Phase transitions and spin-state of iron in FeO at the conditions of Earth’s deep interior

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Abstract

Iron-bearing oxides undergo a series of pressure-induced electronic, spin and structural transitions that can cause seismic anomalies and dynamic instabilities in Earth’s mantle and outer core. We employ x-ray diffraction and x-ray emission spectroscopy along with state-of-the-art density functional plus dynamical mean-field theory (DFT+DMFT) to characterize the electronic structure and spin states, and crystal-structural properties of wüstite (Fe_{1-x}O) – a basic oxide component of Earth’s interior – at high pressure-temperature conditions up to 140 GPa and 2100 K. We find that FeO exhibits complex polymorphism under pressure, with abnormal compression behavior associated with electron-spin and crystallographic phase transitions, and resulting in a substantial change of bulk modulus. Our results reveal the existence of a high-pressure phase characterized by a metallic high-spin state of iron at about the pressure-temperature conditions of Earth’s core-mantle boundary. The presence of high-spin metallic iron near the base of the mantle can significantly influence the geophysical and geochemical properties of Earth’s deep interior.

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Iron monoxide, wüstite (Fe$_{1-x}$O), is among the most representative of compounds making up the terrestrial planets: as an electrically insulating oxide, it is akin to the constituents of rocky mantles, yet it can also be a metallic alloy, such as comprises planetary cores [1–3]. Because it is likely a major component of Earth’s core, and may also be present near the mantle-core boundary due to interactions between Earth’s rocky and liquid-metal regions, characterization of wüstite at high pressures and temperatures is fundamental to understanding the nature and evolution of our planet’s deep interior [4–9]. Notably, this one oxide exhibits a richness of condensed-matter phenomena that can significantly influence mantle convection, plume stability and other aspects of planetary internal dynamics, including i) crystal-structural phase transformations and melting; ii) electronic (e.g., insulator-metal) transitions; and iii) spin transitions that affect atomic structure, size and magnetic moments [10, 11]. An end-member of magnesiowüstite [(Mg, Fe)O], the second most abundant mineral of Earth’s mantle, wüstite exhibits spin transitions and other key features of our planet’s most abundant but more complex mineral compound, (Mg,Fe)SiO$_3$ bridgmanite [10].

Wüstite has a rich phase diagram featuring at least five crystallographic phases, from the rock-salt B1 (NaCl) (or low-temperature rhombohedral rB1) to cubic B2 (CsCl) structure [4–9, 12–15]. A Mott-Hubbard insulator with a relatively large band gap of $\sim$2.4 eV at ambient conditions, it is known to undergo a Mott insulator-metal transition under pressure [5, 12–14, 16, 17]. This metallization transition has been claimed to be accompanied by a high-spin to low-spin electronic transition in iron [14, 16, 17]. Contraction of the iron ionic volume by up to $\sim$20-40 percent at the spin transition results in dramatic changes in seismological (density, elasticity) and transport properties (e.g., electrical and thermal conductivity), as well as in chemical partitioning of iron-bearing minerals [10, 11, 18, 19]. Therefore, documenting the electronic state of iron in FeO (and other iron-bearing minerals) is thought to be essential for understanding the structure and evolution of Earth’s lower mantle and core-mantle boundary. However, despite being an archetype for terrestrial planetary materials, FeO is poorly understood, and its phase diagram and electronic properties remain controversial, especially at high pressure and temperatures [5, 9, 12, 17, 20, 22].

To address these gaps in understanding, we examine the phase diagram of FeO using state-of-the-art quantum mechanical calculations, and check the reliability of the calculations by way of experimental measurements at simultaneously high temperatures and pres-
sures \[23\]. More specifically, we use density-functional plus dynamical mean-field theory (DFT+DMFT) \[24–27\], along with x-ray diffraction and x-ray emission spectroscopy, to determine the crystal structures, electronic and spin states of FeO over a wide range of pressures. Our results document the interplay between electron correlation and delocalization (i.e., metallic character) that – along with changes in crystal structure and iron spin-state – makes for rich allotropic behavior and significant variations in elastic properties.

We compute the pressure-temperature phase diagram of FeO at temperatures above 1200 K using DFT+DMFT, taking into account the B1 (NaCl-type), B2 (CsCl-type), B8 (NiAs-type) and inverse B8 (Fe and O sites interchanged from B8) crystal structures (Figs. 1, 2). The effects of electron correlations in the Fe 3\textit{d} shell are described using a Coulomb interaction \(U\) ranging from 7 to 9 eV, as estimated for the different crystallographic phases within constrained DFT \[28, 29\]; also, we take the Hund exchange energy \(J = 0.86\) eV, and account for the thermal contribution to the free energy using the Debye-Grüneisen model \[30\] and local-moments contribution \[31\] (see Supplementary Materials for details). As an example, the phase stability, equation of state and local magnetic moments calculated for a temperature near 1200 K are summarized in Fig. 2.

Our calculations indicate that FeO is a B1-structured Mott insulator at pressures below \(\sim 40-60\) GPa, with a large (\(\sim 2\) eV) energy gap between iron 3\textit{d} states (Fig. 3), in agreement with previous findings \[14, 16, 17\]. Fluctuating atomic-scale magnetic moments of \(\sim 3.6\ \mu_B\) imply a high-spin \(S = 2\) state for the Fe\(^{2+}\) ion, as expected for the 3\textit{d}^6 configuration in an octahedral crystal field (e.g., see Fig. 2 of Ref. \[10\]). Under increased pressure, FeO exhibits electronic transitions, followed by crystal-structural transformations. We find a Mott insulator-metal transition for the B1 phase at about 70 GPa and 1500 K, in accord with past shock-wave and static measurements \[4–8\], and obtain a negative Clapeyron slope for the transition, suggestive of Fermi-liquid behavior and consistent with recent experimental results \[9, 12, 15, 21\]. As the volume change is calculated to be small (\(< 1\)%), even a small (positive) entropy change can explain the temperature-dependence of the metallization transition.

We emphasize that, in contrast to conclusions reached from previous calculations, the insulator-metal transition does not overlap with the high- to low-spin transition of iron. Instead, the spin and metallization transitions appear to be decoupled, and our calculations reveal the existence of a novel high-spin (paramagnetic) metallic state over the \(\sim 40-150\)
GPa pressure range at temperatures between 1500 and 4000 K, with transition to the low-spin state at conditions close to those of the core-mantle boundary (Fig. 1). The spin-state transition in the metallic B1 phase has a positive $P$-$T$ slope, and is accompanied by a collapse in unit-cell volume and increase in bulk modulus of up to 9% and $\sim 48\%$, respectively, at about 110 GPa and 2500 K. These values for property changes are upper bounds, because we neglect intermediate phase transitions in calculating the equation of state of FeO. It is also likely that the spin transition is spread out over a finite pressure range – hence depth interval – in Earth’s mantle, despite the sizeable change of properties involved. The B1 structure remains stable at the high temperatures of Earth’s mantle and outer core, and the high-spin metallic form of this structure is predicted to be stable near core-mantle boundary conditions (Fig. 1).

Below 1500 K, the non-metallic, high-spin B1 phase transforms to the inverse B8 (iB8, anti-NiAs) structure above $\sim 62$ GPa (Fig. 1). We estimate that its volume collapses by $\sim 10.7\%$, with only a slight increase in bulk modulus, from 140 to 143 GPa. The iB8 phase is still in a high-spin state (local moment $\sim 3 \mu_B$ upon compression to $\sim 0.7 V_0$), but the trigonal prismatic coordination of the iron site causes orbital-selective collapse of the local moments [32]. That is, while the Fe $a_{1g}$ states are metallic and show a quasiparticle peak at the Fermi level, a small energy gap remains for the iB8 $e_g$ states pointing between nearest-neighbor oxygens (Fig. 3).

The iB8 phase then transforms to the normal B8 (NiAs) structure above 89 GPa (at $\sim 1200$ K), with a small reduction in unit-cell volume ($\sim 2.1\%$) but a near doubling of the bulk modulus to 274 GPa. The transition involves a collapse of local magnetic moments into a low-spin state ($\sim 0.9 \mu_B$: Fig. 2), and appearance of correlated metallic behavior. The B2 (CsCl) structure, which is stable above 290 GPa at $\sim 1200$ K, is also a low-spin, correlated-electron metal, as indicated by the lack of a band gap in the spectral density and the low value of local moments (Figs. 2, 3).

Our results thus suggest that wüstite, which may appear in the lowermost mantle due to chemical reactions at the core-mantle boundary, is metallic and could produce seismological anomalies caused by spin-state transitions at deep-mantle depths ($\sim 1700$-$2000$ km). Enhanced electrical conductivity due to the presence of metallic FeO would influence heat transfer from Earth’s core into the mantle, as well the temporal evolution of magnetic field lines crossing into the lower mantle. From the perspective of phase stability, it is notable
that the metallization and spin-state transitions are decoupled for the B1 phase of FeO at high temperatures (Fig. 1).

To check these results, and specifically to confirm the existence of the high-spin state in the metallic B1 phase, we used x-ray emission spectroscopy and x-ray diffraction to characterize FeO at 60-140 GPa and temperatures up to 2100 K (Fig. 4). Such a combined experimental study is technically challenging, and has rarely been attempted [23, 33]. Our x-ray spectroscopy was conducted on samples with stoichiometry Fe$_{0.94}$O (see Supplementary Materials for the details) at beamline 13-IDD of the Advanced Photon Source, Argonne National Laboratory. For combined diffraction and spectroscopic measurements at high pressures and temperatures, a x-ray emission spectroscopy system was added to the 13-IDD beamline that includes laser heating for x-ray diffraction with diamond-anvil cells. Our diffraction measurements were performed at a wavelength of $\lambda = 0.4959$ Å with a Mar165 CCD detector. Iron $K_{\beta_{1,3}}$ spectra were collected using an excitation energy of 10.75 keV with a spot size of $\sim 4 \times 4$ µm, and a curved Si 440 analyzer ($a = 5.431$ Å) in a Rowland circle spectrometer geometry having nominal spherical diameter of $\sim 1000$ mm (an Fe wire is used to calibrate the analyzer angle of 66.18°, assuming that the main peak is at 7058 eV). Spectra were collected from 7018 to 7078 eV in $\sim 0.3$ eV steps (1-10 s collection time for each step), with each measurement repeated an even number of times (2-10). At each step the entire region-of-interest on the detector is summed, and the final spectrum is a summation of all repetitions. A sample of siderite FeCO$_3$ at 60 GPa is our low-spin standard [34], and further details are in the Supplementary Materials.

At room temperature, we find the iron to be in the high-spin state up to 74 GPa, with low-spin iron appearing on further compression: the ratio of high- to low-spin iron in FeO drops to about 50% by 110 GPa (Fig. 5). This is in agreement with Mössbauer measurements [18] and recent room-temperature DFT-DMFT calculations [14], but is not entirely consistent with prior x-ray emission work [19]. We attribute this difference to the previous x-ray spectroscopy having probed the sample from the side (through a Be gasket), across the sample’s full pressure distribution, making it difficult to see the disappearance of the $K_{\beta}$ shoulder that is the signature of the low-spin state. We note that FeO is in the distorted (rB1) form of the B1 structure over most of this pressure range [4, 12, 13], with the sluggish spin transition starting in the rB1 phase and being followed by transformation to the B8 phase at room temperature. That is, the electronic-spin and structural transitions are decoupled.
With increasing temperature near 90 GPa, x-ray diffraction shows the presence of the low-temperature rB1 structure up to about 1800 K, and completion of the rB1-to-B1 phase transition – with the iron 100% in the high-spin state – upon heating to 2050 K (Fig. 1). Our experiments do not confirm the previously reported low-spin B1 phase of FeO above ~70 GPa at temperatures above 1300 K [14, 16, 17], but they are in qualitative agreement with our DFT+DMFT calculations. Furthermore, we note the sensitivity of the spin state to changes in the crystal-field splitting of the Fe 3d energy levels across the rB1-B1 phase transformation of FeO.

We thus conclude from both experiment and theory that a novel high-spin B1-type phase of FeO appears at conditions relevant to Earth’s core-mantle boundary. Therefore, if present in this region, as might be expected due to chemical reactions between mantle rock and liquid metal of the core, FeO can contribute to the seismological anomalies of the D” region, and cause lateral variations in heat flow into the base of the mantle (e.g., Ref. [11]).

Our DFT+DMFT results are for crystalline phases, so it is premature to make quantitative predictions about the properties of Earth’s fluid outer core. Nevertheless, the evidence we have found for significant changes in bulk sound velocity (\(\sqrt{K/\rho}\)) across both structural (B8-B2: about -5%) and electronic (HS-LS: about +10%) transitions in metallic FeO raises the possibility of anomalous variations in seismic-wave velocity with depth through the core. Specifically, it may be imprudent to treat the outer core as though it followed the isentropic equation of state of a single phase, because changes in liquid and electronic structures could cause subtle variations in the depth dependence of seismic-wave velocity throughout this region. Our results also prompt further investigation of the electronic states of Earth’s lower-mantle minerals as possible sources of seismic and chemical heterogeneity, as well as thermal instabilities.

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Author contributions

R.N. and I.L. performed the DFT+DMFT calculations and analyzed the results. R.N., A.L., and R.Q.H. performed the DFT theoretical analysis. E.G., J.Y., B.H., V.B.P, V.V.S., and G.Kh.R. designed and setup the experiment, carried out the experiments and analyzed the experimental data. All the authors contributed to the interpretation of the data and to the writing of the final manuscript. I.L., G.Kh.R., and R.J. conceived and supervised the project.

Competing interests

The authors declare that they have no competing interests.
Data and materials availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

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| Phase | $V_0^{HS}$ (a.u.\(^3\)) | $K_{0,T}^{HS}$ (GPa) | $V_0^{LS}$ (a.u.\(^3\)) | $K_{0,T}^{LS}$ (GPa) | $P_{tr}^{HS-LS}$ (GPa) | $\Delta V/V$ (%) |
|-------|------------------|------------------|------------------|------------------|------------------|------------------|
| B1    | 144.1            | 140              | 122.4            | 210              | 73               | 9                |
| B2    | 133.7            | 136              | 110.8            | 256              | 116              | 6                |
| iB8   | 138.1            | 143              | 119.6            | 227              | 62               | 7                |
| B8    | 143.3            | 128              | 114              | 274              | 43               | 13               |

TABLE I: Parameters of the third-order Birch-Murnaghan equation of states of paramagnetic FeO phases, as evaluated from the DFT+DMFT total energy results at an electronic temperature $T = 1160$ K. $V_0$ is volume and $K_{0,T}$ isothermal bulk modulus (subscript zero indicates zero pressure, $P = 0$, and $dK_{0,T}/dP$ is fixed to 4.1).
Supplementary Material

A. Theoretical methods

We calculate the electronic structure, magnetic state, and phase stability of paramagnetic FeO using the DFT+DMFT approach that allows us to determine on the same footing a pressure-induced Mott insulator-metal transition, change in crystal structure, and collapse of local magnetic moments of FeO (DFT+DMFT: density functional plus dynamical mean-field theory) [16, 17, 24–27]. The phase stability is evaluated from total-energy calculations fully self-consistent in charge density, and implemented with plane-wave pseudopotentials [16, 17, 37]. To this end, we have computed the total energy and local moments of all fundamental crystal structures of FeO found at high pressure-temperature conditions: the rock-salt B1 (NaCl), inverse and normal B8 (anti-NiAs and NiAs), and B2 (CsCl) structures as a function of lattice volume. To evaluate the equation of states for each of these phases, the total energy results are fitted to the third-order Birch-Murnaghan equation separately for the high-spin (HS) and low-spin (LS) states. This allows us to determine the pressure evolution of the electronic state and structural changes of FeO upon compression.

The DFT+DMFT method exactly describes the quantum dynamics of the many-electron problem, neglecting non-local effects. It includes the effects of electronic correlations on the electronic structure and lattice of correlated materials, where standard DFT fails to predict reliable results. We start by constructing the effective low-energy O 2p–Fe 3d Hamiltonian \( \hat{H}_{\sigma,\alpha\beta}^{\text{DFT}}(\mathbf{k}) \) using the projection onto Wannier functions to obtain the \( p-d \) Hubbard Hamiltonian (in the density-density approximation)

\[
\hat{H} = \sum_{\mathbf{k},\sigma} \hat{H}_{\sigma,\alpha\beta}^{\text{DFT}}(\mathbf{k}) + \frac{1}{2} \sum_{i,\sigma,\sigma',\alpha\beta} U_{\alpha\beta} \hat{n}_{i,\alpha\sigma} \hat{n}_{i,\beta\sigma'} - \hat{H}_{\text{DC}},
\]

where \( \hat{n}_{i,\sigma\alpha} \) is the occupation number operator for the \( i \)-th Fe site with spin \( \sigma \) and (diagonal) orbital indices \( \alpha \). For this purpose, for the partially filled Fe 3d and O 2p orbitals we construct a basis set of atomic-centered symmetry-constrained Wannier functions using a full energy range spanned by the Fe 3d and O 2p band complex [28, 38, 39]. To solve this realistic many-body problem, we employ a continuous-time hybridization-expansion (segment) quantum Monte-Carlo algorithm [40]. The calculations are performed in the paramagnetic state at temperatures \( T = 1160 \, \text{K}, 2320 \, \text{K}, \) and \( 4640 \, \text{K} \).
The Perdew-Burke-Ernzerhof exchange-correlation functional \[41\] was used for the DFT calculations, with a cut-off energy of 45 Ry for the wave functions and 450 Ry for the charge density. The $k$-space summation is performed on a converged $12 \times 12 \times 12$ grid. To introduce correlation effects in the Fe $3d$ shell, we use the average Coulomb interaction $U = 7$ eV in the B1 and iB8 phases, $U = 9$ eV in the B8 and $U = 8$ eV in the B2 phase of FeO, as estimated by constrained DFT \[28, 29\]. We note that our results suggest the phase diagram of FeO cannot be explained using a single value of the Hubbard $U$ parameter for all the phases. We also note that we use the same Hund’s exchange energy $J = 0.89$ eV for all FeO phases. The Coulomb interaction is treated in the density-density approximation and spin-orbit coupling is neglected in the present calculations. Moreover, the $U$ and $J$ values are assumed to remain constant upon variation of the lattice volume. We employ the fully localized double-counting correction, evaluated from the self-consistently determined local occupations, to account for the electronic interactions already described by DFT, $\hat{H}_{DC} = U(N - \frac{1}{2}) - J(N_\sigma - \frac{1}{2})$, where $N_\sigma$ is the total Fe $3d$ occupation with spin $\sigma$ and $N = N_\uparrow + N_\downarrow$. Here, we employ a fully self-consistent in charge density DFT+DMFT scheme in order to take into account the effect of charge redistribution caused by electronic correlations and electron-lattice coupling. The spectral functions were computed using the maximum entropy method.

Our results for the total-energy phase equilibria of all the fundamental phases of FeO discussed in the paper are summarized in Fig. S1. We computed the evolution of the total energy as a function of volume. Using these results, we evaluate equation of states of FeO by fitting the calculated total energy to the third-order Birch-Murnaghan equations of state separately for the HS and LS regions. This allowed us to determine the phase stability of paramagnetic FeO and to compute the pressure values of the structural phase transformations. The resulting phase diagram of FeO shown in Fig. S1 is obtained by a least square fitting of the phase boundary lines by taking into account the existence of triple points.

In Fig. S2 we present our results for the phase equilibria of paramagnetic FeO evaluated by different band structure methods. The DFT-CPA-DLM calculations have been performed within the exact muffin-tin orbitals technique (EMTO) in conjunction with the coherent approximation (CPA) and the disordered local moment approximation (DLM) \[42\]. The DFT calculations within non-magnetic generalized gradient approximation are depicted by PBE. CPA: DFT within the coherent potential approximation calculations in which the
paramagnetic state of FeO is modeled on the basis of disordered local moment approach. We note that neither PBE nor CPA techniques are able to describe the phase complexity of paramagnetic FeO at high pressures. This implies the importance of correlations effects to determine the electronic properties and phase stability of paramagnetic FeO.

We note that vibrational contributions to the phase equilibria require an evolution of the phonon dispersions as a function of pressure and temperature. The latter is a very challenging problem within DFT+DMFT [43–45]. We therefore employ the so-called Debye-Grüneisen model [30] which allows to estimate the thermal contribution of the lattice degrees of freedom to the free energies. The effects of quasiharmonic contributions are taken in this model by approximate description of the Grüneisen parameter using the Dugdale-McDonald’s formula. It gives a reliable estimate for the evolution of the Poisson ratio, Grüneisen ratio, and Debye temperature as a function of lattice volume. Thereby it becomes possible to make a realistic estimate of the effect of vibrational contributions to the free energy [46]. The effects of local-moment contribution are estimated in accord with Chuang et al. [31] using the relation $\Delta S_{\text{mag}} = R \ln(\sqrt{\langle \mu^2 \rangle} + 1)$, where $\sqrt{\langle \mu^2 \rangle}$ is the instantaneous local moment per iron atom. We note that this relation is approximate, i.e., there is no rigorous theoretical derivation for this equation even in the case of pure metals [31].

We note that the inclusion of the lattice vibrations on the level of the Debye-Grüneisen model does not qualitatively affect the calculated phase diagram of FeO. The transition pressures between the B2, B8, and iB8 phases are modified by less than 8%. It is changed by less than $\sim 16\%$ for the transitions between B1 FeO and other structural phases. The effect of vibrational contributions has the biggest effect for the B1 HS-LS transition, increasing the critical pressure by $\sim 12\%$ at 1160 K and by $\sim 23\%$ at 2320K. This substantial increase leads to a positive Clapeyron slope for the HS-LS B1 phase transition boundary (the phase transition line shifts towards the core-mantle boundary). This behavior is related to remarkably different mechanical properties of the HS and the LS B1 phases. The bulk modulus of the LS B1 phase is substantially higher by about 48% than that for the HS B1 phase at 1160 K. This implies that more rigid phonons destabilize the LS B1 phase as compared to the HS B1 phase.

We show our results for the evolution of the angle-resolved spectral function of paramagnetic FeO under pressure in Fig. S3. At ambient pressure, the B1-type FeO is a Mott insulator with a relatively large Fe d-d energy gap of about 2 eV [14, 16, 17]. The top of the
valence band has a mixed Fe 3d and O 2p character, with a resonant peak in the filled \( t_{2g} \) band located at about -0.4 eV. It can be ascribed to the formation of a Zhang-Rice bound state \[47\]. The energy gap of \( \sim 0.8 \) eV lies between the occupied states with a mixed Fe 3d-O 2p character and empty Fe 4s state which is seen as a broad, parabolic-like band at the \( \Gamma \)-point above the Fermi energy, in agreement with photoemission and optical experiments. In fact, the optical spectroscopy measurements show a weak absorption between 0.5 and 2.0 eV, assigned to the Fe 3d-O 2p to Fe 4s transitions. The strong absorption edge associated with the Fe d-d transitions is found to appear in optical spectroscopy at about 2.4 eV.

Upon compression, the energy gap of B1 FeO is found to gradually decrease. It is followed by a phase transition into the iB8 structure with formation of an orbital-selective Mott insulating state \[32\]. In fact, in the iB8 phase, the Fe \( t_{2g} \) \( (a_{1g} \text{ and } e_{g}^{\pi}) \) states are delocalized (i.e., metallic), while the \( e_{g} \) electrons remain localized (insulating). Furthermore, upon transition into the B8 phase above 89 GPa, our calculations show an entire reconstruction of the electronic structure of FeO associated with the HS-LS state transition. The B8-structured FeO is a correlated metal with an almost completely occupied \( t_{2g} \) \( (a_{1g} \text{ and } e_{g}^{\pi}) \) band, which is located in the vicinity of the Fermi level, and a broad disperse spectral weight originating from the Fe \( e_{g} \) band crossing the Fermi level. Moreover, the Fe \( t_{2g} \) states exhibit a resonant Zhang-Rice bound state \[47\] below the Fermi level, at about -0.15 eV. The O 2p states are shifted to about -8 eV below the Fermi level, and have a moderate contribution near the Fermi level. Upon further compression above 290 GPa, FeO undergoes a phase transition to the B2 phase. We note that this transition is accompanied by a change of coordination from six to eight, resulting in a complete reconstruction of the electronic structure of FeO. Thus, the Fe \( t_{2g} \) states are now less occupied than the Fe \( e_{g} \) orbitals. B2 FeO exhibits a correlated metallic behavior.

**XES and XRD data**

High-pressure x-ray emission spectroscopy (XES) experiments were conducted at beamline 13-IDD, GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS), at the Advanced Photon Source synchrotron (APS), Argonne National Laboratory (ANL). For XES measurements a Pilatus 100K Si detector was held in a fixed position, and the region of interest (ROI) was chosen according to a calibration of the required window as a
function of analyzer angle. We note that due to technical difficulties conducting a simultaneous high-temperature high-pressure in situ XES combined with XRD study there is so far no dedicated beamline with such capabilities. The 13-IDD beamline is designed for high-pressure high-temperature structural studies using a combination of x-ray diffraction (XRD), laser-heating and diamond anvil cells. An additional XES setup was combined with the existing setup in order to perform both XES and XRD measurements at high-pressure and high-temperature conditions.

For each x-ray emission spectrum of the sample at certain $P$-$T$ conditions and for the LS standard we fit a line to the values below 7030 eV and above 7070 eV to obtain a background for subtraction. We then normalize the background-subtracted spectrum to a unit area by integrating:

$$I_{\text{norm}}(E) = I(E)/\int_{7018}^{7065} |I(E)|dE,$$

where $I(E)$ is the observed background-subtracted intensity at energy $E$, and the absolute value is to allow us to fit a straight line and subtract the contribution of the noise. We fit a Gaussian to the main $K_{\beta 1,3}$ peak to determine the shift required for aligning the peak position to the peak of the standard. The integrated absolute difference (IAD) between the sample and the LS standard was calculated as a cumulative sum:

$$IAD = \int_{E_i}^{E_f} |I_{\text{norm}}^{\text{shifted}}(E) - I_{\text{FeCO}_3}^{\text{norm}}(E)|dE,$$

where $E_i \sim$ 7030 eV, just before the satellite peak, and $E_f = 7054$ eV, above which the main contribution to the difference is the shape and intensity of the main peak. A linear fit to the region below $E_i$ was used to remove the contribution of the noise to the IAD. Error estimates were determined by varying the point used for normalization (7065 eV to 7069 eV) and by artificially adding noise to a simulated data set.

X-ray diffraction measurements were performed with a wavelength of $\lambda = 0.4959$ Å and a Mar165 CCD detector. LaB$_6$ was used to calibrate the tilts and position of the detector, which was placed at a distance of $\sim$195 mm from the sample and shifted to the side by $\sim$70 mm.

Diamond anvils with 200 $\mu$m or beveled $150 \times 220 \mu$m culets were used to induce pressure. A beryllium gasket was pre-indentated up to a pressure of 15 GPa and a hole, with diameter
\(\sim 20 \, \mu m\) smaller than the culet was drilled in the center [48]. The hole was filled with a mixture of cubic boron-nitride (cBN) and epoxy and the gasket was recompressed to a pressure of \(\sim 20 \, \text{GPa}\). The cBN gasket is more suitable for reaching higher pressures, and is safer to use in laser-heating experiments. A hole with diameter \(\sim 70 \, \mu m\) was drilled in the center of the cBN+epoxy insert, and the FeO sample, sandwiched between two layers of KCl was placed inside the cavity. The KCl serves as a thermal insulator between the sample and the diamond anvils, as a pressure-transmitting medium and as an additional pressure marker during the diffraction measurements. Diamond Raman edge was used as the primary pressure marker [49]. We used a 90\(^\circ\) geometry, so that only the incoming x-rays pass through a diamond, and the XES signal passes through the low-Z gasket material. The samples were enriched in \(^{57}\Fe\) (95\%), and have stoichiometry \(\text{Fe}_{0.94}\text{O}\) based on the measured lattice parameter [50].

High-temperature is induced using a dual-sided laser-heating system consisting of two IPG 1064 nm lasers [51]. Glassy carbon mirrors with a silver coating are used to reflect the lasers onto the sample. In this case, to avoid absorption of the low energy x-rays by the up-stream optical setup, the mirror was shifted to beyond the line of the x-ray and then tilted accordingly.
FIG. 1: Pressure-temperature phase diagram of paramagnetic FeO evaluated from DFT+DMFT crystal-structural calculations. Our results for the phase equilibria among rock-salt B1 (NaCl), normal and inverse B8 (NiAs and anti-NiAs), and cubic B2 (CsCl) crystal phases are shown, as is the distinction between high-spin (HS) and low-spin (LS) iron. The bold black line indicates the Mott insulator-metal transition, which occurs within the B1 crystal structure and is determined from the $P$-$T$ evolution of the DFT+DMFT spectral function of FeO (Fig. 3). Entropic contributions, as estimated using the Debye-Grüneisen model and local-moments contribution, do not qualitatively affect the calculated phase diagram of FeO, although the effects of vibrational excitations and fluctuating local magnetic moments do influence the spin transition in B1 FeO (purple band showing a positive $P$-$T$ slope with an increase in the HS-LS transition pressure up to $\sim$110 GPa at $\sim$1500 K). The melting curve (dashed black lines) is from previous experimental studies \cite{20}, and the pressures at the core-mantle boundary (CMB) and inner-core boundary (ICB) are indicated at the top, along with inferred temperatures inside Earth (geotherm: gray). Our x-ray emission spectroscopy and x-ray diffraction at pressures near 90 GPa show only the presence of the high-spin B1 phase at $\sim$2000 K and about 67% high-spin Fe in a mixture of rB1 and B1 structures at $\sim$1800 K (red squares).
FIG. 2: Total energy (bottom) and (instantaneous) local magnetic moment $\sqrt{\langle \mu_z^2 \rangle}$ (top) of paramagnetic FeO as a function of volume compression, as evaluated from the DFT+DMFT calculations for different phases at a temperature $T = 1160$ K. Colors indicate the stability ranges of B1 (blue), iB8 (magenta), B8 (red) and B2 (green) structures.
FIG. 3: Partial spectral functions showing the electron-orbital contributions to bonding in different phases of paramagnetic FeO, as calculated by DFT+DMFT at $T = 1160$ K. Contributions from Fe 3$d$ states ($t_{2g}$, or its split $a_{1g}$, $e_{g}^\pi$ components, and $e_{g}$ states) are shown by solid curves, and O 2$p$ states are given by shaded area (cyan). Under pressure, the electronic structure of FeO evolves from that of a Mott insulator (B1 phase with equilibrium volume $V_0$) to an orbital-selective Mott insulating state (iB8, upon compression beyond $\sim 0.7 V_0$), and then to a correlated metal (B8 and B2 phases, beyond $\sim 0.59 V_0$ and $\sim 0.5 V_0$, respectively). The inset shows a Matsubara plot of the imaginary part of the self-energy.
FIG. 4: Representative Fe $K_{\beta}$ x-ray emission spectra collected from FeO at high pressure as a function of temperature. The spectra have been normalized and shifted so that the main peak is centered around 7058 eV. Inset: Integrated absolute difference (IAD) for a few of the collected spectra. The abundance of the high-spin state remains close to 100% up to 74 GPa, and decreases appreciably upon further compression (90 GPa quenched (Q) and 135 GPa room temperature (RT)). We observe complete recovery (with 100% abundance) of the high-spin state, and completion of the rB1-B1 structural transition, upon heating to 2050 K (spectrum at 90 GPa, 2050 K).
FIG. 5: Abundance of the high-spin (HS) state relative to that at zero pressure (subscript zero) at high pressures and either room temperature (RT) or high temperature (HT), as calculated from the IAD values obtained from x-ray emission spectroscopy (squares, triangles and circles represent room-temperature, high-temperature and quenched data, respectively). Colors represent data collected from different sample runs. Note that Ozawa et al. and Mattila et al.’s data were obtained after laser-heating, resulting in a structural transition into the B8 phase [21, 35]. Inset: HS/HS\textsubscript{0} abundance at room temperature (unheated samples), revealing the sluggish spin transition induced by pressure alone. Open magenta and orange squares represent room temperature Mössbauer spectroscopy results obtained by Hamada et al. [36] and Pasternak et al. [18].
FIG. S1: Phase diagram of paramagnetic FeO as obtained from the total-energy DFT+DMFT calculations (with no vibronic and local-moment entropic contributions). The transition pressure values evaluated from EOS are shown by colored squares. Colors indicate the corresponding structural phase transitions (red: B1-to-B1, green: B1-B2, blue: B1-B8, magneta: iB8-B8, orange: B1-iB8, cyne: B8-B2). The phase boundaries are determined by least square fitting of the transition pressures taking into account the existence of triple points. The inferred temperature profile inside Earth (geotherm) is shown in gray. The locations of core-mantle boundary (CMB) and inner-core boundary (ICB) are indicated with arrowheads. The melting phase boundary is taken from experiment [20].
FIG. S2: Phase equilibria of the B1, iB8, B8, and B2 phases of paramagnetic FeO evaluated by different electronic structure methods. PBE: band structure calculations within nonmagnetic generalized gradient approximation. CPA: DFT calculations within the coherent potential approximation implemented with disordered local moment approach [42]. The DFT+DMFT calculations performed at an electronic temperature $T = 1160$ K.
FIG. S3: \( \mathbf{k} \)-resolved spectral function of paramagnetic FeO as calculated by DFT+DMFT at \( T = 1160 \) K. The B1 phase is evaluated for the equilibrium volume \( V_0 \). The iB8, B8, and B2 phases of FeO are computed under compression at \( \sim 0.7, 0.59, \) and \( 0.5 \) \( V_0 \), respectively. The Fe \( 3d \), O \( 2p \), and Fe \( 4s \) orbital contributions are shown.
FIG. S4: Synchrotron XRD data at ∼90 GPa: Before heating (at room temperature), then at 2000 K and then quenched to room temperature (RT). We observe that at 2000 K FeO adopts the rock-salt B1 crystal structure, as the four expected XRD peaks [(111), (200), (220), and (311)] in this range are observed. At RT, both before and after heating, there appears to be a mixture of the B1 and rB1 phases. Due to the experimental limitations (a nearly single-crystal sample with no ability to rotate the sample) there was no possibility to perform accurate peak indexation. We note, however, that the observation of the B1 phase at 2000 K is in complete agreement with our theoretical calculations and previous thorough experiments by Fischer et al. [12, 13]. From the indexed peaks we obtain a unit-cell volume of 59.02(15) Å³, in agreement with the expected 59.1 Å³ interpolated from the EOS reported in Fischer et al. [12, 13].