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High-pressure experimental evidence for metal FeO with normal NiAs-type structure

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We measured the electrical conductivity ($\sigma$) of Fe$_{0.955}$O (FeO hereafter) at high pressures and temperatures up to 169 GPa and 2050 K, simultaneously with the synchrotron x-ray diffraction measurements. The results showed that a B8-structured FeO (B8 FeO) synthesized above 140 GPa adopts a normal NiAs-type structure and has an electrical conductivity of about $3 \times 10^5$ S/m at 150 GPa and 300 K. The conductivity of B8 FeO decreased with increasing temperature, which is a metallic behavior, in contrast to the semiconducting behaviors of the B1 and rhombohedrally distorted B1 (rB1) phases. However, the conductivities of the B1 and rB1 phases are not much different from that of the metallic B8 phase at equivalent pressures.

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I. INTRODUCTION

FeO wüstite has the rock-salt type (B1) cubic structure and is known to be a typical Mott insulator under ambient conditions. Since iron oxide is one of the fundamental components in the Earth’s interior, its structural phase transition and possible metallization at high pressure are of great geo-physical importance. The B1 phase undergoes a structural transformation into rhombohedrally distorted B1 (rB1) structure above 16 GPa (Fig. 1).1 Shock-wave compression experiments first suggested a discontinuous density increase2 and a possible metallization3 above 70 GPa and 1300 K. The density change and metallization were later attributed to a phase transition into NiAs-type (B8) structure.4,5 Nevertheless, the metallization of FeO has been controversial,6 partly because the resistance measurement has never been performed simultaneously with the crystal structure measurement. The NiAs-type FeO has two possible polytypes; Fe occupies either Ni or As position, which is called normal or inverse B8 structure, respectively. Previous x-ray diffraction (XRD) studies on the structure of B8 FeO at 80–100 GPa were not in agreement,4,5,7,8 although normal B8 was repeatedly reported at very high pressures above 180 GPa.9,10 Note that normal B8 could be a metallic phase, while inverse B8 would be an insulator (semiconductor).

Here we report simultaneous measurements of the structure and electrical conductivity of Fe$_{0.955}$O at high pressure ($P$) and high temperature ($T$). In a laser-heated diamond-anvil cell (DAC), FeO with normal NiAs-type B8 was synthesized above 140 GPa. The electrical resistance of FeO, from which the conductivity was obtained, was then measured with increasing temperature up to 2050 K at 169 GPa. The measurements were conducted also for rB1 and B1 phases at 21 and 59 GPa. Results show that normal B8 FeO has the metallic nature, while low-pressure rB1 and B1 phases are semiconductors.

II. EXPERIMENTAL PROCEDURES

We performed the electrical resistance measurements of FeO at high $P$-$T$ conditions in a laser-heated DAC at BL10XU of SPring-8. Starting material was fine powdered Fe$_{0.955\pm0.002}$O. For simplicity, the sample will be described as FeO hereafter. The same starting material was also used in our previous phase equilibrium study (Fig. 1).9 We used a Re+ cubic-BN (cBN) composite gasket. Finely powdered SiO$_2$ glass was used as a pressure medium which also served as a thermal insulator. The disk of the starting material and foils of gold electrodes (3 μm thick) were sandwiched between SiO$_2$ glass layers in the sample chamber with a 30–50 μm diameter at the center of the gasket. The sample and electrodes were electrically insulated against the metal part of the gasket by the cBN layer. This configuration was similar to those employed in our previous studies.11,12

We compressed the sample by beveled 90 and 150 μm culet diamond anvils. The samples were subsequently heated in a double-sided heating system with a fiber laser. The size of the heated spot was larger than the distance between the two electrodes. We measured the sample temperature above 1400 K by a spectroradiometric method.13 The temperatures below 1400 K were estimated from the relationship between laser output power vs measured sample temperature.14 Radial variations in temperature within the area from which the sample resistance and XRD were obtained were about ±10%.9,14 Pressures at high $T$ were determined from the unit-cell volume of gold (electrode) obtained by the XRD measurements (Fig. 2), using its pressure-volume-temperature equation of state.15 The uncertainty in pressure was smaller than ±3 GPa, mainly due to the uncertainty in temperature when the equation of state of gold was applied (Fig. 1). We also estimated the pressure at room temperature based on the Raman spectrum of the diamond anvil whose error should be smaller than ±10%.16

The electrical resistance of the sample was measured based on a quasi-four-terminal method with a multimeter...
(Keithley 2700) under the direct current of 1 mA. Accuracy of the measurement with this device is within ±0.01%. The electrical conductivity was then estimated from the measured resistance and the sample geometry that is defined by the distance between the electrodes, the size of the laser spot, and the thickness of the sample. The sample thickness was measured after decompression and therefore the correction for pressure was made (see Ref. 11 for details). The errors in conductivity measurements were derived mainly from the uncertainty in the sample thickness, which should be smaller than ±25%. Concurrently with the resistance measurements, the structure of FeO was monitored by the in situ XRD (Fig. 2) measurements.

III. RESULTS

We performed four separate runs of electrical resistance measurements in a pressure range from 21 and 169 GPa (Fig. 1). In the first run, FeO was first compressed at room temperature. The resistance of the rB1 phase was measured from 40 to 153 GPa at 300 K. The estimated conductivity substantially increased with compression from $\sim 5 \times 10^2$ S/m at 40 GPa to $\sim 1 \times 10^5$ S/m at 150 GPa (Fig. 3). Upon heating to about 1800 K, rB1 phase was completely transformed into the B8 phase (Fig. 2). The diffraction pattern showed intense 102 and weak 101 lines which may indicate the normal NiAs-type structure, in agreement with the previous works.8,9 The conductivity at 300 K increased by a factor of 2 at the phase transition from rB1 to B8 phase (Fig. 3). The electrical resistance of B8 FeO was subsequently measured with increasing temperature; it increased from 3.8 $\Omega$ at 300 K to 5.6 $\Omega$ at 2050 K [Fig. 4(a)]. The obtained conductivity showed a mild decrease from $4.4 \times 10^2$ S/m at 300 K to $3.0 \times 10^5$ S/m at 2050 K (Fig. 5). In the second experiment, similarly to the first run, B8 FeO was synthesized as a single phase at 150 GPa by laser heating. The resistance was 22.3 $\Omega$ at 2150 K which was higher than 18.5 $\Omega$ at 300 K. Although the number of data obtained in this run was limited due to the anvil breakage, the negative temperature dependence of the electrical conductivity of normal B8 FeO was confirmed (Fig. 5).

In the third run at 143 GPa, the starting material was mostly transformed into the B8 phase upon heating. A trace amount of the B1 phase (rB1 upon temperature quench) was
Temperature dependence above 70 GPa found by Knittle and Jeanloz (Ref. 8) is consistent with that of B1 phase which is a semiconductor.

The present results demonstrate that Fe0.96O adopts the normal NiAs-type structure at least above 140 GPa, in good agreement with the earlier XRD studies on Fe0.95–0.99O performed above 180 GPa.8,10 Note that the previous experimental studies made at 80–100 GPa were inconsistent with each other on the crystal structure of B8 FeO; Kondo et al. (Ref. 8) suggested the inverse structure, while the XRD patterns obtained by Fei and Mao (Ref. 4) and by Murakami et al. (Ref. 7) matched neither normal nor inverse structures. The stable structure of B8 FeO at such relatively low pressures still remains unsettled.

The negative temperature effect on the electrical conductivity of normal B8 FeO clearly indicates its metallic nature (Fig. 5). This is consistent with the theoretical prediction that the normal B8 phase is possibly metallic, while the inverse structure phase should be an insulator.5,17 In contrast, both rB1 and B1 were found to be insulators at 21–59 GPa in this study. The conductivity of the rB1 phase increased remarkably with increasing temperature. Such strong temperature dependence and low electrical conductivity of rB1 FeO is possibly due to a widening of the band gap as a consequence of the rhombohedral distortion. The conductivity of the cubic B1 phase has much weaker but certainly positive temperature dependence.

Similar electrical conductivity measurements were previously carried out on FeO at 64–73 GPa above 1000 K in a laser-heated DAC. Knittle and Jeanloz (Ref. 18) reported that the temperature effect on the conductivity suddenly changed at 70 GPa, suggesting an insulator to metal transition. However, their measurements were made at the P-T conditions all within the stability field of B1 FeO (Fig. 1), and the phase identification was not performed. The weak temperature dependence above 70 GPa found by Knittle and Jeanloz (Ref. 18) is consistent with that of B1 phase which is a semiconducting phase (Figs. 4 and 5).
FeO should adopt the B1 structure at the P-T condition of the Earth’s core-mantle boundary (136 GPa and ~4000 K). It could exist as a separate phase there as a consequence of the subduction of banded iron formations or the dissolution from outer core liquid by secular cooling. Although B1 FeO is most likely a semiconductor at that P-T condition, its electrical conductivity would be as high as 10^5 S/m, not much different from the values of the metallic B8 phase. Presence of such highly conductive B1 FeO at the bottom of the mantle might play an important role in electromagnetic coupling between the solid mantle and the liquid core, which could cause the anomalous features in observed Earth’s nutation.

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