Magnetic phase diagram of FeO at high pressure

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Abstract. FeO is an insulator with anti-ferromagnetic (AFM) spin ordering at ambient pressure. At increased external pressure, the Néel temperature of FeO first increases at the pressure below 40 GPa. Experiments predict that the AFM ordering will collapse above 80 GPa, but the mechanism of the high pressure magnetic collapse is still unknown. Using the combination of density functional theory and dynamical mean-field theory (DFT+DMFT), the nature of the magnetic collapse of FeO is examined and its magnetic phase diagram up to 180 GPa is discussed.

1. Introduction

The electrical and magnetic properties of FeO at high pressure attracts long lasting attention. FeO is the endmember to magnesiowüstite, the second most abundant materials in Earth’s mantle. FeO has cubic rock salt structure (B1) at ambient pressure [1]. As external pressure is increased, it first transferred to rhombohedrally distorted (rB1) structure at about 17 GPa and room temperature [2, 3], next to the B8 structure as pressure is further increased [4, 5, 6, 7]. At ambient condition, FeO is an insulator. At high pressure and temperature, it has been proved both theoretically and experimentally there is an insulator to metal transition [8]. At ambient pressure and below 200 K [9], the magnetic moments of iron in FeO ordered ferromagnetically in planes perpendicular to [111] direction, but ordered antiferromagnetically between adjacent planes. As pressure is increased, the Néel temperature $T_N$ increases linearly at pressure below 40 GPa [10, 11]. At higher pressure (P>80 GPa), the magnetism of FeO collapse, whereas the mechanism of such collapse is in debating. Mössbauer spectroscopy experiment by Pasternak et al. suggests such magnetic collapse results from high spin to low spin transition (HS-LS) in iron atom and FeO is in LS state at P>80 GPa [12]. But later x-ray emission spectroscopy experiment by Badro et al. suggests the collapse of magnetism comes from antiferromagnetism to paramagnetism (AFM-PM) transition [13]. Badro et al. proposed an arch shape Néel temperature as a function of pressure, which peaks at around 50 GPa and the magnetic moments is finite up to 143 GPa. Such discrepancy calls for a theoretical proof. But the known numerical researches on the Néel temperature of FeO are mostly limited to the low pressure region [14]. Due to underestimation of strong correlations among d-electrons of iron, DFT fails to give out insulate FeO at ambient condition [15]. Here we employ state – of – the – art density functional theory and dynamical mean-field theory (DFT+DMFT) [16, 17] in investigation of magnetic phase diagram of stoichiometric FeO in cubic B1 structure up to 200 GPa and 1000 K. We found two coexisted magnetic transitions in FeO when external pressure is increased, the on-site
HS to LS crossover in iron atom and the ordering (AFM) to non-ordering (PM) transition of iron atoms. The HS state of iron atom crossover to LS state due to the electron transformation from $e_g$ orbitals to $t_{2g}^*$ orbitals and the pairing of these $d$-electrons.

2. Methods

In DFT+DMFT, the crystal problem is treated by solving the DFT equations, whereas the strong correlations are included by solving the DMFT equations. The outputs of DFT with self-energy correction are used to construct impurity levels and hybridization function for the DMFT calculation. After the DMFT iteration is converged, new charge density and self-energy are used for next DFT iteration. Our DFT+DMFT formalism iterates until full convergence of charge, chemical potential and self-energy. The WIEN2K package is used for the DFT part. Hybridization expansion continuous time quantum Monte Carlo (CTQMC) method [18, 19] is used as impurity solver of the DMFT equation to introduce all local electron-electron scattering. More details for the DFT+DMFT method is referenced to [16, 17]. The parameterized Hubbard $U$ of 3d electrons is 8.0 eV, and the corresponding Hund’s $J$ is calculated from the Yukawa screening.

In the paramagnetic region, the bulk magnetic susceptibility has Curie-Weiss behavior

$$\chi_{m}^q \propto \frac{1}{T - T_N}$$

as the temperature is decreasing, and diverges at the Néel temperature $T = T_N$. In order to derive the bulk magnetic susceptibility from magnetic susceptibility on the DMFT impurity site, we calculated the magnetic vertex function from Bethe-Salpeter equation, which connects the bulk magnetic susceptibility with the impurity magnetic susceptibility.

$$\frac{1}{\chi_{m,i}} - \frac{1}{\chi_{m,q}} = \Gamma_m = \frac{1}{\chi_{m,q}} - \frac{1}{\chi_{m,q}}$$

in which $i$ is impurity index, $q$ is moment, $m$ indicates the magnetic susceptibility. Due to numerical efficiency, we truncated number of Fermionic frequency in our CTQMC measurements of the impurity magnetic susceptibility and in derivation of bulk magnetic susceptibility. We use bare magnetic susceptibility in real frequency to recover the lost part due to truncation of Fermionic frequency.

3. Results

![Figure 1: Magnetic moment of iron atom in FeO as a function of volume at temperature from 300 K to 1000 K. The magnetic moment of iron decreases as lattice volume is decreased, and the process of decrement is enhanced at lower temperature.](image1)

![Figure 2: Electron occupancy on $e_g$ and $t_{2g}$ orbitals of iron atom in FeO at 300 K and 1000 K. As lattice volume is decreased, electrons on $e_g$ orbitals transfer to $t_{2g}$ orbitals. At lower temperature, the process of electron transfer is enhanced.](image2)
In Fig. 1, the magnetic moment $M = g\sqrt{\langle S^2 \rangle}$ of iron in FeO is plotted as a function of lattice volume at temperatures from 300 K to 1000 K. As volume is compressed, magnetic moment of FeO gradually decreases. When temperature is decreased, the magnetic moment versus volume curves get steeper in the region of decrement. The magnetic moment versus volume curves converge at $T<300$ K. It indicates there is HS-LS transition in FeO as lattice volume is decreased, and the HS-LS transition is a crossover. The magnetic moments and the corresponding HS-LS transition in transition metal compounds usually result from partitioning and pairing of their d-electrons. This scenario is presented in Fig. 2. At $V=540$ bohr$^3$, there are about 4 electrons on $t_{2g}$ orbitals and about 2 electrons on $e_g$ orbitals. In atomic electron configuration, 4 up spins and 2 down spins give out atomic magnetic moment of $4\mu_B$. As volume is decreased from 500 bohr$^3$ to 360 bohr$^3$, electrons on $e_g$ orbitals gradually transfer to $t_{2g}$ orbitals. At 300 bohr$^3$, there is no electrons on $e_g$ orbitals. The pairing of all 6 electrons on $t_{2g}$ orbitals leads to the LS state. The speed of electron transfer is enhanced as temperature is decreased. The electron transfer from $e_g$ orbitals to $t_{2g}$ orbitals results from shifts of density of state (DOS) from $e_g$ orbitals to $t_{2g}$ orbitals, as shown in Fig. 3. In Fig. 3a, there are finite DOS on both $e_g$ orbitals and $t_{2g}$ orbitals above and below the Fermi level. The Fermi level falls in the gaps of $e_g$ orbitals and $t_{2g}$ orbitals, which indicates FeO is both Mott insulator and charge transfer insulator. The insulator state of FeO in our numerical calculation at the ambient condition is consistent with experiment results. In contrast, although in Fig. 3b FeO is still an insulator at 300 bohr$^3$, the DOS of $e_g$ orbitals is zero below the Fermi level and the DOS of $t_{2g}$ is zero above the Fermi level. There is no DOS available on $e_g$ orbitals for electrons to occupy. All $d$-electrons are pushed to $t_{2g}$ orbitals. FeO is no longer a Mott insulator at 300 bohr$^3$.

Figure 3: Density of states (DOS) on $e_g$ and $t_{2g}$ orbitals of iron atom in FeO at 300 K, (a) 540 bohr$^3$ (b) 420 bohr$^3$ (c) 300 bohr$^3$. As volume is decreased, DOS on $e_g$ orbitals transfers to $t_{2g}$ orbital, until at 300 bohr$^3$ there is no DOS below the Fermi level on $e_g$ orbitals. FeO is always an insulator at all volumes.

Inverse bulk magnetic susceptibility $\chi_m^{-1}$ at $q = (\pi,\pi,\pi)$ as a function of temperature at various volumes in the paramagnetic region is plotted in Fig. 4. Since the bulk magnetic susceptibility $\chi_m(q = (\pi,\pi,\pi), T)$ behaves as $1/(T - T_N)$ in the paramagnetic region, which diverges at $T = T_N$, inverse of the bulk magnetic susceptibility $\chi_m^{-1}(q = (\pi,\pi,\pi), T)$ is linear with temperature. When we extrapolate the linear fit of $\chi_m^{-1}(q = (\pi,\pi,\pi), T)$ as a function of decreased temperature, the Néel temperature $T_N$ is derived at the temperature where the linear fit crosses the temperature-axis. The derived Néel temperature at each volume is presented in the legend of Fig. 4. The Néel temperature first increase as volume is compressed (or the pressure is increased); it peaks at 380 bohr$^3$ and then decrease at smaller volumes (or at higher pressures).

To summarize, we have find there are two magnetic transitions in FeO at increased pressure: a HS-LS transition as well as a AFM-PM transition. At above 80 GPa, the magnetic moment
of iron atom in FeO is nonzero. Our derived Néel temperature first increase then decrease with increased pressure. These results are consistent with previous experiment on FeO [20] and theoretical [21, 22] results of magnesiowstite.

3.1. Acknowledgments
This research used the NSF Extreme Science and Engineering Discovery Environment (XSEDE) supercomputer Stampede as well as the supercomputer Mw in Geophysical Laboratory, Carnegie Institution of Washington.

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