The Role of On-site Coulomb Interaction on Electronic Structure of FeO

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Abstract: We report our density functional theory (DFT) calculation on FeO in order to describe its electronic properties. FeO exhibits an antiferromagnetic at the ground state with cubic structure and Néel temperature T_N = 198 K. The DFT calculation is as powerful tool to describe electronic properties but known to be failed to describe the electronic properties of system with strong on-site Coulomb interaction such as FeO. Here, we introduce the Hubbard correction, U, in order to take into account the on-site Coulomb interaction of d-electron at Fe ion. Hybridization of $3d$-electron of Fe and $2p$-electron of O splits the energy level to become upper Hubbard band (UHB) and low Hubbard band (LHB). Based on the DFT+U calculation, the band structure of FeO shows an insulator feature with the band gap of 1.65 eV, and its density of state (DOS) implies that this gap arise from splitting $3d$-electron of Fe.

Keywords: DFT; FeO; Hubbard; On-site Coulomb Interaction; Energy gap

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I. INTRODUCTION

The transition metal oxide (TMO) has been actively studied due to the rich of physical phenomena. Iron oxide (FeO) is one of the TMO system which is interesting due to the wide application and can be synthesized from the large availability of natural iron sand in Indonesia [1]. FeO can be used as pigments color in paint, as catalysts [2], and as micro-nutrient in fertilizers. High grade FeO have been widely used in electrical and electronic products.

FeO has a cubic structure which exhibits an antiferromagnetic ordering with a Néel temperature (T_N) of around 200 K. The magneto-crystalline distortion below T_N produces a rhombohedral structure [3]. The theoretical study of its electronic structure was done to support the experimental results. Based on band theory, if all band are full or empty then the system will be in the insulating state. On the other hand, if band is partially occupied, the system will be in the metallic state [4]. The strong correlation effect which caused by strong hybridization of Cu $3d$-orbital and $2p$-orbital play crucial role in electronic properties of FeO [5].

The density functional theory (DFT) calculation is a very successful theory to solve the Schrödinger equation for many body system [6, 7]. The DFT is well known to be able to predict energy level for metallic system [8] but failed to treat the correlation effect in TMO. The local density approximation (LDA) and generalized gradient approximation (GGA) scheme is not able to treat the on-site Coulomb interaction of d-electron [4] which raised from correlation effect. Here, we study the electronic structure by taking into account the on-site Coulomb interaction among d-electrons and analyze its effect on band structure and density of states (DOS)of FeO by adding the Hubbard U (DFT+U). The calculation results is compared with the available experimental data.

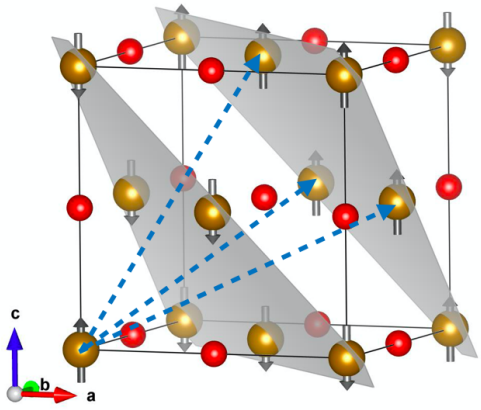

FIG. 1: The crystal and magnetic structure of FeO. The small red circle represents oxygen (O) atom, and the large brown circle illustrates iron (Fe) atom having antiferromagnetic spin ordering.

II. METHOD

The DFT calculation was done on the basis plane wave and pseudopotential approximation as implemented in Quantum Espresso [9]. The Perdew, Burke, Ernzerhof (PBE) approach of GGA exchange correlation function was used for all calculations [10]. The crystal structure of FeO is shown in the Fig. 1 with type II antiferromagnetic ordering. The ferromagnetic ordering in (111) plane can be reduced into rhombohedral symmetry which is used in our calculations with a =

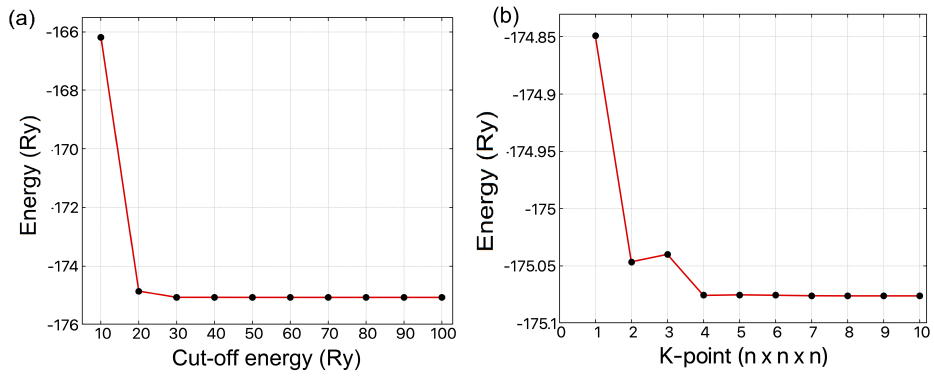

FIG. 2: (a) the total energy as function of cut-off energy of plane wave, and (b) the total energy as function of k-point mess.

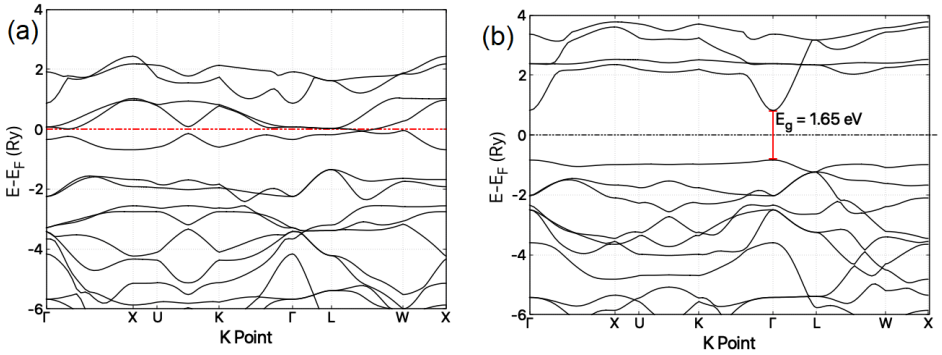

FIG. 3: Band structure of FeO: (a) Without Hubbard U correction, (b) With Hubbard U = 4.3 eV.

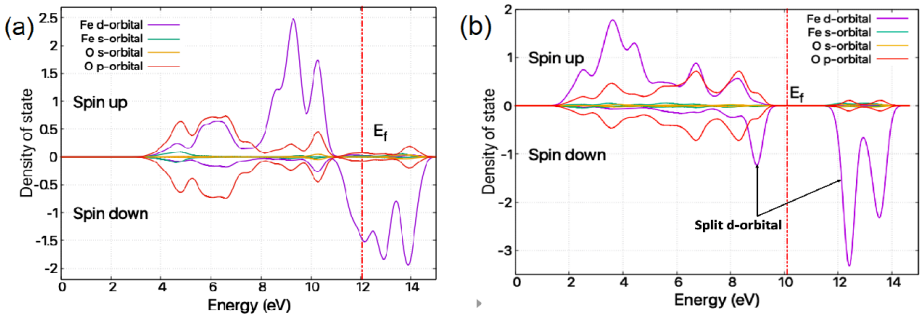

FIG. 4: Partial density of state (DOS) of FeO: (a) Without Hubbard U correction, (b) With Hubbard U = 4.3 eV.

8.1900 Å.

First we calculated the total energy as a function of cut-off energy of plane wave and k-point mesh, where the results are show in Fig. 2(a) and 2(b), respectively. The total energy starts to converge from 30 Ry, while that of k-points mesh is at 4x4x4. We then used those values for the structural optimization and DOS and band structure calculations. The crystal structure is chosen to be rhombohedral with an antiferomagnetic ordering of Fe-ion. The band structure and DOS were calculated with and without on-site Coulomb interaction (U parameter). For the calculation with U, the U value was set to be 4.3 eV for Fe ion [11].

III. RESULTS AND DISCUSSION

Fig. 3(a) and 4(a) show the band structure and DOS of FeO with ignoring the on-site Coulomb interaction (U = 0). The Fermi energy is 11.6426 eV, and several band across this Fermi energy. This result suggests that FeO is metal in the ground state. On the other hand, the experimental results showed that FeO is insulator with energy gap $\approx$ 2.4 eV [12]. The d-electron splits into e_g at higher energy and t_{2g} at the lower energy state due to the octahedral crystal fields [13]. The hopping of unpaired electron in t_{2g} is prevented by on-site Coulomb interactions which make FeO become insulator.

The antiferromagnetic ordering below Néel temperature T_N = 198 K is also observed in this system [14].

We then included Hubbard U parameter in our DFT calculations to take into account the on-site Coulomb interactions. The U value is set to be 4.3 eV. We can observed the clear direct energy gap $\approx$ 1.65 eV at the Γ point as shown in the Fig. 3(b). This results indicate that in addition to the crystal field, the on-site coulomb interaction plays the key role to describe the electronic properties of FeO with opening the gap around Fermi level by splitting into upper Hubbard band (UHB) and lower Hubbard band (LHB) [15]. Further detail, the projected DOS as shown in the Fig. 4(b) indicates the splitting occurs in the d-orbital of Fe. The underestimate of the band gap from DFT+U from the experimental data is caused by fact that DFT+U is carried out in the 0 K, while the experimental results were obtained below Néel temperature.

IV. SUMMARY

We study the role of the on-site Coulomb interaction parameter, U, in electronic structure of FeO by DFT+U Calculations. The value of U = 4.3 eV gives result that FeO is insulator in the ground state with E_{g} = 1.65 eV. The gap arises from the splitting of the $3d$-orbital of Fe due to the hybridization with $2p$-orbital of O. This results consistent with the previous experimental results.

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