Metal-insulator and magnetic collapse transitions in FeO at high pressure: predictions of the LDA+U method

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The accuracy of LDA + $U$ total energies is tested by predicting the high pressure behavior of rocksalt-structured FeO, including metal-insulator and magnetic transitions, equation of state, and lattice strain, as functions of the Coulomb repulsion $U$. For $U = 4.6$ eV, 6.0 eV and 8.0 eV, two self-consistent solutions, one with rhombohedral and one with monoclinic electronic symmetry, are found, and for $U = 4.6$ eV the monoclinic solution becomes more stable than the rhombohedral solution at 100 GPa, leading to an insulator-metal transition. With increasing $U$, metallization occurs at higher pressures. Despite the insulator-metal transition, the high-spin magnetic state persists to pressures greater than 300 GPa for $U > 0$. The LDA + $U$ method also gives improved agreement with experiments for ground state properties as compared to LDA and GGA methods.

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FeO is a prototypical transition metal oxide (TMO) and Mott insulator, and the high-pressure behavior of FeO will help discriminate among possible theoretical models for correlated magnetic insulators. Non-stoichiometric FeO (wüstite) is also important in geophysics as an end-member of the magnesiowüstite solid solution, a major phase in the Earth’s lower mantle. At ambient conditions, FeO has a rhombohedrally-strained B1 structure, which transforms to the cubic rocksalt structure above the Néel temperature, 198 K, where the spins disorder. At high temperatures and pressures (P>120 GPa and T>1000 K), FeO transforms from the rhombohedrally-strained B1 phase to a NiAs (b8)-anti-NiAs (ib8) superlattice. At room temperature, the cubic B1 phase transforms to the strained B1 structure at ∼ 15 GPa. The B1 structure is maintained up to at least 140 GPa at room temperature. We concentrate here on the behavior of FeO in the strained B1 structure to generate predictions that can be compared with experiments on the compression of a Mott insulator with this prototypical structure. Recent experiments are also in conflict regarding the high pressure magnetic behavior of strained B1 FeO. Mössbauer spectroscopy has shown a high- to low-spin transition at 90 GPa, but x-ray spectroscopy indicates that the high-spin state is preserved at least to 140 GPa. Although at low pressure FeO contains ∼ 4-8% Fe vacancies, we consider only stoichiometric FeO, since non-stoichiometry is less important in FeO at high pressure.

The LDA and GGA predict an antiferromagnetic, metallic ground state for FeO, but it is actually an insulator with an optical band gap of 2.4 eV. This arises from the underestimation of the local Coulomb repulsion in LDA. The LDA + $U$ method is designed to remedy this by applying an orbital-dependent potential between correlated states, and then subtracting a double-counting correction. LDA + $U$ has been well tested at zero pressure, and gives insulating behavior in reasonable agreement with experiment. Dynamical mean field theory (DMFT) also includes an energy-dependent self-energy, but is not yet tractable for the large number of computations necessary to understand the behavior of FeO under a wide range of compressions, strains, and symmetries. Indications are that DMFT should be even more reliable, though slower, than LDA + $U$.

We use the rotationally invariant LDA + $U$ formalism within the full-potential, linear muffin-tin orbital (FP-LMTO) method, and the GGA for the local exchange-correlation functional. In agreement with previous LDA and GGA calculations carried out with the linearized augmented plane wave (LAPW) method, the LMTO calculation gives a high- to low-spin transition at 124 GPa with $\Delta V = 9.7$% for the cubic lattice with the GGA ($U = 0$). When the rhombohedral strain is optimized, however, GGA gives a continuous loss of Fe magnetic moment from 80 GPa to ∼ 250 GPa, also in agreement with LAPW.

$U$ may be determined from constrained density-functional computations, the most careful study giving $U = 4.6$ eV. We also consider $U = 6.0$ eV and 8.0 eV since many estimates are higher than that found by Pickett et al. Non-overlapping muffin-tin sphere radii were fixed at 1.8 bohr for Fe and 1.5 bohr for O. The value of $J$, 0.89 eV, is also determined by the constrained LDA.
We find two self-consistent insulating solutions for both unstrained (cubic) and strained lattices. The first is obtained by constraining the electronic symmetry to have the same rhombohedral symmetry as the lattice, and the second by reducing the imposed electronic symmetry to monoclinic and then perturbing the d-orbital occupation matrix. In the rhombohedral case, the spin-down $a_{1g}$ orbital has one electron; the other four spin-down orbitals (two $e_g$ pairs) are empty and therefore raised in energy, forming an insulating gap. The monoclinic solution was found by starting with the d-orbital occupancies from the GGA calculation on cubic FeO. In this solution, the $e_g$ state (lower in energy than $a_{1g}$ in the cubic lattice) splits into two singly-degenerate states ($e_g \rightarrow a_g + b_g$), and the $a_{1g}$ state becomes $a_g$. The $e_g$-derived states are lowest in energy, and therefore one of these ($a_g$) is stabilized, while the companion ($b_g$) state is destabilized along with the other $a_g$ (formerly $a_{1g}$) orbital.

For the unstrained lattice at zero pressure, $U = 4.6$ eV produces a band gap of 0.48 eV for the rhombohedral solution and 0.13 eV for the monoclinic solution. Strained FeO has smaller gaps (0.23 eV and 0.08 eV respectively), reflecting the increase in band width with rhombohedral strain. We find that the band gap at zero pressure is between Fe 3d and Fe 4s states, in agreement with optical spectroscopy, which shows weak absorptions beginning at about 0.5 eV, assigned to Fe 3d/O 2p→Fe 4s transitions, and much stronger absorptions beginning at 2.4 eV, assigned to Fe 3d/O 2p→Fe 3d transitions \[22, 25\]. Our calculations show somewhat less Fe 3d-Fe 2p mixing at the top of the valence band as compared to the spectroscopic results. For the upper and lower Fe 3d (Mott-Hubbard) splitting in the unstrained lattice, we find that $U = 4.6$ eV gives 1.9 eV for the rhombohedral solution and 1.2 eV for the monoclinic solution, while for unstrained FeO, we obtain gaps of 1.5 eV and 1.1 eV, respectively. The character of the band gap is constant for all values of $U$, and increases approximately 0.25 eV for each 1 eV increase in $U$. The Fe 3d-Fe 3d splitting increases by approximately 0.8 eV for each 1 eV increase in $U$, in accordance with the model proposed by Zaanen, Sawatsky and Allen [23]. With $U = 6$ eV, we obtain a Fe 3d-Fe 3d gap of 2.40 eV, in agreement with optical experiments.

At low pressures, the calculated ground state of FeO has rhombohedral symmetry and a rhombohedral strain that increases with pressure for all values of $U$, in agreement with experiment, as shown in Fig. 1. We find a weak first-order transition from rhombohedral to monoclinic symmetry at approximately 110 GPa when $U = 4.6$ eV, with a very small volume change ($\Delta V = 0.3\%$). The minority-spin states for the monoclinic solutions are much broader ($\sim 0.6$ Ry) than for the rhombohedral solutions ($\sim 0.3$ Ry), and increased hybridization results in a favoring of the monoclinic solution over the rhombohedral at high pressure. The existence of two self-consistent solutions with strain-dependent energies explains the results of Mazin and Anisimov [24], who found the low-symmetry state for a highly strained lattice along with the high-symmetry state for the unstrained lattice, and considered this an anomaly of the LDA + $U$ method.

In the ground state, rhombohedral solution for strained FeO, the band gap closes at approximately 180 GPa with $U = 4.6$ eV, a compression of 38% (Fig. 2). The strained monoclinic solution, however, becomes stable at 110 GPa (Fig. 1a; the band gap has already closed in this solution). For all cases, we find that the band gap initially increases before decreasing with pressure in the expected manner, similar to what was seen in NiO [14]. Since the band gap is Fe 3d-Fe 4s in character, increasing pressure causes the Fe 4s states (unaffected by the application of $U$) to be raised in energy, leading to an initial increase in the band gap with pressure. At higher pressures, the Fe 4s states rise in energy above the minority-spin 3d states; band broadening then becomes dominant, and the band gap begins to narrow. Higher values of $U$ cause the gap to close at higher pressure, and increase the pressure of the rhombohedral-monoclinic transition.

The effect of pressure on $U$ is not known. $U$ is thought to be rather pressure independent, being an atomic prop-
FIG. 2: Band gaps as a function of pressure for different LDA + U solutions: (a) $U = 4.6$ eV, (b) $U = 6.0$ eV, (c) $U = 8.0$ eV. Squares, unstrained rhombohedral; circles, strained rhombohedral; down triangles, unstrained monoclinic; down triangles, strained monoclinic.

property, but screening of $U$ might increase with pressure. If so, that would reduce the transition pressures. Furthermore, if screening increases significantly in the metallic state, a dramatic drop in $U$ at metallization could help to precipitate a magnetic collapse transition coincident with or close to the insulator-metal transition. Both Anderson model simulations [26] and dynamical mean field theory [27, 28] show the growth of a quasiparticle peak at the Fermi level with increasing pressure prior to the overlap of spin-up and spin-down states, suggesting that $U$ decreases with pressure but does not become negligible. We do not find a high- to low-spin transition with $U \geq 4.6$ eV up to 250 GPa.

Without spin-orbit coupling, our moments at zero pressure (3.41-3.49 $\mu_B$ for $U = 4.6$-8.0 eV) are slightly higher than experiment (3.32$\mu_B$) [29], as expected with LDA + $U$. Previous work has suggested that spin-orbit coupling is also important in FeO [30, 31], but an orbital moment at Fe$^{2+}$ would increase the discrepancy with experiment. In the absence of spin-orbit coupling and for $U = 0$, the rhombohedral strain in FeO splits the spin-down $t_{2g}$ states with $a_{1g}$ below $e_g$, and the effect of $U$ does not induce an orbital moment. If we begin with the higher-energy LDA+U solution with $e_g$ below $a_{1g}$ and then turn on the spin-orbit coupling, we do obtain a converged solution with an orbital moment of 0.56 $\mu_B$ using $U = 4.6$ eV, essentially in agreement with the result of Ref. [30], which gave an orbital moment of 0.88 $\mu_B$ for $U = 8.0$ eV. However, we find this solution to be $\sim 10$ mRy higher in energy than the solution without an orbital moment, so our computations do not support a large orbital moment in FeO.

We find that the LDA + $U$ treatment gives more accurate structural properties than does the GGA; the equation of state and strain predicted by LDA+U are in good agreement with experiment (Table 1). Also very encouraging is the excellent agreement with experiment obtained for the rhombohedral strain and its pressure dependence using $U = 4.6$ eV (Fig. 3). Our ground state structure with optimized strain gives $\alpha = 58.6^\circ$; the value extrapolated from experimental strain as a function of vacancy concentration suggests $\alpha = 58.4^\circ$ for stoichiometric FeO [3]. Larger values of $U$ also result in improved agreement with experiment as compared to GGA, but not nearly as satisfactory as the results obtained with $U = 4.6$ eV. This suggests that the observed rhombohedral strain and its value with increasing pressure are also strongly dependent upon electron correlation.

The present results represent the first comprehensive study of the applicability of the LDA+U method at pressures above 100 GPa. An upper bound of 110 GPa is derived for the proposed transition from a rhombohedral strained B1 structure to a monoclinic structure at high pressure, which is coincident with the transition from an insulating to a metallic state. No high- to low-spin transition in the magnetic moment at high pressure is predicted with this model, although a strong dependence of $U$ on pressure or metallicity could precipitate such a transition. Conductivity experiments on FeO at high pressure should help to clarify the picture presented here, particularly with respect to the variation of the band gap with pressure. Since many models can give insulating states for FeO at zero pressure, high pressure behavior will be a good testing ground for this and other theories of transition metal oxides.

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| $K_0$ (GPa) | 182 | 158 | 189 | 187 | 193 | 193 | 153 |
| $K''_0$ | 3.88 | 3.05 | 4.49 | 4.30 | 4.08 | 3.72 | 5.55 |
| $V_0$ ($A^3$) | 19.91 | 19.64 | 19.83 | 19.93 | 19.86 | 19.91 | 19.97 |
| $E_0$ (Ry) | -2.154 | -2.174 | -1.856 | -1.854 | -1.859 | -1.856 |

TABLE I: Equation of state parameters for the universal (Vinet) equation of state [2] for the high-spin states of FeO obtained with the GGA and the LDA+U methods for cubic and rhombohedral strained lattices compared with experiment [3]. For LDA+U, $U = 4.6$ eV, $J = 0.89$ eV, R, rhombohedral symmetry; M, monoclinic symmetry. Volumes correspond to one formula unit of FeO. A constant 5390 Ry was added to total energies.
of FeO available prior to publication.

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