Mössbauer spectroscopy at elevated pressures and temperatures: Spin transition in (Mg$_{0.8}$Fe$_{0.2}$)O ferropericlase

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Summary
The experimental methodology of simultaneous high pressure and high temperature Mössbauer spectroscopy using a resistively heated diamond anvil cell is given. As an example, the spin state of iron was studied over a wide range of pressure (up to 105 GPa) and temperature (up to 600 K). The low-spin state of Fe$^{2+}$ ions was first detected at ~55 GPa and the transition is completed only above one Mbar pressure. The amount of low-spin ions was found to be independent of temperature within experimental uncertainty.

Introduction
$^{57}$Fe Mössbauer spectroscopy is one of the most reliable techniques available to determine the valence, magnetic, and spin state of iron. An in situ Mössbauer spectroscopy study at ultrahigh pressures using the diamond-anvil cell (DAC) can provide information on the electronic, structural and magnetic state of iron atoms at a pressure range encompassing the entire Earth's mantle and core. The addition of high temperature significantly enhances the relevance of the data. Conventional Mössbauer spectroscopy at high pressures does not allow the use of laser heating in the diamond anvil cell, because each spectrum is collected for many hours (or days) and it is impossible to maintain high temperatures over such long periods of time. Therefore only a resistively heated DAC is valid for this purpose. A newly developed heating assembly for the DAC allows us to perform such experiments routinely.

(Mg$_{x}$Fe$_{1-x}$)O ferropericlase with x ~ 0.8 is probably the second most abundant phase in the Earth's lower mantle after (Mg,Fe)SiO$_3$ perovskite, and therefore its properties and stability field are important for geophysical and geochemical models of the Earth's deep interior. One of the most important transformations that occurs in ferropericlase at elevated pressures is a high-spin to low-spin transition of iron ions. Knowledge of the iron spin state in different lower mantle minerals at appropriate conditions (high pressures and temperatures) is of great importance, because of its influence on density, element partitioning, transport properties, etc. A high- to low-spin transition of iron in ferropericlase of (Mg$_{0.83}$Fe$_{0.17}$)O was observed between 60 and 70 GPa using X-ray emission spectroscopy (Badro et al., 2003). Mössbauer spectroscopy is a technique that is also quite sensitive to the spin state of iron: a smaller isomer (chemical) shift and absence of quadrupole splitting are expected for low-spin Fe$^{2+}$. We therefore undertook a Mössbauer study of ferropericlase at high pressure and elevated temperature to investigate the high-spin to low-spin transition.

Experimental Method
We used a modified three-pin Merill-Basset type diamond anvil cell in this study (Dubrovinskaia and Dubrovinsky, 2003). Diamonds with a culet size of 250 µm were mounted in the DAC. A rhenium 250 µm thick foil was preindentated to ~30 µm thickness to form a gasket. A 125 µm diameter hole was drilled in the gasket and filled completely with the sample powder and several small (~1 µm) ruby chips as pressure sensors (Mao et al., 1978).

DACs were adapted for the present study by fitting platinum internal resistive heaters (Fig. 1). Resistive heating overcomes many of the disadvantages of laser heating, where temperatures can be maintained within narrow limits over long periods of time, stresses are
reduced, heating is relatively homogeneous, and moderate temperatures are easily accessible. The current apparatus allows heating in air up to 1100 K.

The internal resistive heater consists of a ceramic (fired pyrophyllite) ring that fits into the cell, and has ~ 0.5 mm diameter holes for 24 wire loops. We tested Pt, Pt-Ir and Nichrome wires, and found that the best performance was obtained with pure Pt wire of 0.3 to 0.5 mm in diameter.

Fig. 1. New heating assembly for high P, T Mössbauer measurements: 1 – diamond anvil cell, 2 – ceramic (pyrophylite) heater, 3 – thermocouple, 4 – platinum wires, 5 – mica for electrical isolation, 6 – one Euro coin for scale, 7 – entire assembly.

We used ceramic rings for thermal isolation and mica as an electrical insulator. We fixed a fine R- or S-type thermocouple using high temperature Ceramobond (Amerco Inc.) at a distance of less than 0.5 mm from the pressure chamber, allowing direct and precise temperature measurements. Temperature distribution is homogeneous within the DAC sample chamber, and varies no more than ±10 K at 800 K within a 2 mm diameter circle around the anvils.

One of the difficulties of resistively heated DAC experiments is that pressure usually changes during heating. For example, if at room temperature the pressure is ~70 GPa, at 600 K the pressure might decrease to ~55 GPa. The experimental setup described in this study allows the DAC to be dismounted from the Mössbauer spectrometer and moved to the micro-Raman spectrometer for measurements of ruby fluorescence without disconnecting the power supply at high temperature (Fig. 2). Therefore, we are able to measure directly both temperature (with the thermocouple) and pressure (with the Raman spectrometer) during the
experiment. The temperature dependence of the ruby fluorescence scale used was that of Rekhi et al. (1999).

The ferropericlase sample used in this study had a nominal $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$ composition. It was synthesized by mixing stoichiometric amounts of $\text{MgO}$ and $\text{Fe}_2\text{O}_3$ (50% enriched with $^{57}\text{Fe}$), heating overnight at 1200°C in reducing conditions ($\log f_{\text{O}_2} = -17.4$) using a CO/CO$_2$ gas-flow furnace and quenching into water. The amount of ferric iron was constant over the entire pressure range and the $\text{Fe}^{3+}/\sum\text{Fe}$ ratio was measured to be 0.043. At ambient conditions the lattice constant $a$ of the sample was 4.2389(5) Å. Before and after the experiments the chemical composition of the sample was checked by scanning electron microscopy and X-ray microprobe: no changes in chemical composition were detected, and no evidence for chemical inhomogeneity on the length scale of the measurements (ca. 1 µm) was observed.

Results and discussion

The observed Mössbauer spectra of ferropericlase below 55 GPa (Fig. 3) could be fitted with two doublets (one for $\text{Fe}^{2+}$ and one for $\text{Fe}^{3+}$ sites) according to the model of Dobson et al. (1998).

Fig. 3. Mössbauer spectrum of ferropericlase at 47(1) GPa. Circles – experimental data, black line – total fit; purple – high-spin $\text{Fe}^{2+}$ doublet, blue – $\text{Fe}^{3+}$ doublet. The residual is shown above the spectrum.
At higher pressures a new subspectral component appeared, which was fitted to a Lorentzian singlet with isomer shift significantly lower than that of high-spin Fe$^{2+}$ (Fig. 4). This new component was assigned to a low-spin state of Fe$^{2+}$. The relative area of the low-spin component increases linearly with pressure and reaches 100% only above 100 GPa (Fig. 5). We performed several measurements at high temperatures in order to investigate the temperature effect on the spin transition in ferropericlase. Within the studied $P,T$ range the amount of the low-spin phase was found to be independent of temperature (Fig. 5). Note, however, that this observation does rule out a volumetric effect of temperature on the spin transition: a temperature difference of 300 K between room temperature and 600 K corresponds to ~1 GPa pressure change, which is within the pressure uncertainty.

Fig. 4. Mössbauer spectra of ferropericlase at 78(1) GPa (left, intermediate state) and 105(2) GPa (right, low-spin state). Circles – experimental data, black line – total fit, blue – Fe$^{3+}$ doublet, purple – high-spin Fe$^{2+}$, green – low-spin Fe$^{2+}$. Residuals are shown above each spectrum.

Fig. 5. Relative amount of the low-spin component in Mössbauer spectra of ferropericlase at different $P$ and $T$.

In general our observations are consistent with the previous study (Badro et al., 2003), where the spin transition was observed between 60 and 70 GPa. The main difference is that the Mössbauer data show a significantly wider pressure range over which the low- and high-spin components co-exist. Our data indicate the appearance of the low-spin component at ~56 GPa and the disappearance of the high-spin component at ~101 GPa. Such a broad transition is unusual for spin transitions and implies a continuous reduction of volume over a large (~50 GPa) pressure range, which implies that the effect of a spin transition in ferropericlase does not influence significantly the partitioning of iron between (Mg,Fe)SiO$_3$ perovskite and (Mg,Fe)O ferropericlase in the Earth’s lower mantle.

**Conclusions**

A newly developed resistive heating assembly for the DAC allows Mössbauer spectroscopic experiments to be performed at high pressures and temperatures. Using the described methodology a high- to low-spin transition in (Mg$_{0.8}$Fe$_{0.2}$)O ferropericlase was observed. The transition starts at 56 GPa and is only complete at 101 GPa, showing a wide pressure range over which the high- and low-spin states of iron co-exist.
References cited


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