

## Theoretical Investigation of effect of cobalt doping on properties of Iron Oxide by ADF

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### ABSTRACT

Iron Oxide has gained much interest in biomedical and spintronics applications due to its unique and novel properties. Amsterdam density functional (ADF) software is used for the first time in order to theoretically investigate the structural properties of cobalt doped iron oxide at 0K. TZ2P is used as basis set. Using GGA geometry optimization was achieved to observe structural properties. Inverse spinel cubic structure with lattice parameter of 8.39 Å is confirmed after geometry optimization by using GGA. 2X1X1 super cell of cobalt doped iron oxide is formed and GGA:PBE method is used to obtain total density of states (DOS) along with partial DOS of iron, cobalt and oxygen, respectively. Increase in band gap energy at 0K is observed after applying Hubbard potential (U=3 and 4 eV) for cobalt and iron, respectively.

### 1. INTRODUCTION

Iron oxide has gained much interest of the researchers due to its existence in three most widely used stoichiometric phases ( $\text{Fe}_3\text{O}_4$  (magnetite),  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) and  $\alpha\text{-Fe}_2\text{O}_3$  (hematite)) (Riaz et al. 2014a). Depending on the presence of iron oxide in such unique and novel phases it is widely used in various fields like in biomedical (Riaz et al. 2014b, Riaz et al. 2012a) and spintronics (Riaz et al. 2013).

Among them magnetite possesses crystal structure of cubic inverse spinel with general formula  $\text{AB}_2\text{X}_4$ . X is a divalent anion while A and B are divalent cation and trivalent cation, respectively. In this stoichiometric formula of spinel ferrites tellurides, oxides and sulfides are mostly used (Hou et al. 2010). In case of maghemite, cubic close-packed arrangement is formed by oxygen ions and divalent iron cations occupy the octahedral sites, whereas trivalent iron cations have arbitrarily distributed on octahedral and tetrahedral sites. Hence, in magnetite, the presence of  $\text{Fe}^{+3}$  and  $\text{Fe}^{+2}$  cations make its structure complicated (Riaz et al. 2014b, Riaz et al. 2013).

With the doping of cobalt in magnetite,  $\text{CoFe}_2\text{O}_4$  spinel ferrite is formed which has its

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wide applications in magnetic tunnel junction (Caffrey et al. 2013) and spin filter devices (Fritsch and Ederer 2011).  $\text{CoFe}_2\text{O}_4$  spinel ferrite is insulating ferrimagnet with large experimentally observed direct band gap value of 2.7 (Holinsworth et al. 2013).

Density functional theory (DFT) has gained much importance for the prediction and understanding of various properties of wide range of materials at 0K (Cramer and Truhlar 2009). Although its importance is world wide but there are certain challenges for archers while using it such as to find properties at finite temperature and to examine the effect of that temperature on the stability. The standard band theory with GGA and/or LDA cannot sufficiently described transitions metals with *d* electrons. This failure is due to the strong correlation of these *d* electrons and hence they are placed near the Fermi level. By applying Hubbard potential *U*, GGA + *U* or LDA + *U* approach can be used to obtain correctly described properties of those materials with transition metals. That's why experimentally observed band gap was achieved by using density functional theory with Hubbard *U* (DFT+*U*) approach, whereas metallic solution with no charge ordering was achieved by using conventional DFT calculations (Odkhuu et al. 2014). Many researchers have carried out theoretical investigations of properties of cobalt doped iron oxide by using various softwares such as Holinsworth et al. (2013) reported about variation in band gap of two spinel ferrites by using Vienna ab initio simulation package (VASP). Caffrey et al. (2013) reported about the use of VASP, SIESTA and SMEAGOL packages for the calculation of real band structures along with DOS and of the complex band structure, respectively. Odkhuu et al. (2014) reported about the first principle investigations of the  $\text{Fe}_3\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  by using Vienna ab initio simulation package (VASP) with projector augmented wave pseudopotential method. By applying Hubbard potential ( $U=4.5$  eV) they observed that variation in band gap was observed with variation in charge.

Among these various softwares, Amsterdam Density Functional (ADF), have gained much interest to calculate density functional theory of various materials especially transitions metal containing compounds. It has various advantages as compared to other softwares such as it uses slater-type orbitals instead of Gaussian-type orbitals. It can evaluate post-SCF energies for materials with hybrid functionals although it performs SCF calculations only for local functionals. Reduced computational cost achieved by using density fitting in ADF. While periodic calculations for surfaces and bulk crystals can be performed by using BAND program (Cramer and Truhlar 2009).

In this research work, structural properties along with optical properties of  $\text{CoFe}_2\text{O}_4$  were investigated by using density functional theory. According to our best knowledge, Amsterdam density functional software was first time used to perform density functional calculations of  $\text{CoFe}_2\text{O}_4$  at 0k.

## **2. COMPUTATIONAL DETAILS**

Amsterdam density functional program was used to investigate density functional theory's computations on cobalt doped iron oxide. Generalized gradient approximation (GGA) functional was used which is parameterized by Perdew, Burke, and Ernzerhof (PBE) (Perdew et al. 1996). Self-interaction error in GGA was corrected by assigning *U* value (Hubbard Potential) of 3 and 4 eV to cobalt and iron, respectively. This additional Coulomb interaction on the *d* shell of iron and cobalt results in correct energetic

ordering in crystal structure of  $\text{CoFe}_2\text{O}_4$ . All calculations were performed spin-polarized with TZ2P, triple-zeta quality basis set. This basis set was improved by sets of polarization functions for 2s and 3p on oxygen atom and 2p and 3d on iron atoms. That results in increased band gap by applying Hubbard potential ( $U$  eV) (Schron and Bechstedt 2013). Hence, Hubbard potential was applied to achieve improved explanation of 3d orbitals of iron in  $\text{CoFe}_2\text{O}_4$ . All the computational results were taken at 0K. Frozen-core Perdew-Burke-Ernzerhof (PBE) potentials with lattice parameter 8.39 Å was used. The Brillouin zone was sampled by a  $3 \times 3 \times 3$  mesh of k-points for the calculation of density of states and band structure of  $\text{CoFe}_2\text{O}_4$ .

### 3. RESULTS AND DISCUSSION

We first optimized the structures of  $\text{CoFe}_2\text{O}_4$  by using in BAND tool in ADF. Fig. 1 shows inverse cubic spinel structure of  $\text{CoFe}_2\text{O}_4$  with  $2 \times 1 \times 1$  super cell. Octahedral Fe sites are occupied by cobalt atoms, in this inverse cubic spinel structure of  $\text{CoFe}_2\text{O}_4$ , with space group of  $Fd\bar{3}m$  (Odkhuu et al. 2014). In Fig. 1 red, blue and golden spheres represents oxygen, cobalt and iron atoms, respectively.

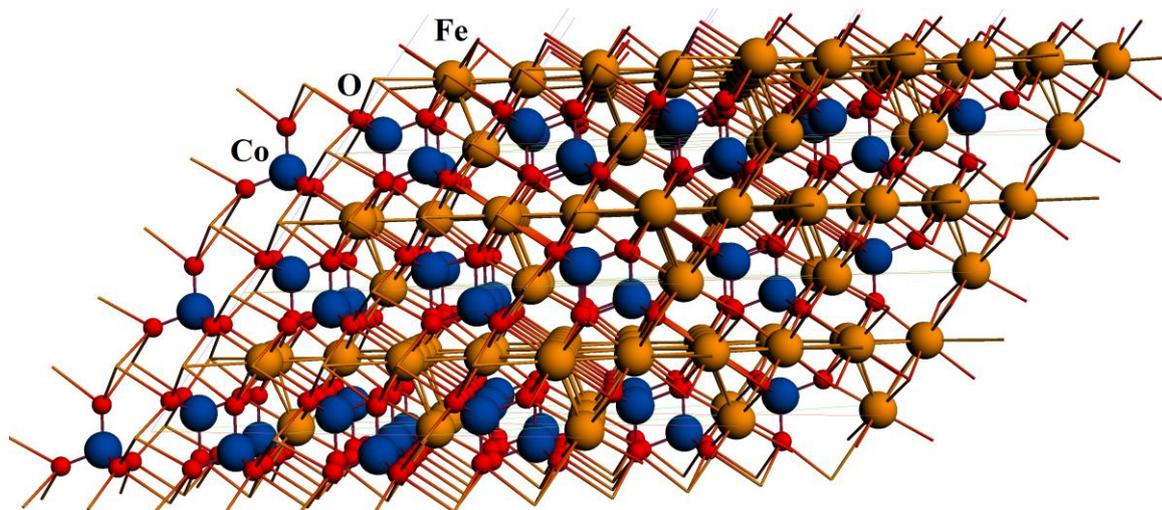


Fig. 1 Structure of Cobalt doped iron oxide

Conventional unit cell contains eight formula units and 8a and 16d positions are occupied by cations occupy 8a and 16d at  $(0, 0, 0)$  and  $(5/8, 5/8, 5/8)$ , respectively. While 32e positions at  $(u, u, u)$  is occupied by oxygen. Where “u” is the positional parameter used for oxygen (Hou et al. 2010). Lattice parameter “a” is observed to be 8.39 Å after geometry optimization, which is very close to the experimentally observed value (Zhang et al. 2010, Fritsch and Ederer 2011).

Fig. 2 shows band structure obtained by applying Hubbard potential  $U$ . According to the crystal field theory the d band of iron is split in two sub-bands; in doubly degenerate  $e_g$  and triply degenerate  $t_{2g}$  (Shorikov et al. 2010). In tetrahedral crystal field  $t_{2g}$  levels

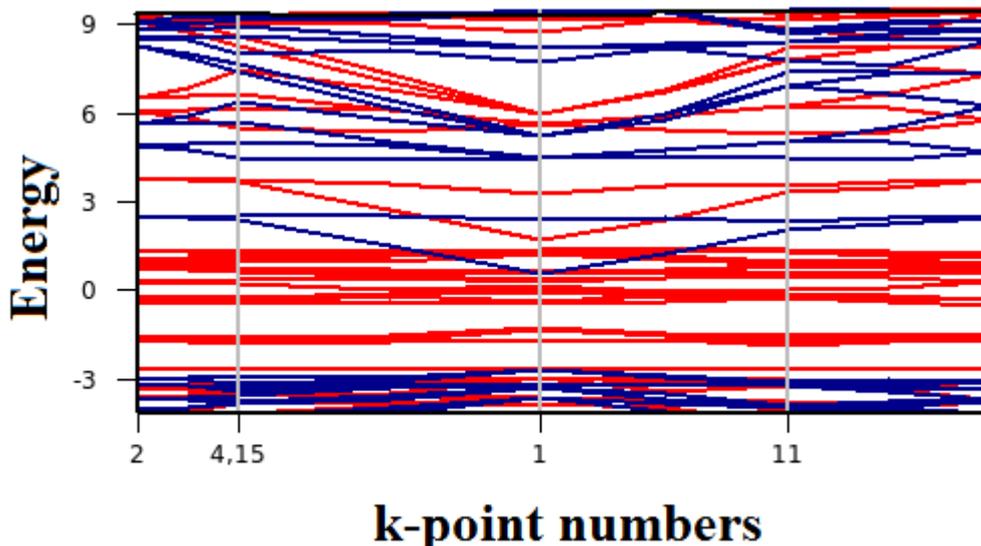
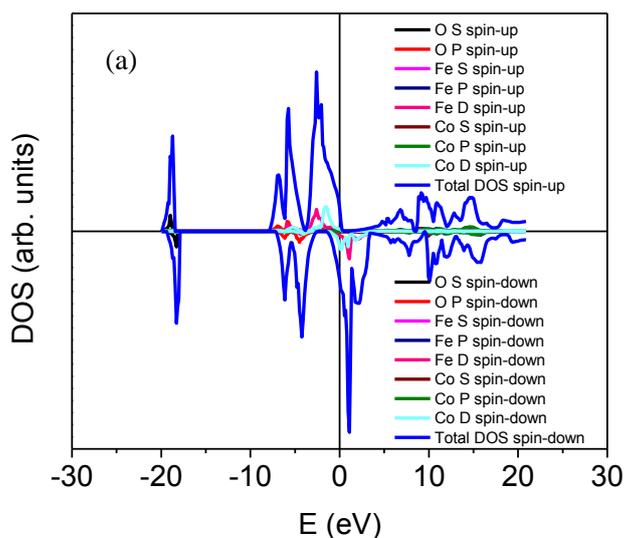


Fig. 2 Band structure of Cobalt doped iron oxide with GGA+U (Red color for spin-up states and blue color for spin-down states)

are higher than  $e_g$  levels. This is might be due to the direct electrostatic repulsion between surrounding anion orbitals and  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals. While in case of octahedral environment order remains reserved due to direct repulsion between  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals. Relative strength of the crystal field strongly defines the electronic configuration (Hou et al. 2010).



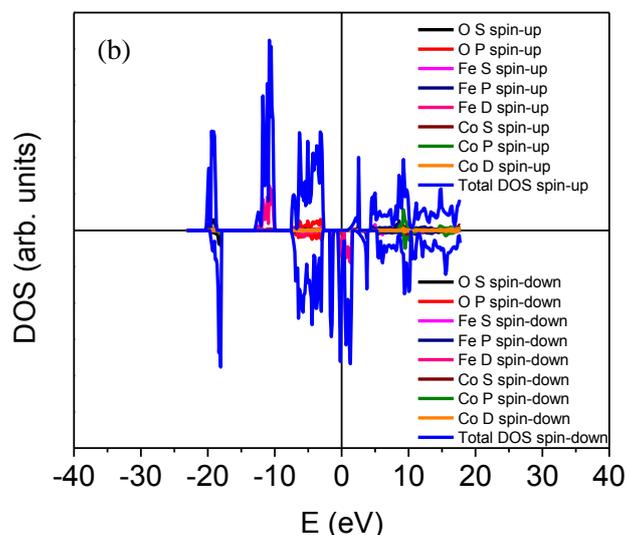


Fig.3 Total DOS and partial density of states in case of a) GGA and b) GGA+U (U=3 and 4 eV for cobalt and iron atoms)

Total and partial density of states of  $\text{CoFe}_2\text{O}_4$  given by GGA and GGA+U is given in Fig. 3(a) and (b), respectively. The majority DOS is set to positive, while the minority part is set to negative.

The indirect band gap value in our case, which is observed by using GGA+U is 0.86 eV, this is value of the band gap energy as compared to observed in literature i.e. 1.6 eV by using VASP method (Holinsworth et al. 2013). Fig. 3(a-b) corresponds that high spin configuration is achieved for iron and cobalt at octahedral and tetrahedral sites respectively. Hence, five and three unpaired electrons are likely to be predicted for  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$ , respectively. For  $\text{Co}^{2+}$  ion  $t_{2g}$  levels are half filled due to unpaired electrons, while at the tetrahedral sites  $e_g$  levels are completely filled. While in case of  $\text{Fe}^{3+}$ , due to Un-paired electrons, both  $e_g$  and  $t_{2g}$  levels are half occupied at octahedral and tetrahedral sites (Hou et al. 2010).

From Fig. 3(a) and (b) it shows that  $\text{CoFe}_2\text{O}_4$  is half metallic in case of GGA calculation with inverse spinel structure and with Hubbard potential i.e. in case of GGA+U calculations, it becomes insulating with the band gap energy of 0.86 eV. This is the enhanced value as compared to reported in literature such as Szotek et al. (2006) reported about the observed 0.8 eV value of band gap by using self-interaction corrected local spin density approximation in DFT. Walsh et al. (2007) reported about the band gap value of 0.63 eV by applying LDA+U approximation. Hence, the results obtained by GGA+U give enhanced structural and electronic properties as compared to those obtained by GGA (Odkhuu et al. 2014). Caffrey et al. (2013) reported about 0.52 eV band gap with GGA+U. To the best of our knowledge it is first time reported investigations of structural and optical properties of inverse cubic spinel  $\text{CoFe}_2\text{O}_4$  by using Amsterdam density functional theory at 0k.

### 3. CONCLUSIONS

In summary, the density functional theory based first principle calculations of  $\text{CoFe}_2\text{O}_4$  have been conducted to clarify the effect of cobalt doping in iron oxide at 0K. According to our best knowledge structural properties of cobalt doped iron oxide were performed by using Amsterdam density functional (ADF) software for the first time. Generalized gradient approximation (GGA) along with TZ2P basis set was used for geometry optimization. Hubbard potential (U) of 3 and 4 eV was used for two transition metals i.e. cobalt and iron, respectively. Inverse spinel structure with lattice parameter of 8.39 Å was observed after geometry optimization. Indirect band gap energy of 0.86 eV at 0K is observed after applying Hubbard potential.

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