Iron spin crossover and its influence on post-perovskite transitions in MgSiO$_3$ and MgGeO$_3$

Gaurav Shukla$^a$, Mehmet Topsakal$^b$, Renata M. Wentzcovitch$^{a,b,c,d}$

$^a$School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455, USA
$^b$Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA
$^c$Minnesota Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455, USA
$^d$Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 OoKayama, Meguro-ku, Tokyo, 152-8550, Japan

Abstract

MgGeO$_3$-perovskite is known to be a low-pressure analog of MgSiO$_3$-perovskite in many respects, but especially in regard to the post-perovskite transition. As such, investigation of spin state changes in Fe-bearing MgGeO$_3$ might help to clarify some aspects of this type of state change in Fe-bearing MgSiO$_3$. Using DFT+U calculations, we have investigated pressure induced spin state changes in Fe$^{2+}$ and Fe$^{3+}$ in MgGeO$_3$ perovskite and post-perovskite. Owing to the relatively larger atomic size of germanium compared to silicon, germanate phases have larger unit cell volume and inter-atomic distances than equivalent silicate phases at same pressures. As a result, all pressure induced state changes in iron occur at higher pressures in germanate phases than in the silicate ones, be it a spin state change or position change of (ferrous) iron in the perovskite cage. We showed that iron state transitions occur at particular average Fe-O bond-length irrespective of mineral composition (silicate or germanate) or functionals (LDA+U sc or GGA+U sc). Ferrous iron substitution decreases the perovskite to post-perovskite (PPv) transition pressure while coupled ferric iron substitution increases it noticeably.

Keywords: Iron-spin crossover, Ferrous and ferric iron, P$_v$ to PPv transition

Corresponding author

Email addresses: shukla@physics.umn.edu (Gaurav Shukla), mtopsaka@umn.edu (Mehmet Topsakal), wentz002@umn.edu (Renata M. Wentzcovitch)

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1. Introduction

Iron-bearing MgSiO$_3$ perovskite (Si-Pv) is one of the major constituent minerals of Earth’s lower mantle along with (Mg,Fe)O ferropericlase (Fp). Unraveling the composition and thermal structure of the lower mantle requires a detailed understanding of the influence of iron (Fe) on these host minerals. It is well known that iron in (Mg,Fe)O undergoes a pressure induced spin crossover from high-spin ($S=2$) to low-spin ($S=0$) state and affects elastic properties \cite{Badro2003, Badro2004, Goncharov2006, Crowhurst2008, Tsuchiya2006, Marquardt2009, Wu2009, Antonangeli2011, Wu2013, Hsu2014, Wu2014}. In the case of Si-Pv, deciphering the iron spin state has been quite challenging due to complex perovskite structure and possibility of different valence states of iron (ferric and ferrous). Si-Pv is also known to undergo a perovskite (Pv) to post-perovskite (PPv) phase transition at $\sim 125$ GPa and this will have geophysical consequences in deep lower mantle region \cite{Murakami2004, Tsuchiya2004, Oganov2004}. Understanding the effect of iron, especially, on Pv to PPv transition and on elastic properties of Pv and PPv phases is crucial to constrain lower mantle composition.

In (Mg,Fe$^{2+}$)SiO$_3$-Pv, the pressure induced increase in Mössbauer quadrupole splitting (QS) above $\sim 30$ GPa (low-QS to high-QS transition) \cite{Jackson2005, Li2004, Li2006, McCammon2008, McCammon2010, Lin2012, Lin2013} has been explained by lateral displacement of Fe$^{2+}$ ion which remains in the high-spin (HS) state in the entire lower-mantle pressure range \cite{Bengtson2009, Hsu2010, Hsu2014}. In the case of (Mg,Fe$^{3+}$)(Si,Fe$^{3+}$)O$_3$-Pv, however, first-principles calculations by \cite{Hsu2011} reported that Fe$^{3+}$ in B-site undergoes a high-spin (S=$5/2$) to low-spin (S=$1/2$) state change at approximately 41 GPa and 70 GPa using LDA+$U_{sc}$ and GGA+$U_{sc}$ methods, respectively, while in the A-site Fe$^{3+}$ remains in the high-spin state. These findings were in good agreement with experimental observations of \cite{Catalli2010a}. There have also been several experimental \cite{Lin2008, Catalli2008, Mao2010} and first-principles \cite{Zhang2006, Caracas2008, Yu2012} studies about the spin crossover in
MgSiO$_3$-PPv (Si-PPv). The consensus regarding the spin crossover in iron-bearing Si-
PPv is that Fe$^{2+}$ in the A-site remains in the high-spin and high-QS state throughout
the lower mantle pressure range, while Fe$^{3+}$ undergoes a high to low spin transition in
the B site and remains in the high spin state in the A-site (Yu et al., 2012). In spite of
these efforts to pin down the state of iron at high pressures, it has been very difficult
to ascertain the exact role of iron with its varying spin and valence state on Pv to PPv
transition, especially because of the extreme pressure and temperature conditions in the
deep lower mantle region.

MgGeO$_3$-perovskite (Ge-Pv) is a low pressure analog of MgSiO$_3$ perovskite (Ross
and Navrotsky, 1988; Leinenweber et al., 2004; Hirose et al., 2005; Kubo et al., 2006;
Merkel et al., 2006; Range et al., 2006; Shim et al., 2007; Tsuchiya and Tsuchiya
2007; Duffy, 2008; Ito et al., 2010) and would be a promising candidate to investigate
iron spin crossover and its structural influence on MgSiO$_3$-Pv and PPv phases. In this
study, we have used first-principles DFT+U (LDA+U$_{sc}$ and GGA+U$_{sc}$) calculations to
investigate the iron spin states and their crossover in the Pv and PPv phases of Fe$^{2+}$-
and Fe$^{3+}$-bearing MgGeO$_3$. Comparing enthalpy of the different spin states, we have
determined the stability of the different states and transition pressure. Using these
results, we have also investigated the effect of Fe$^{2+}$ and Fe$^{3+}$ substitution on Pv to PPv
transition.

2. Method

We have used density functional theory (DFT) within the local density approxima-
tion (LDA) (Ceperley and Alder, 1980) and generalized gradient approximation (GGA)
(Perdew et al., 1996) augmented by the Hubbard U (LDA/GGA+U$_{sc}$), calculated self-
consistently and structurally consistently (Cococcioni and de Gironcoli, 2005; Kulik
et al., 2006; Hsu et al., 2009, 2011; Himmetoglu et al., 2014). Ultrasoft pseudo-
potentials, generated by Vanderbilt’s method (Vanderbilt, 1990), have been used for
Fe, Si, Ge, and O. For Mg, norm-conserving pseudo-potential generated by von Barth-
Car’s method, has been used. The plane-wave kinetic energy and charge density cutoff
are 50 Ry and 300 Ry, respectively. Self-consistent U$_{sc}$, calculated by Hsu et al. (2010)
and Yu et al. (2012) using the linear response approach (Cococcioni and de Gironcoli}
have been used. All calculations were performed in a 40-atoms super-cell. Electronic states were sampled on a shifted $2 \times 2 \times 2$ and $3 \times 2 \times 3$ k-point grid for Pv and PPv structure, respectively (Monkhorst and Pack, 1976). Structural optimization at any arbitrary volume has been performed using variable cell-shape damped molecular dynamics approach (Wentzcovitch, 1991, Wentzcovitch et al., 1993). Structures are optimized until the inter-atomic forces are smaller than $10^{-4}$ Ry/a.u. For every possible spin and valence state, structures are optimized at twelve volumes in the relevant pressure-range and the 3rd-order Birch-Murngharn equation of state has been used to fit these compression data.

3. Iron spin states in Pv and PPv phases

Iron spin states have been investigated in Fe$^{2+}$ and Fe$^{3+}$-bearing MgGeO$_3$ and MgSiO$_3$ in a 40-atom super-cell. One Fe$^{2+}$ ion is substituted for a Mg$^{2+}$ ion in the A-site in (Mg$_{0.875}$Fe$_{0.125}$)GeO$_3$ and (Mg$_{0.875}$Fe$_{0.125}$)SiO$_3$ while two Fe$^{3+}$ ions are substituted for one Mg$^{2+}$ and one first neighbor Ge$^{4+}$ or Si$^{4+}$ as in (Mg$_{0.875}$Fe$_{0.125}$)(Ge$_{0.875}$Fe$_{0.125}$)O$_3$ and (Mg$_{0.875}$Fe$_{0.125}$)(Si$_{0.875}$Fe$_{0.125}$)O$_3$. The nearest-neighbor Fe$^{3+}$-Fe$^{3+}$ substitution has been chosen as it has been found to be the lowest energy configuration in previous first-principles studies (Hsu et al., 2011, 2012; Yu et al., 2012). Relative enthalpies have been used to calculate transition pressures ($P_t$) and the stability of a state or phase in a given pressure range. Effects of disorder have not been addressed at this point, but it is expected to produce a two-phase loop. Here we wish to analyze (a) the potentially different effects of Fe$^{2+}$ and Fe$^{3+}$ in the Pv to PPv transition and (b) whether the germanate phase could serve as a good low pressure analog to investigate spin transitions in iron.

3.1. Spin states of Fe$^{2+}$ in Ge-Pv

As in the case of Fe$^{2+}$ in Si-Pv (Bengtson et al., 2009; Hsu et al., 2010; Hsu and Wentzcovitch, 2014), Fe$^{2+}$ in Ge-Pv remains in the high-spin (HS, S=2) state in the entire lower-mantle pressure range (0-135 GPa). However, it undergoes a pressure-induced lateral displacement producing a transition from low to high Mössbauer quadrupole splitting (QS). The atomic structures for the low- and high-QS states of iron in Si-Pv...
are shown in Fig. 1(a) indicating the lateral displacement of iron in the perovskite A-site.

The pressure dependence of enthalpy differences between high-QS and low-QS states ($\Delta H = H_{\text{high-QS}} - H_{\text{low-QS}}$) gives the low- to high-QS transition pressure. It is well-known that LDA usually underestimates transition pressures while GGA usually overestimates it. In this study, we present both LDA+$U_{sc}$ and GGA+$U_{sc}$ results to provide lower and upper bounds for this transition, as shown in Fig. 1(b). The low- to high-QS state change in Ge-Pv occurs at $\sim 28.5$ GPa with LDA+$U_{sc}$ and at $\sim 40.5$ GPa with GGA+$U_{sc}$. These transition pressures are quite large compared to those in Si-Pv, i.e., $\sim 9.5$ GPa and $\sim 22.5$ GPa respectively as presented in Table 2.

Owing to the larger ionic radius of Ge$^{4+}$ (0.53 Å) compared to that of Si$^{4+}$ (0.40 Å), the unit-cell volume and inter-atomic distances in Ge-Pv are larger than in Si-Pv. Zero pressure Fe-O bond-lengths in Si-Pv and Ge-Pv obtained with LDA+$U_{sc}$ are shown Fig. 2(a). The average of Fe-O bond-lengths, $\langle \text{Fe-O} \rangle$, is also shown in Fig. 2(b). The larger $\langle \text{Fe-O} \rangle$ value in Ge-Pv allows Fe$^{2+}$ to sustain higher pressures than in Si-Pv before changing to the high-QS state. It is also interesting to note that this transition occurs when the $\langle \text{Fe-O} \rangle$ reaches a particular value ($\sim 2.22$ Å) whether in Ge-Pv or in Si-Pv, whether using LDA+$U_{sc}$ or GGA+$U_{sc}$ methods (Fig. 2(b)). It should be noted that the Pv to PPv transition is expected to occur at approximately $\sim 63$ GPa in MgGeO$_3$ (Hirose et al., 2005) and at $\sim 125$ GPa in MgSiO$_3$ (Murakami et al., 2004). These pressures are much higher than low- to high-QS transition pressures in both Fe$^{2+}$-bearing compounds. Consequently, this transition has not been investigated in Si-PPv or Ge-PPv phases.

3.2. Spin states of Fe$^{3+}$ in Ge-Pv and -PPv

Next, we investigate spin states of Fe$^{3+}$ in the B-site of Ge-Pv (low-pressure) and PPv (high-pressure) phases. The crystal structures of Si-Pv and Si-PPv phases are shown in Fig. 3(a). Si-PPv has a layered structure characterized by corner-sharing and edge-sharing SiO$_6$ octahedra extending along the a-c plane. The pressure dependence of calculated enthalpy differences between high-spin (HS) and low-spin (LS) states of Fe$^{3+}$ ($\Delta H = H_{\text{B(HS)}} - H_{\text{B(LS)}}$) in Pv and PPv phases are shown in Fig. 3(b) and (c),
respectively. The calculated HS to LS transition pressures in Ge-Pv are 56.5 GPa with LDA+U_{sc} and 85.0 GPa with GGA+U_{sc}. Similarly, these transition pressures in Ge-PPv are 49.5 GPa and 82.5 GPa with these methods. Our calculated transition pressures in Si-Pv are 41.0 GPa with LDA+U_{sc} and 69.5 GPa with GGA+U_{sc}, which are in very good agreement with previous first-principles study \cite{Hsu11}. In the case of Si-PPv, our calculated transition pressures are 28.0 GPa and 59.5 GPa, respectively, which are quite larger than previously reported values of -30 GPa and 36 GPa \cite{Yu12}. These transition pressures in Si-Pv and Si-PPv are also very similar to those reported by \cite{Hsu12} in (Mg,Al)(Si,Fe)O_{3}-Pv and PPv phases where it was observed that the presence of aluminum does not affect the spin transition pressure significantly. Considering the overall agreement of the stability of the iron spin states and pressure induced crossover in Si-Pv and Si-PPv phases with previous studies \cite{Hsu10, Hsu11, Hsu12}, the present calculations about HS to LS transition in Fe^{3+} at B site seems to be consistent and reliable.

In order to explain the increase of HS to LS transition pressures in MgGeO_{3} phases, we compare atomic configurations around Fe^{3+} in the B-site of Si-Pv and Ge-Pv phases. As shown in Fig. 4(a), the coordination number of Fe^{3+} is six and Fe-O bond lengths in this site are smaller than those of Fe^{2+} in the A-site. The pressure dependence of the average bond-length, \langle Fe-O \rangle, for Fe^{3+} in the B-site in Si-Pv and Ge-Pv phases are shown in Fig. 4(b). As in the case of low- to high-QS transition in Fe^{2+} (Fig. 1), the HS to LS transition in Fe^{3+} in Ge-Pv and Ge-PPv phases are also large compared to those in Si-Pv and Si-PPv phases (Fig. 3) due to relatively larger Fe-O bond-lengths and unit-cell volumes in germanate phases at a given pressure (Fig. 4). Similar to low- to high-QS transition, the HS to LS transition also occurs only when the (Fe-O) reaches a particular value (i.e., \sim 1.86 Å in the present case) irrespective of Ge-Pv or Si-Pv, or of the exchange-correlation functional used (Fig. 4(b)). This is a useful insight for predicting pressure induced spin state changes in different materials.

4. Effect of Fe^{2+} and Fe^{3+} in the Pv to PPv transition

Having investigated the stability of different iron states in the lower mantle pressure range in the previous section, we now focus on the potential effect of Fe^{2+} and Fe^{3+}
substitution on the Pv to PPv transition. This is a plain static calculation to access the overall influence of iron substitution on the Pv to PPv transition in these phases. We have not included finite temperature entropic or vibrational effects, therefore, we are not able to produce a full phase diagram with a two phase loop region. This is simply the first step towards the calculation of such phase diagrams.

It is well known that the LDA functional underestimates the equilibrium volume while GGA overestimates it. After inclusion of vibrational effects LDA equations of state and elastic properties tend to agree better with experimental data than GGA results \cite{Karki2019, Karkietal2000, Wentzcovitch2004, Nunez-Valdez2012a, Nunez-Valdez2012b, Nunez-Valdez2013}. Therefore, we have chosen LDA+U_sc results to investigate the effect of Fe^{2+} and Fe^{3+} in the Pv to PPv transition in both compounds. Previous studies based on \textit{ab initio} calculations \cite{Tsuchiya2004, TsuchiyaTsuchiya2007} and experimental measurements \cite{Murakami2004, Hirose2005} have reported the Pv to PPv transition in MgSiO_3 and MgGeO_3 to occur around \(\sim 125\) GPa and \(\sim 63\) GPa, respectively, at \(\sim 2500\) K.

As indicated in Fig. 1(b) and in Table 2, the low- to high-QS transition in Si-Pv and Ge-Pv occurs at much lower pressures than the Pv to PPv transition in these minerals \cite{Murakami2004, Hirose2005}. Considering this fact, only the high pressure high-QS state of Fe^{2+} was considered in the investigation of the Pv to PPv transition. Similarly, near the Pv to PPv transition pressure, the stable state of Fe^{3+} substituted in both Si-Pv and Si-PPv phases is HS state in the A-site (HS-A) and LS state in the B-site (LS-B). However, in germanate phases, the HS-B to LS-B transition pressure (Fig. 3 and Table 2) is near the Pv to PPv transition pressure. In order to find the appropriate spin states of Fe^{3+} across the transition we have considered all possibilities in the calculation of enthalpy differences (\(\Delta H = H_{PPv} - H_{Pv}\)) (see Fig. 5).

As indicated in Fig. 5(b) the transition pressure 55.5 GPa involves a transition between HS-B in Ge-Pv to LS-B in Ge-PPv. Obviously iron in the A site remains in the HS state. At high temperatures, contributions by other states might be relevant as well, but this issue is well beyond the scope of this paper. This transition and transition pressure, i.e., HS-B in Pv and LS-B in PPv, is the only combination consistent with B(HS) to B(LS) transition pressures of 56.5 GPa and 49.5 GPa in Ge-Pv and Ge-PPv, respectively.
The effect of Fe$^{2+}$ and Fe$^{3+}$ on the Pv to PPv transition in Si-Pv and Ge-Pv is summarized in Fig. 6, showing the pressure dependence of enthalpy differences ($\Delta H=H_{PPv}-H_{Pv}$) for the configurations indicated in the previous paragraph. Static (zero temperature) Pv to PPv transition pressures in iron-free ($x=0$) MgGeO$_3$ and MgSiO$_3$ are 43.2 GPa and 94 GPa, respectively. The Clapeyron slope for the Pv to PPv transitions have been previously estimated to be $\sim$ 7.5 MPa/K for MgSiO$_3$ (Tsuchiya et al., 2004) and 7.8 MPa/K for MgGeO$_3$ (Tsuchiya and Tsuchiya, 2007). Taking these Clapeyron slopes approximately into account, transition pressures at $\sim$2500 K should be $\sim$ 62.7 GPa and $\sim$ 112.8 GPa for MgGeO$_3$ and MgSiO$_3$, respectively. These results are in good agreement with previous experimental measurements and ab initio LDA calculations (Murakami et al., 2004; Hirose et al., 2005; Tsuchiya et al., 2004; Tsuchiya and Tsuchiya, 2007).

A summary of transition pressure shifts caused by iron in silicate and germanate phases is indicated in (Fig. 6, Table 3). As indicated, Fe$^{2+}$ decreases the Pv to PPv transition pressure in both MgGeO$_3$ and MgSiO$_3$. These observations are consistent with previous experimental (Mao et al., 2004; Shieh et al., 2006) and ab initio studies (Caracas et al., 2005; Stackhouse et al., 2006). However, in the case Fe$^{3+}$, the Pv to PPv transition pressure increases noticeably. To the best of our knowledge, this fact has not been verified experimentally yet.

To understand these opposite effects of Fe$^{2+}$ and Fe$^{3+}$ substitution on the Pv to PPv transition, the volume difference between Si-Pv and Si-PPv phase ($\Delta V=V_{PPv}-V_{Pv}$) is shown in Fig. 7(a). With respect to iron-free case, the volume difference is smaller and larger in magnitude with Fe$^{2+}$ and Fe$^{3+}$ substitution, respectively. These smaller and larger volume difference will contribute to enthalpy difference between Pv and PPv phase in such a way that will decrease the transition pressure with Fe$^{2+}$ substitution while it will increase when Fe$^{3+}$ is substituted. This can be seen explicitly in Fig. 7(b and c), where pressure dependence of energy ($\Delta E$) and $P\times V$ term [$\Delta(PV)$] of relative enthalpy ($\Delta H$) are shown separately. Transition pressure points, where $\Delta E$ and $\Delta(PV)$ terms cancel each other, are shown by vertical dashed lines.
5. Conclusions

Using *ab initio* DFT+U calculations, we have undertaken a comparative investigation of state changes of ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) iron in MgSiO$_3$ and MgGeO$_3$ perovskite (Pv) and post-perovskite (PPv) phases. The goal was to verify the possibility of using MgGeO$_3$ as a low pressure analog of MgSiO$_3$ for better understanding of spin state changes in iron. Unfortunately, owing to the larger ionic radius of germanium, Fe-O inter-atomic distances in the germanate phases are larger than in the silicate phases, allowing the germanates to sustain higher pressures than analog silicates before state changes in iron take place. It has been clearly shown that such state changes, whether the displacement transition (low- to high-QS) of Fe$^{2+}$ in the A-site or the HS to LS state change in Fe$^{3+}$ in the B-site, take place at approximately the same average Fe-O, $\langle$Fe-O$\rangle$, distance irrespective of the chemistry or the exchange and correlation functional used in the calculations.

This encompassing investigation also allowed us to address the effect of Fe$^{2+}$ and Fe$^{3+}$ substitutions on the Pv to PPv transition. Despite the simplicity of these static calculations, previously measured and calculated effect of Fe$^{2+}$ on this transition in MgSiO$_3$ is well reproduced: Fe$^{2+}$ substitution decreases the transition pressure, whether in germanate or silicate phases. However, we report the opposite effect for Fe$^{3+}$ substitution in the B-site. This transition should involve the LS-B state in both Pv and PPv silicate phases but HS-B and LS-B states in Pv and PPv germanates, respectively. For both types of transitions the effect is the same: coupled substitution of Fe$^{3+}$ increases the Pv to PPv transition in both materials. This observation has not been validated by experiments yet and should be relevant for better understanding the D'' discontinuity and the nature of the deep lower mantle.

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Table 1: Self-consistent Hubbard $U_{sc}$ (eV) for ferrous and ferric iron calculated by Hsu et al. (2010, 2011) in Pv and by Yu et al. (2012) in PPv structures.

|        | Fe$^{2+}$ | Fe$^{3+}$ |
|--------|-----------|-----------|
|        | High-QS   | Low-QS    | A(HS) | B(HS) | B(LS) |
| Pv     | 3.1       | 3.1       | 3.7   | 3.3   | 4.9   |
| PPv    | 2.9       | –         | 4.0   | 3.5   | 5.6   |

Table 2: Spin state transition pressures, $P_t$ (GPa), in iron-bearing MgGeO$_3$ and MgSiO$_3$ calculated within LDA+$U_{sc}$ and GGA+$U_{sc}$ methods.

|        | Low-QS to High-QS in Fe$^{2+}$-bearing Pv phase | B(HS) to B(LS) in Fe$^{3+}$-bearing Pv and PPv phases |
|--------|-------------------------------------------------|------------------------------------------------------|
|        | LDA+$U_{sc}$ | GGA+$U_{sc}$ | LDA+$U_{sc}$ | GGA+$U_{sc}$ | LDA+$U_{sc}$ | GGA+$U_{sc}$ |
| MgGeO$_3$ | 28.5      | 40.5        | 56.5        | 85.0        | 49.5        | 82.5        |
| MgSiO$_3$ | 9.5       | 22.5        | 41.0        | 69.5        | 28.0        | 59.5        |

Table 3: Perovskite to post-perovskite transition pressures, $P_C$ (GPa), calculated within LDA+$U_{sc}$ methods. $x$ represents the iron concentration.

|        | 0 | 0.125 (Fe$^{2+}$) | 0.125 (Fe$^{3+}$) |
|--------|---|-------------------|-------------------|
| MgGeO$_3$ | 43.2 | 40.5             | 57.5             |
| MgSiO$_3$ | 94.0 | 88.5             | 104.0            |
Figure 1: (Color Online) (a) Atomic structure around low-QS and high-QS Fe$^{2+}$-bearing MgSiO$_3$ in Pv phase at ambient pressure. Fe, Mg, O, and Si are represented as purple, orange, red, and blue sphere, respectively. MgGeO$_3$-Pv structures are similar and not shown here. (b) Enthalpy difference (ΔH=H$_{high-QS}$-H$_{low-QS}$) for Fe$^{2+}$-bearing Si-Pv (blue) and Ge-Pv (red). Lower and upper bounds correspond to LDA+U$_{sc}$ and GGA+U$_{sc}$ results, respectively.
Figure 2: (Color Online) Atomic environment around iron in $Fe^{2+}$-bearing Si-Pv and Ge-Pv phases. (a) Fe-O distances (in Å) in Si-Pv, and Ge-Pv structures at ambient pressure are shown next to the oxygen atoms. (b) Pressure dependence of average Fe-O distance. Vertical lines represent the low-QS to high-QS transition. Lower and upper bounds correspond to LDA+$U_{ic}$ and GGA+$U_{ic}$ results, respectively.
Figure 3: (Color Online) (a) Atomic structure of Fe\(^{3+}\)-bearing MgSiO\(_3\) Pv and PPv phase. Structures of Pv and PPv phases of Fe\(^{3+}\)-bearing MgGeO\(_3\) are similar and not shown here. Fe, Mg, O, and Si are represented as purple, orange, red, and blue sphere, respectively. Enthalpy difference ($\Delta H = H_{LS} - H_{HS}$) for Fe\(^{3+}\)-bearing MgSiO\(_3\) (blue) and MgGeO\(_3\) (red) in (b) Pv and (c) PPv phases. Lower and upper bounds correspond to LDA+U\(_w\) and GGA+U\(_w\) results, respectively.
Figure 4: (Color Online) Atomic environment around Fe$^{3+}$ in Si-Pv and Ge-Pv phases. (a) Zero pressure Fe-O bond lengths (Å) in Si-Pv and in Ge-Pv obtained with LDA+$U_{xc}$. (b) Pressure dependence of average Fe-O bond lengths for MgSiO$_3$ (blue) and MgGeO$_3$ (red) phases. Vertical lines represent the high-spin (HS) to low-spin (LS) transitions in the B-site. Lower and upper bounds correspond to LDA+$U_{xc}$ and GGA+$U_{xc}$ results, respectively.
Figure 5: (Color Online) Enthalpy difference ($\Delta H = H_{PPv} - H_{Pv}$) between Fe$^{3+}$-bearing Ge-Pv and Ge-PPv phase using LDA+$U_{xc}$ method with different possible spin-state combinations of Fe$^{3+}$ at B-site. (a) $P_{v}(HS)$ and $PP_{v}(HS)$, (b) $P_{v}(HS)$ and $PP_{v}(LS)$, (c) $P_{v}(LS)$ and $PP_{v}(HS)$, (d) $P_{v}(LS)$ and $PP_{v}(LS)$.

Figure 6: (Color Online) Enthalpy difference ($\Delta H = H_{PPv} - H_{Pv}$) obtained using LDA+$U_{xc}$ for (a) iron free, (b) Fe$^{2+}$-$+$, and (c) Fe$^{3+}$-bearing Si-Pv and Ge-Pv.
Figure 7: (Color Online) Difference in (a) volume ($\Delta V = V_{PPv} - V_{Pv}$), (b) internal energy ($\Delta E = E_{PPv} - E_{Pv}$), and (c) PV term ($\Delta(PV) = (PV)_{PPv} - (PV)_{Pv}$) of the enthalpy for iron-free (red), Fe$^{2+}$-bearing (blue), and Fe$^{3+}$-bearing (green) MgSiO$_3$. Results represent LDA+$U_{\mu\nu}$ calculation. Vertical dashed lines represent Pv to PPv transition point.