



HAL
open science

Local structure and electronic-spin transition of Fe-bearing MgSiO perovskite up to the earth's lower mantle conditions

Changming Fang, Rajeev Ahuja

► **To cite this version:**

Changming Fang, Rajeev Ahuja. Local structure and electronic-spin transition of Fe-bearing MgSiO perovskite up to the earth's lower mantle conditions. *Physics of the Earth and Planetary Interiors*, 2008, 166 (1-2), pp.77. 10.1016/j.pepi.2007.11.004 . hal-00532132

HAL Id: hal-00532132

<https://hal.science/hal-00532132>

Submitted on 4 Nov 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accepted Manuscript

Title: Local structure and electronic-spin transition of Fe-bearing MgSiO₃ perovskite up to the earth's lower mantle conditions

Authors: Changming Fang, Rajeev Ahuja

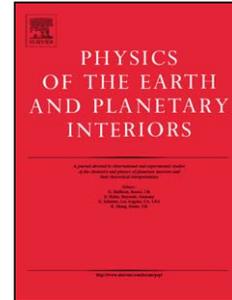
PII: S0031-9201(07)00232-4
DOI: doi:10.1016/j.pepi.2007.11.004
Reference: PEPI 4879

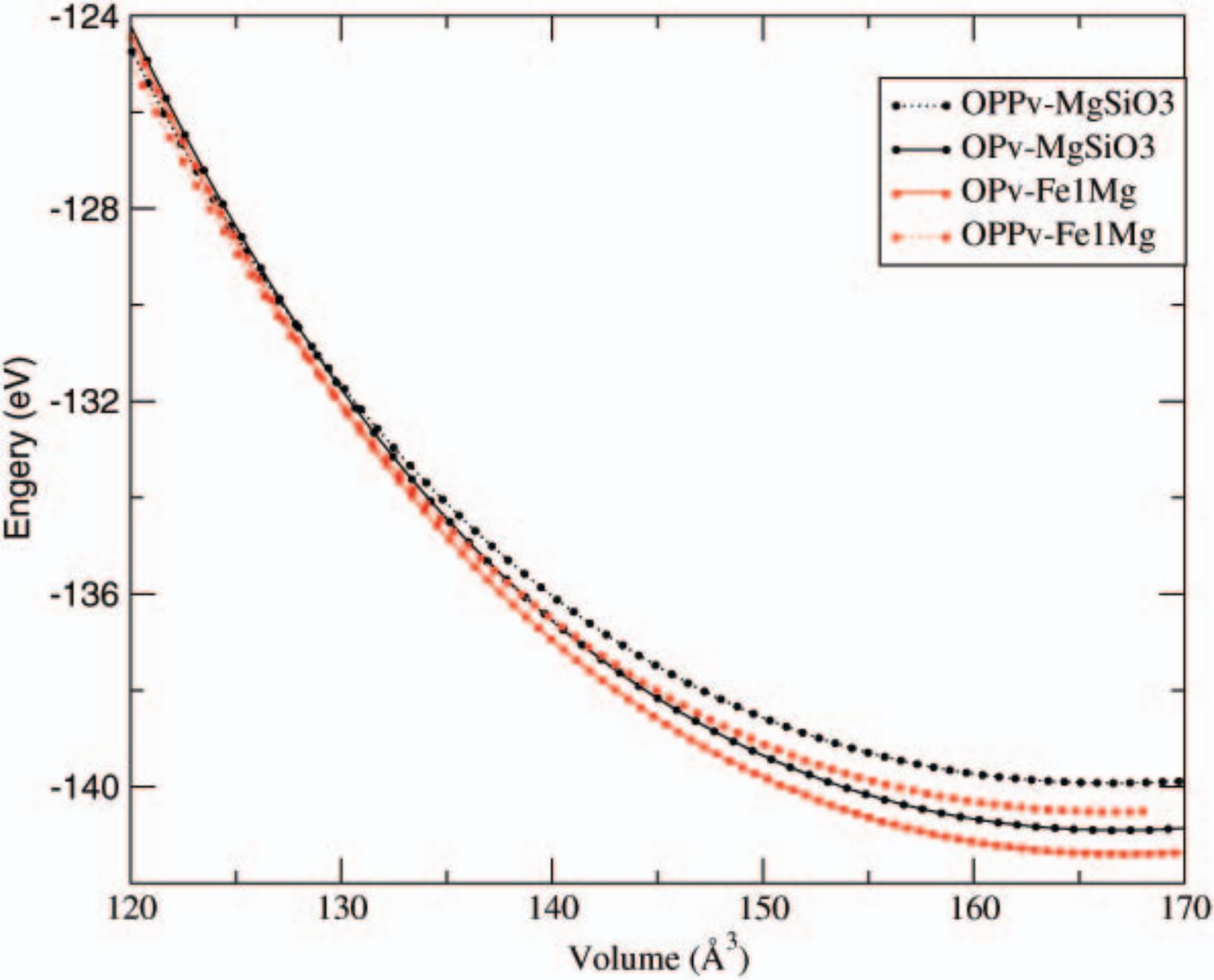
To appear in: *Physics of the Earth and Planetary Interiors*

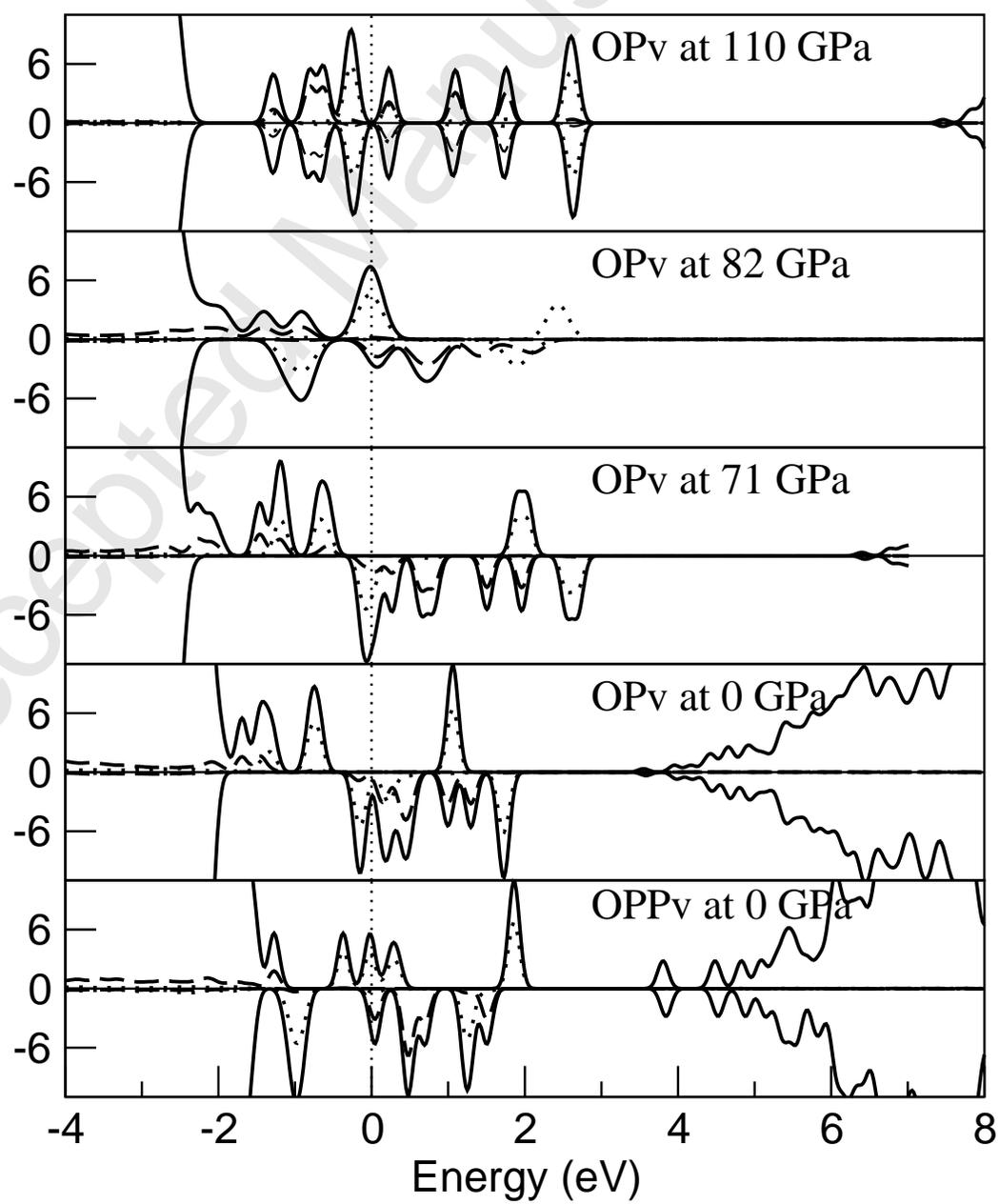
Received date: 20-3-2007
Revised date: 1-11-2007
Accepted date: 5-11-2007

Please cite this article as: Fang, C., Ahuja, R., Local structure and electronic-spin transition of Fe-bearing MgSiO₃ perovskite up to the earth's lower mantle conditions, *Physics of the Earth and Planetary Interiors* (2007), doi:10.1016/j.pepi.2007.11.004

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.







Local structure and electronic-spin transition of Fe-bearing MgSiO_3 perovskite up to the earth's lower mantle conditions

Changming Fang and Rajeev Ahuja

Condensed Matter Theory Group, Department of Physics, Uppsala University,

Box 530, S-750 21, Uppsala, Sweden

ABSTRACT: We report first-principles electronic structure calculations on the structural and electronic-spin behaviours of Fe-bearing MgSiO_3 crystals up to the pressure of Earth's mantle. The transition pressure of the Fe-bearing MgSiO_3 from the orthorhombic perovskite (OPv) to the orthorhombic post-perovskite (OPPv) phase decreases with increasing Fe concentration. The lattice distortion has impacts on the electronic-spin behaviour of the Fe ions in the PVs. The spin-polarizations of the Fe ions in the $(\text{Fe,Mg})\text{SiO}_3$ OPvs and OPPvs keep unchanged up to the pressures in the lower mantle. Meanwhile the Fe-bearing MgSiO_3 OPv containing $\text{Fe}_{\text{Mg}}\text{-Fe}_{\text{Si}}$ pairs exhibits multiple magnetic moments co-existing in a large pressure range (from about 78 to 110 GPa), and finally becomes non-magnetic at pressure higher than 110 GPa. These results provide a mechanism to understand the recent experimental results about Fe valence states and the electronic transitions of the Fe-bearing MgSiO_3 under high pressure.

Key words: Iron-bearing; MgSiO_3 -perovskite and post-perovskite; *Ab initio* method; phase transition; Electronic and spin transitions.

1. Introduction

As the dominant component in the Earth's lower mantle, pure and Fe-bearing MgSiO_3 phases have been intensively studied for several decades (Dziewonski & Anderson, 1981; Cohen, 1987; Hemley and Cohen, 1992; Stixrude and Cohen, 1993; Knittle & Jeanloz, 1991; Marton, *et al* 1994; Farges, *et al.* 1994; Keppler, *et al.* 1994; Dubrovinsky, *et al.* 1999; Helffrich & Wood, 2001; Struzhkin, *et al.* 2004; Mao, *et al.* 2004, 2005; Jackson, *et al.* 2005; Dobson & Brodholt, 2005; Cyrannoski 2006; Zhang & Oganov, 2006; Spera, *et al.* 2006; Caracas and Cohen, 2006; Stackhouse, *et al.*, 2007; Tateno, *et al.* 2007). These compounds have an orthorhombic perovskite (OPv, in short) structure which is stable up to high-pressure (Matsui, *et al.* 1991; Karki, *et al.* 1997; Duffy, 2004). Recent discovery of a phase transition for pure MgSiO_3 from the OPv phase to an orthorhombic post-perovskite (OPPv, in short) by Murakami, *et al.* (2004) has stimulated new interests in the Fe-bearing MgSiO_3 perovskites. Mao, *et al.* (2004, 2005) have performed high-pressure experiments on the OPvs containing high Fe concentrations, $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ ($x = 0.12$ to 1.00). They found that all samples convert entirely or partially into the OPPv structure at high pressures and the transition pressure decreases with increasing the concentration of Fe in the samples. Meanwhile, from the high-pressure experiments on solid-solutions of FeO in $(\text{Mg,Fe})\text{SiO}_3$, Tateno, *et al.* (2007) have concluded that incorporation of FeO stabilizes the OPv to higher pressures. Apart from the structural phase transition, another interesting topic is to understand the electronic-spin behaviours of the Fe-bearing MgSiO_3 crystals under-pressure. From the X-ray emission spectroscopy, Badro, *et al.* (2004) discovered two

electronic transitions for the $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ ($x = 0.10$) OPv at pressures about 70 and 110 GPa. Li *et al.* (2004) reported that the Fe ions in both Al-bearing and Al-free $(\text{Mg,Fe})\text{SiO}_3$ OPv samples exhibit a mixed-valences state at about 100 GPa. Multi valences and many forms of the Fe ions in MgSiO_3 perovskites have been suggested by the experimentalists (Keppler, *et al.* 1994; Dubrovinsky, *et al.* 1999; Helffrich & Wood, 2001; Jackson, *et al.* 2005). Using a synchrotron Mössbauer spectroscopy technique, Jackson, *et al.* (2005) have studied the electronic environments of the Fe ions in the $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ ($x= 0.05$ and 0.10) samples pressures up to about 120 GPa . They have concluded that there are two kinds of Fe^{2+} ions and one kind of Fe^{3+} ions (the so-called ‘three-double’ model) in the samples. They have also discovered that pressure alone does not alter the valence states of the iron ions in $(\text{Mg, Fe})\text{SiO}_3$ OPv samples. Around 70 GPa, they observed a change in the isomer shift, which was interpreted as an electronic transition.

Theoretical efforts have been made to build up a clear picture about the phase relationship and electronic-spin properties of the Fe-bearing MgSiO_3 crystals under pressure. Theoretical calculations for the pure MgSiO_3 OPv and OPPv have been reported by several authors (Iitaka, *et al.*, 2004; Oganov & Ono, 2004; Caracas and Cohen, 2006). Cohen *et al.* (1997) performed first-principles calculations about the high-pressure behaviours of iron ions in different compounds, including novel FeSiO_3 and MgFeO_3 OPvs. Mao *et al.* (2004) also reported the results of their first-principles calculations for $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ ($x = 0.5, 1.0$) and found that the transition pressure from the OPv to the OPPv phase decreases with pressure. Caracas and Cohen (2005) also reported their results on the first-principles calculations on the stability and

elasticity of the Opv and OPPv phases in the MgSiO₃-FeSiO₃-Al₂O₃ system. Meanwhile, Stackhouse, *et al.* (2007) have investigated the electronic-spin states of the iron ions in FeSiO₃ perovskites under pressures employing the Density-Functional Theory (DFT) and found that spin transitions over a range from 60 to 160 GPa.

In order to have a complete knowledge about behaviour of Fe in the MgSiO₃ perovskites, more efforts are needed (Keppeler, *et al.* 1994; Dubrovinsky, *et al.* 1999; Helffrich & Wood, 2001, Tateno, *et al.* 2007). In the present paper, we have investigated the structural and electronic-spin behaviours of iron in (Mg_{1-x}Fe_x)SiO₃ (x = 0.0625 and 0.125), as well as in (Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O₃ (x = 0.0625) using first-principles method within a super-cell approach. Different atomic arrangements of the Fe ions have been taken into account. Meanwhile, one has to keep in the mind that the configurations of the local structure around Fe we employed in the calculations are limited and our calculations only give a rough approximation of a real solid solution (Seko, *et al.* 2006). However, the information obtained here will be useful to understand local structure, phase relationship and electronic properties of the complicated solid solution of Fe-bearing MgSiO₃ perovskites up to the pressure of the Earth's lower mantle.

2. Theoretical Method

A super-cell approach is employed in our calculations to have reasonable chemical compositions. The super-cells of $2a_{\text{opv}} \times 2b_{\text{opv}} \times 1c_{\text{opv}}$ and of $4a_{\text{oppv}} \times 1b_{\text{oppv}} \times 1c_{\text{oppv}}$ were employed for the OPv and OPPv structure, respectively.

Theoretical calculations were carried out using the computer-code VASP (Vienna *ab initio* simulation program) (Kresse & Hafner, 1993,1994; Kresse & Furthmüller, 1996a,1996b). Both lattice parameters and coordinates of atoms have been fully relaxed. The calculations were carried out in the spin-polarized Generalized Gradient Approximation (GGA) (Perdew, *et al.*1996) within the Projector-Augmented Wave (PAW) method (Blöchl, 1994; Kresse & Joubert, 1999). The electronic wave functions were sampled on $6\times 6\times 4$, $10\times 4\times 4$ k -point meshes, or 18, 30 k -points in the Brillouin zone of the pure MgSiO_3 OPv and OPPv, respectively. We use a $2\times 2\times 2$ k -point mesh, or 2 to 8 k -points in the irreversibly BZ for the super-cells, depending on the symmetry. The kinetic energy cut-off on the wave functions was 500 eV. The cut-off energy for the augmented wave functions was 605 eV. Convergence of the total energy with the number of k -points and the plane-wave cut-off energy has been checked. The energy-volume relationship is fitted by Murnaghan equation of state (Murnaghan, 1944).

3. Results and discussion

First, we report the calculated results on pure MgSiO_3 . As shown in Table 1, our calculations reproduce the experiments and agree well with other theoretical work. This can serve as a test of our calculation techniques.

Figure 1 shows the calculated energy-volume relationships for the pure OPv- and OPPv- MgSiO_3 . At low pressures (larger volumes) the OPv structure is more stable. The two curves cross at volumes of about 130 \AA^3 per unit cell. A phase transition under pressure at zero K is determined by the Gibbs energy difference, $\Delta G = \Delta U + P\Delta V$. Here ΔU is the difference of the cohesive energies (it is expected that the differences of the

zero-vibration energies of the OPvs and OPPvs are very small since the two structures have similar coordination), ΔV is the volume difference at pressure P . The calculated transition pressures are listed in Table 2. The (equation of state) EOS parameters of energy-volume relationship by Murnaghan equation of state (Murnaghan, 1944) are listed in Table 3. It is noted that the fitting parameters (B_p) are smaller than 4 due to the large pressure ranges. However, since we use this equation for both OPv and OPPv phases, the systematic error is minimized.

The calculated transition pressure for MgSiO₃ is about 101 GPa (Table 2). That is slightly smaller than the experimental value (about 120 GPa) (Iitaka, *et al.* 2004), but agrees well with the former theoretical value (about 99 GPa) by Oganov and Ono (2004).

Both MgSiO₃ OPv and OPPv crystals are calculated to be insulators with the band-gaps larger than 5.0 eV at ambient conditions. The valence bands are dominated by the O 2p states and the bottom of the conduction bands consists of mainly Si 3s states admixing with O 3s states. The band-gaps increase with increasing pressure.

Fang and Ahuja (2006) have analysed the lattice deviations of MgSiO₃ OPv and OPPv structures from the corresponding cubic perovskite (CPv) under pressure and found that the lattice distortions of MgSiO₃ OPv are moderate (about 1.7 %) relative to that of CPv, as compared with those (about 10 %) of OPPv-phase. The lattice distortions increase with pressure for both OPv- and OPPv-MgSiO₃. Correspondingly, the local symmetries around the Mg and Si ions in OPv- and OPPv-MgSiO₃ are lower as compared with those in CPv.

Under the conditions of the oxygen fugacity in the Earth's mantle, Fe ions occupy the Mg sites to form compounds with the chemical formula $(\text{Fe,Mg})\text{SiO}_3$ (Karato & Murthy, 1995, Terasaki, *et al.* 2005). Each Fe^{2+} ion in the $(\text{Fe,Mg})\text{SiO}_3$ crystals has six 3d electrons, which indicates three possible spin-polarization status of $(3d^5\uparrow, 3d^1\downarrow)$, $(3d^4\uparrow, 3d^2\downarrow)$ and $(3d^3\uparrow, 3d^3\downarrow)$ in the Ising model, and which gives magnetic moments of 4.0 (HS), 2.0 (MS), and 0.0 (LS) μ_B per Fe, respectively. Here the HS represents high-spin, MS medium-spin and LS low-spin or non-magnetic status.

The structural relaxations showed that the Fe-bearing MgSiO_3 structures have slightly larger volumes as compared with the corresponding Fe-free crystals, due to the larger ionic size of Fe^{2+} than that of Mg^{2+} . In the both OPv and OPv- $(\text{Fe,Mg})\text{SiO}_3$ lattices, the Fe-O bonds become slightly longer than those of Mg-O bonds. For example, at about 120 GPa, the three shortest Fe-O distances in the OPv lattice are 1.88 ($\times 3$) Å, longer than the three corresponding Mg-O bonds (1.82, 1.85, 1.85 Å), due to the ionic sizes. One should note that the three Mg-O bonds have different lengths due to the structural distortion (Fang and Ahuja 2006). Similar behaviour was also observed in the $(\text{Fe}_x\text{Mg}_{1-x})\text{SiO}_3$ ($x = 0.125$) OPvs. Using the same method for the pure MgSiO_3 as mentioned above, we obtained the transition pressures of the $(\text{Fe}_x\text{Mg}_{1-x})\text{SiO}_3$ compounds. The transition pressure decreases with increasing Fe concentration: from 101 GPa for $x = 0$ to about 96 GPa $x = 0.0625$ and further to about 89 GPa for $x = 0.125$, as shown in Table 2. This differs from the conclusion that solution of FeO would stabilize the OPv by Tateno, *et al.* (2007). The calculated trend is in agreement with the recent calculations by Mao, *et al.* (2004, 2005) for the compounds with high iron concentrations.

The Fe^{2+} 3d states form narrow bands in the energy gaps of the pure MgSiO_3 OPv and OPPv, corresponding to the pseudo t_{2g} - e_g splitting in the dodecahedral coordination. For the spin-up electrons, the Fe 3d states are fully occupied with the density of states (DOS) positioned around 0.5 to 1.0 eV below the Fermi level. While for the spin-down electrons, the Fe 3d orbitals are occupied by only one electron, and the Fermi level is at the middle of the peak of 3d states for OPv, while it is at the fall of two peaks for the OPPv structure. This is due to the fact that OPPv structure is more distorted.

In order to have better understanding about the stability of the electron-spin state of the Fe atoms, calculations with the fixed spin-polarization method were performed for the Fe^{2+} ions in the $(\text{Fe}_x\text{Mg}_{1-x})\text{SiO}_3$ ($x = 0.0625$ and 0.125) OPv and OPPv structures under different pressures. The calculations showed the Fe ions in the perovskites have ferro-magnetic ordering. That the high-spin state is most stable at the ambient conditions for Fe^{2+} ions in the $(\text{Fe}_x\text{Mg}_{1-x})\text{SiO}_3$ ($x = 0.0625$). The order of relative stability is $\text{HS} > \text{MS} \gg \text{LS}$, as shown in the energy difference (Table 4): $(E_0 - E_4) = 1.6$ eV and $(E_0 - E_2) = 1.2$ eV. The relative stability of the HS and MS states compare to the LS states decreases with pressure. However, the HS and MS are still much stable than the LS at high-pressure: at 220 GPa $(E_0 - E_4) = 0.8$ eV and $(E_0 - E_2) = 0.4$ eV. This indicates that there is no electronic-spin transition for the OPvs at pressures up to that of the Earth's lower mantle. The same conclusion is obtained for $(\text{Fe}_x\text{Mg}_{1-x})\text{SiO}_3$ ($x = 0.125$) OPvs. This differs from the conclusions by Stackhouse, *et al.* (2007) who found spin transitions of the Fe^{2+} ions at about 128 to 139 GPa when the calculations were performed within the GGA and 76 to 93 GPa of the LDA.

Experiments have shown that the Fe ions in the MgSiO₃ samples exist probably in more complicated forms (Keppler, *et al.* 1994; Dubrovinsky, *et al.* 1999; Helffrich & Wood, 2001). Jackson, *et al.* (2005) suggested the co-existence of Fe²⁺ and Fe³⁺ in the Fe-bearing MgSiO₃ at high-pressures. At high-pressures, it was reported that Fe₂O₃ exists in the OPv-form in the pressure range from about 30 to 96 GPa and transform to the OPPv-form at about 96 GPa (Rozenberg, *et al.*, 2002, Ono and Ohish, 2005). Therefore, it is reasonable to consider the possibilities of Fe occupying both Si and Mg sites to form Fe_{Si}-Fe_{Mg} pairs with chemical formula (Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O₃. Herewith we limit to x=0.0625.

We have performed total-energy calculations for different Fe_{Si}-Fe_{Mg} arrangements. The calculations show that in both OPv and OPPv the two iron ions prefer to sit closer, in line with the results of dilute Mn in ZnO crystals (Sharma, *et al.* 2003) where two Mn atoms like to sit closer. Therefore, we limit our discussion to the results for (Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O₃ (x=0.0625) OPPv and OPv with the shortest Fe(Si)-Fe(Mg) distances.

At ambient pressure, there is a short Fe_{Si}-Fe_{Mg} bond (about 2.8 Å) in the OPv, which is slightly longer than that in the OPPv crystal (2.6 Å). Structural optimisations have shown that the Fe²⁺ ion in the OPv has Fe-O distances almost the same as other Mg ions. This is different from the cases of (Mg_{1-x}Fe_x)SiO₃ OPv and OPPv, in which the Fe-O bonds are longer than the corresponding Mg-O ones. At ambient pressure, the Fe_{Si} ion in the OPv form has the Fe-O inter-atomic distances of (about 1.90 to 1.92 Å), significantly longer than the Si-O bonds (about 1.79 to 1.82 Å). This indicates that in

the $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ OPv crystals both Fe_{Si} and Fe_{Mg} ions exhibit 3+ state, corresponding to the itinerant nature of the 3d electrons.

We have also calculated the electronic-spin states of the Fe ions at different pressures. Figure 2 shows the calculated total DOS close to the Fermi level for $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPv crystal at about 0, 70, 81 and 110 GPa. The total DOS for the OPPv at 0 GPa is included for comparison. At ambient conditions in the $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPv, the splitting of the Fe 3d orbitals is very apparent. For the spin-up electrons the Fermi level is at the energy gap with the width of about 1.6 eV, while for the spin-down electrons, the Fermi level is between two peaks. For the Fe at the Mg site, the 3d states for the spin-up electrons are fully occupied while the 3d states for spin down electrons are occupied by only one electron. For the Fe at the Si site, three 3d orbitals are occupied by the spin-up electrons as well, while only one electron occupies the spin-down 3d states. The total magnetic moment for the OPv is $6 \mu_{\text{B}}/\text{cell}$. For the $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPv, the Fermi level is at the fall of the two peaks for the spin-down electrons, which is caused by the local relaxation and the short Fe-Fe bonding (bond of about 2.8 \AA). It is also shown that with increasing pressure, the structure distortion causes the increasing width of the Fe 3d bands. One can also see this in Figure 2, at about 70 GPa, the three lower bands for the spin-down electrons re-constructed and the Fermi level is at the peak of the lowest band. Further, increasing pressure causes change of the electronic structure. At about 82 GPa, the $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPv becomes ferri-magnetic (Figure 2). The Fe at the Mg site is still in the high-spin status, however, the Fe at the Si site has a smaller magnetic moment (about $-0.5 \mu_{\text{B}}/\text{Fe}$). That results the total magnetic moment to

be about $3.5 \mu_B$ for the $(Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O_3$ ($x=0.0625$) OPv at about 82 GPa. At higher pressure (about 90 GPa), the OPv becomes non-magnetic, as shown in Figure 2. However, the energy differences between different spin states are still small, and multi-spin state may coexist in a wider pressure range (Table 4). Calculations for OPPv crystal showed that the two Fe ions have magnetic moments of $6 \mu_B$ at pressure up to about 150 GPa, indicating no electronic transitions. This is related to the fact that OPPv lattice is more distorted compare to OPv (Fang and Ahuja 2006).

The local symmetry and structure as well as the valence status of Fe ions in $MgSiO_3$ OPv were intensively investigated by experimentalists. Keppler, *et al.* (1994) from the measurements on $Mg_{0.94}Fe_{0.06}SiO_3$ OPv samples concluded that the Fe^{2+} in the dodecahedral site. Farge, *et al.* (1994) studied the local structure of Fe in $(Mg_{0.9}Fe_{0.1})SiO_3$ OPv using X-ray absorption spectroscopy measurements. They found very complicated coordination of Fe by oxygen as compared with that of Mg by oxygen atoms. Recently, Jackson, *et al.* (2005) using a synchrotron Mössbauer spectroscopy studied the electronic environments of the Fe ions in $(Mg_{1-x}Fe_x)SiO_3$ ($x = 0.05$ and 0.10) OPv samples. They built a ‘three doublet’ model, that is, two different kinds of Fe^{2+} ions and one kind of Fe^{3+} ions in the samples. The amount of Fe^{3+} is measured to be about 40% of the whole iron ions for both samples, and the ratio of $Fe^{3+}/\Sigma Fe$ keeps almost unchanged up to the pressure in the Earth’s lower mantle. They also found increasing local distortion with in increasing pressure. They measured changes in the volume-pressure relation at about 70 GPa, which was suggested as an electronic transition. Badro, *et al.* (2004) measured a two-step electronic transitions in the $(Mg_{0.9}Fe_{0.1})SiO_3$ OPv at pressure around 70 to 110 GPa using an X-ray absorption

spectroscopy. Furthermore, recent high-pressure experiments by Mao, *et al.* (2004, 2005) found strong reduction of transition pressures from Fe-bearing MgSiO_3 OPvs to OPPvs with increasing the Fe concentration.

Our calculations have shown that there are no electronic transitions, for the structure models like Fe in $(\text{Mg,Fe})\text{SiO}_3$. Electronic transitions were found in the $(\text{Mg,Fe})(\text{Si,Fe})\text{O}_3$ OPv containing $\text{Fe}_{\text{Si}}\text{-Fe}_{\text{Mg}}$ pairs. Combined with these calculated results and experimental data, it is reasonable to suggest that in most Fe bearing MgSiO_3 high-pressure-prepared samples, Fe ions exist not only at the dodecahedral (Mg) sites, but also the octahedral (Si) sites to form $\text{Fe}_{\text{Si}}\text{-Fe}_{\text{Mg}}$ pairs or such clusters. The $\text{Fe}_{\text{Si}}\text{-Fe}_{\text{Mg}}$ pairs and Fe_{Mg} at the Mg sites would result in the ‘double triplet’ model proposed by Jackson, *et al.* (2005). Such mixed Fe^{2+} ions and $\text{Fe}_{\text{Si}}\text{-Fe}_{\text{Mg}}$ clusters would cause further distortions of the Si-O network in the OPvs and OPPvs. As a result, the transition pressure decreases with increasing Fe concentration.

Badro *et al.* (2004) have discovered two electronic transitions at about 70 GPa (high-spin to mixed spin) and at about 110 GPa (mixed spin to low-spin). Our calculations showed that at about 70 GPa, the magnetic moment of the Fe_{Si} ions in the $\text{Fe}_{\text{Si}}\text{-Fe}_{\text{Mg}}$ clusters decreases first and at about 91 GPa, the magnetic moments of both Fe_{Si} and Fe_{Mg} ions are quenched to zero. However, the energy differences among the different magnetic configurations are very small. This indicates the coexistence of multiple-magnetic status for the Fe-ion clusters in a large pressure range, which is enforced by the inhomogeneous characters of the samples.

In summary, we have performed first-principles calculations for the structural and electronic-spin behaviours of Fe-bearing MgSiO_3 crystals up to the pressure of the

Earth's lower mantle. The calculations have shown that the transition pressure from the OPv to the OPPv phase decreases as the Fe concentration increases. The Fe^{2+} ions in the $(\text{Mg,Fe})\text{SiO}_3$ crystals have the high-spin ($S=4/2$ for $\text{Fe } 3d^6$) at pressure up to that of the Earth's mantle. Electronic transitions have been found for the $(\text{Mg,Fe})(\text{Si,Fe})\text{O}_3$ OPv containing $\text{Fe}_{\text{Si}}\text{-Fe}_{\text{Mg}}$ pair-like clusters. The energy differences of the different magnetic moments of the Fe ions are very small in a wide pressure range. In these Opvs, multiple-valences of Fe ions may exist in a large pressure range (e.g. 78 to 110 GPa). Based on our calculations, we suggest that in the high-pressure and high-temperature prepared Fe-MgSiO₃ crystals, Fe ions are positioned not only at the Mg sites, but also at the Si and Mg sites, forming $\text{Fe}_{\text{Si}}\text{-Fe}_{\text{Mg}}$ pairs and even complicated clusters.

We would like to acknowledge the financial support from the Swedish Research Council (VR) and EuroMinSI. Parts of the calculations were carried out at NSC, Linköping.

References

- Badro, J., Rueff, J.-P., Vanó, G., Monaco, G., Figuet, G. & Guyot, F., (2004), Electronic transitions in perovskite: possible nonconvecting layers in the lower mantle, *Science*, 305, 383-386.
- Blóchl, P. E., (1994) Projector augmented-wave method, *Phys. Rev. B* 50, 17953-17979.
- Caracas, R. and Cohen, R.E. (2005), Effect of chemistry on the stability and elasticity of the perovskite and post-perovskite phases in the MgSiO_3 - FeSiO_3 - Al_2O_3 system and implications for the lowermost mantle, *Geophys. Res. Lett.* 32, L16310.
- Caracas, R. and Cohen, R. E.,(2006) Theoretical determination of the Raman spectra of MgSiO_3 perovskite and post-perovskite at high pressure, *Geophys. Res. Lett.*, 33, L12S05.
- Cohen, R. E. (1987) Elasticity and equation of state of MgSiO_3 perovskite, *Geophys. Res. Lett.* 14, 1053-6.
- Cohn, R. E., Mazin, I. I., & Isaak, D. G., (1997) Magnetic collapse in transition metal oxides at high pressure: implications for the Earth, *Science*, 275, 654-657.
- Cyranoski, D., (2006) Geophysics: magical mantle tour, *Nature*, 440, 1108-1110.
- Dobson, D. P. & Brodholt, J. P., (2005) Subducted banded iron formations as a source of ultralow-velocity zones at the core-mantle boundary, *Nature*, 434, 371-374.
- Dubrovinsky, L. S., Saxena, S. K., Rekh, S., Serghiou G., Zerr, A., & Boehler, R., (1999) $(\text{Mg,Fe})\text{SiO}_3$ -perovskite stability and lower mantle conditions, *Science*, 285, 983.
- Duffy, T. S. (2004) Deeper understanding, *Nature*, 430, 409-410.

- Dziewonski, A. M. & Anderson, D. L. (1981) Preliminary reference earth model, *Phys. Earth Planet. Int.*, 25, 297-356.
- Fang, C. M., & Ahuja, R., (2006) Structures and stability of ABO₃ orthorhombic perovskites at the Earth's mantle conditions from first-principles theory, *Phys. Earth Planet. Int.*, 157, 1-7.
- Farges, F., Guyot, F., Andraut, D. & Wang, Y. (1994) Local-structure around Fe in Mg_{0.9}Fe_{0.10}SiO₃ perovskite-An X-ray-absorption spectroscopy study at Fe-edge, *European Journal of Mineralogy*, 6, 303-310.
- Fei, Y., Virgo, D., Mysen, B. O., Wang, Y. & Mao, H. K., (1994) Temperature-dependent electron delocalization in (Mg,Fe)SiO₃ perovskite, *Am. Miner.* 79, 826-837
- Helfrich, G. R. & Wood, B. J. (2001) The Earth's mantle, *Nature* 412, 501.
- Hemley, R. J. and Cohen, R. E., (1992) Silicate perovskite, *Ann. Rev. Earth and Planetary Sci.*, 20, 553-600.
- Iitaka, T., Hirose, K., Kawamura, K., & Murakami, M. (2004) The elasticity of the MgSiO₃ perovskite phase in the earth's lowermost mantle. *Nature* 430, 442-445.
- Jackson, J. M., Sturhahn, W., Shen, G. Y., Zhao, J. Y., Hu, M. Y., Errandonea, D., Bass, J. D. & Fei, Y. W. (2005) A synchrotron Mössbauer spectroscopy study of (Mg,Fe)SiO₃ perovskite up to 120 GPa, *Am. Miner.* 90, 199-205.
- Karato, S., and Murthy V. R., (1997) Core formation and chemical equilibrium in the Earth - I. Physical considerations, *Phys. Earth Planet. Inter.* 100, 61-79.
- Karki, B.B., Stixrude, L., Clark, S. J., Warren, M. C., Ackland, G. J., & Grain, J. (1997) Elastic properties of orthorhombic MgSiO₃ perovskite at lower mantle pressures, *Am. Miner.* 82, 635-638.

- Keppler, H., McCammon, C. A., & Rubie, D. C. (1994) Crystal-field and charge-transfer spectra of (Mg, Fe)SiO₃ perovskite, *Am. Mineral.* 79, 1215-1218.
- Knittle, R. E. & Jeanloz, R. (1991) Earth's core-mantle boundary: results of experiments at high pressures and temperatures, *Science*, 251, 1438-1443.
- Kresse, G., & Hafner, J. (1993) Ab initio *molecular dynamics for liquid metals*, *Phys. Rev.* B47, 558-561.
- Kresse, G. & Hafner, J. (1994) Ab-initio molecular-dynamics simulation of the liquid-metal amorphous-semiconductor transition in germanium, *Phys. Rev.* B49, 14251-14269.
- Kresse, G. & Furthmüller, J. (1996a) Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set *Comput. Mat. Sci.* 6, 15-50.
- Kresse, G. & Furthmüller, J. (1996b) Efficient iterative schemes for ab initio total energy calculations using a plane-wave basis set, *Phys. Rev.* B54, 11169-11186.
- Kresse, G. & Joubert, D., (1999) From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev.* B59, 1758-1775.
- Li, J., Struzhkin, V. V., Mao, H.-K., Shu, J. F., Hemley, R. J., Fei, Y. W., Mysen, B., Dera, P., Prakapenka V. B. & Shen, G. Y. (2004) Electronic spin state of iron in lower mantle perovskite, *PNAS*, 101, 14027-14030.
- Mao, W. L., Shen, G. Y., Prakapenka, V. B., Meng, Y., Campbell, A. J., Heinz, D. L., Shu, J. F., Hemley, R. L. & Mao, H.-K. (2004), Ferromagnesian postperovskite silicates in the D'' layer of the Earth, *PNAS*, 101, 15867-69.

- Mao, W. L., Meng, Y., Shen, G. Y., Prakapenka, V. B., Campbell, A. J., Heinz, D. L., Shu, J. F., Caracas, R., Cohen, R. E., Fei, Y. W., Hemley, R. J. & Mao, H.-K. (2005) Iron-rich silicates in the Earth's D'' layer, *PNAS*, 102, 9751-9753.
- Marton, F. C., Ita, J. and Cohen, R. E., (2001), P-V-T equation of state of MgSiO₃ perovskite from molecular dynamics and constraints on lower mantle composition, *J. Geophys. Res.* 106, 8615-27.
- Matsui, M., & Price, G. D. (1991) Simulation of the pre-melting behaviour of MgSiO₃ perovskite at high pressures and temperatures, *Nature*, 351, 735-737.
- Murakami, M. Hirose, K. Kawamura, K. Sata, N. & Ohishi, Y. (2004) Post-perovskite phase transition in MgSiO₃, *Science*, 304, 855-858.
- Murnaghan, F. D. (1944) The compressibility of media under extreme pressures, *PNAS*, 30, 244-47.
- Oganov, A. R., & Ono, S. (2004) Theoretical and experimental evidence for a post-perovskite phase in MgSiO₃ in Earth's D'' layer, *Nature*, 430, 445-448.
- Ono, S., and Ohishi, Y., (2005), *In situ* X-ray observation of phase transformation in Fe₂O₃ at high pressures and high temperatures, *J. Phys. Chem. Solids*, 66, 1714-1720.
- Perdew, J.P., Burke, S., & Ernzerhof, M., (1996) Generalized gradient approximation made simple, *Phys. Rev. Lett.*, 77, 3865.
- Ringwood, A. R., and Hibberson, W. H., (1991) Solubility of mantle oxides in molten iron at high pressures and temperatures: implications for the composition and formation of Earth's core, *Earth and Planetary Sci. Lett.* 102, 235-251.
- Rozenberg, G. K., Dubrovinsky, L. S., Pasternak, M. P., Le Bihan, T. and Ahuja, R., (2002) High-pressure structural studies of hematite Fe₂O₃, *Phys. Rev.* B65, 064112.

- Sharma, P., Gupta, A., Rao, K. V., Ownes, F. J., Sharma, R., Ahuja, R., Guillen, J. M. O., Johansson, B., & Gehring, (2003) Ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO, *Nature Materials*, 2, 673-677.
- Seko, A., Yuge, K., Oba, F., Kuwabara, A., and Tanaka, I., (2006) First-principles study of cation disordering in MgAl₂O₄ spinel with cluster expansion and Monte Carlo simulation, *Phys. Rev. B* 73, 094116.
- Spera, F. J., Yuen, D.A., & Giles, G. (2006) Tradeoffs in chemical and thermal variations in the post-perovskite phase transition: Mixed phase regions in the deep lower mantle? *Phys. Earth Plan. Inter.*, 159, 234-246.
- Stackhouse, S., Brodholt, J. P., & Price, G. D. (2007) Electronic spin transitions in iron-bearing MgSiO₃ perovskites, *Earth Planet. Sci. Lett.* 253, 282-290.
- Stixrude L. and R. E. Cohen, (1993) Stability of orthorhombic MgSiO₃ perovskite in the Earth's lower mantle from first-principles, *Nature* 364, 613-615.
- Tateno, S., Hirose, K., Sata, N., & Ohish, Y., (2007) Solubility of Fe in (Mg,Fe)SiO₃ perovskite and the post-perovskite phase transition, *Phys. Earth Planet Inter.*, 160, 319-25.
- Terasaki, H., Frost, D. J., Rubie, D. C., and Langenhorst, (2005) The effect of oxygen and sulphur on the dihedral angle between Fe-O-S and silicate minerals at high pressure: Implications for Martian core formation, *Earth and Planetary Sci. Lett.* 232, 379-392.
- Zhang, F & Oganov, A. R. (2006) Valence state and spin transitions of iron in Earth's mantle silicates, *Earth Planet. Sci. Lett.*, 249, 436-443.

Table 1. Results of structure optimisations for MgSiO₃, compared with the available experimental and theoretical results in literature.

Lattice	OPv-MgSiO ₃ Space group: Pbnm				OPPv-MgSiO ₃ Space group: Cmcm			
	PAW-GGA		exp.&,%	GGA ^{\$}	PAW-GGA		exp.&,%	GGA ^{\$}
<i>a</i> (Å)	4.819	4.275	4.777	4.318	2.711	2.457	2.456	2.474
<i>b</i> (Å)	4.972	4.574	4.927	4.595	9.181	8.032	8.042	8.121
<i>c</i> (Å)	6.969	6.261	6.898	6.305	6.717	6.099	6.093	6.138
<i>V</i> (Å ³)	166.96	122.43	162.35	125.10	167.18	120.39	120.39	123.32
<i>P</i> (GPa)	0	134*	0	120	0	136*	121	120

*The fixed volume from experiments at 121 Gpa (% refers to Iitaka, *et al.*, 2004).

& refers to Murakami, *et al.*, 2004.

\$ refers to Oganov & Ono, 2004.

Table 2. Transition pressures of the Fe-free and Fe-bearing MgSiO₃ OPv to OPPv from the DFT-PAW-GGA calculations. $\Delta V/V$ indicates volume collapses at the transition pressure (P_{tran}) from the OPv to the OPPv phase.

Composition	P_{tran} (GPa)	$\Delta V/V$ at P_{tran}
MgSiO ₃	101	1.5 %
(Fe _{0.0625} Mg _{0.9375})SiO ₃	96	1.5 %
(Fe _{0.125} Mg _{0.875})SiO ₃	89	1.3 %

Table 3. EOS fitting parameters for pure and Fe-bearing MgSiO_3 perovskites from DFT-GGA calculations.

EOS param.	MgSiO_3		$(\text{Fe}_{0.0625}\text{Mg}_{0.9375})\text{SiO}_3$		$(\text{Fe}_{0.125}\text{Mg}_{0.875})\text{SiO}_3$		$(\text{Fe}_{0.0625}\text{Mg}_{0.9375})(\text{Fe}_{0.0625}\text{Si}_{0.9375})\text{O}_3$	
	OPv	OPPv	OPv	OPPv	OPv	OPPv	OPv	OPPv
V_0 ($\text{\AA}^3/\text{fu}$)	167.0	167.2	167.1	166.9	167.2	168.1	167.5	167.6
$-E_0$ (eV/fu)	140.879	139.926	141.399	140.522	141.943	141.283	140.345	140.256
B (GPa)	249.9	226.5	246.1	224.6	247.6	212.6	247.0	217.5
B_p	3.3	3.4	3.5	3.5	3.4	3.7	3.3	3.7

Table 4. Energy differences ($\Delta E = E_i - E_0$, E_i represents the calculated cohesive energy of a $\text{Fe}_{\text{Si}}\text{-Fe}_{\text{Mg}}$ pair of total magnetic moment i) of different spin-polarization states relative to that (E_0) of non-magnetic states of the $(\text{Fe}_x\text{Mg}_{1-x})(\text{Fe}_x\text{Si}_{1-x})\text{O}_3$ ($x=0.0625$) OPv at different pressures.

$P(\text{GPa})$	29	72	81	92	97	106
$\Delta E(\text{eV})$						
$E_2 - E_0$	-1.25	-0.50	+0.08	+0.11	+0.16	+0.18
$E_4 - E_0$	-1.52	-0.56	+0.05	+0.12	+0.13	+0.37
$E_6 - E_0$	-1.70	-0.64	+0.02	+0.07	+0.21	+0.35

Legends for the Figures

Figure 1. The calculated volume-energy relationships for OPv and OPPv for $(\text{Fe}_{0.0625}\text{Mg}_{0.9375})\text{SiO}_3$ (Fe1Mg, in short) and MgSiO_3 . The representations of the symbols are included in the Figure. The lines are used to guide the eyes.

Figure 2. DOS of the $(\text{Fe}_{0.0625}\text{Mg}_{0.9375})(\text{Fe}_{0.0625}\text{Si}_{0.9375})\text{O}_3$ -OPv at different pressures. The DOS of $(\text{Fe}_{0.0625}\text{Mg}_{0.9375})(\text{Fe}_{0.0625}\text{Si}_{0.9375})\text{SiO}_3$ -OPPv at 0 GPa is included for comparison. The filled black lines represent the total DOS, the dots for the Fe 3d at the Si site and the short-lines the Fe 3d at the Mg site.