Ab initio computation on the Fe L-edge X-ray emission spectroscopy of Fe-bearing MgSiO₃ perovskite

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ABSTRACT

We systematically investigated the L-edge X-ray emission spectroscopy (XES), a 3d-to-2p transition, of Fe²⁺- and Fe³⁺-bearing MgSiO₃ perovskite under high pressure based on the internally consistent LSDA+U technique combined with the Slater-transition method. The Fe L-edge XES spectra can be used to directly interpolate the distribution of Fe-3d electrons including the spin states and coordination environments of iron. Our results show that the spin transition from the high-spin state to low-spin state of Fe²⁺ and Fe³⁺ can be identified easily by the L-edge XES technique. The valence state of Fe (2+ or 3+) can be verified by this, since a shift of the first main peak of Fe²⁺ across the spin transition of 2 eV, in good agreement with the experimental value (~1.6 eV), is significantly smaller than that of Fe³⁺ of 4 eV. The width of the L-edge XES of Fe³⁺ also depends strongly on the substitution sites (Mg or Si), meaning that its coordination environments might also be distinguishable based on the Fe L-edge XES spectra. These strong sensitivities to the Fe’s states suggest that the high-resolution Fe L-edge XES would be a useful experimental technique to investigate Fe-bearing silicate minerals.

Keywords: First-principles method, L-edge XES, Fe-bearing MgSiO₃ perovskite, high pressures

INTRODUCTION

Iron is one of the dominant impurities in the minerals of the potential Earth’s lower mantle (LM) such as in MgSiO₃ and MgO (e.g., Hemley and Cohen 1992; Irifune and Tsuchiya 2007). Therefore, behavior of Fe in different spin states, valence states, and coordination environments needs to be clarified to improve our understanding of the LM. Researchers have already focused extensively on the behavior of Fe in LM minerals, which can be affected by several factors such as pressure and concentration of dissolving trivalent aluminum (Al³⁺), which is believed to be another dominant impurity in LM minerals (Irifune 1997; Badro et al. 2003, 2004; Li et al. 2004, 2006; Frost and Langenhorst 2002; Nishio-Hamane et al. 2005; Lin et al. 2005; Catalli et al. 2010; Fujino et al. 2012). Frost and Langenhorst (2002) confirmed that a fraction of Fe³⁺, Fe⁵⁺/2Fe, in Fe-bearing MgSiO₃ perovskite (Pv) increases with the concentration of increasing Al. The pressure-induced spin transition of Fe in Fe-bearing MgO (ferropericlase) and MgSiO₃ Pv and postperovskite (PPv) was observed via Fe K-edge X-ray emission spectroscopy (XES) or Mössbauer spectroscopy (Badro et al. 2003, 2004; Li et al. 2004, 2006; Lin et al. 2005; McCammon et al. 2008; Catalli et al. 2010; Fujino et al. 2012). However, interpretations of the results obtained by these techniques are sometimes ambiguous. For example, very similar spectral variations observed with increasing pressure were assigned to the spin transition of Fe from the initial high-spin (HS) to the final low-spin (LS) state (Li et al. 2004, 2006) or to the final intermediate-spin (IS) state (McCammon et al. 2008) in Mg-Pv. Furthermore, not only the stable spin states but also their site dependence continued to be debated. Jackson et al. (2005) reported that in Fe³⁺-bearing Mg-Pv, iron at the Mg site (hereafter denoted A site) became LS in the LM pressure range. Nevertheless, some other experimental results showed that Fe²⁺ in the A site remains HS even up to 136 GPa (Li et al. 2006; Catalli et al. 2010). Recently, based on spectral measurements, Fujino et al. (2012) proposed that Fe³⁺ in the A site of Mg-Pv would move to the Si site (hereafter denoted B site) after 40 GPa and then would undergo a spin transition. Meanwhile, theoretical simulations were also conducted for better understanding of the spin transition behavior of Fe (Tsuchiya et al. 2006; Hsu et al. 2011; Fukui et al. 2012; Tsuchiya and Wang 2013), since the spin transition of Fe was suggested to impact physical properties of LM minerals such as density, sound velocity, thermal conductivity, and so on (Lin and Tsuchiya 2008; Catalli et al. 2010). Theoretical results also showed that the Fe spin transition strongly depends on its substitution sites and valence charges. Fe²⁺ incorporated into MgO and Fe³⁺ at the B site of Mg-Pv went through the HS→LS transition in the LM pressure range, while no spin transition was observed when Fe was substituted at the A site of Mg-Pv with geophysically relevant Fe concentrations (Tsuchiya et al. 2006; Bengtson et al. 2009; Hsu et al. 2011, 2012; Metsue and Tsuchiya 2011, 2012; Fukui et al. 2012; Tsuchiya and Wang 2013). In those studies, no stability of the IS state was ensured, suggesting that there are still technical difficulties in high-pressure experiments to identify the valence state and coordination environment of Fe clearly. Indeed, the Fe K-edge XES technique often used in experiments (Badro et al. 2003, 2004; Li et al. 2004, 2006; Lin et al. 2005, 2008; McCammon et al. 2008; Catalli et al. 2010; Fujino et al. 2012) can only illustrate the spin state of Fe clearly, whereas it is not easy to distinguish between Fe²⁺ and Fe³⁺ and to identify the position, the A or B site, since the K-edge XES detects the