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Resonant X-ray emission study of the lower-mantle ferropericlase at high pressures

Jung-Fu Lin,[1,*] Zhu Mao,[1] Ignace Jarrige,[2] Yuming Xiao,[3] Paul Chow,[3] Takuo Okuchi,[4] Nozomu Hiraoka,[5] and Steven D. Jacobsen[6]

[1]Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, Austin, Texas 78712, U.S.A.
[2]Synchrotron Radiation Research Unit, Japan Atomic Energy Agency, Hyogo 679-5148, Japan
[3]HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, U.S.A.
[4]Institute for Study of the Earth's Interior, Okayama University, Yamada 827, Misasa, Tottori 682-0193, Japan
[5]National Synchrotron Radiation Research Center, Hsinchu 30077, Taiwan
[6]Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois 60208, U.S.A.

Abstract

Electronic states of iron in Earth's mantle minerals including ferropericlase, silicate perovskite, and post-perovskite have been previously investigated at high pressures and/or temperatures using various experimental techniques, including X-ray emission and Mössbauer spectroscopies. Although such methods have been used to infer changes in the electronic spin and valence states of iron in lower mantle minerals, they do not directly probe the 3*d* electronic states quantitatively. Here we use 1*s*2*p* resonant X-ray emission spectroscopy (RXES) at the Fe *K* pre-edge to directly probe and assess the 3*d* electronic states and the crystal-field splittings of Fe^{2+} in the lower-mantle ferropericlase [$(Mg_{0.75},Fe_{0.25})O$] at pressures up to 90 GPa. The pre-edge features from X-ray absorption spectroscopy in the partial fluorescence yield (PFY-XAS) and RXES results explicitly show three excited states for high-spin Fe^{2+} (a lower-energy $^4T_{1g}$ state, a $^4T_{2g}$ state, and a higher-energy $^4T_{1g}$ state) and a single ^2E_g state for low-spin Fe^{2+}, attributed to the $(t_{2g})^0(e_g)^3$ excited configuration. This latter feature begins to appear at 48 GPa and grows with pressure, while the peaks related to high-spin Fe^{2+} vanish above 80 GPa. The observed pre-edge features are consistent with purely quadrupolar transitions resulting from the centrosymmetric character of the Fe^{2+} site. The *K* pre-edge RXES spectra at the incident energy of 7112 eV, which are similar to the Fe *L*-edge spectra, are also used successfully to quantitatively obtain consistent results on the spin transition of Fe^{2+} in ferropericlase under high pressures. Owing to the superior sensitivity of the RXES technique, the observed electronic states and their energy separations provide direct information on the local electronic structures and crystal-field splitting energies of the 3*d* electronic shells of Fe^{2+} in ferropericlase at relevant pressures of the Earth's lower mantle.

Keywords: Ferropericlase, diamond anvil cell, spin transition, resonant X-ray emission spectroscopy, partial fluorescence yield, high pressures