# The effect of iron spin transition on electrical conductivity of (Mg,Fe)O magnesiowüstite

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(Communicated by Ikuo Kushiro, m.j.a.)

**Abstract:** We measured the electrical conductivity of $Mg_{0.81}Fe_{0.19}O$ magnesiowüstite, one of the important minerals comprising Earth's lower mantle, at high pressures up to 135 GPa and 300 K in a diamond-anvil cell (DAC). The results demonstrate that the electrical conductivity increases with increasing pressure to about 60 GPa and exhibits anomalous behavior at higher pressures; it conversely decreases to around 80 GPa and again increases very mildly with pressure. These observed changes may be explained by the high-spin to low-spin transition of iron in magnesiowüstite that was previously reported to occur in a similar pressure range. A very small pressure effect on the electrical conductivity above 80 GPa suggests that a dominant conduction mechanism changes by this electronic spin transition. The electrical conductivity below 2000-km depth in the mantle may be much smaller than previously thought, since the spin transition takes place also in (Mg,Fe)$SiO_3$ perovskite.

**Keywords:** electrical conductivity, high-pressure, magnesiowüstite, spin transition

## Introduction

The electrical conductivity is one of the important physical properties of the Earth's mantle.[1] It is highly sensitive to chemical composition, especially iron and water, as well as pressure and temperature. The pyrolitic lower mantle consists of 78% Al-bearing (Mg,Fe)$SiO_3$ perovskite (Mg-perovskite), 16% (Mg,Fe)O magnesiowüstite, and 6% $CaSiO_3$ perovskite in volume,[2] and the electrical conduction occurs through these iron-bearing phases, Mg-perovskite and magnesiowüstite. Previous study by Wood and Nell[3] reported that the electrical conductivity of magnesiowüstite is similar to that of Mg-perovskite plus magnesiowüstite assemblage, suggesting that magnesiowüstite may be the dominant conductor in the lower mantle although it is a volumetrically minor phase compared to Mg-perovskite.

Recently, Badro *et al.*[4] discovered a pressure-induced high-spin to low-spin transition of iron in $Mg_{0.83}Fe_{0.17}O$ magnesiowüstite between 58 to 75 GPa at room temperature. Subsequent studies have shown that this electronic spin transition is accompanied by the volume reduction[5),6] and significant changes in bulk elastic properties,[5)–7] optical absorption spectrum,[8),9] and possibly iron partitioning with (Mg,Fe)$SiO_3$ perovskite.[4] The electrical conductivity of magnesiowüstite was previously measured at high pressures and high temperatures to 32 GPa and 2000 K.[10),11] The spin transition of iron may have significant effect on electrical conductivity, but it has not been examined yet. In this study, we conduct the electrical resistance measurements of $Mg_{0.81}Fe_{0.19}O$ magnesiowüstite up to 135 GPa and report its anomalous behavior above 60 GPa due most likely to the effect of iron spin transition. All the measurements were done at room temperature, because spin transition occurs in smaller pressure range at lower temperature.[12),13]

## Materials and methods

We measured the electrical conductivity of polycrystalline magnesiowüstite containing 19 mol% iron with $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratio of 0.013. The ferric iron content in our sample was estimated according to the method by Dobson *et al.*[14] High-pressure conditions were generated in a DAC (Fig. 1). The

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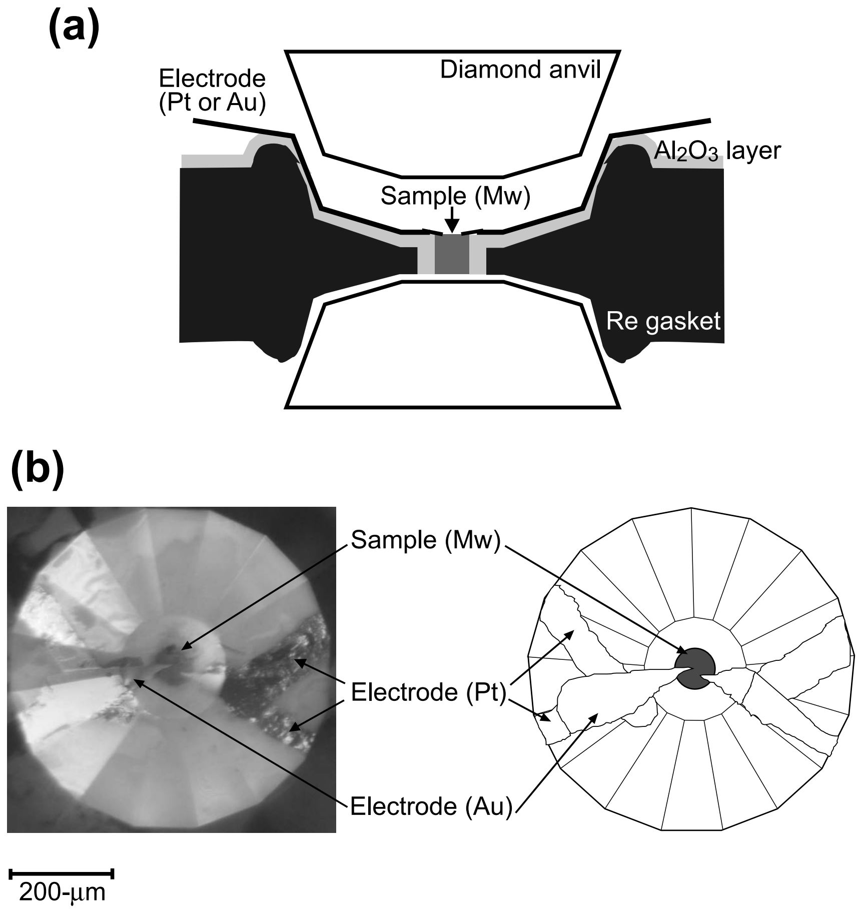


Fig. 1. (a) Cross section of experimental set up. (b) Photograph and schematic drawing showing the configuration of the sample and electrodes on the diamond-anvil. The gold foils were attached to the sample and connected to platinum electrodes outside the sample hole.

beveled diamond anvils with 150- or 200-µm culet were used. We indented the rhenium gasket to about 50-µm thick, and then made a hole at its center, and put $Al_2O_3$ powder in it and on the rhenium. They were subsequently compressed for $Al_2O_3$ to be transparent. The magnesiowüstite sample was loaded into a hole with 60-µm diameter that was drilled in $Al_2O_3$. Two electrodes made of platinum foil were placed on the $Al_2O_3$ layer, which electrically insulated the sample and electrodes against rhenium. From these Pt electrodes, we put another platinum or gold electrodes directly attached to the sample. No pressure medium was loaded so as to ensure a good contact between sample and electrodes.

Pressure was determined by the ruby fluorescence technique[15] and by the Raman spectrum of diamond-anvil above 60 GPa.[16] The uncertainty in our pressure measurements may be less than 10%. The electrical resistance measurements were performed using the two-terminal method with an electrometer (Keithly 6517A). The electrical conductivity was estimated from measured resistance, length and width of the sample between electrodes at high pressure, and sample thickness. The thickness of the sample was measured as a function of pressure by separate experiments with the same configuration.

## Results

We conducted three separate sets of experiments. The position and shape of the electrodes on the sample did not change during compression above 20–30 GPa in each run. The resistance of electrodes was checked before measuring the sample resistance at each pressure. In the first run, the sample resistance was measured during both compression and decompression (Fig. 2). On compression, it decreased from 530 MΩ at 12 GPa to 98 MΩ at 55 GPa, and then conversely increased with pressure to 470 MΩ

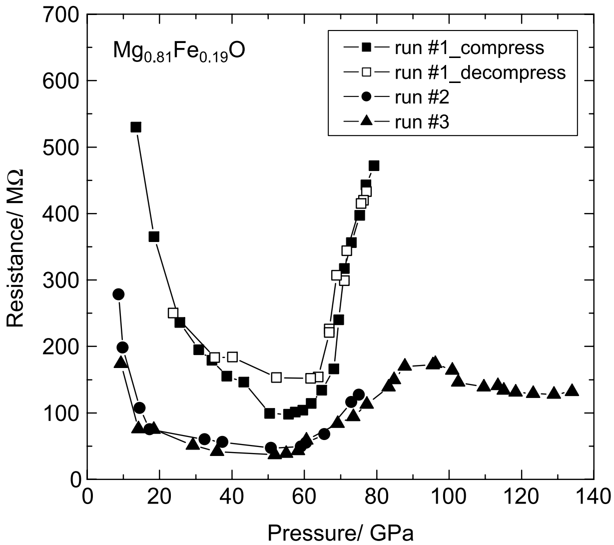


Fig. 2. Changes in the electrical resistance of magnesiowüstite measured at 300 K as a function of pressure. The measurements were perfomed during both compression and decompression in run #1. Squares, run #1; circles, run #2; triangles, run #3.

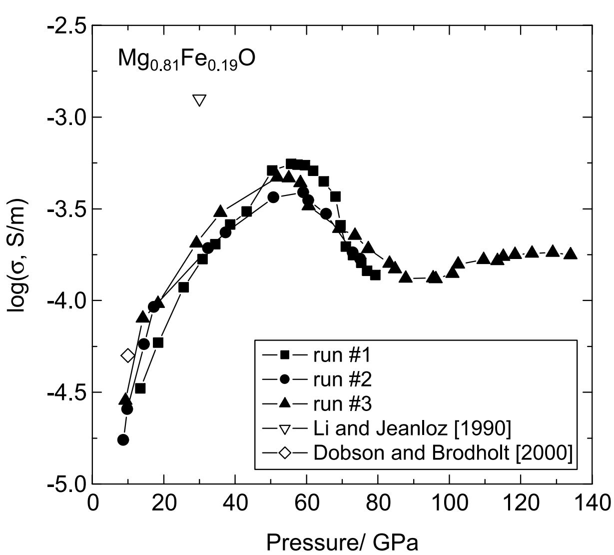


Fig. 3. Electrical conductivity ($\sigma$) of magnesiowüstite at 300 K as a function of pressure. Filled symbols, present study; open symbols, Li and Jeanloz [1990] and Dobson and Brodholt [2000].

at 80 GPa. We also observed similar change in the resistance during decompression to 23 GPa. The estimated electrical conductivity is shown in Fig. 3.

In the second run, we squeezed and measured the sample resistance from 7 to 80 GPa. The measured resistance was low compared to that observed in the first run at equivalent pressure, but the calculated electrical conductivity shows very similar values. The conductivity increased to around 60 GPa and then decreased with increasing pressure (Fig. 3). In the third run, the sample resistance was measured up to 135 GPa. The calculated electrical conductivity profile is quite consistent with those obtained in the previous two runs (Fig. 3). It increased by more than one order of magnitude with increasing pressure from 7 to 60 GPa, and then decreased by a factor of four to 80 GPa. The conductivity again increased very mildly with pressure to about 120 GPa and showed constant value at higher pressures.

## Discussion

These results demonstrate that the electrical conductivity of $Mg_{0.81}Fe_{0.19}O$ magnesiowüstite increases remarkably with pressure to about 60 GPa and exhibits anomalous behavior at higher pressures. Our data are consistent with a previous report[11] at 10 GPa for magnesiowüstite containing the same iron content (Fig. 3). In contrast, they are substantially lower than that by Li and Jeanloz[10] at 30 GPa, which may be due to the possible difference in ferric iron concentration.

Previous X-ray emission spectroscopy measurements have shown that the high-spin to low-spin transition of iron takes place in $Mg_{0.83}Fe_{0.17}O$ magnesiowüstite between 58 and 75 GPa at 300 K.[4] We observed the reduction in electrical conductivity at similar pressure range, suggesting that it is most likely caused by the effect of this electronic spin-pairing transition. The change in electrical conductivity is a reversible process (Fig. 2), which is also in good agreement with the X-ray emission spectroscopy observations by Badro *et al.*[4]

The electrical conduction of magnesiowüstite including more than 7.5 mol% iron is dominated by a small-polaron process of electron hopping between ferric and ferrous iron ions at temperatures below 1000 K.[11] Such electron hopping occurs predominantly by unpaired electrons. The ferrous iron in high-spin state has four unpaired electrons in the 3*d* orbital, whereas all electrons are paired in the low-spin state. The observed reduction in electrical conductivity above 60 GPa is thus reasonably explained by the spin-pairing transition. In addition, the measurements above 80 GPa show nearly uniform values (Fig. 3). A predominant electrical conduction mechanism in magnesiowüstite with low-spin iron may be different from the small-polaron process.

Such electronic spin-pairing transition was reported to occur also in (Mg,Fe)$SiO_3$ perovskite above 70 GPa.[8),17)] This most likely causes the reduction in electrical conductivity of (Mg,Fe)$SiO_3$ perovskite as well. The electrical conductivity in the deep lower mantle has been estimated from the extrapolation of laboratory measurements at relatively low pressures below 25 GPa,[18)] where iron is present in high-spin state; however, the high-spin to low-spin transition of iron in both magnesiowüstite and Mg-perovskite may remarkably reduce their electrical conductivity below about 2000-km depth.

**Acknowledgements**

We thank J.-F. Lin and T. Tsuchiya for discussions. The sample was provided by H. Ozawa. The reviewers' comments were helpful in improving the manuscript.

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(Received Feb. 19, 2007; accepted Feb. 26, 2007)