First-Principles Study of Iron Oxide Polytypes: Comparison of GGA+U and Hybrid Functional Method

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ABSTRACT: Iron oxides are materials of wide interest that exhibit diverse electric, magnetic, optical, and catalytic properties; therefore, many studies to gain complete understanding of their polytypic phase boundary have been pursued. However, first-principles investigations of iron oxides using conventional density functional theory (DFT) calculations often yield a gross error due to the strong electron correlation that is poorly described within (semi) local approximations. This limitation often can be overcome using either the Hubbard correction (DFT+U) or a hybrid functional DFT method. Here, we investigate the diverse polytypic phases of iron monoxide (FeO) by comparing DFT+U and the hybrid-functional method (particularly B3PW91). We found that both methods show reasonable agreement in predicting the properties of the experimentally observed phases (B1, B8, iB8, and B2). However, the DFT+U method overestimates the equilibrium volume of B1 phase and predicts the experimentally undiscovered B4 phases to be nearly as stable as the naturally abundant B1 phase. In addition, B3PW91 predicts a local Jahn–Teller distortion pattern of the B1 phase that is more similar than that predicted by DFT+U to the result of a reported low-temperature neutron diffraction experiment. Using B3PW91, which is considered more convincing, we further discuss that there is no clear phase boundary between the monoclinic and rhombohedral B1 phases under compression but that the compression gradually reduces the local anisotropy to yield a rhombohedral-like phase, which agrees with previous experimental diffraction results. We expect that our comprehensive study demonstrates the virtue of using hybrid-functional DFT methods, particularly in exploring various known and unknown polytypic phases of transition-metal oxides.

1. INTRODUCTION
Iron oxides are one of the most valuable and stable materials utilized in many types of applications, such as pigments, soil- or groundwater-remediation processes, catalysts, etc. In particular, ferrous oxide (FeO), often referred to as wustite, is a major component of the Earth and is abundant in the lower mantle as a solid solution with magnesiowustite (MgO).1 As a result, many studies on the structural characteristics and the phase behavior of FeO have been performed to elucidate the chemophysical properties of the outer core.2–11

Depending on the pressure (P) and temperature (T), FeO exhibits the following complicated polymorphic phase transitions:

- FeO forms a diamagnetic cubic NaCl-type structure (B1) under ambient conditions.12
- FeO forms an antiferromagnetic NiAs-type structure (B8 or iB8) at ~290 GPa and 2400 K13–15
- FeO forms a metallic CaCl-type structure (B2) at ~300 GPa and 4100 K, which resembles the P–T conditions of the Earth’s core.16

On the other hand, the possibility of symmetry breaking of the cubic B1 structure during the magnetic transition has been suggested. When the P–T conditions are below the Néel temperature, e.g., at a low temperature (<198 K17) at ambient pressure or at a high pressure (> ~12 GPa) at room temperature, the magnetic phase of FeO is transformed from a paramagnetic state into an antiferromagnetic state, which may accompany a structural phase transition among the cubic, rhombohedral, and monoclinic phases.18 However, the detailed experimental characterizations of various iron oxide phases under high-temperature and high-pressure conditions are limited, and the control of oxygen partial vacancies (yielding FeO1−x) over the experimental samples introduces additional complications in determining the phase boundaries among the complex polymorphs.

Density functional theory (DFT) is the practical method of choice for accurate quantum mechanics, and it provides the capability of exploring the structural and electronic properties of naturally occurring or hypothetical and/or undiscovered materials based on first principles without experimental uncertainties. Although (semi) local approximation in the
exchange-correlation energy functional of DFT introduces a nonphysical electron self-interaction energy,\textsuperscript{19} much of the success of this theory is attributable to the cancellation of this self-interaction energy between the various calculations that are combined into a property. However, predicting the relative energies of compounds with very different electronic environments is significantly more challenging, as this error cancellation cannot be relied upon. Particularly, the self-interaction error (SIE) is particularly large in the d or f orbitals; thus, the DFT results of transition-metal oxides are usually unacceptably erroneous. For example, semiconducting or insulating materials are mispredicted as metallic.

One method to mitigate the SIE is the Hubbard correction method (often termed the LDA/GGA+U method),\textsuperscript{20} which selectively adds an energy correction to localized electron states. The Hubbard correction method sometimes correctly reproduces the relative energetics, magnetic ground states, and electronic structure for systems in which generalized gradient approximation (GGA) fails,\textsuperscript{21,22} however, the choice of the Hubbard parameter (usually termed the U parameter) is often arbitrary, although it drastically affects the physical properties. As an alternative, the exact exchange energy is included in the conventional DFT energy by mixing the Hartree–Fock (HF) Hamiltonian to the Kohn–Sham Hamiltonian; this is referred to as a hybrid-functional method. Because HF includes no SIE in the calculation of the total energy (but the correlation energy is completely ignored), hybrid-functional methods often balance errors in HF and in DFT to improve the atomization energies, structures, vibrational frequencies, and band gaps.\textsuperscript{23,24} For hybrid-functional methods, the mixing ratio of HF ($\alpha$) is the adjustable free parameter as the U parameter of Hubbard correction methods, and many previous studies have discussed that $\alpha \sim 0.2$–0.3 is the optimal choice to reproduce the experimental band gaps.\textsuperscript{25,26}

In this work, we examined various polymorphic phases of FeO using three different DFT methods: (1) a conventional DFT method based on the GGA using the functional form of Perdew, Burke, and Enzerhof (PBE);\textsuperscript{27} (2) a Hubbard correction method applied to GGA (i.e., PBE+U);\textsuperscript{28} and (3) the B3PW91 hybrid-functional theory method in which Becke’s three parameters were used to mix HF and GGA Hamiltonians.\textsuperscript{29} By comparing the relative energetics, cell parameters, and equations of state, we discuss the reliability of the various DFT methods, and we further address the pressure-induced symmetry breaking of the B1 phase.

2. COMPUTATIONAL DETAILS

We investigated six different polymorphic phases of iron oxide: (1) the most stable B1 phase (for which the mineral name is wüstite; Figure 1a); (2) the high-pressure B2 phase (Figure 1b); the intermediate phases (3) B8 and (4) iB8 (panels c and d of Figure 1, respectively); and the hypothetical phases (5) B3 and (6) B4 (panels e and f of Figure 1, respectively). Superexchange interactions exist for the B1, B8, and iB8 phases because an oxygen atom is linearly bridging two iron atoms, leading those magnetic states to be antiferromagnetic. To properly assign the antiferromagnetic spin directions for the B1 structure along the (111) direction, we transformed the cubic unit cell (consisting of eight atoms in the cell) into a hexagonal supercell as shown in Figure S1 in Supporting Information (consisting of 12 atoms in a cell), and we also used hexagonal cells for B3 and B4 structures. For the B2, B3, and B4 structures, we simply assumed that the magnetic state was ferromagnetic because the strength of the interspin coupling is expected to be low because of the lack of a superexchange interaction, and thereby, the energy differences among the various magnetic states are expected to be marginal.

We performed DFT calculations based on GGA. We used the widely using Vienna ab initio simulation package (VASP)\textsuperscript{30} with a PBE exchange correlation functional, planewave basis sets, and pseudopotential descriptions using the projected augmented wave method.\textsuperscript{31} We also used the GGA+U method. We calibrated the Hubbard parameter to reproduce the experimental band gap energy of B1 of 2.4 eV,\textsuperscript{32,33} leading to $U$ = $U_{\text{eff}}$ = 4.2 eV (see Figure S2 in Supporting Information), which is comparable to the choices of $U_{\text{eff}}$ in previous theoretical works.\textsuperscript{34–37} We set the kinetic energy cutoff ($E_{\text{cut}}$) at 700 eV (the $E_{\text{cut}}$ convergence test is shown in Figure S3a in Supporting Information).

Additionally, we performed DFT calculations with a hybrid functional, using the B3PW91 method. For the B3PW91 calculations, because of the computational efficiency of using the linearly combined atomic orbital (LCAO) basis set for exact exchange calculations, we used the CRYSTAL program\textsuperscript{38} coupled with the triple-$\zeta$ level of Gaussian basis sets (pob-TZVP).\textsuperscript{39}

For the sampling of reciprocal space, we used a $15 \times 15 \times 3$ mesh for B1, a $15 \times 15 \times 5$ mesh for B2, a $15 \times 15 \times 5$ mesh for B3, and $15 \times 15 \times 9$ meshes for B4, B8, and iB8 (the $k$-
space grid convergence test is shown in Figure S3b in Supporting Information). For the hexagonal cells of B1, B3, B4, B8, and iB8, we used a Γ-centered mesh and a Monkhorst mesh for the cubic cells of B2.

3. RESULTS AND DISCUSSION

Figure 2 shows the equations of state for the various polymorphic phases of FeO computed using the PBE (Figure 2a), PBE+U (where $U-J$ is denoted as $U_{\text{eff}} = 4.2$ eV; Figure 2b), and B3PW91 methods (Figure 2c), respectively. We denote the relative energies of the various phases with respect to the energy of the B1 phase at the equilibrium density. From the PBE results, the iB8 structure is more stable than the B1 structure, although B1 is the most stable phase under ambient pressure conditions. PBE+U predicts a very stable B4 phase that is even comparable to B1. B3PW91 predicts the most reasonable energetics among various phases.

Inclusion of the Hubbard U correction slightly ameliorates the problem in the relative energetics; the ground state predicted from PBE+U is the B1 phase, which is consistent with the experimental observations. We note that a similar tendency has been reported in the literature, in which the DFT energetics based on a local density approximation (LDA) and that based on LDA+U were compared. However, the energy of the B4 phase is still separated by only 0.09 eV/FeO-pair compared to the energy of the B1 phase, although the B4 phase, to our knowledge, has never yet been experimentally observed.

In contrast, we find that the relative energetics from the B3PW91 method explains all of the experimental observations reasonably as follows:

1. The B1 phase is the ground state, and all of the other phases are less stable than B1 by at least >0.2 eV/FeO-pair.
2. The B2 phase is much less stable than the B1 phase (by 1.04 eV/FeO-pair), and its equilibrium density is the largest. This explains the phase transition to the B2 phase at a very high pressure.
3. Both the B3 and B4 phases are significantly destabilized by ∼1 eV/FeO-pair compared to the B1 phase. Because the equilibrium densities of the B3 and B4 phases are smaller than that of B1, it is difficult to experimentally achieve these phases using previous compression experiments.
4. The B8 and iB8 phases have similar stabilities, and both are destabilized by ∼0.2 eV/FeO-pair. The equilibrium of the iB8 phase is slightly higher than that of B1, which explains the phase transition of B1 to iB8 at the intermediate pressure regime.

Thus, it is concluded that the B3PW91 method is the most reliable in predicting the relative energetic orderings among the various polymorphic phases.

We compared the pressure−volume ($P−V$) curves from the PBE, PBE+U, and B3PW91 methods to the $P−V$ curve from the experiment in Figure 3. We note that only the B1 phase and its variants are relevant to this pressure regime (<25 GPa).
We find that the B3PW91 calculations result in the best agreement with the experimental values in the low-pressure regime (<20 GPa), whereas PBE becomes better than B3PW91 in reproducing the experimental $P-V$ curve in the high-pressure regime (>20 GPa). In all pressure regimes, PBE+U predicts significantly expanded volumes. For example, the equilibrium density ($\rho_0$) of the B3PW91 method is 6.024 g/cm$^3$; $\rho_0$ of the PBE method is 6.139 g/cm$^3$, and $\rho_0$ of the PBE+U method is 5.662 g/cm$^3$; and the experimental $\rho_0$ is 6.002 g/cm$^3$ at 300 K and 5.939 g/cm$^3$ at 10 K. This demonstrates that the inclusion of the Hubbard correction expands the cell volume by 7.8% (Figure S4 in Supporting Information), leading the PBE+U method to yield a noticeably low density, although the electronic structure, such as a band gap, becomes more accurate.

We further calculated the bulk modulus ($B_0$) and the derivative of bulk modulus ($B'_0$) of various polymorphic phases as shown in Table S1 in Supporting Information. For B1 phase where the comparison with experimental values is only available, we found that B3PW91 predicts the mechanical properties comparable to the experimental values while PBE+U shows a non-negligible error ($B_0 = 167.5$ GPa and $B'_0 = 3.70$ for B3PW91; $B_0 = 138.8$ GPa and $B'_0 = 4.81$ for PBE+U; $B_0 = 175$ GPa and $B'_0 = 4$ from 300 K experiment$^{15}$).

We further compared the electronic structures, particularly the energy band gaps ($E_g$) predicted from the various DFT methods in Table 1. It is unsurprising that PBE significantly underestimates $E_g$ because of the SIE, leading all polymorphic phases of FeO to be metallic or nearly metallic. The Hubbard U correction modifies the band gaps for the B1, B3, B4, B8, and iB8 phases, yielding $E_g = 2.4$ eV for B1, $E_g = 1.6$ eV for B3 and B4, $E_g = 2.1$ eV for B8, and $E_g = 1.7$ eV for iB8. The exact match of the theoretical $E_g$ for B1 to the experimental value is obvious because we calibrated the $U$ values in that manner (vide supra). On the other hand, the B3PW91 method predicts $E_g = 2.7$ eV for B1, $E_g = 2.5$ eV for B3, $E_g = 2.0$ eV for iB8, which are consistently ~0.3 eV higher than the PBE+U predicted values. We note that the B3PW91 method predicted a slightly higher but still appreciable $E_g$ value for B1 compared to the experimental value. The B2 phases are predicted as metallic by both methods. The most drastic difference was observed in predicting the electronic structure of the B3 and B4 phases; B3PW91 predicts them as metallic, whereas PBE+U predicts them as semiconducting. On the basis of (1) the more reasonable energetics of the B3PW91 method in predicting the relative energetics and equilibrium density$^{43}$ and (2) many previous studies showing the importance of the inclusion of exact exchange for systematic predictions of band gaps,$^{36,44}$ we conclude that the B3PW91 result is more convincing.

Moreover, we closely examined the optimized B1 structures using three different DFT methods, showing the presence of symmetry breaking due to the strong antiferromagnetic superexchange interaction. We symmetrized the optimized structures with a tight tolerance of 0.01−0.08 Å, yielding a rhombohedral structure for the PBE-optimized structure (R$^m_3$) and monoclinic structures for the PBE+U and B3PW91 optimized structures (C2/m). Thus, in a strict sense, it should no longer be termed the B1 phase because its unit cell is no longer cubic; rather, we named it either rB1 for rhombohedral B1 or mB1 for monoclinic B1.

To compare our 0 K DFT results to the experimental data properly, it is necessary to examine the low-temperature experiments performed at least below the Néel temperature of FeO (198 K). From the neutron powder diffraction experiment measured at 10 K in 2002,$^{45}$ Fjellvag et al. determined that the ground state of FeO at ambient pressure is a mB1 structure with C2/m symmetry, which contradicted a previous result that the ground state below the Néel temperature would be an rB1 structure with R$^3m$ symmetry. They further determined that such symmetry breaking perturbs the octahedral environment of iron, resulting in two long (2.165 Å) and four short (2.154 Å) Fe−O bonds. Additional experimental data supporting the presence of the monoclinic ground state of FeO was provided by XRD studies.$^{48}$

These experimental findings are clearly supported by our B3PW91 results. The monoclinic B3PW91-optimized structure consists of iron atoms with two long (2.176 Å) and four short (2.134 Å) Fe−O bonds, whereas the rhombohedral PBE-optimized structure consists of iron atoms with six equivalent Fe−O bonds (2.145 Å), and the monoclinic PBE+U-optimized structure consists of iron atoms with four long (2.242−2.267 Å) and two short (2.077 Å) Fe−O bonds, as summarized in Table 2.

Conventional Jahn–Teller (J−T) distortion explains the origin of the observed symmetry breaking. FeO has high-spin d$^6$ irons (Fe$^{2+}$), and thereby the unevenly occupied t$_{2g}$ orbitals
prefer to elongate two axial bonds out of the six bonds, as shown in Figure 4a. Within the crystalline arrangement, we found that the B3PW91-optimized structure prefers to locate four short bonds in a plane to maximize the superexchange coupling. Overall, this yields two-dimensionally interconnected Fe–O layers connected via the short bonds, and the interlayer is connected via the long bonds, as shown in Figure 4b. This implies that the inclusion of the exact exchange is advantageous in adequately describing the balance of the crystal field splitting effect and the superexchange interaction.

One interesting question remaining in the field is if there will be a phase boundary between the mB1 and the rB1 phases upon compression. Experimentally, hydraulic compression is loaded using pressurized gas; thus, the majority of experimental investigations have been performed at room temperature (RT) for XRD experiments. Under ambient pressure, RT is above the Néel temperature, yielding the cubic phase of FeO because of the lack of antiferromagnetic spin ordering. When pressure is applied, the overlap between the d-orbital of Fe and the p-orbital of O becomes larger, which enhances the superexchange interaction and elevates the Néel temperature. Therefore, researchers have reported a phase transition from the paramagnetic state to the antiferromagnetic state at ∼20 GPa, at which XRD experiments and Mössbauer spectroscopic study claimed that the RT antiferromagnetic state formed at >25 GPa is rhombohedral. Considering that the antiferromagnetic structure under ambient pressure (at low temperature) is monoclinic, there have been many debates on the existence of a monoclinic-to-rhombohedral phase transition during hydraulic compression.

To provide insight into this debate, we analyzed the FeO structures optimized using the B3PW91 method under various isotropic pressure conditions, spanning from 0 GPa to ∼32 GPa. The structural distinctions of the mB1 phase from the rB1 phase, which have been provided as evidence for the existence of the monoclinic phase, are (1) the splitting of the (110) peak of R3m symmetry to the (111) and (020) peaks of C2/m symmetry, (2) the splitting of the (104) peak of R3m symmetry to the (311) and (202) peaks of C2/m symmetry, and (3) the splitting of the (204) peak of R3m symmetry to the (400) and (222) peaks of C2/m symmetry.

Figure 5a,b shows the relevant XRD peaks simulated using the DFT-optimized structures (wavelength, 1.8857 Å). From the in silico hydraulic compression experiment at 0 K, no rhombohedral phase formation has been observed until ∼30 GPa compression. However, the extent of the peak splitting was gradually decreased as the pressure increased; therefore, resolving one peak from the other is expected to be difficult under high-pressure conditions. We think that this has led many previous experimental studies to conclude that the structure is rhombohedral.

Figure 6a,b shows the difference and relative ratio of the bond lengths between the short and long bonds as a function of the pressure. This shows that the monoclinic structure gradually becomes more symmetrized as the pressure is loaded, although it is inadequate to consider that there is a clear phase boundary between the monoclinic and the rhombohedral phases.

**4. CONCLUSION**

We examined several polymorphic phases of FeO using three different, widely used DFT methods: (1) PBE, (2) PBE+U in which a Hubbard U correction parameter is added to correct the self-interaction error, and (3) the hybrid-functional DFT method B3PW91 that includes the exact-exchange contribution.
The application of the Hubbard correction can overcome certain apparent problems of the conventional GGA method, leading the naturally observed phase B1 to be the most stable phase and creating a band gap; however, it simultaneously induces the following additional problems: an overly expanded equilibrium volume for the B1 phase, Jahn–Teller distortion is suppressed as the pressure increases, which gradually transforms the monoclinic phase into the rhombohedral phase with six equivalent-length Fe–O bonds. However, we note that we find no clear phase boundary between the monoclinic and rhombohedral phases.

The phase behavior between the monoclinic (m) and rhombohedral phases of FeO at high pressures was investigated by employing the most reliable B3PW91 method, which predicts reasonable energetic and electronic properties of various FeO phases in general: equations of state comparable to those for the experimental data, reasonable relative energetics among various polymorphic phases and band gap properties, and accurate local structural distortion. Most interestingly, we found that the B3PW91 and PBE+U methods exhibit a drastic difference in predicting the electronic properties of the B3 and B4 phases; the former predicts that it is metallic, whereas the latter predicts it to be a material with a band gap.

By employing the most reliable B3PW91 method, we further investigated the phase behavior between the monoclinic (m) and rhombohedral (r) B1 phase of wüstite upon hydraulic compression. Our DFT study detects no clear phase boundary between the mB1 and rB1 phases, although the mB1 phase acquires greater symmetry during the 0 K compression. We believe that this gradual transformation of the mB1 phase into a rB1-like phase has led previous experimentalists to barely resolve the reduced diffraction peak splitting, leading them to conclude that there is no monoclinic phase below >25 GPa.

We expect that our current study shows the critical importance of including exact exchange in DFT methods, particularly in exploring the structural and electronic properties of unknown phases and materials using first-principles-based methods beyond the empirical Hubbard $U$ corrections.

## Supporting Information

Computational details (Figures S1–S4), partial density of states (Figures S5 and S6), equation of state parameters (Table S1), and orbital occupancies (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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