Metal-insulator transition and the role of electron correlation in FeO₂

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Iron oxide is a key compound to understand the state of the deep Earth. It has been believed that previously known oxides such as FeO and Fe_2O_3 will be dominant at the mantle conditions. However, the recent observation of FeO_2 shed another light to the composition of the deep lower mantle (DLM), and thus understanding of the physical properties of FeO_2 will be critical to model the DLM. Here, we report the electronic structure and structural properties of FeO_2 by using density functional theory and dynamic mean-field theory. The crystal structure of FeO_2 is composed of Fe^{2+} and O_2^{2-} dimers, where the Fe ions are surrounded by the octahedral O atoms. We found that FeO_2 shows a metal-insulator transition (MIT) under high pressure. The MIT is not a Mott type but a band insulator type which is driven by the O_2 dimer bond length change. However, the correlation effect of Fe $3d$ orbitals should be considered to correctly describe O_2 dimer bond length of FeO_2 and the MIT.

Iron oxides are basic and important materials of the Earth's interior. Among them, FeO and Fe_2O_3 are two end members and the most well-known compounds. However, other kinds of iron oxides with new stoichiometry, such as Fe_4O_5 [1] and Fe_5O_6 [2], are also discovered under the high pressure and temperature. Although molecular FeO_2, which holds an excessive amount of oxygen, is a well-known molecular iron-oxygen system [3], the crystalline form of FeO_2 was identified recently with both first-principles calculation and experiments near 76 GPa [4]. This new iron oxide receives great attention because it suggests an alternative scenario for describing geochemical anomalies in the lower mantle and the Great Oxidation Event. Thus, it is important to understand the correct electronic and structural properties of FeO_2.

FeO_2 possesses an FeS_2-type pyrite structure. FeS_2 is a nonmagnetic compound where the six Fe d electrons occupy the t_{2g} ground states [5–8]. $NiS_{1-x}Se_x$ also has a same crystal structure with FeO_2. It exhibits a complex phase diagram including the metal-insulator transition (MIT) and magnetic phase transition depending on composition x, temperature, and pressure due to the partially filled e_g orbital [9,10]. Several previous studies have reported that the p orbitals of S_2 dimer play an important role in describing the electronic structures of these compounds [9,10], so we can expect that the O_2 dimer may also be a driving factor for determining the electronic and physical properties of FeO_2.

It is well known that standard density functional theory (DFT) fails to reproduce the electronic structures of many transition-metal compounds because the correlation effect of d orbitals cannot be described properly. It also fails to predict Fe-anion bond length, which plays a crucial role in determining the physical properties of Fe-based superconductors [11–13]. Alternatively, DFT$+U$, which includes the correlation effect of localized orbitals, gives better results for structural properties, magnetic moments, and electronic structures. Dynamic

mean-field theory (DMFT) has been believed to be a more advanced technique which deals with local electronic correlation problems exactly [14,15]. DMFT can describe weakly correlated electron systems because it can capture both the itinerant and localized nature of spectral function. DMFT has been combined with DFT (DFT+DMFT), and it has been widely used to describe the correlated physics of real materials in a first-principles manner [16,17].

In this paper, we investigate structural properties and electronic structure using DFT and DFT+DMFT approaches. First, the electronic structure of experimentally reported FeO_2 is calculated from DFT+DMFT. The calculated electronic structures indicate that the $\sigma*$ band of the O_2 dimer plays an important role in determining the physical properties of this system. We also study that the correlation effect of Fe d orbitals should be considered to describe the crystal structure of FeO_2 properly. Last, we find that MIT can occur by varying volume based on the crystal structure predicted by DFT$+U$ ($U = 5$ eV) calculation. O_2 dimer bond length is a governing parameter to determine the MIT in this system, which is sensitively affected by the correlation strength of Fe d orbitals.

We use the DFT+DMFT code [17] based on WIEN2K code [18], which uses a full-potential augmented plane-wave method. We use the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange-correlation functional [19]. A $12 \times 12 \times 12$ k-point mesh is used for self-consistent calculation. An effective one-electron Hamiltonian is generated from WIEN2K calculation, and the electronic correlation effect of Fe d orbitals is treated by local self-energy, which is considered by using a continuous time quantum Monte Carlo (CTQMC) impurity solver [20]. We consider a paramagnetic state at temperature $T = 200$ K. For structural optimization at different volumes, we use the Vienna *ab initio* package (VASP) [21], where a plane-wave cutoff is set to 500 eV and a $10 \times 10 \times 10$ k-point mesh is used.

Figure 1 shows the experimental crystal structure of FeO_2 at 76 GPa, which contains four Fe atoms and eight O atoms in the unit cell. It possesses a simple cubic structure with a space group Pa$\bar{3}$, where the four Fe atoms are located at (0, 0, 0), (0, 0.5, 0.5), (0.5, 0, 0.5), and (0.5, 0.5, 0). The eight O atoms

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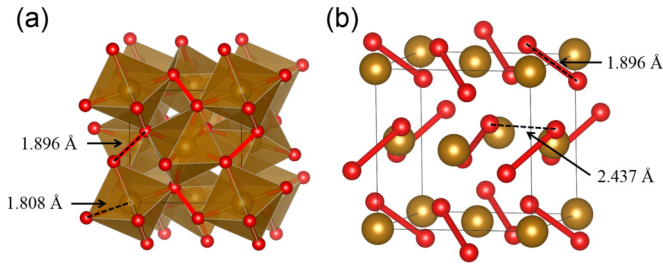†jhshim@postech.ac.kr

FIG. 1. Crystal structure of FeO_2. Brown and red spheres indicate Fe and O atoms, respectively. (a) Fe atom surrounded by six O atoms makes octahedral symmetry, where the Fe-O bond length is 1.808 Å. (b) O-O dimers in FeO_2 crystal. Fe-O bond is omitted for clarity. The bond length of the O_2 dimer is 1.896 Å, and the distance between the second-nearest O atom is 2.437 Å.

are located at $\pm(a,a,a), \pm(0.5-a,-a,0.5+a), \pm(-a,0.5+a,0.5-a)$, and $\pm(0.5+a,0.5-a,-a)$, where $a = 0.3746$ at the experimental structure. An Fe atom surrounded by six O atoms makes slightly distorted octahedral symmetry where the Fe-O bond length is 1.808 Å. Each octahedron shares oxygen atoms at the vertex or it is connected by O-O bonding which makes O_2 dimer, as shown in Fig. 1. The bond length of O_2 dimer is 1.896 Å, and the distance between second-nearest O atoms is 2.437 Å, which is quite large compared to the O_2 dimer bond length. Thus one can expect that O_2 dimer forms σ and π molecular orbitals, which may play an important role in this system.

First, we perform calculations of the electronic structures using the DFT and DFT+DMFT method on the reported crystal structure of FeO_2 at 76 GPa. Figure 2(a) displays spectral functions from standard DFT calculation and DFT+DMFT calculation. In DFT+DMFT, we use an on-site Coulomb
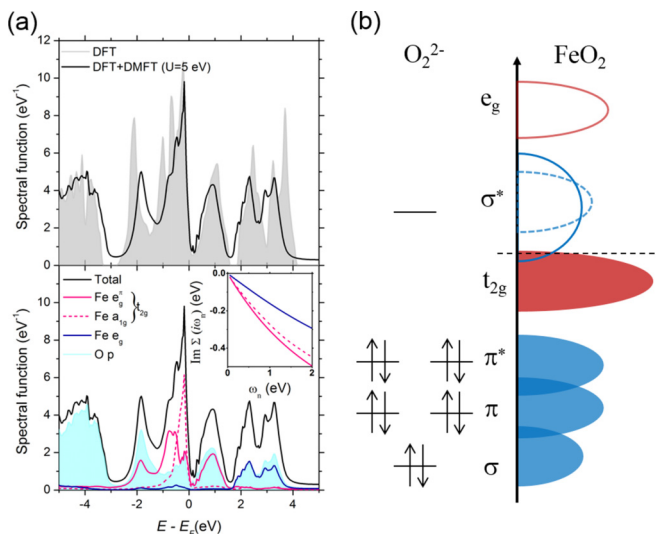

FIG. 2. (a) Calculated spectral functions from standard DFT and DFT+DMFT ($U = 5$ eV, $J = 0.8$ eV, and $T = 200$ K) (upper panel) and orbital-resolved spectra from DFT+DMFT (lower panel). Inset shows imaginary part of electron self-energy on Matsubara frequency for each orbital. (b) Molecular orbital diagram of O_2^{2-} and schematic DOS of FeO_2. FeO_2 shows metallic behavior due to the broad O_2 σ^* band.

interaction $U = 5$ eV and a Hund coupling constant $J = 0.8$ eV. The spectral function of DFT+DMFT calculation is slightly renormalized from that of DFT calculation, which indicates that the correlation effect on the spectral function is very weak. The inset figure displays the imaginary part of electron self-energy on Matsubara frequency. Fe t_{2g} and e_g bands show mass enhancement of m^*/m of ~ 1.4 and ~ 1.2, respectively.

The spectral function in Fig. 2(a) clearly shows metallic behavior of FeO_2 at 76 GPa. Its e_g orbitals, which are well above Fermi level by ~ 2–4 eV, are fully empty, which leads to the low spin states, resulting in the corresponding local magnetic moment being zero. The t_{2g} bands split into an e_g^π doublet and an a_{1g} singlet due to distorted FeO_6 octahedron symmetry [9]. The overall bandwidth of the t_{2g} bands is around 2 eV and is located just below Fermi level, while the broad σ^* band of the O_2 dimer is just above the Fermi level, with the bandwidth of around 3 eV. Thus, the O_2 dimer takes two electrons from a nearest Fe atom, forming hyperoxide O_2^{2-}, and electrons are occupied up to π^* antibonding orbitals. A schematic of the electronic structures is shown in Fig. 2(b) based on the molecular orbital energy diagram. The π and σ bands from the O_2 dimer are completely filled, making broad bands well below the Fermi level. In the calculated electronic structures of FeO_2 at 76 GPa, there is an overlap between the t_{2g} band and the σ^* band due to their large bandwidth, and it forms a metallic ground state. We also perform DFT+DMFT calculations at a given crystal structure with bigger U value, but the band gap does not open due to the broad σ^* band at the Fermi level, as shown in Fig. 2. This implies that it is governed by the O_2 dimer σ^* band rather than the Mott physics with partially filled d orbitals.

Note that the bandwidth and the position of the σ^* band is subject sensitively to the bond length of the O_2 dimer. In Fig. 2(b), a schematic DOS shows a possible insulating ground state by reducing the bandwidth of σ^* bands. We speculate that this system may be located near the metal-insulator transition point, which is controlled by the O_2 dimer. In the following, we investigate further the effect of pressure on the crystal structure and its effect on the electronic properties.

We investigate the change of the electronic structures with respect to volume. Before optimizing the crystal structure at several volumes, we check whether standard DFT captures the experimental structure at 76 GPa properly. However, standard DFT calculation overestimates O_2 dimer bond length by ~ 0.2 Å, which originates from underestimated Fe-O bond length. At a given volume, O_2 dimer bond length and Fe-O distance are determined by the oxygen position parameter a in the unit cell. As the position parameter a increases, the Fe-O distance increases slowly while the O_2 dimer bond length decreases rapidly (Supplemental Material, Sec. II [22]). When the Fe-O distance increases by 0.05 Å, the O_2 dimer bond length decreases by ~ 0.5 Å. So the O_2 dimer bond length is easily affected by small changes of the Fe-O bond length. DFT calculation predicts the Fe-O distance to be shorter than that of the experimental report, and thus the corresponding O_2 dimer bond length is estimated to be longer. It is expected that the standard DFT calculation cannot describe a localized picture of Fe d orbitals properly and overestimates the bonding strength between Fe and O.
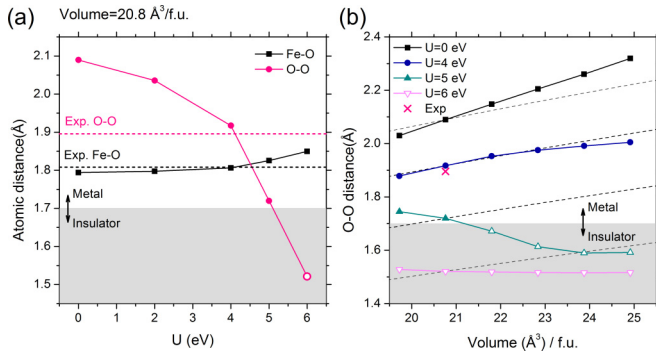
FIG. 3. (a) Variation of Fe-O and O-O distance in experimental volume (20.8 Å^3/f.u.) at 76 GPa with respect to Coulomb interaction energy U. (b) Calculated O$_2$ dimer bond length with respect to volume for several U values from DFT+U calculation. Below critical O$_2$ dimer bond length ($\sim$1.7 Å), it turns into insulator from metal. The filled symbols and open symbols indicate the metallic and insulating states, respectively.

Furthermore, we perform DFT+U calculation to check the change of crystal structure depending on the onsite Coulomb interaction U. We find that the O$_2$ dimer bond length is very sensitively affected by a choice of U value, as shown in Fig. 3(a). Although the change in Fe-O distance, which is directly affected by U, is small, the O$_2$ dimer bond length is rapidly changed as we discussed above. With an increase of U value, the hybridization between O$_2$ p orbitals and Fe t_{2g} bands decreases to make the Fe-O bond length increase. The O$_2$ dimer bond length is affected sensitively by this change and becomes closer to that of the experimental value. This indicates that the correlation effect on Fe d orbitals should be considered to describe properly the crystal structure of FeO$_2$, especially the O$_2$ dimer bond length.

The O$_2$ dimer bond length also affects the electronic structure of FeO$_2$. As O$_2$ dimer bond length decreases, the interaction between the adjacent dimers decreases, making the bandwidth of O$_2$ $\sigma*$ orbitals narrow. Splitting between bonding and antibonding orbitals of O$_2$ dimer increases by pushing up the O$_2$ $\sigma*$ orbitals above the Fermi level, as shown in Fig. 2(b). We notice that O$_2$ $\sigma*$ bands are completely removed from the Fermi level at $U = 6$ eV to make a gap between Fe t_{2g} bands and the O$_2$ $\sigma*$ band. FeO$_2$ eventually turns into an insulator, as described in Fig. 2(b) with a dotted $\sigma*$ band.

We obtain the optimized structures at several volumes with varying U value, as shown in Fig. 3(b). The O$_2$ dimer bond length increases as volume increases with a choice of U value up to 4 eV. However, this trend is reversed at higher U value. It can be understood as a competition between Fe-O bonding strength and the correlation effect of Fe 3d orbitals. Note that a stronger Fe-O bonding strength gives a shorter Fe-O bonding, which results in a longer O$_2$ dimer bond length. The gray dashed reference lines in Fig. 3(b) exhibit a simple O$_2$ dimer bond length change in accordance with volume expansion without atomic position relaxation. When the slope of the O$_2$ dimer bond length with respect to volume is steeper than that of the guided line, the effect of Fe-O bonding strength predominates over the correlation effect. In this case, the O$_2$ dimer bonding becomes weaker with increasing volume at

small U value. Although the O$_2$ dimer bond length keeps increasing at $U = 4$ eV, the slope is smaller than the guided line, which indicates that the formation of O$_2$ dimer becomes preferable at bigger volume. When the U value is larger than 5 eV, the correlation effect becomes more dominant than the Fe-O bonding strength so that the formation of O$_2$ dimer is much preferred. At $U = 5$ eV, Fe d orbitals become too localized to interact with O p orbitals at large volume so that O$_2$ dimer bond length decreases as volume increases. The O$_2$ dimer bond length remains almost constant at $U = 6$ eV, because the interaction between Fe d orbitals and O p orbitals is negligible in that volume range. We already discussed that the tiny change in Fe-O bond, which is induced by the change of U, makes a big difference in O$_2$ dimer bond length, which can affect the electronic structure of FeO$_2$ significantly. Comparison of the O$_2$ dimer bond length between experiment and theory will be a useful test to confirm the importance of the correlation effect. We suggest that exact measurements of O$_2$ dimer bond length with respect to volume can verify which U value is proper for the correct description of this system.

We find that FeO$_2$ turns into an insulator below the critical O$_2$ dimer bond length of about 1.7 Å. MIT is observed at $U = 5$ eV with varying the volume, as shown in Fig. 3(b). It is also observed at constant volume by optimizing the internal atomic position with different U value, as shown in Fig. 3(a).

Figure 4 shows the predicted spectral functions from DFT+U calculations. The Fe d orbital contribution in the O$_2$ $\sigma*$ band, the lowest conduction band, keeps decreasing as the U value increases. Also, the $\sigma*$ band becomes narrower and its position gradually moves up from the Fermi level as the O$_2$ dimer bond length decreases, which lead to large bonding–antibonding splitting. Finally, MIT is observed between volumes 20.8 Å^3 and 21.8 Å^3 at $U = 5$ eV. DFT+DMFT calculations based on the structures obtained with DFT+U ($U = 5$ eV) also show MIT between 20.8 Å^3 and 21.8 Å^3 (see Supplemental Material, Sec. III [22]). It is worth to noticing that the MIT is a band insulator type not a Mott-type, because it is driven by the change of the bandwidths and positions of O$_2$ $\sigma*$ and Fe t_{2g} bands, which are determined by O$_2$ dimer bond length. As we discussed above, the electronic structure is robust only with the change of U values, while the O$_2$ dimer bond length is fixed. Even if an exaggerated U value is used for electronic structure calculation, the insulating state cannot be obtained based on the crystal structure obtained from simple DFT relaxation. On the other hand, simple DFT calculation on the the crystal structure obtained from DFT+U ($U = 5$ eV) also gives an insulating state at large volume because it is a simple band-type insulator determined by O$_2$ dimer bond length (see Supplemental Material, Sec. IV [22]). It is interesting that the correlation effect is very limited directly to the spectral function, but it plays an important role in the MIT through the change of the crystal structure.

It should also be noted that the O$_2$ dimer bond length can be easily tuned by an external condition such as chemical doping and/or oxygen vacancy, which can affect the correlation strength of Fe d orbitals [23]. As we discussed above, a small change of Fe-O bond length affects the O$_2$ dimer bond length significantly. If the Fe-O distance increases only by $\sim$0.02 Å from the experimental distance, it easily turns into an insulator
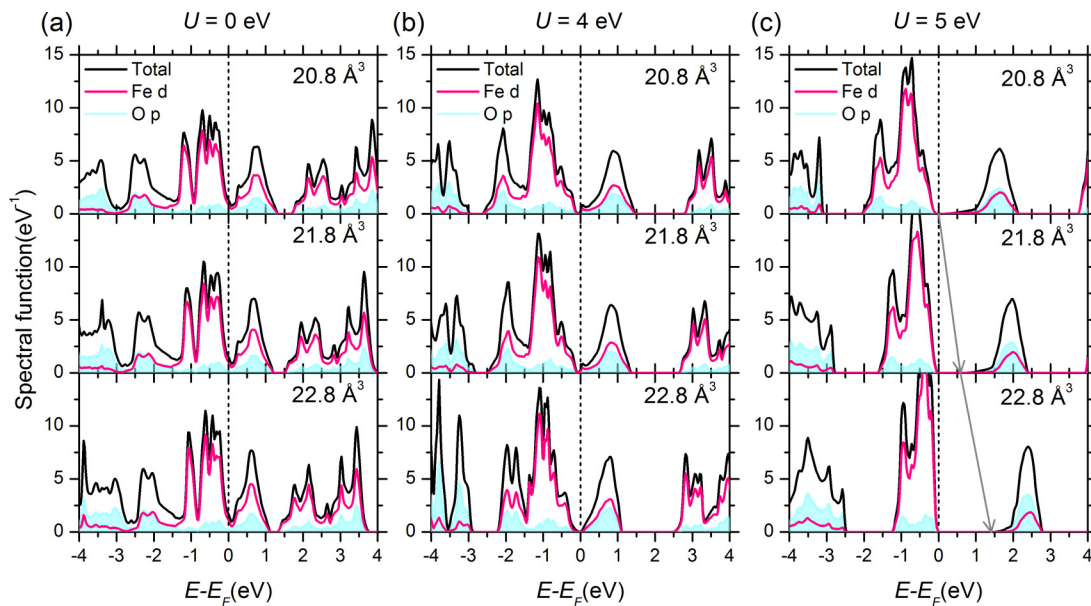
FIG. 4. The spectral functions of relaxed structure from DFT+U calculation for (a) $U = 0$ eV, (b) $U = 4$ eV, and (c) $U = 5$ eV. The metal-insulator transition is observed within the structures relaxed with $U = 5$ eV.

due to the sensitive change in O_2 dimer distance, as shown in Fig. 3(a), so the electronic properties can be significantly changed by external conditions.

A stable phase of FeO_2 was observed under deep lower mantle conditions with very high pressure and temperature. To simulate the mantle condition, we also investigate the electronic structure of FeO_2 at high temperature up to 2000 K. When DFT+DMFT calculations are performed on the experimental structure at 76 GPa, electronic structures of FeO_2 exhibit a metallic nature at any temperature of our interest. So, we expect that the O_2 dimer bond length is the most important parameter to determine the physical properties under the lower mantle condition. On the other hand, the magnetism also might be an important parameter to the electronic structures at very low temperature, although FeS_2, which has the same crystal structure, is reported to be a nonmagnetic compound for whole temperature range [5–8].

Using DFT and DFT+DMFT calculation, we investigated the electronic structure and structural properties of FeO_2 under high pressure. Calculated spectral function from DFT+DMFT indicates that the correlation effect on the electronic structure of a given crystal structure is small. However, the correlation effect of Fe d orbitals plays an important role in determining the crystal structure of FeO_2. Specifically, O_2 dimer bond length is sensitively affected by the choice of U value. We find that FeO_2 shows MIT at the critical O_2 dimer bond length of $\sim$1.7 Å, which can be induced by changing the U value or volume. We suggest that the correlation effect should be considered to describe correct structural and electronic properties of FeO_2.

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