Resonant X-ray Emission Study of the Lower-mantle Ferropericlase at High Pressures

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Electronic states of iron, including total spin momentum and valence charge, have been studied extensively at high pressures in lower-mantle ferropericlase, silicate perovskite, and post-perovskite because changes in electronic configurations of iron can influence a range of physical properties relevant to understanding the state and dynamics of the Earth's deep interior. In particular, a high-spin to low-spin transition of Fe2+ has been reported in ferropericlase [(Mg,Fe)O] at high pressures using Mössbauer, X-ray emission spectroscopy (XES), and optical absorption spectroscopy. These techniques have long played important and complementary roles in studying the electronic structures of planetary materials in extreme environments. Although many experimental techniques allow inference of changes in spin and valence states through changes in electronic, optical, vibrational, magnetic, or structural properties, few directly probe the 3d electronic states quantitatively.

Here we use 1s2p resonant X-ray emission spectroscopy (RXES) on the Fe K pre-edge to directly probe and assess the 3d 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. Our partial fluorescence yield (PFY) and two-dimensional 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 ^2Eg state for low-spin Fe2+ above 80 GPa. The ^2E_g state begins to appear at 48 GPa and is attributed to the occurrence of low-spin Fe_{2+} with the $(t_{2g})^0(e_g)^3$ excited configuration. The observed pre-edge features are consistent with purely quadrupolar transitions as a result of the centrosymmetric character of the Fe^{2+} site. Our results provide direct information on the local electronic structures and crystal-field splitting energies of the 3d electronic shells of the Fe^{2+} in ferropericlase at relevant pressures of the Earth's lower mantle.

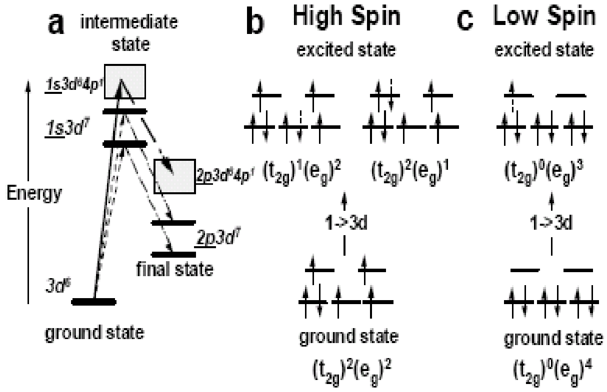

Fig. 1: Schematic representation of 1s2p RXES transitions for octahedrally-coordinated Fe^{2+} in ferropericlase at the Fe K pre-edge based on crystal field theory. (a), a two-step RXES transition process within a mono-electronic picture. The quadrupolar and dipolar transitions are indicated by thick and thin lines, respectively; (b), ground and excited states of the octahedrally-coordinated high-spin Fe^{2+}; (c), ground and excited states of the octahedrally-coordinated low-spin Fe^{2+}.

Reference

[1] J. F. Lin *et al.*, submitted to American Mineralogists, (2010).