

# Fe<sub>0.91</sub>O at High Pressure and High Temperature: Normal or Inverse B8 Structure?

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## Introduction

FeO is one of the transition-metal monoxides with the rock salt structure (B1) at ambient conditions, known as a Mott insulator. It has two pressure-induced structural transitions. The higher structural transition in FeO was observed in an externally heated diamond anvil cell (DAC) at 70-100 GPa by energy dispersive x-ray diffraction (XRD) [1]. The high-pressure, high-temperature phase was assigned to the B8 structure ( $P6_3/mmc$ ). On the basis of the same diffraction pattern, Mazin et al. [2] interpreted the diffraction pattern as a stacking of normal B8 structure [Fe at  $(x,y,z) = (0,0,0)$  and O at  $(2/3,1/3,1/4)$ , here denoted as nB8] and inverse B8 structure [Fe at  $(x,y,z) = (2/3,1/3,1/4)$  and O at  $(0,0,0)$ , here denoted as iB8]. Crystal structure is strongly related to other properties. Theoretical calculations have predicted that the nB8 phase is metallic but the iB8 phase is an insulator [2-4]. This phase transition, especially metallization, has strong implications with regard to the properties of the Earth's core (e.g., Reference 5). We conducted synchrotron angle-dispersive XRD experiments with a laser-heated DAC under high pressures and high temperatures. The diffraction patterns allowed us to clarify the structure of the high-pressure, high-temperature phase of FeO.

## Methods and Materials

The DAC, beveled with a small culet size of 150  $\mu\text{m}$  from a culet of 300  $\mu\text{m}$ , and the stainless-steel guided boron gasket were used for generating high-pressure conditions. The sample was synthetic Fe<sub>x</sub>O with  $x = 0.912 \pm 0.002$  (hereafter denoted as Fe<sub>0.91</sub>O), estimated from the cell parameter of  $4.2917 \pm 0.0011$  Å. NaCl was used as a pressure medium and thermal insulating layers for laser heating. The NaCl powder was dried in a vacuum oven to eliminate any moisture. Sample loading was performed in an argon atmosphere in a glove bag. Angle-dispersive XRD experiments under high pressures and high temperatures were performed at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) beamline 13-ID-D at the APS. A double-sided YLF laser heating system [6] was used for the experiments. The laser heating spot size at the sample position was about 20 to 30  $\mu\text{m}$  in diameter. A monochromatic x-ray beam (energy of 30.491 keV) was produced by a channel-cut crystal [silicon (220)]. The

x-ray beam size was controlled by a slit system to  $150 \times 150 \mu\text{m}^2$  and subsequently focused by Kirkpatrick-Baez mirrors to a beam size of 7  $\mu\text{m}$  (vertical)  $\times$  10  $\mu\text{m}$  (horizontal) at full width at half maximum (FWHM). A charge-coupled device (CCD) detector (Bruker-2k) was used for diffraction measurements. Exposure time for the CCD was 2 min. Pressures were determined from the lattice parameters of the NaCl B2 phase [7] after heating.

## Results

Our experimental procedure was to increase the pressure at room temperature to a desired point and then obtain x-ray diffraction patterns before, during, and after laser heating. The heating temperatures were fixed at  $1500 \pm 150\text{K}$ . Up to 131 GPa, only the B1 phase was observed at 1500K, and upon temperature quenching, it transformed to the rB1 phase with weak and broad diffraction peaks. At 137 GPa and 1500K, six new sharp peaks appeared. These new peaks were assigned to the B8 phase. The lattice refinement results were found to be  $a = 2.4822 \pm 0.0026$  Å,  $c = 4.9847 \pm 0.0073$  Å, and  $c/a = 2.0082 \pm 0.0051$  with the UnitCell program. To investigate the hysteresis of the transition pressure, we gradually decreased pressure and measured x-ray diffraction during laser heating. At 124 GPa, diffraction from the B8 phase became weaker than it was at 127 GPa. The B8 phase was still observed with the coexisting B1 phase, even at 121 GPa. However, it disappeared after keeping its load at room temperature for 18 h. It was not observed upon further heating to 1500K. The transition pressure between the B1 and B8 phases at 1500K was then constrained to be  $130 \pm 7$  GPa.

## Discussion

The rB1-B8 phase transformation had been previously observed in externally heated DAC experiments [1]. However, those data were explained by stacking of the nB8 and iB8 structure [2]. To clarify whether the high-pressure, high-temperature phase has the nB8 or iB8 structure, we used the GSAS and EXPGUI programs to analyze our observed data at 137 GPa and 1500K (Table 1). The structural parameters for the B1 phase, NaCl, background, and thermal factors of the B8 phase were fixed, and the unit cell parameter, intensity, and peak width of the B8 phase were refined. The preferred

Table 1. Observed and calculated XRD pattern of FeO at 137 GPa and 1500 K.

hkl	$d_{\text{obs}}^{\text{a}}$ (Å)	$d_{\text{cal}}^{\text{b}}$ (Å)	$d_{\text{obs}} - d_{\text{cal}}$ (Å)	$I_{\text{obs}}$ (%)	$I_{\text{cal}}^{\text{c}}$ nB8 (%)	$I_{\text{cal}}^{\text{c}}$ iB8 (%)
002	2.48780(41)	2.49237	-0.00457	16	24	22
100	2.14964(53)	2.14967	-0.00003	32	69	4.6
101	-	1.97392	-	-	7.3	100
102	1.62612(11)	1.62783	-0.00171	100	100	41
103	-	1.31463	-	-	5.5	27
004	<sup>d</sup>	1.24111	-	<sup>d</sup>	7.9	7.3
110	1.24170(13)	1.24110	0.00060	32	23	22
112	1.11065(10)	1.11099	-0.00034	6.4	20	12
104	1.07842(14)	1.07813	0.00029	35	20	1.5
200	<sup>e</sup>	1.07482	-	<sup>d</sup>	7.4	0.7

<sup>a</sup>The numbers in parentheses are uncertainties in the last digit(s).

<sup>b</sup>Unit cell parameters are estimated by the UnitCell program with  $a = 2.4822 \pm 0.0026$  Å and  $c = 4.9847 \pm 0.0073$  Å, which gives  $c/a = 2.0082 \pm 0.0051$  Å.

<sup>c</sup>Calculated by PowderCell program.

<sup>d</sup>Overlap with (110).

<sup>e</sup>Overlap with (104).

orientation of the B8 phase was not introduced. Figure 1 shows the observed data and the fit with the nB8 structure. The residual without background ( $R_{\text{wp}}$ ) is 0.0277. If iB8 structure is assumed instead of nB8 structure, the residual is larger at every diffraction line of the B8 phase, and the  $R_{\text{wp}}$  is more than two times larger (0.0651). This shows that the observed high-pressure phase has the nB8 structure. The B8 phase observed by Fei and Mao [1] may be explained as an intermediate phase in the rB1 to nB8 phase transition. First-principle calculations [3, 4] predicted that for stoichiometric FeO, the iB8 structure is more stable than the nB8 structure in the ground state. More studies are needed that consider the temperature effects, nonstoichiometry, and/or magnetic ordering state.

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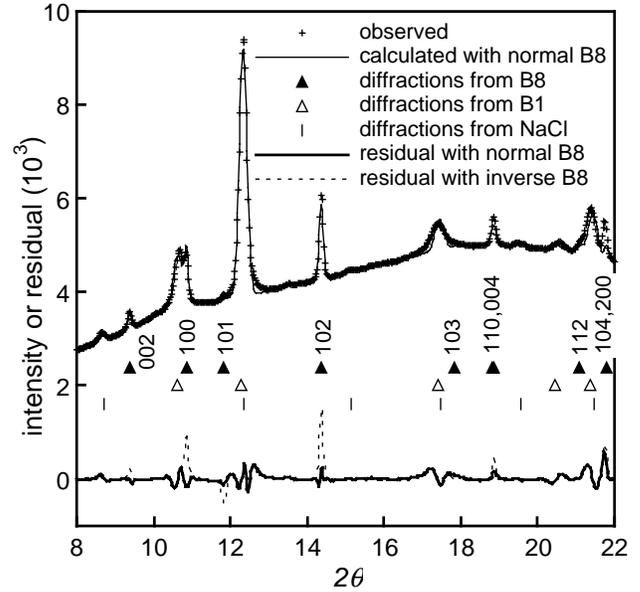


FIG. 1. The integrated 1-D pattern ( $\lambda = 0.4066$  Å) from XRD for  $\text{Fe}_{0.91}\text{O}$  at 137 GPa and 1500K. The GSAS and EXPGUI programs were used for fitting. If the structure is assumed to be iB8 instead of nB8, the residual is larger at every diffraction line of the B8 phase.

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