Spin state of ferric iron in Mg-perovskite up to 160 GPa by X-ray emission spectroscopy

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Pressure-induced high spin - low spin transition of iron in the lower mantle minerals has been attracting many researcher's interest because the spin transition of iron largely affects the mineralogy and dynamics of the lower mantle. Among the lower mantle minerals, the spin transition of iron in Mg-perovskite is the subject of controversy. Recent studies indicate that the predominant valence state of iron in Mg-perovskite is ferric rather than ferrous, and in the presence of Al, ferric iron enters into Mg-perovskite as an $FeAlO_3$ component. Therefore, the spin state of ferric iron in $FeAlO_3$-bearing Mg-perovskite is important to understand the dynamics of the lower mantle.

We measured the spin state of ferric iron in Mg-perovskite of the composition $Mg_{0.85}Fe^{3+}{}_{0.15}Al_{0.15}Si_{0.85}O_3$ by X-ray emission spectroscopy (XES) at BL-12XU of Spring-8. The samples were loaded in a diamond anvil cell using a Be gasket to obtain the emitted k-beta' X-ray intensity. The incident X-ray beam of 11 keV was inserted through the diamond in the direction parallel to the opposing axis of the diamond anvils, and the emitted k-beta' X-ray through the Be gasket in the direction perpendicular to the incident X-ray beam was focused by the bent Si analyzer on the detector. A collimator of 20 micrometer was used to avoid the X-ray emitted from iron contained in the Be gasket around the specimen.

We could measure the XES data at pressures up to 160 GPa at room temperature. This is the highest pressure at which the XES data of iron in Mg-perovskite have been ever reported. We also measured XES data of powdered Fe_2O_3 at 0 GPa (high spin) and 77 GPa (low spin) at room temperature, as the reference spectra of ferric iron.

The obtained XES data suggest that the spin state of ferric iron in Mg-perovskite is high spin at pressures nearly up to 120 GPa, and then the spin number begins to decrease at higher pressures. However, even at 160 GPa, far beyond the pressure of the bottom of the lower mantle, the spin state is not yet low spin.

The present XES data were measured at room temperature, and to evaluate the spin state of ferric iron in Mg-perovskite in the lower mantle, we must consider the temperature dependence of the spin transition. If the Clapeyron slope of the spin transition in the pressure-temperature space is positive, then the spin state of ferric iron in Mg-perovskite in the lower mantle would be still high spin, while if the Clapeyron slope of the spin transition is negative, then the low spin state of ferric iron in Mg-perovskite may be possible in the lower mantle.