

Structure, metal-insulator transitions, and magnetic properties of FeO at high pressures

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ABSTRACT

The high-pressure behavior of rocksalt-structured FeO has been investigated using the LDA + U method, a first-principles computational technique that allows treatment of correlated electrons with strong localized repulsions. Within the local density approximation (LDA) FeO is predicted to be a metal, but with LDA + U , an insulating state is obtained at zero pressure. Electronic and magnetic behavior, the equation of state, and lattice strain are determined for three values of the Coulomb repulsion U . We find two self-consistent solutions, one with rhombohedral and one with monoclinic electronic symmetry. For $U = 4.6$ eV, the monoclinic solution becomes more stable than the rhombohedral solution at 110 GPa, leading to an insulator-metal transition; with increasing U , metallization occurs at higher pressures. Results from the LDA + U calculation suggest that the high-spin magnetic state should persist to pressures greater than 300 GPa. The method gives improved agreement with experiments for ground state properties as compared to LDA and GGA methods that do not explicitly include a local Coulomb repulsion.

INTRODUCTION

Almost all minerals containing magnesium accommodate significant ferrous iron in solid solution. Although first-principles theoretical methods have been very successful in understanding and predicting properties of iron-free systems (Bukowinski 1994; Cohen 1999; Stixrude et al. 2000), the situation for iron-bearing oxides and silicates, which are critical for an accurate description of mantle mineralogy, has been less encouraging. Here we use the LDA + U method to study stoichiometric wüstite, FeO, a prototypical Mott insulator (Mott 1974), which is the simplest iron-bearing oxide, and an end-member to magnesiowüstite, thought to be the second most abundant mineral in the Earth's lower mantle. We know that the LDA + U method properly predicts a band gap in FeO and other transition metal oxides (Anisimov et al. 1991; Dudarev et al. 1998), but the accuracy of other predictions made using the LDA + U method is not known because it has not yet been thoroughly tested except at low pressure, and in cases where the correct answer was already determined experimentally. Here we test the LDA + U formalism by investigating the high-pressure behavior of FeO. Subsequent experiments will prove whether or not these predictions are accurate, and whether LDA + U is reliable as a general predictive tool for iron- and other transition metal ion-bearing minerals.

At ambient pressure and low temperature, FeO adopts a distorted B1 structure, and transforms to the cubic rocksalt structure above the Néel temperature, 198 K (Willis and Rooksby 1953), where the Fe magnetic moments disorder. The distorted B1 structure has a rhombohedral strain due to the antiferromagnetic ordering of Fe²⁺ moments in hexagonal planes stacked along the [111] direction of the crystal. At high temperatures and pressures ($P > 120$ GPa and $T > 1000$ K), FeO transforms

from the rhombohedrally distorted B1 phase to a NiAs (B8)-anti-NiAs (iB8) superlattice (Fei and Mao 1994; Mazin et al. 1998; Fang et al. 1998; Fang et al. 1999). At room temperature, the cubic B1 phase transforms to the distorted B1 structure at ~15 GPa, and this structure is maintained up to at least 140 GPa (Yagi et al. 1985; Badro et al. 1999). Recent experiments are in conflict regarding the high pressure magnetic behavior of distorted B1 FeO. Results from Mössbauer spectroscopy show a high- to low-spin transition at 90 GPa (Pasternak et al. 1997), but X-ray spectroscopy indicates that the high-spin state is preserved to at least 140 GPa (Badro et al. 1999). Although at low pressure FeO contains ~4–8% Fe vacancies, non-stoichiometry is less important in FeO at high pressures (McCammon 1993), so the use of stoichiometric FeO in modeling its high pressure behavior is justified. The recent report of a rhombohedral-to-monoclinic phase transition at ambient pressure and low temperature in FeO (Fjellvåg et al. 2002) suggests that a monoclinic modification may also be stable at high pressure.

Computational methods based on density functional theory (DFT; Hohenberg and Kohn 1964; Kohn and Sham 1965) and employing the local density approximation (LDA; see Lundqvist and March 1987 for a review) and generalized gradient approximation (GGA; Perdew 1991; Perdew et al. 1996) predict an antiferromagnetic, metallic ground state for FeO, whereas it is actually an insulator with an optical band gap of 2.4 eV (Bowen et al. 1975). This discrepancy arises from the fact that the local Coulomb repulsion is not taken explicitly into account in LDA and GGA methods, and is therefore underestimated. The LDA + U method (Anisimov et al. 1991) is designed to remedy this situation through the application of an orbital-dependent potential between correlated states, and then subtracting a correction for the double-counting of these interactions. The LDA + U method has been well tested for ambient

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pressure properties, and gives insulating behavior in reasonable agreement with experiment (Dudarev et al. 1998). Other methods that include local Coulomb repulsions, such as the self-interaction correction method (Svane and Gunnarsson 1990; Szotek et al. 1993) and dynamical mean field theory (Savrasov et al. 2001), can also give insulating behavior for transition metal oxides. These methods are not yet computationally tractable, however, for the large number of computations necessary to understand the behavior of FeO under the wide range of compressions, strains, and symmetries studied in the present work.

The parameter U represents the energetic penalty for doubly occupying a local orbital. The total energy of the system then depends explicitly on orbital occupancies, whereas in DFT, the energy depends explicitly only on the charge density, not the occupancies of each orbital. Interactions between two correlated states are specified by U , which is the Coulomb repulsion, and J , the local exchange interaction. The former is much more important than the latter in determining the properties of transition metal oxides because U is roughly an order of magnitude larger than J . Although U and J can be calculated self-consistently, it is computationally time consuming, and different approximations have given different results. U may also be computed using constrained density-functional calculations (Anisimov et al. 1991 gives $U = 6.8$ eV), in which the energy is computed as a function of orbital occupancy. The most careful study gives $U = 4.6$ eV for FeO (Pickett et al. 1998), but we also considered $U = 6.0$ eV and 8.0 eV in order to investigate a range of values about the most common theoretical estimates. The value of J , 0.89 eV, is also determined in the constrained LDA + U calculation (Anisimov et al. 1991) and is close to the atomic value, 1.23 eV; small changes in J in this range do not affect the results significantly.

The effect of pressure on U is not known. Since it is an atomic property, U is thought to be rather independent of pressure, but as interatomic distances decrease with pressure and the overlap of charge densities increases, the effective Coulomb repulsion may actually be reduced (screening of the interelectronic repulsion). If so, the transition pressures determined with the LDA + U method would therefore decrease. 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. More advanced treatments of this problem (Georges et al. 1996; McMahan et al. 1998; Chitra and Kotliar 1999) suggest that U decreases with pressure but does not become negligible.

COMPUTATIONAL METHODS

The rotationally invariant LDA + U formalism (Liechtenstein et al. 1995; Anisimov et al. 1997) within the full-potential, linear muffin-tin orbital (FP-LMTO; Savrasov and Savrasov 1992) method is used to calculate the total energies and magnetic moments of both cubic and distorted FeO (static lattice at 0 K) from -10% to 40% compression. In this method, the potential is expanded in terms of spherical harmonics within the atomic spheres and in plane waves in the interstitial region. We use the generalized gradient approximation (GGA; Perdew 1991; Perdew et al. 1996) for the density functional. Non-overlap-

ping muffin-tin sphere radii were fixed at 1.8 bohr for Fe and 1.5 bohr for O, consistent with those applied in an earlier work (Isaak et al. 1993). For the self-consistent calculation of total energies, a triple- κ basis was applied, and the total energies were considered converged when the energy difference between successive iterations was less than 0.01 mRy. The tetrahedron integration method (Monkhorst and Pack 1976; Blöchl et al. 1994) was applied to give 116 k -points in the irreducible wedge of the Brillouin zone of the rhombohedral FeO structure.

Rhombohedral LDA + U solutions arise naturally from the symmetry of the antiferromagnetic rocksalt structure, but it is also possible to explore lower-symmetry solutions by reducing the imposed symmetry of the electronic wavefunction to monoclinic and then perturbing the d -orbital occupation matrix. Thus we investigated the behavior of high-symmetry and low-symmetry solutions for each structure and at each volume, for each of the three values of U . The six volumes studied ranged from 302 bohr³ (44.8 Å³) to 165 bohr³ (24.4 Å³) corresponding to pressures of -20 GPa to 250 GPa for the ground state.

RESULTS AND DISCUSSION

In agreement with previous LDA and GGA calculations carried out with the linearized augmented plane wave (LAPW) method (Issak et al. 1993; Cohen et al. 1997; Cohen et al. 1998), the FP-LMTO calculation gives a high- to low-spin transition at 124 GPa with $\Delta V = -9.7\%$ for the cubic lattice with LDA/GGA. When the pressure-dependent, rhombohedral strain is incorporated, however, LDA/GGA gives a continuous loss of Fe magnetic moment from 80 GPa to ~ 250 GPa, also in agreement with LAPW.

With LDA + U , two self-consistent insulating solutions for both undistorted (cubic) and strained lattices are possible. The initial occupancies and the effect of U on each set are illustrated in Figure 1, which shows the occupancy of the spin-down states of d^6 Fe²⁺ in octahedral coordination. There are two ways to form a band gap in B1 FeO. First, it is possible for the a_{1g} orbital to be occupied, so that U pushes this orbital lower in energy. If the e_g pair is lower in energy, then the only way for a gap to open is for the rhombohedral symmetry to be broken, resulting in a solution with monoclinic symmetry. For the rhombohedral solutions, the spin-down a_{1g} orbital has one electron; the other four spin-down orbitals (two e_g pairs) are empty and therefore the action of U increases the energy, and the insulating gap appears. The monoclinic solution is found by starting with the d -orbital occupancies from the self-consistent LDA/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 to $a_g + b_g$), 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 cubic 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. Distorted FeO has smaller gaps, 0.23 eV and 0.08 eV respectively, reflecting the increase in band width with rhombohedral strain. At zero pressure, the band gap lies between Fe $3d$ and Fe $4s$ states, in agreement with optical spectroscopy, which shows weak absorptions be-

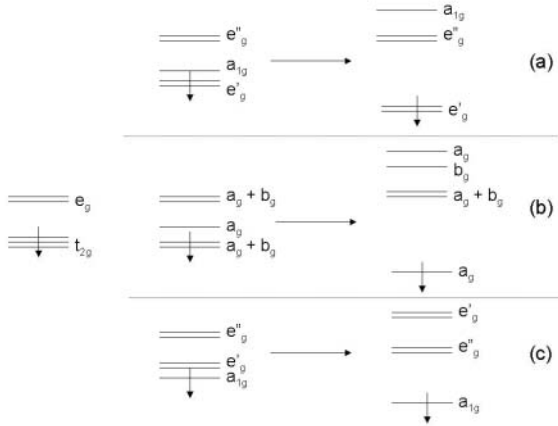


FIGURE 1. Initial occupation and effect of U for generating the monoclinic and rhombohedral LDA + U solutions. For clarity, the five spin-up electrons of Fe^{2+} have been omitted. At left, the spin-down states of purely octahedral Fe^{2+} are shown. (a) In rhombohedral FeO with the cubic lattice, the GGA calculation gives a splitting of the spin-down t_{2g} states with e_g' below a_{1g} . The effect of U is to stabilize the lower e_g' state and destabilize a_{1g} . Still, no band gap can be formed while rhombohedral symmetry is maintained. (b) If the rhombohedral symmetry is broken such that only monoclinic symmetry is imposed, a singly degenerate state becomes lowest in energy, and a band gap can form when U is applied. (c) With the equilibrium rhombohedral strain (elongation along [111]), a_{1g} becomes lower than e_g' while rhombohedral symmetry is enforced. The application of U results in the formation of a band gap while the crystal still has rhombohedral symmetry.

ginning at about 0.5 eV, assigned to the Fe $3d/O\ 2p - \text{Fe}\ 4s$ transitions, and much stronger absorptions beginning at 2.4 eV, assigned to the Fe $3d/O\ 2p - \text{Fe}\ 3d$ transitions (Bagus et al. 1977; Balberg and Pinch 1978). For the upper and lower Fe $3d$ (Mott-Hubbard) splitting in the cubic 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 distorted 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 $3d - \text{Fe}\ 3d$ splitting increases approximately 0.8 eV for each 1 eV increase in U , in accordance with the model proposed by Zaanen et al. (1985). With $U = 6$ eV, the calculated Fe $3d - \text{Fe}\ 3d$ band gap is 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 Figure 2. At 110 GPa, a weak first-order transition from rhombohedral to monoclinic symmetry takes place with $U = 4.6$ eV, with a very small volume change ($\Delta V = -0.3\%$). The minority-spin states for the monoclinic solutions are much broader (~ 0.6 Ry) than for the rhombohedral solutions (~ 0.3 Ry), and increased hybridization results in a favoring of the monoclinic solution over the rhombohedral solution at high pressure. The existence of two self-consistent solutions with strain-dependent energies explains the results of Mazin and Anisimov (1997), who found the low-symmetry state for a highly distorted lattice along with the high-symme-

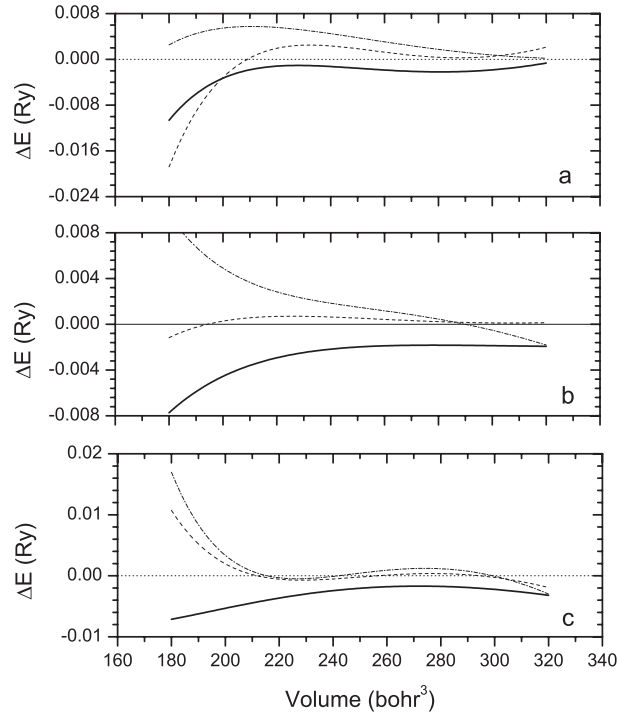


FIGURE 2. Energy difference as a function of volume for LDA+ U solutions for FeO, relative to the undistorted rhombohedral solution. (a) $U = 4.6$ eV, (b) $U = 6.0$ eV, (c) $U = 8.0$ eV. Solid line = distorted rhombohedral; dashed line = distorted monoclinic; dash-dot line = undistorted monoclinic.

try state for the undistorted lattice, and considered this an anomaly of the LDA + U method.

In the ground state, rhombohedral solution for distorted FeO, the band gap closes at approximately 180 GPa with $U = 4.6$ eV, a compression of 38% (Fig. 3). The distorted monoclinic solution, however, becomes stable at 110 GPa (Fig. 2a; the band gap has already closed in this solution at approximately 60 GPa, so that the insulator-metal transition is predicted to occur simultaneously with the symmetry change). Non-hydrostatic stress could also induce the rhombohedral-monoclinic transition, and thus the insulator-metal transition, at lower pressures. For all cases, we find that the band gap initially increases before decreasing with pressure in the expected manner, similar to the behavior observed in NiO (Dudarev et al. 1998). Since the band gap is Fe $3d - \text{Fe}\ 4s$ 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 as expected. Higher values of U cause the gap to close at higher pressure, and increase the pressure of the rhombohedral-monoclinic transition.

In the absence of spin-orbit coupling, our calculated magnetic moments at zero pressure (3.41–3.49 μ_B for $U = 4.6 - 8.0$ eV) are slightly higher than the experimental moments (3.32 μ_B ; Roth 1958), as expected with LDA + U . Previous work has suggested that spin-orbit coupling is also important in stabiliz-

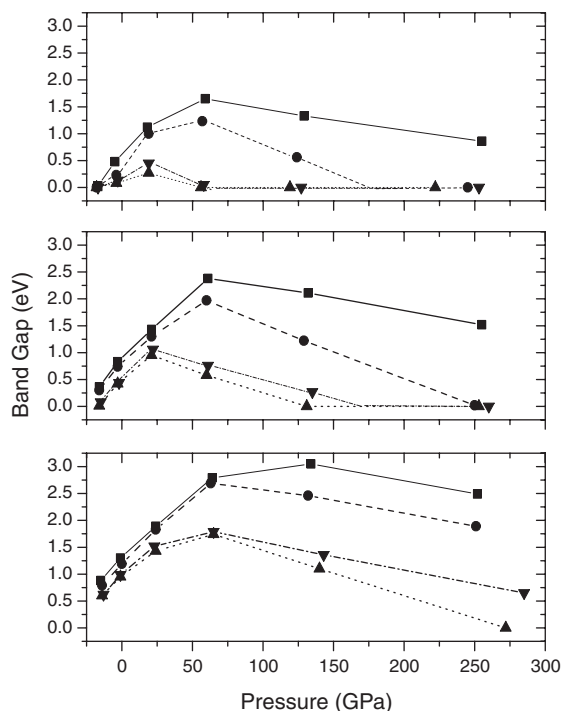


FIGURE 3. Band gaps as a function of pressure for different LDA+ U solutions: (a) $U = 4.6$ eV, (b) $U = 6.0$ eV, (c) $U = 8.0$ eV. Squares = undistorted rhombohedral; circles = distorted rhombohedral; up triangles = undistorted monoclinic; down triangles = distorted monoclinic.

ing strains in FeO (Solovyev et al. 1998a) and CoO (Solovyev et al. 1998b). An orbital moment at Fe^{2+} would, however, increase the discrepancy with experimental results. 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 as in Figure 1, and the effect of U cannot induce an orbital moment, since there can be no spin-orbit coupling in the a_{1g} state ($l = 0$). 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 Solovyev et al. (1998a), which gave an orbital moment of $0.88 \mu_B$ ($U = 8.0$ eV). This particular solution, however, is ~ 10 mRy higher in energy than the solution without an orbital moment, and in our computations this solution is metallic.

For the equation of state, the LDA + U treatment gives properties in good agreement with experiment (Table 1). Even more

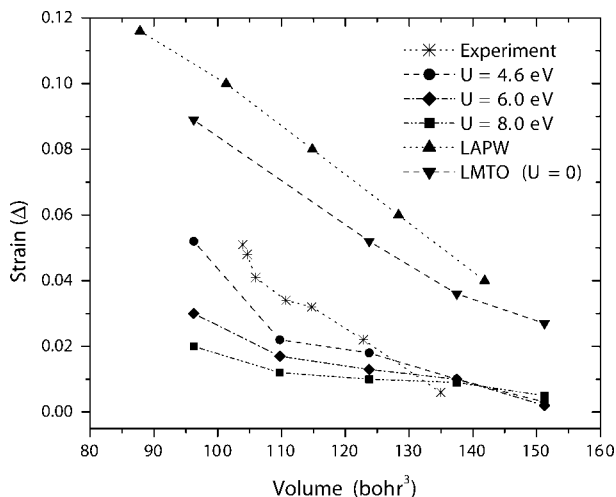


FIGURE 4. Optimized strain for FeO as a function of volume. Up triangles = GGA/LAPW; down triangles = GGA/LMTO; circles = $U = 4.6$ eV; diamonds = $U = 6.0$ eV; squares = $U = 8.0$ eV; stars = experiment.

encouraging, however, is the excellent agreement with experiment obtained for the rhombohedral strain and its pressure dependence using $U = 4.6$ eV (Fig. 4). Our ground state structure with optimized strain gives $\alpha = 58.6^\circ$; the value extrapolated from the experimental strain as a function of vacancy concentration suggests $\alpha = 58.4^\circ$ for stoichiometric FeO (Willis and Rooksby 1953). 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. A pressure 110 GPa is derived for the proposed transition from a rhombohedrally distorted 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. At ambient pressure, values for U in the region of 4-6 eV appear to accurately reproduce the structural and electronic properties of FeO. 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 pres-

TABLE 1. Equation of state parameters for the universal equation of state (Vinet et al. 1987) for the high-spin states of FeO obtained with the LDA/GGA and the LDA + U methods for cubic and rhombohedrally distorted lattices, compared with experimental values (Jacobsen et al. 2002)

	LDA/GGA		LDA + U				Expt.
	cubic	distorted	cubic		distorted		
			R	M	R	M	
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 (\AA^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	

Notes: $U = 4.6$ eV and $J = 0.89$ eV for LDA + U results. R = rhombohedral symmetry; M = monoclinic symmetry. Volumes correspond to one formula unit of FeO. A constant 5390 Ry was added to total energies.

sure. 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. Most importantly, the LDA + U method appears to be a tractable scheme for treating iron- and other transition metal ion-bearing minerals. In order for the LDA + U formalism to be a generally predictive method, however, the computation of U and J in crystalline solids and their behavior with compression and structural changes must be better understood.

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