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Study of structural and electronic properties of iron oxide by ADF

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ABSTRACT

Cubic FeO has been studied by using density functional theory. Generalized gradient approximation (GGA:PBE) and local density approximation (LDA) is used in order to study optical and structural properties of iron oxide. By using BAND tool with basis set of TZ2P geometry optimization is achieved and fcc structure is observed. It is important to mention it here that all the calculations were taken at 0K by using Amsterdam density functional software for the first time to investigate structural and electronic properties of FeO (wüstite). Band gap of 0.615 eV and 0.75 eV is observed by GGA and LDA. While, 2.2 eV and 1.89 eV is obtained by GGA+U and LDA+U respectively. Constant value of Hubbard potential (U) is used for both approximations i.e. 6.4 eV. Total DOS and partial density of states for iron and oxygen is also studied for both approximations. Analysis of the density of states confirms the strong hybridization between Fe 3d and O 2p states in FeO. The bond length between iron and oxygen is examined and found to be 3.74Å with total bonding energy of 15.99 eV.

1. INTRODUCTION

Iron oxides are amongst most important transition metal oxides due to its occurrence in sixteen different phases (Riaz et al. 2012). Among these pure phases of iron oxide, FeO, which is known as wüstite, is simplest one (Riaz et al. 2013a). It has its potential applications in magnetic devices such as magnetic tunnel junctions (Riaz et al. 2013b).

Being the member of transition metal (TM) monoxides, FeO has strongly correlated electron systems. In the narrow 3d bands of transition metals, interaction between delocalized and localized effects results different electronic structure of FeO (Schrettlea et al. 2012). Large number of experimental and theoretical studies has been carried out to investigate properties of transition metal monoxides but only few reports are present about wüstite. Wüstite has been less investigated due to its non-stoichiometric existence at room temperature. Cubic wüstite, ($Fe_{1-x}O$), can only be synthesized at ambient pressure with variation of x in the range of $0.05 < x < 0.15$.While, meta-stable

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wüstite gives mixture of two phases of iron oxide: one is hematite while second is magnetite (Schrettlea et al. 2012).

It possesses stable cubic NaCl (B1) like crystal structure under ambient temperature and pressure (Fischer et al. 2011). Face centered cubic unit cell is formed with oxygen (O^{-2}) lattice and Fe^{+2} substitutes on interstitial sites (Benitez et al. 2011). With variation in temperature and pressure structure deformation is observed such as at room temperature and high pressure of 17GPa monoclinic crystal structure is observed (Fischer 2011). Above room temperature and at high pressure of about 70GPa transformation from B1 to B8 (NaCl to NiAs) crystal structure is observed (Kaercher et al. 2012).

After five decades of formulation of density functional theory (DFT) (Hohenberg et al. 1964, Kohn et al. 1965), it is still in use as a basic computational tool to investigate various calculations on electronic structures of complex systems. Density functional theory was used due to simplicity and high efficiency with providing possibility to represent ground state energies in terms of electronic charge density (Himmetoglu et al. 2014). Various approximations are needed to be used in actual calculations by DFT to give exact expression of the total energy functional. Among these approximations, local density approximation (LDA) and generalized gradient approximations (GGA) are widely used (Himmetoglu et al. 2014, Schron and Bechstedt 2013). However, Underestimation of band gap for insulators and semiconductors is the main problem with both these functional. This underestimation is due to the deficiency of self-interaction cancelation and inappropriate description of and correlation exchange in comparison to changes. In case of materials having transition metals, with d shells, this problem exceeds and may give wrong prediction of electronic structure of that material. For example GGA underestimates the experimentally observed band gap of iron oxide and gives 75% smaller value of band gap energy. In order to improve this underestimation of GGA and LDA for materials having transition metal, Hubbard potential can be added. This leads to the GGA+U and LDA+U methods (Guo et al. 2012).

In this research work, we have investigated the structural and optical properties of wüstite by using density functional theory. According to our best knowledge Amsterdam Density Functional (ADF) program was used for the first time to investigate the properties of wüstite by comparing different approximations with and without Hubbard potential.

2. COMPUTATIONAL DETAILS

Density functional theory was used to theoretically investigate structural and optical properties of wüstite. Amsterdam density functional (ADF) program was used for density functional theory calculations. Generalized gradient approximation (GGA) and local density approximation (LDA) were used for structural optimization of wüstite. Density functional theory may fail to explain electronic properties of wüstite due to lack of consideration of the onsite Columbic repulsion between the Fe 3d electrons. Therefore, in order to avoid this problem Hubbard potential (U) was used (Wang 2013). Generalized gradient approximation with Hubbard potential of 6.4 eV (Wdowik et al. 2013) was used for final optimization of electronic structure. Hubbard potential was

applied to achieve improved explanation of 3d orbitals of iron in wüstite. TZ2P was used as basis set. All the computational results were taken at 0K. We have used frozen-core Perdew-Burke-Ernzerhof (PBE) potentials in case of generalized gradient approximations. Lattice parameter was used 4.33 Å. The Brillouin zone was sampled by a 3 × 3 × 3 mesh of k-points for the calculation of density of states and band structure.

3. RESULTS AND DISCUSSION

Fig. 1 shows cubic structure of wüstite (Cornell and Schwertmann, 1996). Periodic unit cells containing three-layers were used for geometric optimization of the rock salt crystal structure of FeO.

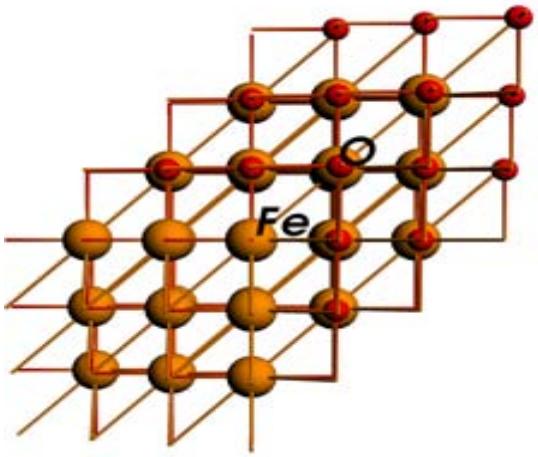

Fig. 1 Structure of FeO at 0K

Experimental lattice parameter a=4.26 (Cavelius et al. 2012) was used in order to get geometry optimization with BAND tool for both approximations. The bond length between iron and oxygen is found to be 3.74Å with total bonding energy of 15.99 eV.

Fig. 2 (a-b) shows the band structures from our calculations using the LDA+U and GGA+U, respectively. Red colour indicates for majority spins (spin-up) and blue colour indicates minority spins (spin-down) in Fig. 2(a-b). According to crystal field theory, d band of iron is splited in t_{2g} and e_g sub-bands which are triply degenerated and doubly degenerated, respectively. Insulating ground state at ambient conditions is failed to obtain by using LDA. Hence, it shows metallic nature for all volumes (Shorikov et al. 2010). In all cases (GGA, GGA+U, LDA and LDA+U), the top of valence band consists of mixed states of 2p states of oxygen and inadequately dispersed d states of iron. Degenerate e_g orbitals are formed by the splitting of five-fold degenerate d orbitals and degenerate t_{2g} orbitals are formed by three-fold degenerate orbitals as a result of octahedral crystal field splitting (Gillen and Robertson 2013).

The fundamental band gap is between 4s band and single band of t_{2g} of iron (Gillen and Robertson 2013). Band gap values obtained at 0K by GGA, GGA+U, LDA and LDA+U are given in table 1 and can be seen that the band gap energy of 2.2 eV obtained in our calculations by using GGA+U, is in slightly better agreement with the experimental value by using GGA+U with Hubbard potential 6.4 (Wdowik et al. 2013).

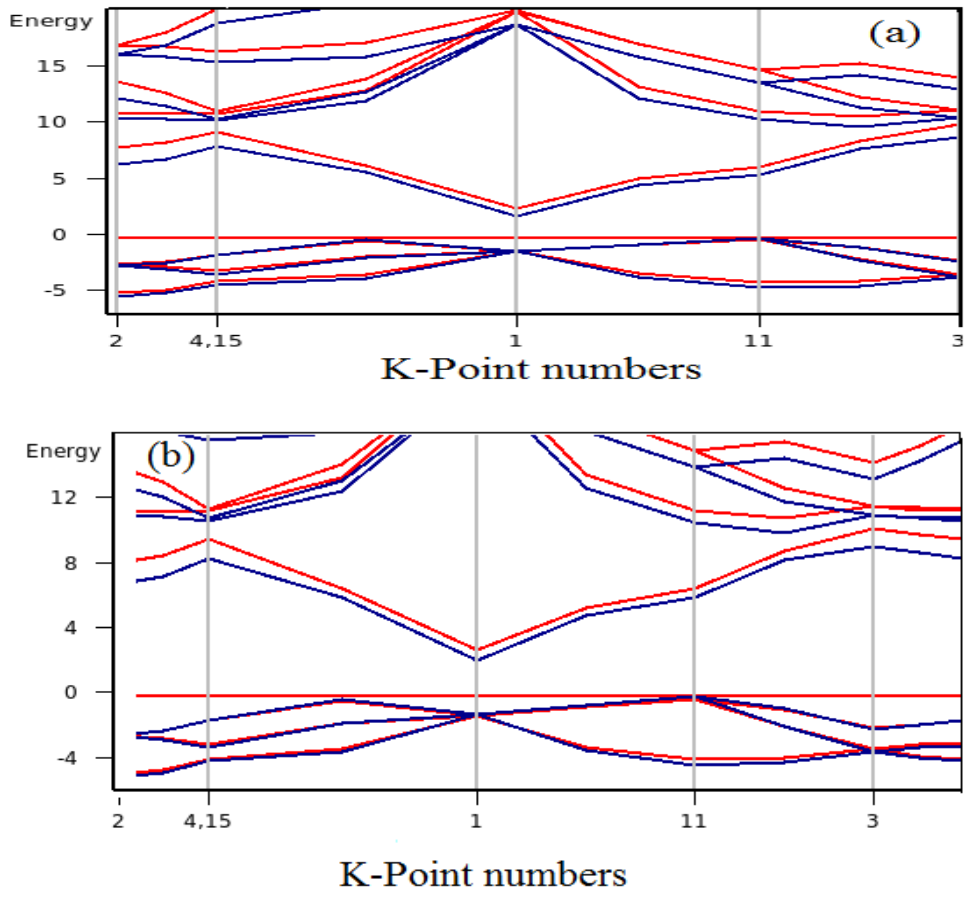

Fig. 2 Band Structure of FeO with a) LDA+U=6.4 and b) with GGA+U=6.4 (Red color for spin-up states and blue color for spin-down states)

The total density of states (DOS) for FeO along with partial density of states with and without Hubbard potential in case of GGA is shown in Fig. 3(a-b). While in case of LDA is shown in Fig. 4 (a-b). Electronic configuration of Fe in FeO is $3d^6$. Hence in FeO, high magnetization configuration is obtained due to division of d electrons in majority spin and minority spin. Normally five d electrons occupy majority spin state and remaining one occupies the minority spin states (Himmetoglu et al. 2014).

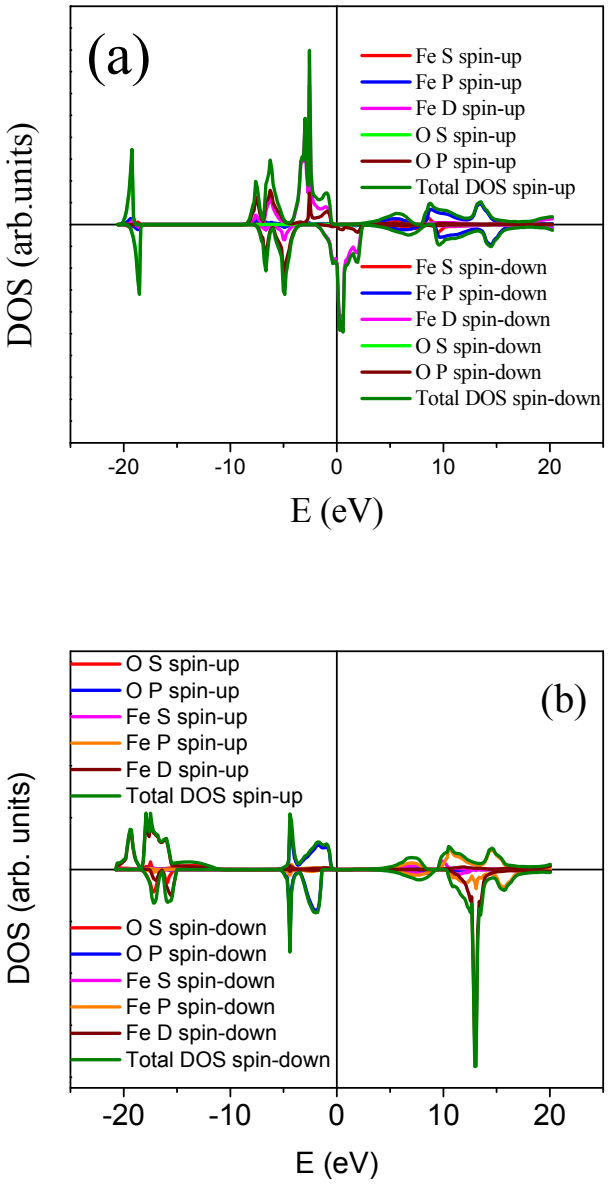

Fig. 3 Partial (Fe and O) and total density of states of FeO a) with LDA and b) with LDA+U=6.4

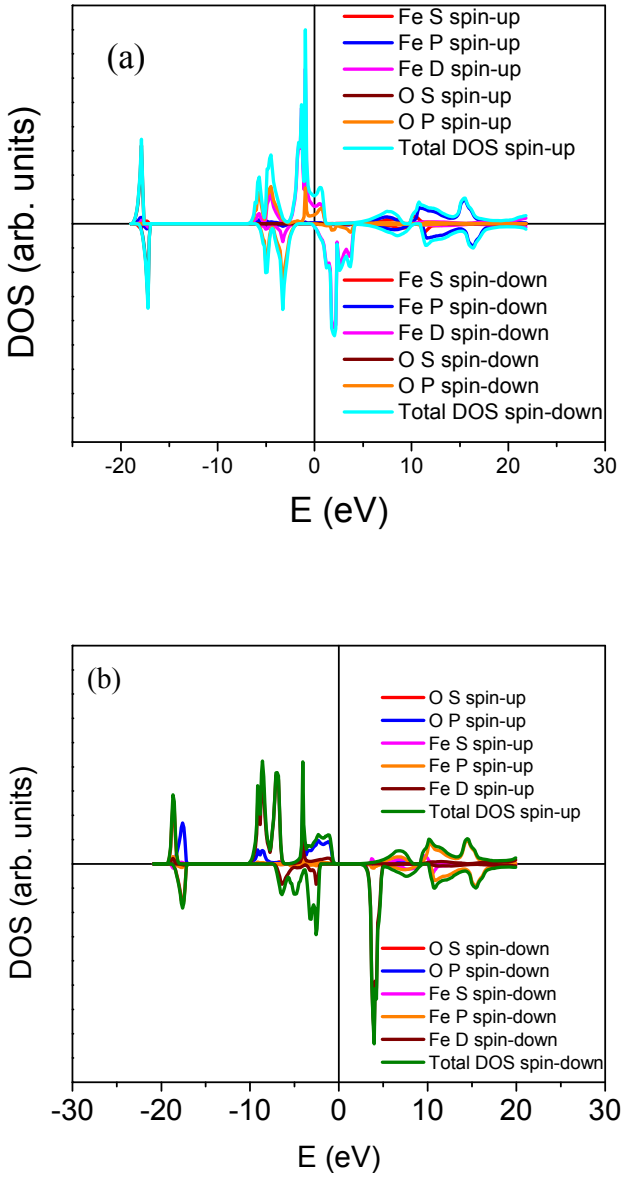

Fig. 4 Partial (Fe and O) and total density of states of FeO a) with GGA and b) with GGA+U=6.4

Occupied energy levels of 3d are lowered due to Hubbard potential U and shifts unoccupied 3d orbitals to higher energy as can be seen in Fig. 3(b) and 4(b). This shifting of unoccupied orbitals is with respect to maxima of the valence band (Zhang et al. 2013). While below the Fermi Energy; 2p states of oxygen are hybridized and occupied by 3d states of iron (Wdowik et al. 2013).

Table 1. Comparison of band gap values by using GGA, GGA+U, LDA and LDA+U (U=6.4 eV)

Approximation	**U (eV)**	**E_g (eV) at 0K**
GGA	0	0.61
GGA+U	6.4	2.2
LDA	0	0.75
LDA+U	6.4	1.89
Experimental (Wdowik et al. 2013)		2.4

4. CONCLUSIONS

Structural, electronic and optical properties of iron oxide (wüstite) were studied by using density functional theory (DFT). Generalized gradient approximation (GGA:PBE) was used in BAND tool. Geometry optimization was achieved with TZ2P basis set. Cubic NaCl crystal structure was confirmed after geometry optimization. Band gap of wüstite with value of 0.615 eV at 0K was observed without addition of Hubbard potential U. With the addition of Hubbard potential (U=6.4) increase in the value of band gap energy was observed (2.2 eV), which is close to the experimentally observed value. Study of density of states revealed that interaction between d states of iron and p states of oxygen were responsible for the stability of the wüstite. This work represents the first attempt to investigate the structural, electronic and optical properties of wüstite (FeO) by using Amsterdam density functional software based on density functional theory.

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