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 endmember 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). Although at low pressure FeO contains ~4–8% Fe vacancies, non-stoichiometry is less important in FeO at high pressures (McCann et al. 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...