The 2014 World Congress on
Advances in Civil, Environmental, and Materials Research (ACEM14)
Busan, Korea, August 24-28, 2014

Structural, electronic and optical properties of γ-Fe_2O_3 by ADF

Robina Ashraf[1)], Saira Riaz[2)], and *Shahzad Naseem[2)]

Centre for Solid State Physics, University of the Punjab, Lahore, Pakistan
shahzad_naseem@yahoo.com

ABSTRACT

Maghemite (γ-Fe_2O_3) is one of the promising candidates for its use in biomedical and in optoelectronics. Density functional theory (DFT) with generalized gradient approximation (GGA:PBE) is used in order to study structural and optical properties of iron oxide. By using BAND tool with basis set of TZ2P, geometry optimization is achieved. Cubic spinel structure is confirmed after geometry optimization with bond length of 3.55 Å between iron and oxygen in γ-Fe_2O_3. Amount of Hirshfeld charge is observed to be 18.02, 28.39 for Fe(1) and Fe(2), respectively instead of 26.00. While for all three oxygen atoms its value increases from 8.00 to 9.85. Indirect band gap of γ-Fe_2O_3 is observed with value of 0.68 eV without applying Hubbard potential U. After applying Hubbard potential U=3 band gap of 2.1eV is achieved which is in agreement to the experimental value of 2.0 eV (Zhu et al. 2013). Total density of states along with partial density of states for iron and oxygen is also studied. It is important to mansion it here that it is the first time to use Amsterdam Density Functional software to investigate properties of maghemite and all these calculations were carried out at 0K.

1. INTRODUCTION

Among various polymorphs of iron oxide, Maghemite (γ-Fe_2O_3) is the second most stable polymorph (Riaz et al. 2012a, Crespo et al. 2010) having potential applications in various fields such as in biomedical (Nan et al. 2014), optoelectronics (Fouineau et al. 2013) and in gas sensors (Capone et al. 2014). Due to its low cost, chemical stability, bio-compatibility and non-toxicity maghemite is widely used in biomedical applications along with other nanoparticles since last 20 years (Crespo et al. 2010, Fouineau et al. 2013). Various nanostructures of iron oxide have gained much interest of researchers as properties of these nanostructures are widely different as compared to properties of that material in bulk form. Nanoparticles of maghemite with less than 20nm size are typically used for specific biomedical applications such as for the treatment of hyperthermia (Nan et al. 2014). Maghemite spheres with doping of various elements have been used in photocatalysis. Optical and ferromagnetic properties of these spheres of 10nm diameter with room temperature high saturation magnetization make applicable for the application separation technology as photocatalysis (Zhu et al. 2013). Structure of maghemite originates from that of spinel magnetite (Riaz et al. 2013). As

[1] Graduate Student
[2] Professor

magnetite structure made up of a face centered cubic oxygen lattice, divalent cations of iron are occupied at octahedral sites and trivalent cations are distributed at tetrahedral. Distribution of divant and trivalent cations along with fcc oxygen lattice can be represented as: $(Fe^{3+})_{Tet}[Fe^{2+}Fe^{3+}]_{Oct}O_4$. While in case of maghemite, spinel structure is observed due to fcc oxygen lattice in which iron cation vacancies are present on octahedral sites (Fouineau et al. 2013).

Maghemite is a semiconductor with energy band gap of 2.0 eV (Zhu et al. 2013). The magnetic moments in maghemite are oriented in opposite directions on the octahedral and tetrahedral sites, just like magnetite. This leads to ferromagnetic behavior of maghemite (Crespo et al. 2010). It has net magnetic moment of 2.5 μB with high Neel temperature of 950 K and Curie temperature of 820-986K (Riaz et al. 2013).

In order to get improved experimental results it is important to theoretically investigate various properties of the materials. Density functional theory (DFT) is the basic method to study electronic properties of materials. Local density approximation (LDA) and generalized gradient approximation (GGA) are the most famous and widely used functionals. However, the main problem during usage of GGA and LDA is the underestimation of band gap for various materials such as insulators and semiconductors (Guo et al. 2012). The reason for this underestimation is the lack of self-interaction cancelation. Specially, in case of materials with transition metals, with d shells, this problem exceeds and as a result wrong prediction of electronic structure of that material was observed. For example GGA gives 75% smaller value of experimentally observed band gap of Fe_2O_3. 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).

There are only a limited number of investigations about of structural and electronic properties of maghemite by using different softwares and approximations, like Guo, et al. (2012) reported about the electronic investigation of Fe_2O_3 by using screened exchange hybrid density functional. They observed wide indirect band gap energy of 2.41 eV of Fe_2O_3 with anti-ferromagnetic behavior. Crespo, et al. (2010) theoretically investigated vacancy ordering and electronic structure of maghemite. They used the Vienna ab-initio simulation program (VASP). Hubbard potential (U=4) was used to observe nature of maghemite as a charge-transfer-type insulator with large band gap of 2eV. Hence, it is important to theoretically investigate various properties of maghemite and the results obtained by these studies can be applied in various experiments.

In this paper, we report about the theoretical investigation of structural and optical properties of maghemite. According to our best knowledge it is the first time to use Amsterdam density functional (ADF) software to study properties of maghemite at 0K.

2. COMPUTATIONAL DETAILS

Density functional theory was used to theoretically investigate structural and optical properties of maghemite. Amsterdam density functional (ADF) program was used for density functional theory calculations. Generalized gradient approximation (GGA) was used for structural optimization of maghemite. The value of Hubbard potential U is set to (U =4 eV) for maghemite in GGA+U method. This additional Coulomb interaction on

the d shell of iron results in correct energetic ordering in crystal structure of maghemite. Hence, increased band gap is obtained by applying Hubbard potential (Schron and Bechstedt 2013). Hubbard potential was applied to achieve improved explanation of 3d orbitals of iron in maghemite. All the computational results were taken at 0K. TZ2P is used as basis set, which is of triple-zeta quality and was improved with two sets of polarization functions: 2p and 3d on iron, 2s and 3p on oxygen. We have used frozen-core Perdew-Burke-Ernzerhof (PBE) potentials. Lattice parameter was used 8.33 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

We first employ geometry optimization to investigate structure of maghemite along with bond length between iron and oxygen, oxygen-oxygen and iron-iron. Fig. 1 shows the cubic spinel-type structure of maghemite in space group fd3m of with bond length of 3.55Å between iron and oxygen atoms (Cornell and Schwertmann 1996). The lattice constant was observed to be 8.34 Å (Riaz et al. 2012b). Smallest interatomic distance of 4.72 Å was observed after geometry optimization at 0K. Red spheres in Fig. 1 represent oxygen atoms while yellow spheres represent iron atoms.

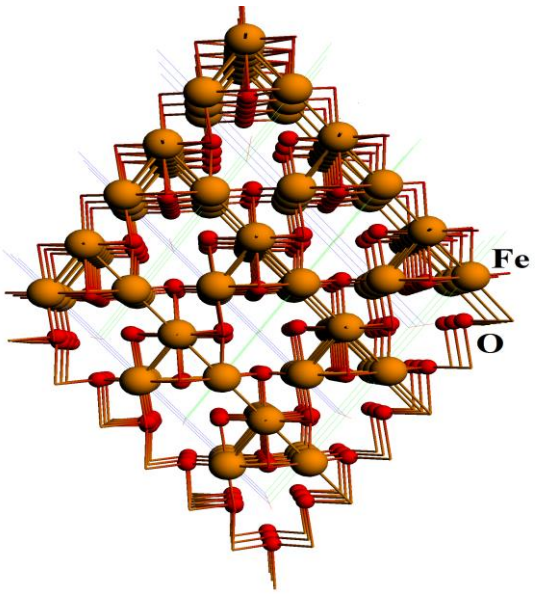


Fig. 1 Structure of maghemite

In this disordered cubic spinel structure, all 32 sites of fcc cubic lattice are fully occupied by oxygen. While 8 tetrahedral sites are occupied by trivalent cations of iron (Fe^{3+}) and 16 octahedral sites are also additional occupied by of one third of the 13 Fe^{3+} cations (Guo et al. 2010). This structure of maghemite is more complicated due to absence of divalent cations and partial occupation of Fe^{3+} cations on octahedral sites.

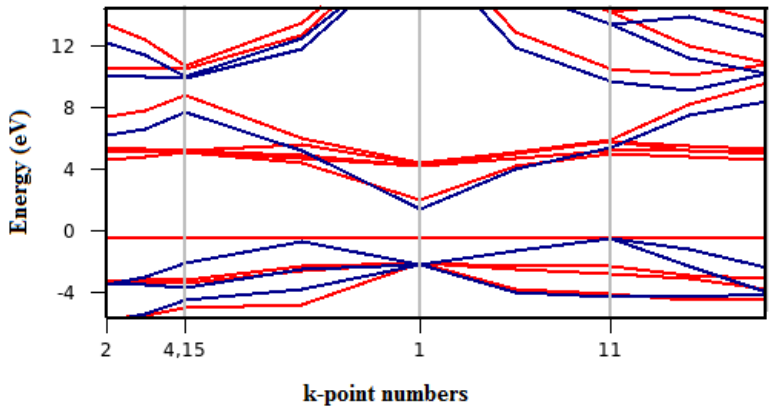
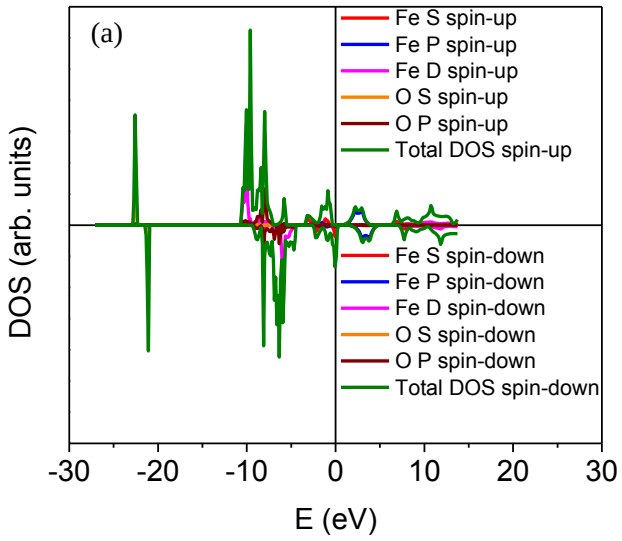


Fig. 2 Band structure of maghemite in case of GGA+U (red colour indicates spin-up and blue colour indicates spin-down states)

Fig. 3(a-b) shows the total and partial density of states (DOS) of maghemite at 0K without and with the effect of Hubbard potential U, respectively. These results indicates that improved description of the band of maghemite can be obtained by using Hubbard potential as band gap value is improved and came close to experimentally observed values (



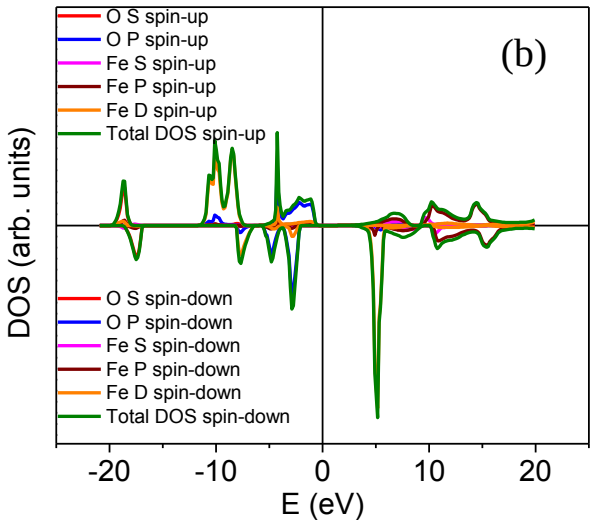


Fig. 3 Total and partial density of states in case of a) GGA and b) GGA+U (U=4eV) at 0K

In this study, the partial density of states of iron is from just one iron atom, in the unit cell of maghemite and just distinguished for s, p and d orbitals by spin-up and spin-down states. Similarly, for oxygen, partial density of states was taken for s and p orbitals and spin-up and spin-down states are given in Fig. 3(a) and (b). Non-symmetric density of states can be seen in Fig. 3(b) around the Fermi level in case of GGA+U. Hence, results indirect energy band gaps at 2.4 eV (Fig. 2) which is comparable to the experimentally observed value band gap energy of 2.2 eV (Abe and Watanabe 2014). For two atoms of iron (Fe1 and Fe2) amount of Hirshfeld charge is observed to be 18.02 C, 28.39C, respectively, instead of 26.00C. While for all three oxygen atoms its value increases from 8.00 to 9.85. Which indicate that it is a charge transfer type insulator and due to this property can be used in spintronics such as in spin-filter devices (Crespo et al. 2010).

4. CONCLUSIONS

Structural and optical properties of iron oxide (maghemite) 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 spinel (defective) structure was confirmed with space group Fd-3m. Amount of Hirshfeld charge was observed to be 18.02, 28.39 for Fe (1) and Fe (2), respectively instead of 26.00. While for all three oxygen atoms its value increased from 8.00 to 9.85. Indirect band gap of γ-Fe_2O_3 with value of 0.68 eV at 0K was observed without addition of Hubbard potential U. With the addition of Hubbard potential (U=4) increase in the

value of band gap energy was observed (2.4eV), 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 maghemite. This work represents the first attempt to investigate the structural, electronic and optical properties of maghemite (γ-Fe_2O_3) by using density functional theory.

REFERENCES

Abe, S. and Watanabe, m. (2014), "Mg-induced phase transformation from hematite to Maghemite," *Mater. Res. Express*, **1**, 026108-026116.

Caffrey, N.M., Fritsch, D., Archer, T., Sanvito, S. and Ederer, C. (2013), "Spin-filtering efficiency of ferrimagnetic spinels $CoFe_2O_4$ and $NiFe_2O_4$," *Phys. Rev. B,* **87**, 024419-024426.

Capone, S., Manera, M.G., Taurino, A., Siciliano, P., Rella, R., Luby, S., Benkovicova, M., Siffalovic, P. and Majkova, E. (2014), "Fe_3O_4/γ-Fe_2O_3 Nanoparticle multilayers deposited by the langmuir−blodgett technique for gas sensors application," *Langmuir*, **30**, 1190−1197.

Cornell, R.M. and Schwertmann, U. (1996), *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses,* VCH, Weinheim, Germany.

Cramer, C.J. and Truhlar, D.G. (2009), "Density functional theory for transition metals and transition metal chemistry," *Phys. Chem. Chem. Phys.,* **11**, 10757–10816.

Crespo, R.G., Al-Baitai, A.Y., Saadoune, I. and Leeuw, N.H.D. (2010), "Vacancy ordering and electronic structure of γ-Fe2O3 (maghemite): a theoretical investigation," *J. Phys.: Condens. Matter,* **22**, 25540-25547.

Fouineau, J., Brymora, K., Ourry, L., Mammeri, F., Yaacoub, N., Calvayrac, F., Merah, S.A. and Greneche, J.M. (2013), "Synthesis, m ssbauer characteri ation and Ab Initio modeling of iron oxide nanoparticles of medical interest functionalized by dopamine," *J. Phys. Chem. C*, **117**, 14295−14302.

Guo, P., Guo, X. and Zheng, C. (2010), "Roles of γ-Fe_2O_3 in fly ash for mercury removal: Results of density functional theory study," *Appl. Surf. Sci.,* **256,** 6991–6996.

Guo, Y., Clark, S.J. and Robertson, J. (2012), "Electronic and magnetic properties of Ti_2O_3, Cr_2O_3, and Fe_2O_3 calculated by the screened exchange hybrid density functional," *J. Phys.: Condens. Matter,* **24**, 325504-325512.

Nan, S.S., Chao, W., Zan, Z.Z., Long, H.Y., Venkatraman, S.S. and Xu Zhi-Chuan, (2014), "Magnetic iron oxide nanoparticles: synthesis and surface coating techniques for biomedical applications," *Chin. Phys. B*, **23**(3), 037503-037512.

Ria , S., Ahmad, P., Akbar, A. and Naseem, S. (2012b), "Improved magnetic properties of sol-gel derived Fe_3O_4 nanoparticles for biomedical applications", *Proceedings of International Conference on Advances in Materials Research (ICAMR'12),* Seoul, South Korea.

Ria , S., Akbar, A. and Naseem, S. (2012a), "Fabrication and magnetic characterization of AAO template assisted growth of Fe_3O_4 nanotubes", *Proceedings*

of International Conference on Advances in Materials Research (ICAMR'12), Seoul, South Korea.

Ria , S., Akbar, A. and Naseem, S. (2013), "structural, electrical and magnetic properties of iron oxide thin films," *Adv Sci. Lett.,* **19**, 828-833.

Schron, A. and Bechstedt, F. (2013), "Magnetic anisotropy of FeO and CoO: the influence of gradient corrections on exchange and correlation," J. Phys.: Condens. Matter, 25, 486002- 486011.

Zhu, L.P., Wang, L.L, Bing, N.C., Huang, C., Wang, L.J. and Liao, G.H. (2013), "Porous fluorine-doped γ‑Fe_2O_3 hollow spheres: synthesis, growth mechanism, and their application in photocatalysis," *Appl. Mater. Interfaces,* **5**, 12478−12487.