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# Theoretical study of spinel structure of $FeAl_2O_4$ using density functional theory

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## ABSTRACT

A first principles calculation of ternary spinel oxides $FeAl_2O_4$ is presented by means of density functional theory. The analysis of structural, magnetic, and electronic properties is performed using the GGA:PBE gradient corrected exchange-correlation functional. The results are presented for the structure and magnetic exchange interactions for a wide range of systems. The partial density of states of Fe, Al and O reveals that Fe cation has dominant source to study the magnetic properties of $FeAl_2O_4$. The electronic band gap is obtained showing the same value as reported in literature. The results and chemical trends are discussed in terms of atomic sites and orbital energies and relation between the valence kinetic and core kinetic energy are estimated using atomic orbital. The bond lengths of O-O, Al-O, Al-Al, Fe-Fe, Fe-O with their energy are estimated. The first-principles investigation of magneto structural coupling is discussed. The presented study can provide valuable information and insight into the physics of structure, especially in case of the magnetic and structural properties.

## 1. INTRODUCTION

In most spinel structures, the temperature has great influence on the cation distribution as proposed by Andrezze et al. (2000). More complications are pointed out when $FeAl_2O_4$ studied with the bulk composition in intracrystalline cation distribution which is mist crucial parameter as pointed out by Andreozzi et al. (2001). However, with the increase in equilibrium temperature the inversion of $FeAl_2O_4$ is more progressive which is characterized by using the normal configuration of $FeAl_2O_4$. The chemistry of $FeAl_2O_4$ is a

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bit complicated due to the change in stoichiometery with the influence of $F^{3+}$ cation vacancy (Andrezze et al. 2000). Waerenborgh et al. (1994), claimed that the substitution of $Fe^{3+}$ in place of $Fe^{2+}$ and cation vacancies provides the discrepancy between the calculated and experimental data. Larsson et al. (1994) investigated the detailed study of $Fe^{2+}$ and Al disordering using the Mossbaur and Power x-ray diffraction techniques. To obtain the photoelectric properties with stability of $FeAl_2O_4$ thin film, the doping techniques being used are very important and have been focused in last decade. Much attention has been paid to Al based spinel structures using different experimental procedures and theoretical analysis using density functional theory (Yang et al., 2013, Yan et al. 2011, Walsh et al. 2007). $TiO_2$ electrodes have great importance in order to decompose the water by induced photon, provides attractive extensive interest for Photoelectrochemical cell (PEC) splitting of water (Bard et al. (1995). Transition metal oxide-based spinel structures have capability to exhibit sustained efficiency. For reasonable PEC application, it is necessary o search the transition metal oxide based materials that can potentially provide lower band gap to absorb in the visible region. The spinel oxide system based on Co-Fe-Al exhibits very interesting behavior as reported by Woodhouse et al. the $Co_3O_4$ and $Fe_3O4$ are two binary oxides which have been focused for PEC applications with optical band gaps between 1.1 and 1.65 eV for $Co_3O_4$ and 0.14 eV for low-temperature $Fe_3O_4$ (Patil et al. 1996, Kim and Park, 2003, Park et al. 1998). Although these materials have shown limited application for PEC applications splitting of water, but enhancement in optical band gap between 1.6 and 2.0 eV is possible when Al is introduced in Co-Fe spinel system to make the Co-Fe-Al oxide spinel system. This spinel oxide system is very important to generate p-type current which is a fundamental source for PEC applications. Furthermore, other interesting behavior has also been reported when experimental work is repeated in the absence of Fe. The photocurrent thus obtained has low value mentioning that the absence of Fe in the spinel system is not important. Co, Fe and Al based ternary oxides have shown a good performance for the spinel structure as reported by Walsh et al. (2007).

There are six spinel structures reported experimentally as $MgAl_2O_4$, $MgFe_2O_4$, $Fe_2AlO_4$, $NiAl_2O_4$, $ZnAl_2O_4$, $ZnFe_2O_4$ (Palin et al. 2007). There are also few theoretical reports available in this context. Computational study on the binary spinel structure of $MgAl_2O_4$-$FeAl_2O_4$ has been Carried out by Monte Carlo simulations. The results were based on the cation distribution of Fe and Mg (Palin et al. 2007. It has been reported various compounds of transition metals have also been studied using GGA analysis (Fritsch et al. 2013, Dixit et al. 2013). According to this analysis, unsatisfactory results have been obtained for high correlated materials using GGA methodology. To overcome this problem, GGA+U analysis was introduced to get the satisfactory bandgap analysis (Xua et al. 2010). Here parameter U presents the applied potential with GGA to obtain the orbital dependent correction (Hou et al. 2010). In this paper, first we have performed the geometry optimization, optical and magnetic properties using the ADF package. After that GGA:PBE approximation was used to find the band gap and density of states. Furthermore, we have employed the Hubbard model in order to obtain appropriate value of U functional for presented spinel system.

## 2. COMPUTATIONAL DETAILS

The conventional unit cell of $FeAl_2O_4$ contains eight formula units as shown in Fig 1. The output coordinates and lattice are optimized using 1x1x1 super cell contains 14 atoms. Fe ions are located at the octahedral sites while Al ions are located at the tetrahedral sites. The calculations of normal spinel of $FeAl_2O_4$ are performed using the density function theory with GGA:PBE gradient corrected exchange correlation functional. The periodic boundary condition is implemented using the BAND tool. This program also provides the various k-space within the Brillouin zone using the method of tetrahedron. Here we used KSPACE = 3 for the study of structural and optical and magnetic properties of $FeAl_2O_4$. We also employed the double zeta basis (Tz2P) function, showing the spin polarization is involved throughout the simulation. Relativistic effect is included in this simulation work. General accuracy parameter considered which is equal to 4.5. Each calculation was initialized in a specific configurations of charge and orbital order and self-consistently converged. The plane wave expansion was truncated at a cutoff energy of $1 \times 10^{-6}$ eV. Ionic radii for Zn, Al and O are set to be 0.74, 1.4 and 0.8 Å, respectively. The valence electron was considered for (Fe: $4s^2\ 3d^6$), (Al: $3s^2\ 3p^1$) and (O: $2s^2\ 2p^4$). For static and energy calculations as well as the geometry optimization, the Brillouin zone is set by 3 x 3 x 3 k-point Monkhorst–Pack mesh.

## 2. STRUCTURE

The spinel $AB_2X_4$ is one of the most important crystalline materials for the application of magnetic materials, ceramics, catalyst, superconductor and photoelectrochemical cell etc. The notation A, B and X represents the divalent cation, trivalent cation and divalent anion, respectively. In this structure, oxygen is packed in a FCC in which A atoms occupy the 1/8 of the tetrahedral sites, while B atoms occupy the 1/2 of the octahedral sites [18]. Due to the distribution of A and B, spinel structure is very interesting material and the chemical properties can largely be characterized by the wide range of cation ions distribution. The cation ion distribution can be derived by the value of x, which provides the fraction of divalent metal cation ions on the octahedral sites such as:

$$(A_{1-x}B_x)_{Tet}[A_xB_{2-x}]_{Oct}O_4$$

In case of (x=0), the divalent and trivalent cation occupied on the tetrahedral and octahedral sites. In case of (x=1), octahedral sites are occupied by divalent cation and tetrahedral and octahedral sites are occupied by trivalent cation. The crystal structure of $FeAl_2O_4$ optimized by ADF:Band tools is shown in Fig 1. There are 56 occupied positions in a single unit cell in which 8a and 16d are resides by the cation ions symmetries as (0,0,0) and (1/8, 1/8, 1/8), respectively. Whereas, the 32e sites of oxygen ion are occupied by (u, u, u). Where, u represents the positional parameter of oxygen. It is noticeable that

spinel structure is open structure in which around 33% of the volume is covered by the octahedral and tetrahedral sites.

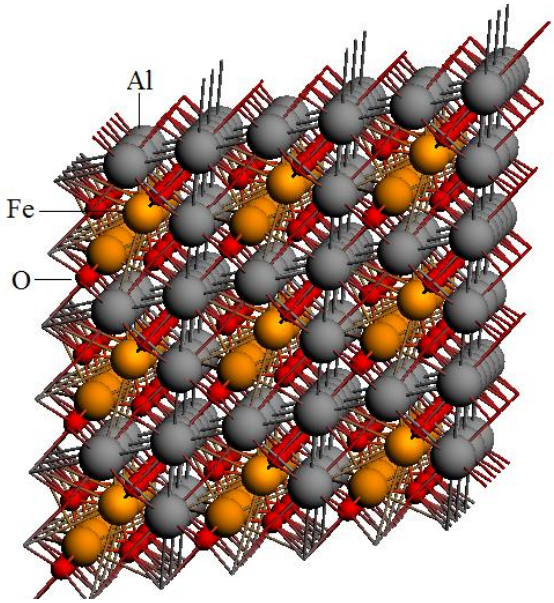


Fig.1 Diagram of $FeAl_2O_4$ spinel structure where Fe atom occupied tetrahedral sites and Al atom occupied octahedral sites.

## 3. RESULTS AND DISCUSSION

The band diagram of $FeAl_2O_4$ simulated from the ADF:Band using GGA approximation is shown in Fig. 2. (a) In figures red lines shows the majority spin while blue lines indicates the minority spin. We calculated the band structure in which the Fermi level lies at energy of 2.4 eV. It is clear that the top of the of the valance band lies at energy value of 2.20 eV and bottom of the conduction lies at energy value of 2.85 eV. The difference between these two values defines the energy band gap which is found to be 0.65 eV. This value is higher than the previous reported theoretical value (Walsh et al. 2007) but has good agreement with the experimental values. The reduction of band gap has several reasons such as we do not consider the localization of d orbital. The GGA approximation calculates the underestimate value of band gap. It is clear from figure that Fermi level shifted into valence band which is highly populated of electron as compared to the conduction band. To avoid the problem regarding improvement in band gap, Fig. 2 represents the band diagram by employing the GGA+U methodology to calculate the band gap reported by experimental value. For this purpose, HubbardU model was employed provides the coulomb-energetic at the same sites of two electrons. It has been observed that for most iron based compound the value of U vary from the 2 to 6 eV for Fe. Meanwhile, the

bandgap value can be enhanced by using the U value. Here we used the U value of 5.4 eV applied to d orbital of the transition metal of Fe (Jeng et al. 2006). The Fermi level lies at energy of 7 eV. It is clear that the top of the of the valance band lies at energy value of 6.80 eV and bottom of the conduction lies at energy value of 8.70 eV. The band gap determined in this case found to be 1.9 eV has good agreements with the experimental predicted value. This value lies in the visible range and most suitable for the photoelectrochemical cell of water splitting.

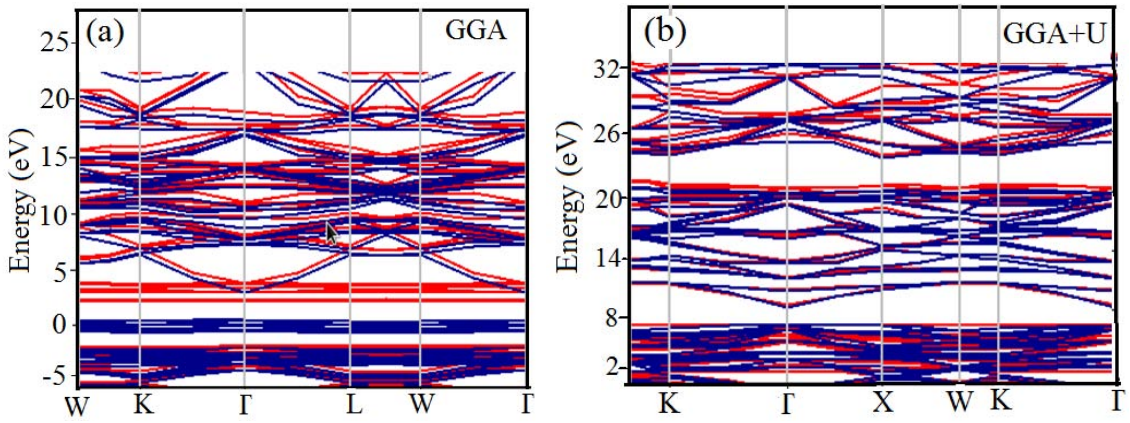


Fig. 2 Band diagram of $FeAl_2O_4$ taken from (a) GGA and (b) GGA+U calculations.

Fig. 3 shows the spin polarized total and partial density of states of $FeAl_2O_4$ taken from the GGA approximation using ADF:Band tool. It is clear from figure that highest peak in the valence band is due to O-2p states while conduction band is formed by the Al-p and Al-s states. The Fermi level located at 2.4 eV. From -20 to 2.4 eV, the valence band is formed by the Al-3d and O-2p states. The maximum density of states located around 2 eV showing the lower valence band. Here we focused spin polarization at the Fermi level in order to study the magnetic properties. We can see from Figure majority spin exist in the valence band while minority spin in the conduction band. We observed that ferromagnetic configuration is more importantly was observed using GGA. The ferromagnetic nature of spinel structure shows the contribution of d state of iron at the Fermi level. According to the crystal field theory, Fe five fold d orbital split into doubly degenerate states $e_g$ and $t_{2g}$ Fig. 3(d) shows the partial density of states crystal field theory of $FeAl_2O_4$ base spinel structure to understand the degeneracy of d orbital of Fe $t_{2g}$ (i.e. $d_{xy}$, $d_{yz}$, $d_{zx}$) states with high energy states and $e_g$ (i.e. $d_z^2$, and $d_{x^2-y^2}$) states at the lower energy. It is clear that minority spin are fully occupied with 5 electrons due to $e_g$ and $t_{2g}$ orbital while one remaining electron in the majority spin occupied by the $e_g$ orbital.

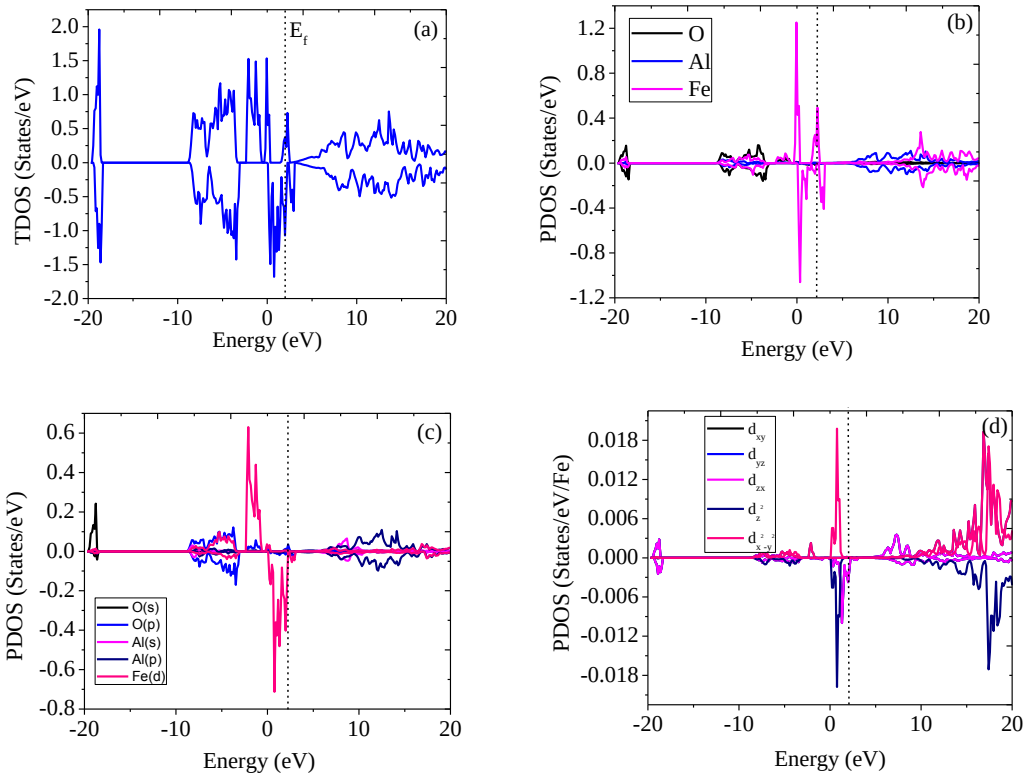


Fig. 3 Total and partial density of states of $FeAl_2O_4$ calculate using GGA:PBE approximation.

Fig. 4 presents the total and partial density of states using the GGA+U approximation. The value of U is equal to 5.4 eV taken from the literature. Here the case in totally different, we observed that no spin configuration exists at the Fermi level after applying the value of U. It has been observed that the $FeAl_2O_4$ have become insulating with band gap of 1.9 eV. It is clear that no states of Fe d orbital presents at the Fermi level with the application of U value. The fully occupied d orbital are push down with respect to Fermi energy. It is clear that Fermi level shifted towards the edge of the valence band with occupied d orbital. It is emphasizing that system has moved towards the high energy region as compared to GGA approximation. To examine the stability of $FeAl_2O_4$ spinel structure we calculated the energy formation of the optimized geometry. The total energy of $FeAl_2O_4$ with GGA and GGA+U are -100 and -39 eV, indicating the stability in structure. Table 1 indicates the average bond length of Fe-Fe, Al-Al, O-O, Al-O and Fe-O. For GGA approximation, the bond lengths are almost identical for Al-O and Fe-O. Increase in bond length with 5.4 and 23% was determined when compared by GGA+U approximation.

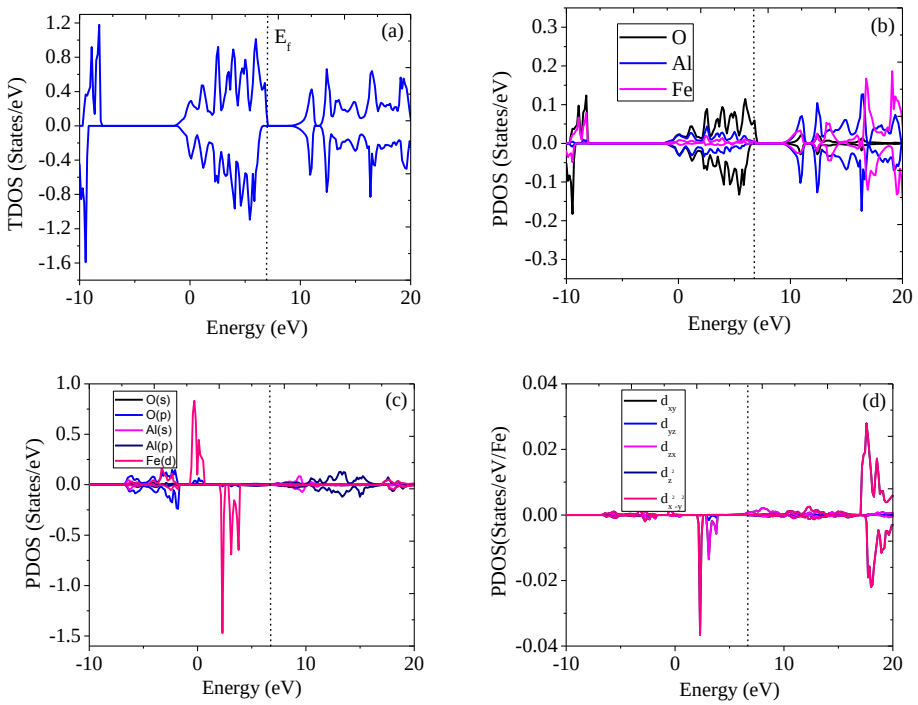


Fig. 4 Total and partial density of states of $FeAl_2O_4$ calculate using GGA+U approximation.

Table 1: Calculated bond length in Å

| | Fe-Fe | Al-Al | O-O | Al-O | Fe-O |
|---|---|---|---|---|---|
| GGA | 3.58 | 3.45 | 2.95 | 2.02 | 2.02 |
| GGA+U | 3.50 | 2.83 | 2.86 | 2.13 | 1.55 |

## 5. Conclusion

In this study, the $FeAl_2O_4$ spinel system has been optimized systematically by GGA and GAA+U calculation within the frame work of DFT. The GGA:PBE exchange correlation function was employed in order to find the accurate calculation. Our results indicated that $FeAl_2O_4$ energetically stable in both cases. We found that, theoretically calculated band gap value by both calculations (GGA and GGA+U) is well agreement with the literature. Furthermore, Fe always prefers high spin polarization at the Fermi level. We have also examined the bond length; results indicated that the bond length decreases from GGA to GGA+U calculation. Finally, the calculated band gap of 1.9 eV using the GGA+U approximation can enhance the efficiency of photoelectrochemical cell of water splitting.

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