

Ab initio computation on the Fe L-edge X-ray emission spectroscopy of Fe-bearing Mg-SiO₃

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Behaviors of iron (Fe) in the minerals of the Earth's lower mantle (LM), including valence state, spin state, and chemical environments, at high pressures are important for more detailed understanding the LM properties. The pressure induced spin transition of Fe-bearing MgO and MgSiO₃ perovskite (Pv) were detected of usually by using high-resolution *K*-edge X-ray emission spectroscopy (XES) [1,2,3] and confirmed by theoretical simulations [4,5]. Since the Fe *K*-edge XES is associated to the 3*p* orbital, which is far from the valence orbitals (3*d* and 4*s*), it provides no information about Fe's coordination environments. However, Fe *L*-edge XES can directly determine the distribution and intensity of Fe-3*d* character. To identify the spin state, valence state and substitution site of Fe in Fe-bearing Pv at the LM pressure range, we systematically investigated the *L*-edge XES of Fe²⁺- and Fe³⁺ (Al³⁺)-bearing Pv under high pressure by using the first-principles method combined with the Slater-transition method. Our results show that the spin transition of Fe²⁺ and Fe³⁺ can be identified easily by the *L*-edge XES technique. The valence state of Fe can be furthermore certified, since the shift of the first main peak of Fe³⁺ is about two times larger than that of Fe²⁺ across the spin transition. The width of the *L*-edge XES of Fe³⁺ is also sensitive to the substitution site, indicating that their coordination environments might also be distinguishable from the Fe *L*-edge XES spectra. These strong sensitivities to the Fe states suggest that the high-resolution Fe *L*-edge XES measurement would be a useful experimental technique to investigate Fe-bearing silicate minerals. Corresponding experiments are expected.

Keywords: First-principles calculation, First-principles calculation, Fe L-edge XES, Mg perovskite