Possible polytypism in FeO at high pressures

IGOR I. MAZIN,* YINGWEI FEI, ROBERT DOWNS,† AND RONALD COHEN

Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Road, N.W., Washington, D.C. 20015, U.S.A.

ABSTRACT

Examination of X-ray diffraction intensities for FeO collected in situ at high pressure and high temperature reveals that the atomic arrangements of FeO in the hexagonal structure are not the same as those in the simple NiAs-type structure (B8) where Fe takes the place of Ni. The observed diffraction intensity can be explained by adding an anti-B8 component (where Fe takes the place of As). Substitution of Fe and O atoms for each other is crystallochemically unique. The exchange of Fe and O positions provides a critical measure of the change in chemical bonding. Our conclusion is consistent with the observed transition of FeO from an ionic bond structure to a strongly covalent and metallic one. First-principles electronic structure computations using the linearized augmented plane wave (LAPW) method with the generalized gradient approximation (GGA) indicate that both B8 and anti-B8 should be antiferromagnetic, but only anti-B8 should be an insulator. The GGA and local density approximation (LDA) incorrectly compute anti-B8 as the ground state structure.

INTRODUCTION

FeO is a major component of the Earth, due to solid solution with magnesiowüstite, believed abundant in the lower mantle and believed to be enriched in the lowermost mantle (D0 region) (Jeanloz and Lay 1993). Important properties of the deep Earth, such as the electrical conductivity, may be controlled by the FeO component. Understanding of FeO is also important for crystal chemistry (Fei 1996). At low pressures there is nearly ideal solubility of Fe2+ for Mg2+ in most minerals, which is surprising because Mg2+ is a simple closed-shell ion, whereas Fe2+ is open shelled and FeO is a Mott insulator, one of a set of exotic transition metal compounds that is insulating due to strong local correlations in electron motions. At high pressures the ionic nature of Fe2+ changes and becomes more covalent (Cohen et al. 1997) and will probably not exchange so easily with Mg2+, which would have important implications for geochemistry, but exactly how this change happens is unclear. Jeanloz and Ahrens (1980) and Knittle and Jeanloz (1986) found a high-pressure, high-temperature phase transition in FeO to a metallic phase, evidence for the change in Fe2+ character at high pressures. Fei and Mao (1994) determined the structure to be based on NiAs from in situ high-pressure, high-temperature X-ray diffraction. However, the observed diffraction intensities were not consistent with the expected values for a single NiAs-type structure.

Understanding FeO is also important for the development of solid-state theory (Mazin and Anisimov 1997 and references therein). Most forms of band theory predict FeO to be a metal, whereas it is observed to be an insulator. Several methods that include effective local coulomb interactions neglected in GGA and LDA such as Hartree-Fock (Mackrodt et al. 1993), SIC (Szotek and Temmerman 1993), or LDA+U (Anisimov et al. 1991; Mazin and Anisimov 1997), or local models (Takahashi and Igarashi 1996) give a band gap, but whether they reproduce the proper high-pressure behavior (a metal-insulator transition) is unknown.

A reexamination of the X-ray diffraction data of FeO and new theoretical computations suggested that the high pressure phase diagram may be more complicated than previously thought. New crystallochemical behavior is suggested, where anions and cations substitute for each other, which has not been seen previously in an oxide.

X-RAY DIFFRACTION INTENSITIES

At ambient pressure FeO assumes the cubic rocksalt (B1) structure, which can be viewed as two interpenetrating face-centered cubic (fcc) sublattices of Fe and O. Another useful visualization of this structure is one of close-packed planes stacked in the [111] direction, with the stacking sequence being, in traditional crystallographic notation, AbCaBcAbCaBc, where lower case letters stand for planes of Fe atoms and upper case letters for planes of O atoms. At low temperature, FeO displays a rhombohedral distortion (rhombohedral angle $\alpha < 60^\circ$),