

Local structure and electronic–spin transition of Fe-bearing MgSiO_3 perovskite under conditions of the Earth's lower mantle

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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 $(\text{Fe},\text{Mg})\text{SiO}_3$ 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. © 2007 Elsevier B.V. All rights reserved.

Keywords: 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 and Anderson, 1981; Cohen, 1987; Hemley and Cohen, 1992; Stixrude and Cohen, 1993; Knittle and Jeanloz, 1991; Marton et al., 2001; Farges et al., 1994; Keppler et al., 1994; Dubrovinsky et al., 1999; Helffrich and Wood, 2001; Murakami et al., 2004; Mao et al., 2004, 2005; Jackson et al., 2005; Dobson and Brodholt, 2005; Cyrannoski, 2006; Zhang and 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 and Price, 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, $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ ($x = 0.12-1.00$). 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 $(\text{Mg},\text{Fe})\text{SiO}_3$, 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 $(\text{Mg},\text{Fe})\text{SiO}_3$ 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 and 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

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samples. They have also discovered that pressure alone does not alter the valence states of the iron ions in (Mg,Fe)SiO₃ 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 MgSiO₃ crystals under pressure. Theoretical calculations for the pure MgSiO₃ OPv and OPPv have been reported by several authors (Iitaka et al., 2004; Oganov and Ono, 2004; Caracas and Cohen, 2006). Cohn et al. (1997) performed first-principles calculations about the high-pressure behaviours of iron ions in different compounds, including novel FeSiO₃ and MgFeO₃ OPvs. Mao et al. (2004) also reported the results of their first-principles calculations for (Mg_{1-x}Fe_x)SiO₃ ($x=0.5, 1.0$) 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 (Keppler et al., 1994; Dubrovinsky et al., 1999; Helffrich and 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 Vienna *ab initio* simulation program (VASP) (Kresse and Hafner, 1993, 1994; Kresse and Furthmüller, 1996a,b). 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 and Joubert, 1999). The electronic wave functions were sampled on a $6 \times 6 \times 4$, $10 \times 4 \times 4$ k -point mesh,

or 18, 30 k -points in the Brillouin zone of the pure MgSiO₃ OPv and OPPv, respectively. We use a $2 \times 2 \times 2$ k -point mesh, or 2–8 k -points in the irreversible 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 MgSiO₃. 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.

Fig. 1 shows the calculated energy–volume relationships for the pure OPv- and OPPv-MgSiO₃. At low pressures (larger volumes) the OPv structure is more stable. The two curves cross at volumes of about 130 Å³ per unit cell. A phase transition under pressure at 0 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).

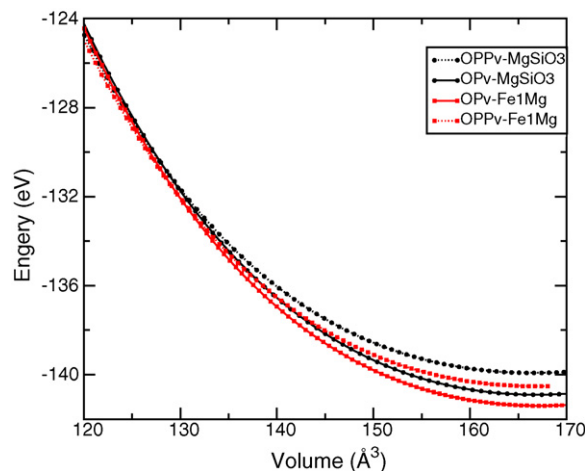


Fig. 1. The calculated volume–energy relationships for OPv and OPPv for (Fe_{0.0625}Mg_{0.9375})SiO₃ (Fe1Mg, in short) and MgSiO₃. The representations of the symbols are included in the figure. The lines are used to guide the eyes.

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