Ab initio study of the roles of Fe in the electronic properties of ferropericlase

Cui Zhou [1, a], Kai Li [1], Rong Zhang [1], Xiao Liu [1], Qingbo Wang [2]

[1]No. 3 Department, Air Force Early Warning Academy, Wuhan 430019, China

[2]School of Mathematics and Physics, China University of Geosciences (Wuhan), Wuhan 430074, China

[a]cuizhou2014@163.com

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Abstract. The effects of Fe doping on the electronic properties of MgO have been studied by ab initio method. Iron (Fe) changes the lattice constants while does not change the cell angels. The calculated band shows MgO is an insulator. Iron doping introduces a band level in the band gap, which increases the conduction of MgO. Iron shift the band to lower energy. The relations between the density of states (DOS) and band have been discussed. Iron increases the electronic peaks and shifts the peaks to higher energy, which can identify Fe in MgO. Our studies provide a reference to identify the Mg0.9375Fe0.0625O in experiment. We also provide data to identify ferropericlase mineral in practical.

Introduction

MgO is an important mineral in the mantle [1]. Iron (Fe) is an important element in the mantle [2, 3]. In the mantle, the Fe is incline to substitute Mg to form MgFeO (ferropericlase) [4, 5]. There are plenty ferropericlase in our mantle [6, 7]. The study of the electronic properties of ferropericlase is important to identify ferropericlase in our laboratory and some geological process. To our knowledge, there are few experiments studies about the properties of ferropericlase because the expensive cost [8].

On the contrary, ab initio method is effective to study the electronic properties of materials [9-11]. With the development of high performance computer [12], more and more experts used the computer to study the properties of materials. In our paper, we intend to use the ab initio method to study the electronic properties of iron doped ferropericlase.

Computational details

Our calculations performed in an initio program (CASTEP), which implemented in Materials Studio software. As shown in Fig. 1, we first built an MgO crystal and then built a $2\times2\times1$ MgO supercell. We used an iron atom to substitute an Mg atom in the supercell. The obtained content of ferropericlase is 6.25%, which can represent the typical content of ferropericlase in the mantle. After test, the used cut-off energy in our calculation is 400 eV. The used k-points of MgO and $Mg_{0.9375}Fe_{0.0625}O$ are $6\times6\times6$ and $3\times3\times6$. The used valence electrons of Mg, Fe and O are $2p^6 3s^2$, $3d^6 4s^2$ and $2s^2 2p^4$, respectively. The SCF tolerance is $1.0e^{-7}$ eV/cell. The ultrasoft pseudopotential was used in our calculations. We first optimized the crystal structure and then calculated the electronic properties.

Results and discussions

Structure and bands. After optimized the crystal structure, the lattice constants of MgO are $a=b=c=4.29$ Å, while the lattice constants of $Mg_{0.9375}Fe_{0.0625}O$ are $a=b=4.31$ and $c=4.27$ Å. The Fe increases a and b while decreases c. The cell angles of MgO are $\alpha=\beta=\gamma=90°$. Though the constants of

$Mg_{0.9375}Fe_{0.0625}O$ are not equal, the cell angels are $\alpha=\beta=\gamma=90°$. The Fe doping affects the constants apparently, while doesn't affect the cell angles apparently.
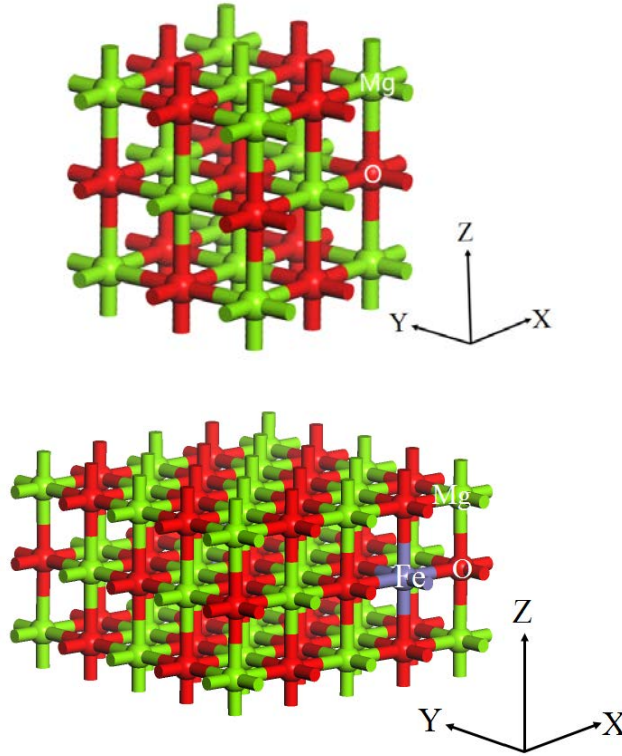

Fig. 1. The schemes of the structure of MgO and $Mg_{0.9375}Fe_{0.0625}O$.
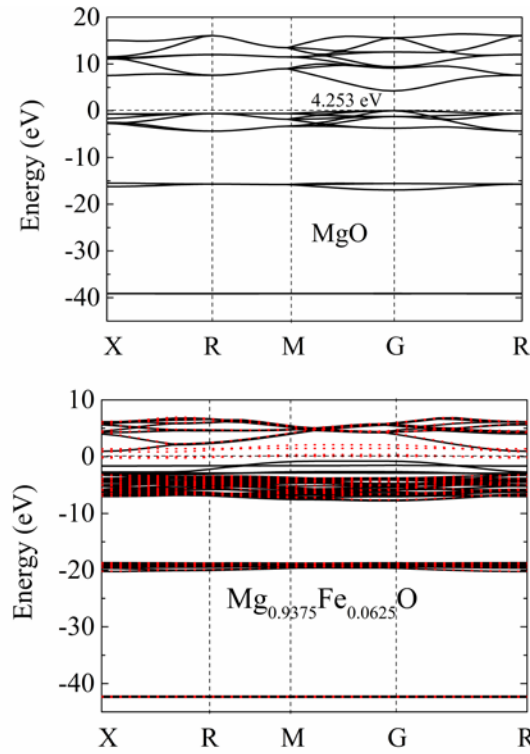

Fig. 2. The calculated bands of MgO and $Mg_{0.9375}Fe_{0.0625}O$.

After optimized the crystal structures, we calculated the bands of MgO and $Mg_{0.9375}Fe_{0.0625}O$ (as shown in Fig. 2). There is a band gap (4.253 eV) of MgO around the Fermi level, which means MgO is an insulator. The calculated band gap is lower than the experiment (7.7 eV). The top of the valence

band at G point and the upper part of the valence band is flat. The bottom of the conduction band is also at G point. So, the top and bottom are all at G point, which means MgO is a direct insulator.

After Fe doping MgO, the alpha and beta band separate from each other. Fe releases electrons and shifts the band to lower energy. Both the conduction and valence band shift to lower energy. The band gap disappears and some band level appears in the origin band gap, which can increase the conduction of MgO. The changes of band will induce a colorful electronic properties, which we will discuss in the following paragraph.

Density of states. The density of states (DOS) are important to discuss the band properties. In this paragraph, we will discuss the calculated DOS of MgO and $Mg_{0.9375}Fe_{0.0625}O$. From the DOS in the left of Fig. 3. We can see the total DOS of MgO mainly come from O $2p$ and Mg $2p$ states. The DOS around the Fermi level mainly come from the O $2p$ state. The state at -15.5 and -39.2 eV mainly come from O $2s$ and Mg $2p$ state. The energy of the according state constitute the according band in Fig. 2.

After Fe doping, the DOS shift to lower energy. There is some state around the Fermi level, which mainly comes from Fe $3d$ state. The appeared state constitutes the band level between the origin band gaps. The spin up and down of Fe state is unequal, which means $Mg_{0.9375}Fe_{0.0625}O$ has spin polarization. The DOS above the Fermi level mainly come from the O $2p$ and Mg $2p$ state. The upper DOS mainly come O $2p$ state. The DOS at -19.0 and -42.2 eV mainly come from O $2s$ and Mg $2p$ state. The according DOS constitute the according band (shown in Fig. 2).
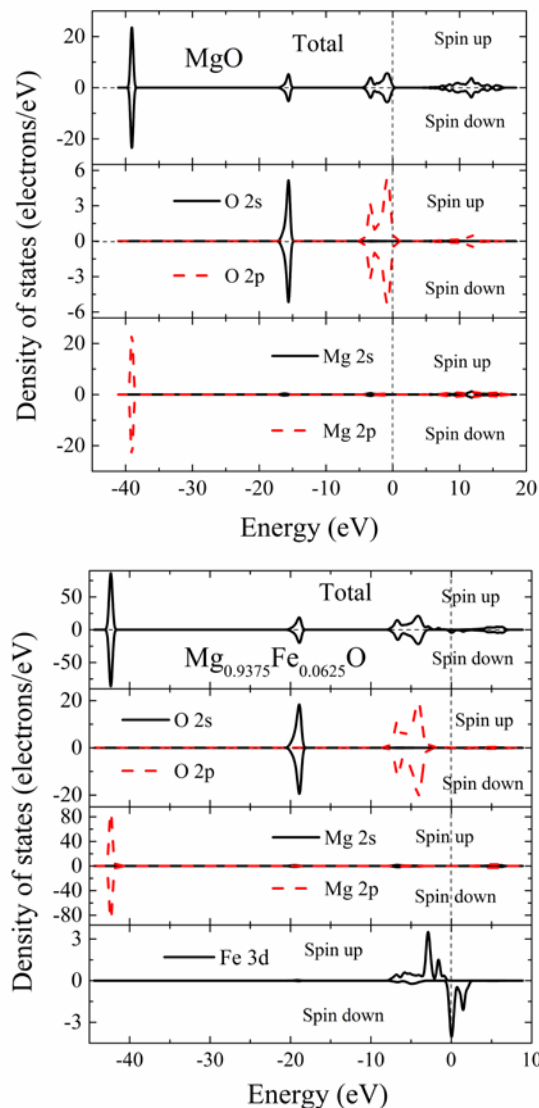

Fig. 3. The density of states (DOS) of MgO (left) and $Mg_{0.9375}Fe_{0.0625}O$ (right).

Conclusions

In this paper, we have studied the electronic properties of MgO and ferropericlase. Iron changes the lattice constant while does not change the cell angles. The calculated band shows MgO is an insulator. Iron introduces some band level in the band gap, which can increase the conduction of MgO. The increased conduction can be used to identify ferropericlase in experiment and mineral specimen. The relations between the density of states (DOS) and band have been discussed. The introduced band level between the band gaps comes from Fe $3d$ state. Our paper not only provides a reference to identify the ferropericlase in experiment and mineral specimen, but also stimulate future experiments.

Acknowledgments

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