In situ X-ray Emission and Diffraction Study on Magnesiowüstite [(Mg,Fe)O] in the Earth's Lower Mantle

Jung-Fu Lin[1], Viktor V. Struzhkin[1], Steven D. Jacobsen[1], Michael Y. Hu[2], Paul Chow[2], Jennifer Kung[3], Haozhe Liu[2], Ho-kwang Mao[1], and Russell J. Hemley[1]

[1]Geophysical Laboratory, Carnegie Institution of Washington, DC, U.S.A.; [2]HPCAT, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.;[3]The Mineral Physics Institute, University of New York at Stony Brook, Stony Brook, NY, U.S.A.

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Introduction

Magnesiowüstite [(Mg,Fe)O] is the second most abundant mineral assemblage in the Earth's lower mantle [1-3]. High-pressure experimental and theoretical studies indicate that pressure-induced electronic spin transitions of iron from high-spin state to low-spin states occur in magnesiowüstite [1,2]. The electronic spin transitions have been postulated to have important geophysical and geochemical consequences, such as causing a large density change and shifting the partitioning of iron between magnesiowüstite and perovskite. However, no significant change in iron partitioning between magnesiowüstite and perovskite has been observed and the effects of the electronic transition on the density and elasticity have not been previously measured. In order to understand the consequences of the electronic transition on the geophysical and geochemical processes of the Earth's interior, we have studied the spin states of iron in magnesiowüstite and the effects of the electronic transitions on the elasticity of magnesiowüstite with *in situ* X-ray emission spectroscopy (XES) and X-ray diffraction under lower mantle pressures.

Methods and Materials

In situ X-ray emission spectroscopy and X-ray diffraction experiments in a diamond anvil cell (DAC) were conducted at the 16-ID sector of HPCAT, Advanced Photon Source, Argonne National Laboratory. A monochromatic X-ray beam of 12 keV was focused down to 20 µm vertically and 60 µm horizontally at the sample position. The Fe-K_β emission spectra were collected through a Be gasket by an one-meter Rowland circle spectrometer in the vertical scattering geometry. A Si (333) single-crystal wafer glued onto a spherical substrate of one-meter radius was used as the analyzer and a Peltier-cooled silicon detector (AMPTEK XR_100CR) was used to detect the emitted X-ray fluorescence.

To understand the isolated effect of the spin transition of iron on the elasticity of magnesiowüstite, we also carried out *in situ* X-ray powder diffraction experiments in a DAC. A polycrystalline magnesiowüstite sample [$(Mg_{0.83},Fe_{0.17})O$ or $(Mg_{0.40},Fe_{0.60})O$] was loaded into a DAC with a neon pressure medium and Pt pressure scale [4,5]. A focused monochromatic beam (0.4246 Å) with a beamsize of approximately 10 µm in diameter was used as the X-ray source for angle-dispersive X-ray diffraction experiments and the diffracted X-ray was collected with an image plate (MAR345). Three diffraction peaks of (111), (200), and (220) were used to calculate the cell parameters of magnesiowüstite, and pressures were calculated from the equation of state (EOS) of Pt. The pressure and volume data were analyzed with the Birch-Murnaghan (BM) EOS and the Vinet EOS using a weighted least squares linear fit to obtain values for the isothermal bulk modulus at ambient conditions (K_{0T}) and pressure derivative of the bulk modulus at ambient conditions (K_{0T}') [6,7].

Results

The XES spectra of the Fe-K_β fluorescence lines in $(Mg_{0.75},Fe_{0.25})O$ and $(Mg_{0.40},Fe_{0.60})O$ reveal that a high-spin to low-spin transition occurs at 54 to 67 GPa and 84 to 102 GPa, respectively (Fig. 1).

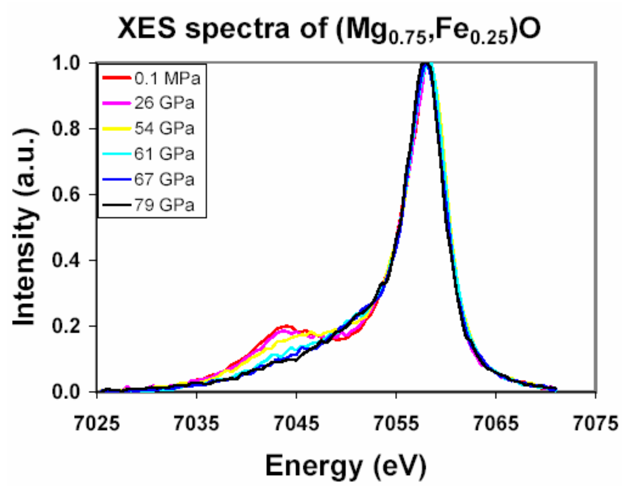

Fig. 1 Representative X-ray emission spectra of Fe-K_β collected from magnesiowüstite [$(Mg_{0.75},Fe_{0.25})O$] at high pressures. The presence of the satellite peak (K_β') below 55 GPa is characteristic of the magnetic state of iron whereas the absence of the satellite peak above 67 GPa indicates the collapse of the magnetization.

Discussion

X-ray emission and X-ray diffraction studies on magnesiowüstite under lower mantle pressures show that the electronic transition significantly affects the incompressibility of magnesiowüstite at lower mantle pressures. An observed high-spin to low-spin transition of iron in magnesiowüstite results in an abnormal compressional behaviour between the high-spin and the low-spin states. The high-pressure low-spin state exhibits a much higher bulk modulus (K_T) and bulk sound velocity (V_Φ) than the low-pressure high-spin state in $(Mg_{0.17},Fe_{0.83})O$. Our current understanding of the equation of state for iron-bearing minerals comprising the bulk of Earth's lower mantle, namely magnesiowüstite and ferromagnesian silicate perovskite, appears to be inadequate considering the effects of the pressure-induced spin-state transitions of iron in its host minerals.

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