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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 (σ) of Fe_{0.96}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 3×10^5 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 geophysical 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 $Fe_{0.96}O$ at high pressure (*P*) and high temperature (*T*). In a laser-heated diamondanvil 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±0.002}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 SiO₂ 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 μ m thick) were sandwiched between SiO₂ glass layers in the sample chamber with a 30–50 μ m 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 μ m 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 $\pm 10\%$.^{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-volumetemperature 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 $\pm 10\%$.¹⁶

The electrical resistance of the sample was measured based on a quasi-four-terminal method with a multimeter



FIG. 1. *P-T* conditions of the electrical conductivity measurements and the phases identified by the simultaneous XRD analyses. B8 phase was observed in run no. 1 (diamonds) and no. 2 (triangles). The B8 plus trace amount of B1 (rB1 upon temperature quench) was confirmed in run no. 3 (squares). In the run no. 4 (at 59 and 21 GPa), B1 (gray closed circles) and rB1 (open circles) phases appeared. Phase boundaries are from previous XRD studies (Refs. 4 and 9).

(Keithley 2700) under the direct current of 1 mA. Accuracy of the measurement with this device is within $\pm 0.01\%$. 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 $\pm 25\%$. 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 Ω at 300 K to 5.6 Ω at 2050 K [Fig. 4(a)]. The obtained conductivity showed a mild decrease from 4.4×10^5 S/m at 300 K to 3.0×10^5 S/m at 2050 K (Fig. 5). In the second experiment, similarly to the first run, B8 FeO was synthesized as a single



FIG. 2. XRD patterns of FeO during conductivity measurements at 59 and 153 GPa. These pressures were the values obtained at 300 K.

phase at 150 GPa by laser heating. The resistance was 22.3 Ω at 2150 K which was higher than 18.5 Ω 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



FIG. 3. Variations in electrical conductivities (σ) of rB1 (open symbols) and B8 FeO (solid symbols) at 300 K as a function of pressure. Different symbols indicate the data obtained in separate runs. Note that the conductivity of semiconducting rB1 is not much different from that of metallic B8 at equivalent pressure.



FIG. 4. Variations in measured resistance of (a) B8 and (b) rB1 (open circles) and B1 (gray closed circles) with increasing temperature. The pressure values are those obtained at 300 K.

observed possibly because the temperature had exceeded the phase-transition boundary between B1 and B8. However, the volume faction of the B1 (or rB1) phase was quite small, and we assume it did not significantly affect the observed values of bulk conductivity. The sample conductivity was indeed comparable to those obtained in the previous two runs in which only the B8 phase was observed. As in the first and the second experiments, the resistance increased with increasing



FIG. 5. Changes in electrical conductivities (σ) of B8 (solid symbols), rB1 (open circles), and B1 FeO (gray closed circles) with increasing temperature. B8 is a metallic phase, whereas both rB1 and B1 are insulators. Pressure values are those obtained at 300 K.

temperature [Fig. 4(a)]. When the sample was decompressed to 80 GPa, the B8 structure was still preserved. The electrical conductivity decreased from 2.7×10^5 S/m at 143 GPa to 6.5×10^4 S/m at 80 GPa, both of which are higher than those of the rB1 phase at the equivalent pressure (Fig. 3).

In the fourth run, the high-T conductivities of the rB1 and B1 phases were examined. We observed the change in structure from rB1 to B1 with increasing temperature (Figs. 1 and 2). This phase transition is second order, since it corresponds to a rhombohedral distortion at low temperatures (<1000 K), while other phase changes in FeO such as rB1 to B8 and B1 to B8 are first order.^{4,8,9} The electrical resistance was measured at 59 GPa after thermal annealing which reduced the deviatoric stress in the sample. The resistance of the rB1 phase dramatically decreased with increasing temperature; from 36 Ω at 300 K to 4 Ω at 1000 K [Fig. 4(b)]. In contrast, much smaller negative temperature dependence was observed in B1 FeO to 1790 K. We then decompressed the sample to 21 GPa and again found similar behavior in the resistance with increasing temperature in both phases [Fig. 4(b)]. Throughout all the experimental runs, any evidence for reaction or decomposition of FeO was not observed.

IV. DISCUSSION

The present results demonstrate that $Fe_{0.96}O$ adopts the normal NiAs-type structure at least above 140 GPa, in good agreement with the earlier XRD studies on $Fe_{0.95-0.96}O$ performed above 180 GPa.^{9,10} 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).⁹ It could exist as a separate phase there as a consequence of the subduction of banded iron formations¹⁹ or the dissolution from outer core liquid by secular cooling.²⁰ 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 (Fig. 3). 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,

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which could cause the anomalous features in observed Earth's nutation. $^{\rm 20}$

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