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Electronic spin states of ferric and ferrous iron in the lower-mantle silicate perovskite

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Abstract

The electronic spin and valence states of iron in lower-mantle silicate perovskite have been previously investigated at high pressures using various experimental and theoretical techniques. However, experimental results and their interpretation remain highly debated. Here we have studied a well-characterized silicate perovskite starting sample [$(Mg_{0.9},Fe_{0.1})SiO_3$] in a chemically inert Ne pressure medium at pressures up to 120 GPa using synchrotron Mössbauer spectra. Analyses of the Mössbauer spectra explicitly show a high-spin to low-spin transition of the octahedral-site Fe^{3+} occurring at ~13–24 GPa, as evidenced from a significant increase in the hyperfine quadrupole splitting. Two quadrupole doublets of the A-site Fe^{2+}, with extremely high-QS values of 4.1 and 3.1 mm/s, occur simultaneously with the spin transition of the octahedral-site Fe^{3+} and continue to develop to 120 GPa. It is conceivable that the spin-pairing transition of the octahedral-site Fe^{3+} causes a volume reduction and a change in the local atomic-site configurations that result in a significant increase of the quadrupole splitting in the dodecahedral-site Fe^{2+} at 13–24 GPa. Our results here provide a coherent explanation for recent experimental and theoretical results on the spin and valence states of iron in perovskite, and assist in comprehending the effects of the spin and valence states of iron on the properties of the lower-mantle minerals.

Keywords: Silicate perovskite, diamond-anvil cell, spin transition, lower mantle, synchrotron Mössbauer spectroscopy, high pressures