We report the results of the investigation of the thermoelectric power (Seebeck effect) on quasi-single-crystalline wüstite (FeO) at a high pressure up to 22 GPa. Using a polaron hopping model, we estimate pressure dependencies of the $Fe^{2+}/Fe^{3+}$ ratio and the stoichiometry. It is found that a typical composition $Fe_{0.93}O$ is unstable against compression, and gradually and irreversibly "shifts" to $Fe_{0.89}O$. Comparative x-ray diffraction and Raman studies confirm, respectively, this change in the stoichiometry and dramatic modification of an incommensurate defect structure. This finding can partly explain discrepant high-pressure properties of Fe$_{1-x}$O, in particular, a strong scattering of bulk modulus data, the high inelasticity, and the differences in the high-pressure phases. This result provides clear evidence of a change in the stoichiometry of FeO under pressure.

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Compressions of solids modify their crystal and electron band structures and related properties and often produces denser forms (states, phases, etc.) whose properties may be essentially distinguished from those of ambient condition forms. There are also several subtle effects of pressure such as, for instance, the introduction of different kinds of defects or the modification of structure of native defects, which are not detected by conventional structural techniques, although they may strongly influence the magnetic, transport, and optical properties.

Iron oxides are materials that are steadily in a focus of high-pressure (HP) studies because of their fundamental importance for the understanding of a state of the earth crust and mantle, and numerous industrial applications. The simplest form of iron oxide (wüstite, Fe$_{1-x}$O) is the most controversial. At ambient conditions it normally adopts a defect rocksalt (RS) structure with iron-related point and cluster defects, while quenching from high temperatures (HTs) may result in its decomposition into iron and magnetite Fe$_3$O$_4$. Neutron-diffraction data suggest that the number of empty octahedral sites is twice as large as iron deficiency (x), hinting that the fraction of iron at the interstitial tetrahedral sites is close to x. This resembles octahedrally and tetrahedrally coordinated iron chains in Fe$_3$O$_4$. The $Fe^{3+}$ ions in Fe$_{1-x}$O are proposed to be randomly distributed. The defect structure of Fe$_{1-x}$O was believed to be a source of its high inelasticity. Analysis of data for a plenty of samples revealed that the stoichiometry of Fe$_{1-x}$O and its lattice parameter a are directly bounded by a linear law: $a(\text{Å}) = 3.856 + 0.478(1-x)$. Compression of Fe$_{1-x}$O results in a variety of remarkable but inconsistent phenomena. Thus, several works reported on magnetic ordering, e.g., above 14–15 GPa (Refs. 8 and 9) and 5 GPa, while a recent neutron study did not confirm it. Under compression RS-FeO transforms to a rhombohedral lattice around 18–25 GPa. Further compression was shown to lead to NiAs (or anti-NiAs) phase under heating at pressures above 70–90 GPa. Very recently another options have been revealed, namely, the persistence of the rhombohedral phase to 142 GPa (Ref. 15) or a distortion to a monoclinic form at ~75 GPa. Standard density-functional approximations fail to determine the stable ground state of FeO. But in recent theoretical calculations both the ambient RS phase and a transition to anti-NiAs phase above 65 GPa have been predicted. Furthermore, zone-axis diffraction study of a single-crystalline Fe$_{0.93}O$ compressed to 35 GPa revealed an inhomogeneity of a sample consisting of four different phases with cubic and orthorhombic (or monoclinic) symmetries in different regions of a sample. This effect could be related to a drastic pressure-driven modification of a defect structure under pressure, as well as spatial fluctuations in the stoichiometry of the sample that could lead to different phases. It was also reported that pressure leads to an irreversible order-disorder transition at which reflexes coming from an incommensurate defect superstructure disappear near 14 (Ref. 21) or 40 GPa. Knowledge of pressure effect on the stoichiometry of Fe$_{1-x}$O could greatly help one to understand these controversial properties, while in situ measurement of the amount of iron atoms that are coming or leaving the lattice is challenging. Normally, samples recovered from HP (except those recovered from HPHT) exhibit reduced lattice parameter a that might hint at possible decrease in the iron content. However, it could be just related to a high inelasticity.

In this work we measured in situ the thermoelectric power of Fe$_{1-x}$O under compression to ~22 GPa. Using a polaron hopping model, the pressure dependencies of the $Fe^{3+}/Fe^{2+}$ ratio and the stoichiometry are estimated. It is found that a typical composition ($x=0.065$) irreversibly shifts to $x\sim0.11$, in agreement with x-ray diffraction (XRD) studies.

HP thermopower experiments were performed in two anvil cells with flat and semispherically concave anvils on, respectively, thin (~200×200×30 μm$^2$) and thick (~200×200×250 μm$^3$) samples (insets in Fig. 1).
Fe2O3 film, chromator. Measuring Raman spectra of Fe1−
were excited with the 514.5 nm line of an Ar laser and were
recorded using a T64000 Jobin-Yvon triple grating mono-

The experiments were performed in three regimes:
at fixed \( \Delta T \) under gradual variation of the pressure \( P \), at
fixed \( P \) and gradual variation of \( \Delta T \), and under monotonic
variations of both \( \Delta T \) and \( P \). All regimes gave similar results.
The experiments were carried out on an automated setup
with motor-driven plungers permitting continuous variation
of pressure and simultaneous measurement of several param-
ers of a sample; other details may be found elsewhere.24–26

We took a quasi-single-crystalline wüstite ingot. Both the
ingot and the recovered samples were probed by XRD and
Raman scattering. In order to evaluate possible inhomogeneities,20
the samples were probed in many points. XRD was performed using a Rigaku diffractometer (wave-
length of 0.7108 Å). For the ingot, the lattice parameter was
repeatedly found as \( a \approx 4.303(4) \) Å, and hence its composi-
tion deduced from Eq. (1) was Fe0.935O. The Raman spectra
were excited with the 514.5 nm line of an Ar laser and were
recorded using a T64000 Jobin-Yvon triple grating monochromator. Measuring Raman spectra of Fe1−
O is a complicated task since it is a weak Raman scatterer, and
furthermore even a tiny laser power is enough to form a Fe2O3 film,
of which strong Raman spectrum completely hides that of
FeO. To avoid any laser-heating effects, the spectra were
excited with immeasurably small laser powers and collected
for 10–20 h.

The “ambient” thermopower \( S \) values in our samples are
around \( +80 \pm 5 \mu V/K \) (Fig. 1). The pressure dependence
of the thermopower measured in both cells for several samples
cut from the same ingot exhibits a similar irreversible drop
of \( |S| \) down to \( +35 \pm 5 \mu V/K \) (Fig. 1). The dominant con-
ductivity mechanism in FeO was established to be a polaron
hopping between Fe2+ and Fe3+ ions on the octahedral
sites.3,23,27 This model toughly binds the Fe3+/Fe2+ ratio
with the thermopower value, and in the approximation of
the “small polaron conductivity” their relation comes as follows:3,23,27

\[
S = -k/|e| \ln \left[ \frac{2(Fe^{3+}/Fe^{2+})_{oct} + A}{} \right],
\]

where \( e \) is the electron charge, \( k \) is the Boltzmann constant,
and \( A \) is a small shift that is related to an “entropy of trans-
port term.”27 This model explains, for instance, the positive
sign of \( S \) in Fe1−xO and, likewise, the negative one in Fe2O3.5
Examination of the model on a set of wüstite samples
(0.05 < x < 0.15) at elevated temperatures revealed a good
linearlike correlation between the Fe3+/Fe2+ ratios deter-
mined from Eq. (2) and from the degree of
nonstoichiometry.3,27 Potentially, a small amount of iron in-
clusions in Fe1−xO may influence both the thermopower
and the electrical resistivity. For instance, for isotropic configu-
ration of inclusions different methods (e.g., Refs. 28 and 29)
find a conductivity threshold close to 30% of the total vol-
ume, and hence in a first approximation for available com-
positions (x < 0.15) a minor contribution to the thermopower
from the iron clusters may be disregarded.

For ambient thermopower values the calculations by Eq.
(2) in fact find that the Fe3+/Fe2+ ratio and the stoichiometry
are, respectively, higher by ~0.04 and lower by ~0.01 than
expected for Fe0.935O (Fig. 2). Pressurization monotonically
and irreversibly enhances the Fe3+/Fe2+ ratio to 0.35 at 17.5
GPa (Fig. 2). Charge balance conservation suggests that iron
is leaving the lattice and thereby the material gradually shifts
to a less stoichiometric composition with \( x \approx 0.115 \) at 17.5
GPa (Fig. 2). One can recognize in the data a tendency to
stabilization of the thermopower to a value above
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FIG. 3. (Color online) Typical x-ray diffraction patterns of the initial and recovered wüstites. The latter exhibits shifts in the positions of the peaks related to Fe1−xO. The upper inset shows the 18.5°–21° range in more details. Two insets near the cures are azimuth patterns. The height covers a full range, 0°–360°, and the width corresponds to a 2θ range of ~12°–28°.

S ~ 20–25 μV/K (Fig. 1) suggesting a limit of pressure-tuned stoichiometry as x ~0.125 (Fig. 2). Although the HP treatment of all the samples investigated leads eventually to consistent compositions (Fig. 2), the difference between the data collected in different experiments points out that the rate of stoichiometry alteration depends on the details of the compression procedure.

The XRD studies on starting and recovered samples found the expected shift in the reflections (Fig. 3) indicating a reduced lattice parameter. The recovered samples subjected to several pressure cycles to 15–22 GPa exhibit consistent lattice parameters close to a=4.283(3) ± 0.0008 Å (average value); Eq. (1) gives x=0.893 ± 0.002, in agreement with the above estimations from the thermopower (Fig. 2). This confirms that Eq. (1) is working for HP-treated samples too, as it was asserted in Ref. 22. This stoichiometric shift should contribute to changes in the elastic properties under pressure. Based on the extant literature, the composition dependence of the bulk modulus of Fe1−xO shows a kink for x ~0.05, and for compositions with 0.05 < x < 0.12 a strong data scattering does not permit us to figure out a trend.2,4,22

Although, the amount of iron in the wüstite lattice is decreasing, we do not observe any enhancement of the reflections of α-Fe in the recovered samples, but on the contrary their weakening (insets in Fig. 3). Such a “dissolution” of iron in FeO under pressure is in fact often observed (e.g., Refs. 21 and 30), and hence there was a long-standing conjecture that the applied pressure “stabilizes” nonequilibrium wüstite lattice to 15 GPa by filling it out with clustered iron. A simple explanation of this contradiction consists in a shredding of the iron clusters, and for this reason structural techniques probing long-range order are unable to detect the iron. A study on diffusivity of Fe in Fe1−xO found a dependence on x (Ref. 31); thus, at 800 °C the diffusion coefficient D strongly diminishes when x increases from ~0.05 to ~0.1. To explain this fact it was proposed that Fe ions diffuse by exchanging sites with “free mobile vacancies,” and increasing vacancy concentration enhances short-range defect-defect interactions and favors defect cluster formation, in which vacancies are “much less mobile.”31

Hypothetical extrapolation of these data to “D → 0” gives x ~0.15,31 i.e., close to our estimation of a limit of the stoichiometric shift under HP (x ~0.125). Therefore, a “stabilization” of FeO under pressure may mean a defect-cluster-related restriction in iron migration that prevents both further leaving or coming of iron into the lattice and a decomposition of FeO into iron and Fe3O4.

To obtain information on HP treatment effect on the modulated defect structure of FeO, we used Raman spectroscopy. For perfect RS lattice the first-order Raman scattering is forbidden by the selection rules. All fresh chips from the ingot exhibited three bands near 298, 524, and 652 cm−1 (Fig. 4), resembling those in Fe3O4. The cubic structures of both FeO and Fe3O4 contain fragments of tetrahedrally bonded Fe ions, which are randomly distributed in the interstices in the former3,4 while ordered in the latter.3 The frequencies of the Raman modes observed in Fe1−xO are lower than those known in Fe3O4. This softening could be related to size or stress effects. The Raman peak of FeO at ~652 cm−1 was already observed in previous studies.33 The samples recovered from HP to ambient conditions exhibited numerous surface defects, and the spectra were measured on flat islands, which kept good crystalline structure aspect (inset in Fig. 4). The peak at ~652 cm−1 remained while widened, and a new one appeared near 217 cm−1. This apparently evidences a variation in the defect structure. The origin of the peak at 217 cm−1 is obscure. Probably it comes from some Fe-O-vacancy-related complexes, while one can also find a correlation with the E2g phonon of α-Fe arising above 13 GPa near 200–210 cm−1.3 The splitting of the main iron XRD reflection at ~20.2° (Fig. 3) could be related to the coexistence of α- and ε-Fe.35

In summary, the thermopower and XRD data gathered and analyzed in two widely accepted models [Eqs. (1) and (2)]
independently evidence that the stoichiometry of wüstite may change under compression. Thus, a typical composition ($\text{Fe}_0.935\text{O}$) after pressure cycling to $\sim20$ GPa eventually shifted to $\sim\text{Fe}_0.89\text{O}$. Since “effective” properties of materials depend on their mesostructure, this could explain the controversial and puzzling high-pressure properties that are ascribed to “ideal” wüstite. In particular, this explains a strong scattering of bulk modulus data, the high $\gamma$ values, and the differences in the high-pressure phases. The finding has important implications for geosciences and also may be utilized in different technologies.

Note added in proof: It is interesting to notice, that a valence disproportionation reaction, namely $3\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{Fe}^{0}$ (metal) was found to be energetically favorable in Al-rich and Fe-rich MgSiO$_3$ silicates at lower mantle pressure. There are also evidences that the mantle is enriched in Fe$^{3+}$ and Fe-rich metallic alloy.

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