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Spin crossover of iron in aluminous $MgSiO_3$ perovskite and post-perovskite

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ABSTRACT

Using density functional theory+Hubbard U (DFT+U) calculations, we investigate how aluminum affects the spin crossover of iron in $MgSiO_3$ perovskite (Pv) and post-perovskite (Ppv), the major mineral phases in the Earth's lower mantle. We find that the presence of aluminum does not change the response of iron spin state to pressure: only ferric iron (Fe^{3+}) in the octahedral (B)-site undergoes a crossover from high-spin (HS) to low-spin (LS) state, while Fe^{3+} in the dodecahedral (A)-site remains in the HS state, same as in Al-free cases. However, aluminum does significantly affect the placement of Fe^{3+} in these mineral phases. The most stable atomic configuration has all Al^{3+} in the B-site and all Fe^{3+} in the A-site (thus in the HS state). Metastable configurations with LS Fe^{3+} in the B-site can happen only *at high pressures and high temperatures*. Therefore, experimental observations of LS Fe^{3+} at high pressures in Al-bearing Pv require diffusion of iron from the A-site to the B-site and should be sensitive to the annealing temperature and schedule. In the Earth's lower mantle, the elastic anomalies accompanying the B-site HS-LS crossover exhibited in Al-free Pv are likely to be considerably reduced, according to the B-site Fe^{3+} population.

1. Introduction

Pressure-induced spin crossovers of iron in Earth minerals have attracted great attention since the discovery of this phenomenon (Badro et al., 2003, 2004). As well studied in ferropericlase (the second most abundant mineral in the Earth's lower mantle), spin crossover can produce elastic, thermodynamic, optical, and conducting anomalies in the host minerals (Crowhurst et al., 2008; Goncharov et al., 2006; Hsu et al., 2010c; Lin et al., 2005, 2007a, 2007b; Tsuchiya et al., 2006; Wentzcovitch et al., 2009; Wu et al., 2009). While the geophysical consequences of these anomalies have been anticipated, further investigations are still necessary. In contrast to ferropericlase, spin crossovers in magnesium silicate ($MgSiO_3$), perovskite (Pv), and post-perovskite (Ppv), the *major* mineral phases in the lower mantle, have been controversial for years. One reason for such controversy is the complicated nature of these minerals. In Pv and Ppv, ferrous iron (Fe^{2+}) and ferric iron (Fe^{3+}) coexist, and they both have three possible spin states: high-spin (HS), intermediate-spin (IS), and low-spin (LS). In addition, Fe^{3+} can occupy the dodecahedral (A)-site and the octahedral (B)-site (Fe^{2+} only occupies the A-site), so there can be up to nine possible states to be considered. Another reason for this iron-spin controversy is the lack of definitive tools to directly identify the iron spin state and occupying site. Indeed, x-ray emission spectroscopy (XES) and Mössbauer spectroscopy have been widely used, but their interpretations can be ambiguous. For example, decreases of the satellite peak ($K\beta'$) intensity observed in XES spectra of Pv containing both Fe^{2+} and Fe^{3+} were interpreted in terms of HS-IS or HS-LS crossover of Fe^{2+} (Badro et al., 2004; Li et al., 2004; McCammon et al., 2008), but a highly similar $K\beta'$ decrease was also observed in Pv containing only Fe^{3+} (Catalli et al., 2010b). Clearly, while the decrease of $K\beta'$ intensity is a signature of the decrease of *average* electron spin moment of iron in Pv, extracting the detailed spin-crossover mechanism in such a complicated system solely based on XES spectra is extremely difficult. Interpretation of Mössbauer spectra without other information can be ambiguous as well. A sudden increase in the nuclear quadrupole splitting (QS) of Fe^{2+} (from 2.4 to 3.5 mm/s) in Pv has been interpreted in terms of HS-IS or HS-LS crossover (Jackson et al., 2005; Li et al., 2006; McCammon et al., 2008). To understand spin crossover in Pv and to explain the above experimental observations, plenty of calculations have been conducted (Bengtson et al., 2008; Hofmeister, 2006; Stackhouse et al., 2007; Umemoto et al., 2008, 2009; Zhang and Oganov, 2006), but consistency with experiments was not achieved until recently (Bengtson et al., 2009; Catalli et al., 2010b; Hsu et al., 2010b, 2011; Lin et al., 2012). It turns out that Fe^{2+} in Pv does not undergo a spin crossover; it remains in the HS state throughout the lower-mantle pressure range (23–135 GPa) with a change in orbital occupancy (and thus QS) occurring at about 20–30 GPa (Hsu et al., 2010b). It is the B-site Fe^{3+} in (Mg,Fe)(Si,Fe)O_3 Pv going through a HS-LS crossover at 50–60 GPa, which is accompanied by a volume reduction

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and suggests a possible source of seismic anomalies (Catalli et al., 2010b; Hsu et al., 2011). As to Ppv, a high QS (3.5–4.0 mm/s) of Fe^{2+} was interpreted as a signature of the IS state (Lin et al., 2008; Mao et al., 2010). However, first-principles calculations have shown it to be the HS state (Yu et al., 2012). Yu et al. (2012) have also shown that for Al-free Ppv in the D″ pressure range (120–135 GPa), the *A*- and *B*-sites Fe^{3+} are in the HS and LS state, respectively, and the calculated QSs of these two states are consistent with Mössbauer spectra (Catalli et al., 2010a; Jackson et al., 2009; Mao et al., 2010).

The success of first-principles calculations in studying Fe-bearing minerals mainly results from the development of density function theory + Hubbard *U* (DFT+*U*) method [see Cococcioni, 2010 for a comprehensive review]. In contrast to standard DFT methods, such as local density approximation (LDA) or generalized gradient approximation (GGA), the on-site Coulomb interaction of iron is more accurately treated by including the Hubbard *U* correction. With this correction, states inaccessible in standard DFT calculations can be obtained, such as the two HS Fe^{2+} with distinct QSs and the *B*-site HS Fe^{3+} in Pv and Ppv (Hsu et al., 2010b, 2011; Yu et al., 2012). In particular, when the Hubbard *U* parameters are computed self-consistently by first principles (referred to as U_{sc}, see Section 2), the predicted transition pressure is in good agreement with experiments (Hsu et al., 2011). So far, the DFT+U_{sc} method has been applied to Al-free Pv/Ppv. With a small fraction of Al_2O_3 known to be accommodated in Pv in the lower-mantle condition (Frost et al., 2004; Irifune, 1997; Kesson et al., 1998; McCammon, 1997), Al-bearing Pv/Ppv is believed to be more important in the lower mantle. However, these mineral phases have been computationally studied via standard DFT methods only (Caracas, 2010; Li et al., 2005; Zhang and Oganov, 2006), and standard DFT calculations cannot fully explain the contradictive experimental results described below. Using Mössbauer spectroscopy, Li et al. (2006) did not observe any crossover in Al-bearing Pv in 0–100 GPa, but Catalli et al. (2011) showed a fraction of Fe^{3+} undergoes a crossover from QS $\sim$1 mm/s to QS $\sim$2.1 mm/s when $P > 80$ GPa, along with a decrease in the $K\beta'$ intensity, which was also reported by Fujino et al. (2012). Furthermore, the transition pressure observed in Al-bearing Pv (Catalli et al., 2011) is significantly higher than that in Al-free Pv (Catalli et al., 2010b). This finding strongly suggests that changes of ironspin state in these two systems may have different mechanisms. To properly address iron spin problems in complicated systems like Al-bearing Pv/Ppv, detailed and carefully conducted DFT+U_{sc} calculations are thus highly desirable, given their previous success in Al-free cases.

2. Computation details

In this paper, we performed structural optimization for 40-atom supercells of Fe- and Al-bearing Pv/Ppv (Fig. 1) using variable cell shape molecular dynamics (Wentzcovitch et al., 1993) implemented in the QUANTUM ESPRESSO code (Giannozzi et al., 2009), in which the plane-wave pseudopotential method is adopted. Pseudopotentials used in this paper have been reported by Umemoto et al. (2008), with a plane-wave energy cutoff of 40 Ry. In our calculations for Al-bearing Pv/Ppv, we find metastable IS Fe^{3+} in both the *A*- and *B*-sites, in contrast to the Al-free cases where IS Fe^{3+} was only found in the *A*-site. We used a linear response approach (Cococcioni and de Gironcoli, 2005) to compute spin-dependent U_{sc}'s until self consistency is achieved (Hsu et al., 2011; Kulik et al., 2006). The U_{sc}'s of the newly found *B*-site IS Fe^{3+} are 4.1 and 4.2 eV for Pv and Ppv, respectively. The U_{sc}'s of other states are the same as the Al-free cases; their numerical values have been reported previously (Hsu et al., 2011; Yu et al., 2012). The volume dependence of these U_{sc}'s is negligible. To be more rigorous, the Hubbard *U* mentioned in this paper is effectively the *U*–*J* introduced by Dudarev et al. (1998). The electric field gradient (EFG) tensors are computed using the WIEN2k code (Blaha et al., 2001), in which the augmented plane-wave plus local orbitals (APW+lo) method (Madsen et al., 2001) is implemented. The EFGs were converted to QSs with the ^{57}Fe nuclear quadrupole moment $Q=0.16$ (Petrilli et al., 1998) and 0.18 barn for the possible uncertainty. A shifted $4\times4\times4$ **k**-point grid was used to calculate the EFG, while a $2\times2\times2$ and a $4\times4\times4$ grids produce the same atomic structure.

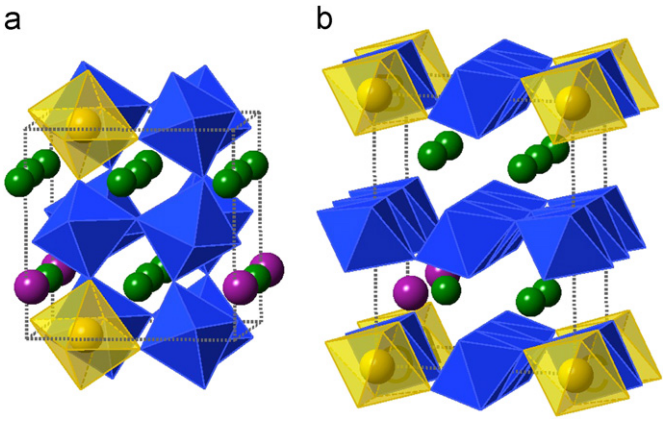

Fig. 1. Atomic structure of Fe- and Al-bearing $MgSiO_3$ perovskite (a) and post-perovskite (b), where the 40-atom supercells are indicated by the dotted lines. Green spheres and blue octahedra indicate Mg and SiO_6 octahedra, respectively. Purple and yellow spheres indicate substituting atoms at the *A*- and *B*-sites, respectively. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Fe- and Al-bearing $MgSiO_3$ perovskite

In Pv, Fe^{3+} can substitute Mg or Si in the *A*- or *B*-site, respectively. To understand how the iron spin state responds to pressure in these two non-equivalent sites, we first consider the coupled substitutions of Fe^{3+} and Al^{3+} in a 40-atom supercell, forming $(Mg_{1-x}Fe_x)(Si_{1-x}Al_x)O_3$ or $(Mg_{1-x}Al_x)(Si_{1-x}Fe_x)O_3$ Pv ($x=0.125$), with Fe^{3+} and Al^{3+} occupying nearest *A*- and *B*-sites [Fig. 1(a)]. For each configuration, relative enthalpies (ΔH) of all possible spin states (HS, IS, and LS) are computed using LDA+U_{sc} and GGA+U_{sc} [PBE-type GGA Perdew et al., 1996], as shown in Fig. 2. The results are very similar to that of Al-free Pv (Hsu et al., 2011): the *A*-site Fe^{3+} remains in the HS state in 0–150 GPa [Fig. 2(a) and (b)], and the *B*-site Fe^{3+} undergoes a HS-LS crossover [Fig. 2(c) and (d)] at a transition pressure $P_T \sim 43$ GPa in LDA+U_{sc} and $P_T \sim 70$ GPa in GGA+U_{sc}. Since LDA+U_{sc} predicts more accurate equation of state and transition pressure (Hsu et al., 2011), we only present LDA+U_{sc} calculations hereafter. The computed QSs of these states are shown in Fig. 2(e), along with those extracted from Mössbauer spectra (Catalli et al., 2011; Li et al., 2006), shown in Fig. 2(f). For the newly found *B*-site IS Fe^{3+}, the EFGs at various pressures are computed. The QS plotted in Fig. 2(e) ranges from the lowest to the highest QS we obtained for this particular state. For the other states, we did not computed their EFGs at every pressure. We tested a few cases and noticed that they are essentially the same as those in Al-free Pv and are in excellent agreement with the measured QS shown in Fig. 2(f). Here, we simply adopt previous Al-free calculation results (Hsu et al., 2011) for these states. Noticeable in Fig. 2(e), the