



## First Principle Study of Effect of Doping on the Lattice Constant and Band Gap of $\text{Fe}_2\text{O}_3$

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### ABSTRACT

Density functional theory (DFT) based first principle study is used to investigate and compare the effect of doping Ge on the lattice constant and band gap of the  $\text{Fe}_2\text{O}_3$ . The investigated crystal structure of both compounds is cubic belongs to the 221-space group. The Perdew-Burke-Ernzerhof (PBE) functional is used for structure optimization and band structure calculations. All calculations were performed using ultrasoft pseudopotentials. As the ionic radii of the halides alter, a systematic shift in the lattice constants and band gap of both compounds is observed.

Keywords: First principle, DFT, lattice constant, band structure

### Introduction

Since ancient times, iron oxide has been recognized, and in many cultures, it has been mandatory for the creation of metal and colors. Two naturally materialize iron oxides are magnetite ( $\text{Fe}_3\text{O}_4$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ). Its implementation dates back thousands of years, particularly in the extracting resources of iron for construction and tools. As modern chemistry in the late 18th century, scientists were capable to understand its structure and features perfectly [1]. Iron oxides make progress into **necessary** industrial materials specially for the manufacturing of steel, that force onward the Industrial Purpose. Iron oxides are now common for an extensive range of uses, for example pigments in paints also coatings and an necessary elements of magnetic storage systems. Magnetic nanoparticles are crucially important in biomedicine noticed through their usage as contrast agents in MRI scans, for medication management and to heal physical condition.

As a consequence of its extraordinary magnetic features and biocompatibility, magnetite ( $\text{Fe}_3\text{O}_4$ ) is a fundamental part of modern technology and medication.  $\text{Fe}_2\text{O}_3$  is the formula for iron oxide, also related to ferric oxide or iron (III) oxide. It commonly present like a reddish-brown, unscented powder that dissolves in acids even so is unable to be solved in water. There are a lot of industrial and technological uses for this material, which is freely available in size and nanoparticles. Hematite, a top most common forms of iron oxide ( $\text{Fe}_2\text{O}_3$ ) in nature, is an important iron material used to manufacture metal. Fundamental element is iron, which is commonly originate inside the crust of the Earth and retains the atomic number 26. Iron in the condition of  $\text{Fe}_2\text{O}_3$  is in the most prevalent oxidation state in nature, which is +3 [1]. Iron oxides can be reduced at a high temperature, like during smelting, to produce the pure metal. Other iron compounds, such iron (III) chloride ( $\text{FeCl}_3$ ), can also be made from iron (III) oxide.

Iron oxide, which comprises  $\text{Fe}_2\text{O}_3$ , is widely utilized in the manufacturing of magnetic compounds, steel, and pigments, magnetic storage media, and catalysis are just a few of the numerous industrial and technological activities that use iron oxide extensively. Furthermore, iron oxide particles that are sold commercially are available in nano and micron sizes. While iron oxide micron powder normally has a particle size of 325 mesh, iron oxide nanoparticles usually range in size from 10 to 50 nm. A highly insoluble and thermally stable material, iron oxide finds extensive use in magnetic fields, ceramics, coatings, and even biological sectors such as medication administration and the treatment of magnetic hyperthermia. Iron oxides, particularly  $\text{Fe}_2\text{O}_3$  (hematite) and ( $\text{Fe}_3\text{O}_4$ ) (magnetite), have magnetic and chemical characteristics that make them valuable as precursors in the manufacturing of steel, electronic components, and catalysis. In this instance, a first-principle investigation can be give useful information about their electrical and electronic properties that will be explored later[2].

Scientists can explore the elementary manner of materials at the atomic level by using density functional theory (DFT), furthermore other first-principles calculations. These computational methods can help us to understand the electrical structure and features of  $\text{Fe}_2\text{O}_3$ . Creating unique materials with particular characteristic for specific applications might enhance from this knowledge. The electrical and electronic properties of  $\text{Fe}_2\text{O}_3$  are determine by defects, substance composition and crystal shape. Investigating these variables by using first-principles calculations, we can determine tendency and interrelationship that able to direct the creation of unique materials with advanced functionality [3].

Lastly, there is a large amount of assurance for the implementation of the  $\text{Fe}_2\text{O}_3$  classifications in electrical and electronic applications. First-principles study can assist us to enhance their properties which will clear the way for the combination of new materials with particular applications. Furthermore, it

can be created on a nanoscale by American Elements in several ways like tablets, nano powder. Most  $\text{Fe}_2\text{O}_3$  is easily available, and refined sub-micron and nano powder forms are available.  $\text{Fe}_2\text{O}_3$  has definite chemical properties, for example a melting and boiling point of roughly  $1565^\circ\text{C}$  ( $2850^\circ\text{F}$ ) due to its high melting point and continuity, hematite generally decompose before it come to a boiling temperature. The melting point of magnetite ( $\text{Fe}_3\text{O}_4$ ) is approximately  $1595^\circ\text{C}$  ( $2900^\circ\text{F}$ ). Due to its high melting point and consistency, magnetite also has a trend to decompose before it comes to a boiling point. The melting point of goethite ( $\text{FeO}(\text{OH})$ ) is approximately  $200^\circ\text{C}$  ( $392^\circ\text{F}$ ). Because of its continuity and low melting point goethite decompose before it comes to a boiling point [4]. The applications of iron oxides in a different industries and specialties are much determined by these chemical characteristics. As already pointed out, iron oxides discover application in an extensive range of industries, e.g. electronics, catalysts, energy storage devices, pigments, and environmental refine. The large number of applications of iron oxides in these fields are changed by their clear chemical and physical characteristics.

$\text{Fe}_2\text{O}_3$  has three main applications the chemical manufacturing industry and catalysts, coatings and pigments, electronics, and magnetic storage. Iron (III) oxide, also referred to as ferric oxide, is an inorganic material having the formula  $\text{Fe}_2\text{O}_3$ . The crystal structure of  $\text{Fe}_2\text{O}_3$ , also known as iron (III) oxide or ferric oxide, is composed of a face-centered cubic (FCC) lattice. In this arrangement, each iron (Fe) atom is surrounded by six oxygen (O) atoms, while each oxygen atom is surrounded by four iron atoms [5].

## Research methodology

Quantum espresso [6] is used to calculate lattice constant and band gaps of both the compounds. The electronic states of  $\text{Fe } 3d^6, 4s^2$  and electronic states of  $\text{O } 2s^2$  and  $2p^4$  are treated as valence states. The convergence values for energy and forces are  $1 \times 10^{-6}$  Ry and  $1 \times 10^{-3}$  Ry/Bohr. The convergence value of cutoff energy is 60 Ry and the cutoff for charge density is selected as 480 Ry i.e. 8 times the cutoff energy. The converged value for k-points grid is  $10 \times 10 \times 10$ .

## Result and discussion

The cubic crystal structure was optimized using the density functional theory (DFT). Figure 1 shows the crystal structure of undoped and doped  $\text{Fe}_2\text{O}_3$ , also known as hematite. Red spheres represent oxygen (O) atoms and grey spheres represent iron (Fe) atoms in a repeating unit cell. The calculated lattice constants for all three cases are  $3.62 \text{ \AA}$  for undoped as shown in figure 1(a),  $3.69 \text{ \AA}$  for center doped Ge as shown in figure 2(b). And when the geometric optimization is performed for face doped Ge in  $\text{Fe}_2\text{O}_3$  as shown in figure 1(c), it changed its crystal structure from cubic to tetragonal crystal structure. And the lattice constants for figure 1(c) are calculated as  $a=b=7.47 \text{ \AA}$  and  $c=5.46 \text{ \AA}$ . We can see that doping of germanium w.r.t to its position in unit cell has different effects. The band structures of these three cases are also calculated to check the band gap. In each case the band gap of doped or undoped cases turn out to be 0 eV. Which means every structure shown in figure 1 (a), (b), (c) are conductor in nature. The band gap is 0 eV because the valence band conduction bands are overlapping.

## Conclusion

The effect of doping on the lattice constant and band gap of  $\text{Fe}_2\text{O}_3$  is investigated. While we can see that the lattice constant has changed form  $3.62 \text{ \AA}$  to  $3.69 \text{ \AA}$  for crystal structures as shown in figure 1 (a) and 1 (b). But when Ge is doped at the face of the cubic structure, the structure has changed into tetragonal structure with lattice constants as  $a=b=7.47 \text{ \AA}$  and  $c=5.46 \text{ \AA}$ . But there is no effect on the band gap as it remains 0 eV for each case.

## Figure

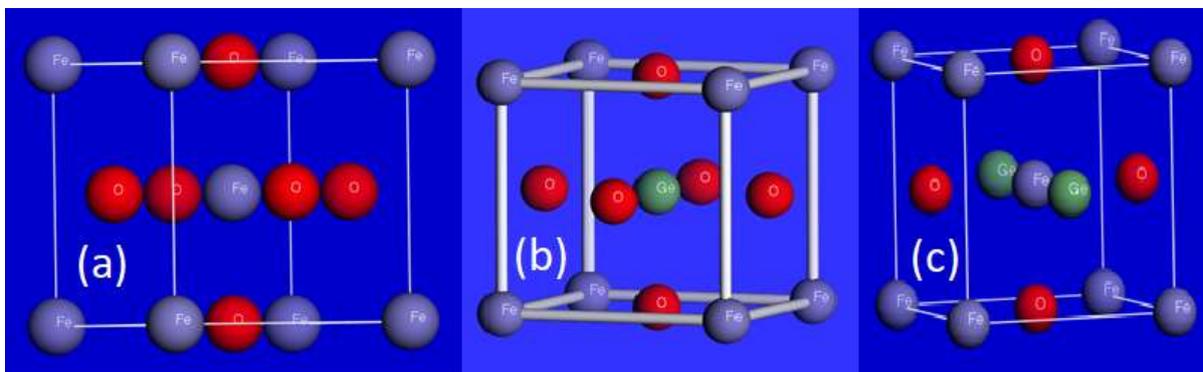


Figure 1: Cubic structure of (a) undoped  $\text{Fe}_2\text{O}_3$  (b) Ge doped at (0.5, 0.5, 0.5) and (c) Ge doped at (0.5, 0.5, 0).

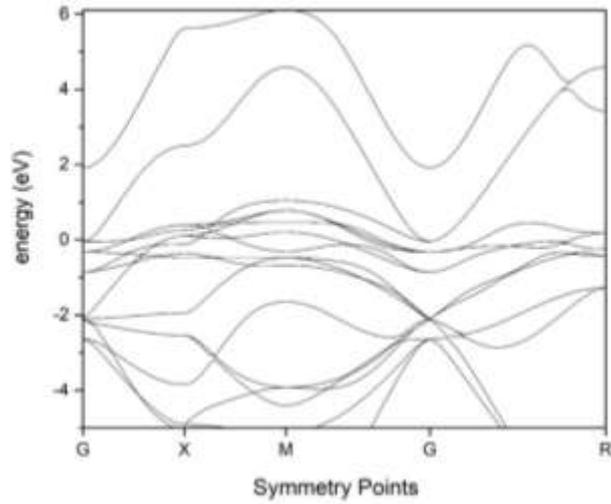


Figure 2: Band structure of the undoped Fe<sub>2</sub>O<sub>3</sub>.

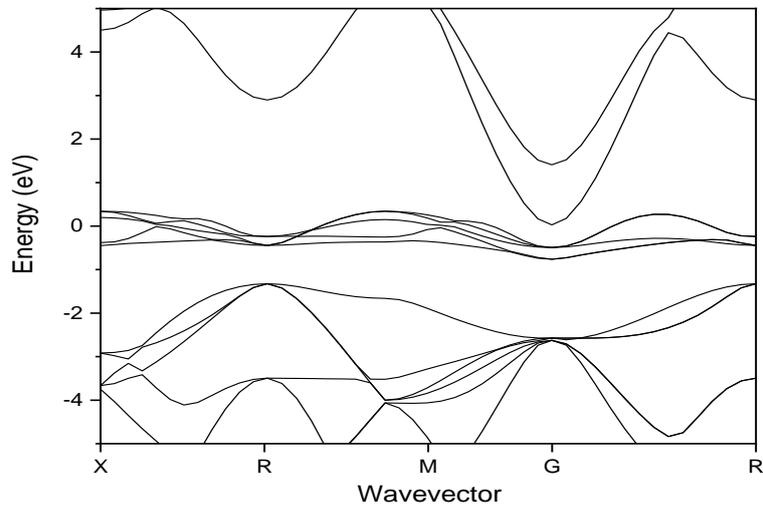


Figure 3: Band structure of Fe<sub>2</sub>O<sub>3</sub> when Ge is doped at center of cubic structure.

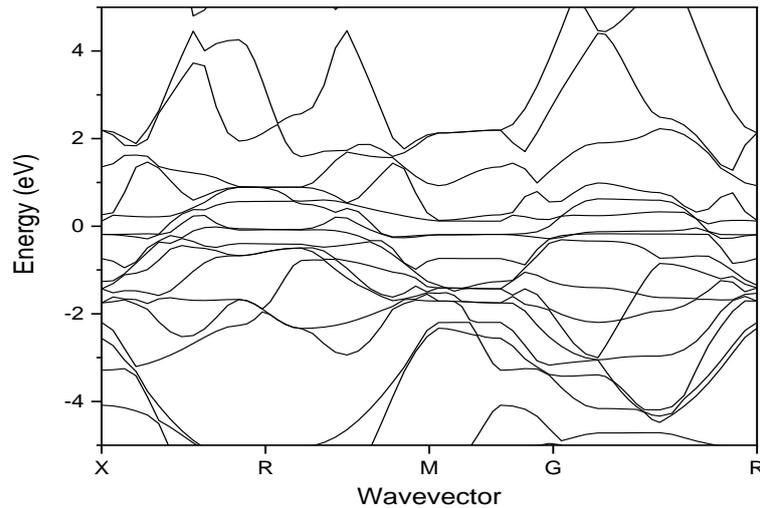


Figure 4: Band structure of the Fe<sub>2</sub>O<sub>3</sub> when Ge is doped at one face of the cubic structure.

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