

Fe-bearing MgSiO₃ perovskite up to the Earth's lower mantle conditions

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Abstract

We investigated structural and electronic behaviors of Fe-MgSiO₃ under pressure up to that in the Earth's lower mantle using the first-principles theory. The Fe- MgSiO₃ crystals have phase transform from the orthorhombic perovskite (OPv) structure into the orthorhombic post-perovskite (OPPv) phase and the transition pressure decreasing with increasing Fe concentration. Electronic transitions occur in the pressure range of about 70 to 90 GPa for an (Mg,Fe)(Si,Fe)O₃ OPv crystal, in which the moment of the Fe⁴⁺ ion decreases gradually to zero at which the magnetic moment of the Fe²⁺ ion becomes zero. That electronic transition provides the possible mechanism to understand experiments.

Keywords: Fe-MgSiO₃, pressure, Earth's lower mantle, first-principles theory.

Perovskita MgSiO₃ con hierro bajo las condiciones del manto inferior de la Tierra

Resumen

Se ha investigado el comportamiento electrónico y estructural de Fe-MgSiO₃ bajo presiones que llegan a la del manto inferior de la Tierra, usando la teoría de primeros principios. Los cristales de Fe-MgSiO₃ experimentan cambio de fase desde una estructura perovskita ortorrómica (OPv) hasta una fase de post-perovskita ortorrómica (OPPv), con una disminución de la presión de transición con el aumento de la concentración de Fe. Las transiciones electrónicas tienen lugar en un rango de presión de unos 70 a 90 GPa para un cristal OPV de (Mg,Fe)(Si,Fe)O₃, en el cual el momento del ion Fe⁴⁺ disminuye gradualmente a cero y el momento magnético del ion Fe²⁺ pasa a ser cero. Esa transición electrónica proporciona el posible mecanismo para entender los experimentos.

Palabras clave: Fe-MgSiO₃, presión, manto inferior de la Tierra, teoría de primeros principios.

Referencia normalizada

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The Earth is formed as a series of chemically distinct concentric shells and understanding structure, chemical composition and dynamics of these shells or layers is the cornerstone of modern Earth sciences. The mantle which extends from near the surface to the depth of 2900 km, formed from mainly magnesium and silicate minerals bearing with Fe, Ca and Al. The structural properties of pure MgSiO₃ is now well understood but the effect of impurity such as Fe is not very well known and also there exist some contradictions in the results obtained by the recent experiments. Fe is one of the abundant metals in the Earth's core and exists as impurity in mantle silicate minerals. Thus, the magnetic properties of iron impurity in

silicate minerals play a crucial role in determining the properties of Earth's mantle mineral such as rheology, electrical and thermal properties *etc.* As the most abundant component in the Earth's lower mantle, MgSiO₃ of pure composition as well as the composition containing Fe has been intensively studied for several decades (Mao *et al.*, 2004; Mao *et al.*, 2005; Jackson *et al.*, 2005; Badro *et al.*, 2003; Cohen *et al.*, 1997). Mao *et al.*, 2004-2005 reported their results of high-pressure experiments on compounds with the chemical formula (Mg_{1-x}Fe_x)SiO₃ (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 (Mao *et al.*, 2005). Meanwhile, much attention has been paid to the electronic behaviors of the Fe dissolving the MgSiO₃ crystals. From X-ray emission spectroscopy, Badro, *et al.*, 2003 discovered two electronic transitions of (Mg_{1-x}Fe_x)SiO₃ (x=0.10) OPv at pressures about 70 and 110 GPa. Using a synchrotron Mössbauer spectroscopy technique, Jackson *et al.*, 2005 studied the electronic environments of the Fe ions in the (Mg_{1-x}Fe_x)SiO₃ (x=0.05 and 0.10) samples at pressures up to about 120 GPa and concluded that there are two kinds of Fe²⁺ ions and one kind of Fe³⁺ ions (the so-called 'three-double' model) in the samples. They also found 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 also been made to build up a clear picture of the electronic properties of the Fe dissolving MgSiO₃ crystals under pressure. Mao *et al.*, 2005 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 OPv with x=0.5 transfer to its OPPv at about 63 GPa and for FeSiO₃ (x=1.00) the OPPv form is more stable at all pressure. However, there is no report on theoretical studies of the FeSiO₃ Pvs and PPvs with dilute Fe concentrations. Here, we present the results of first-principles calculations of the dilute Fe dissolving MgSiO₃ crystals under pressure. The influences of pressure on the lattices and on chemical bonding, as well on the electronic behaviors are investigated.

The forms of Fe existing in the MgSiO₃ samples are still far from clear. Different forms and valences of the Fe ions in the MgSiO₃ samples were suggested (Jackson *et al.*, 2005; Cohen *et al.*, 1997). We have studied one possible type of the Fe dissolving in MgSiO₃: Replacements of one Mg and Si pair by two Fe atoms to form a (Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O₃ (x=0.0625). In the calculations a supercell of $2a_{\text{opv}} \times 2b_{\text{opv}} \times 1c_{\text{opv}}$ and of $4a_{\text{oppv}} \times 1b_{\text{oppv}} \times 1c_{\text{oppv}}$ was employed for the OPv and OPPv structure, respectively. Theoretical calculations were carried out using the VASP code, Vienna *ab initio* simulation program (Kresse *et al.*, 1993; Kresse *et al.*, 1994; Blöchl *et al.*, 1994; Kresse *et al.*, 1999). Both lattice parameters and internal coordinates of the atoms have been fully relaxed.

Experiments have showed that the Fe ions in the MgSiO₃ samples exist in more complicated forms. Different possibilities for the forms of complicated Fe clusters existing in the MgSiO₃ crystals could not be excluded. Here we suggest a simple

configuration by replacing a Mg-Si pair by two Fe ions to obtain $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) in chemical formula.

First we tested the effects of Fe(Si)-Fe(Mg) distances. The calculations showed that in both OPv and OPPv the two iron ions prefer to stay closer, in line with the results of dilute Mn in ZnO crystal (Sharma *et al.*, 2003). Therefore we report the results for $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPPv and OPv with these shortest Fe(Si)-Fe(Mg) distances. The transition pressure at zero K is calculated to be about 24 GPa.

The calculated total DOSs 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 are presented in Figure 1. The total DOS for the OPPv at 0 GPa is included for comparison. At ambient condition for 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 (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 spin-up 3d orbitals are fully occupied while the spin-down 3d orbitals are occupied by one electron. For the Fe at the site, three 3d orbitals are occupied by the spin-up electrons, while only one electron occupies the spin-down 3d orbitals. The total magnetic moment for the OPv is 6 μ_B /cell, indicating the Fe^{2+} ($3d^6$)- Fe^{4+} ($3d^4$) pair. However, the Fe-Fe interaction can also been seen when we compare the DOS of $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPv (Figure 1) with those of $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ and $\text{Mg}(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPvs. 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 Fe-Fe bonding (bond of about 2.8 Å). It is also shown that with increasing pressure, the structure distortion causes the increasing width of the 3d bands. It is also noted as shown in Figure 1, 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 anti-ferrimagnetic (Figure 1). The Fe at the Mg site is still almost fully occupied, however, the Fe at the Si site has smaller magnetic moment (about 0.5 μ_B) μ_B/Fe . That results the total magnetic moment to be about 3.5 μ_B for the $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPv at about 82 GPa. At pressure higher than about 90 GPa, the OPv becomes non-magnetic, as shown in Figure 1 at pressure at 110 GPa. Strong Fe-Fe interaction in the $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPPv can be seen as we compare its DOS with those of the $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ ($x=0.0625$) OPPv and the $\text{Mg}(\text{Si}_{1-x}\text{Fe}_x)\text{O}_3$ ($x=0.0625$) OPPv. The spin-up 3d orbitals of the Fe at Mg site are fully occupied, while there are still some DOS in the spin-down direction below the Fermi level. Also at Fermi level, the DOSs are rather high. That is due to the short Fe-Fe distance (about 2.6 Å) in the compound. However, The calculations shown that the two Fe ions in the OPPv crystal have magnetic moments of 6 μ_B (4 μ_B per Fe^{2+} and 2 μ_B per Fe^{4+}) at pressure up to about 150 GPa, indicating no electronic transitions. That is corresponding to the similarities of the local bonds of the Fe ions. However, complicated electronic behaviors were found for the OPv crystal. The calculated energy differences (total magnetic moments vs. non-magnetic status) for

the OPv are shown in Table 1. At low pressures (lower than about 72 GPa), the calculations showed that the ferromagnetic ordering with total magnetic moment of $6 \mu_B$ (4 for Fe^{2+} and 2 for Fe^{4+}) is more stable than the other states.

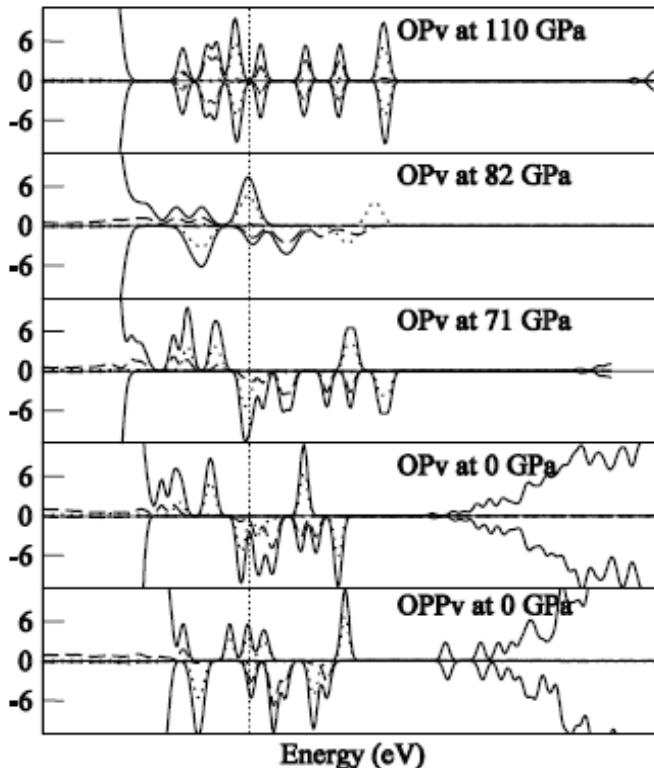


Fig. 1. OPv-($Fe_{0.0625}Mg_{0.9375}$) ($Fe_{0.0625}Si_{0.9375}$) O_3 : (a) at 110 GPa, (b) at 82 GPa, (c) at 0 GPa (d) OPPv-($Fe_{0.0625}Mg_{0.9375}$) ($Fe_{0.0625}Si_{0.9375}$) SiO_3 at 0 GPa. The filled black lines represent the total DOS, the dots for the Fe 3d at the Si site and the short-lines the Fe 3d at the Mg site.

At about 82 GPa the calculations with fully relaxation of the coordinates of atoms and spin-polarization of Fe ions result in a ferri-magnetic ordering with a total magnetic moment of $3.5 \mu_B$ in which the Fe^{2+} has $4 \mu_B$ and the Fe^{2+} ion is partially quenched with the moment of about $-0.5 \mu_B$. The calculated energy of the ferromagnetic status is slightly higher (about 0.01 eV) than that of the non-magnetic status. Above 91 GPa, the Fe ions are in the non-magnetic status. However, between about 78 GPa to 90 GPa, the energies calculated energies for different mag-

netic moments are very close, as shown in Table 1, which indicates coexistence of multiple-magnetic status.

Table 1. Energy differences (E_i , where i represents the value of magnetic moment per Feⁱ⁺) for different spin-polarization states of Fe ions relative to that of Fe⁴⁺ in (Fe_xMg_{1-x})(Fe_xSi_{1-x})O₃ ($x=0.0625$) OPv.

| P (GPa) | 28.6 | 71.8 | 80.8 | 92.3 | 97 | 106 |
|-----------------|-------------|-------------|-------------|-------------|-----------|------------|
| ΔE (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 |

Our calculations showed that electronic transitions were found in the (Mg,Fe)(Si,Fe)O₃ OPv with Fe²⁺-Fe⁴⁺ pairs. Combined with calculated results and experimental data, it is reasonable to suggest that in most Fe dissolving MgSiO₃ high-pressure-prepared samples, Fe ions exist mainly at dodecahedral (Mg) sites, as well as at dodecahedral (Mg) and octahedral (Si) sites to form Fe²⁺-Fe⁴⁺ pairs or such clusters. The Fe^{(2+δ)+}-Fe^{(4-δ)+} pairs and Fe²⁺ at the Mg sites would result in the 'double triplet' model proposed by Jackson *et al.*, 2005. Such mixed Fe²⁺ ions and Fe²⁺-Fe⁴⁺ clusters would cause distortion of the Si-O network in the OPVs and OPPvs, as well as the local symmetry and structure of the Fe ions. Due to the strong itinerant nature of the Fe²⁺-Fe⁴⁺ 3d electrons in the OPvs, the transition pressure lowers down with increasing Fe concentration.

Badro *et al.*, 2003 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 Fe⁴⁺ ions in the pair Fe²⁺-Fe⁴⁺ clusters decreases first. At about 81 GPa, the magnetic moments of both Fe²⁺ and Fe⁴⁺ ions in the Fe²⁺-Fe⁴⁺ clusters are quenched to zero. The small energy differences among the different magnetic configurations also indicate the coexistence of multiple-magnetic status of the Fe-ion clusters in a large transition pressure range. The pressure large range in the electronic transitions may originate from also inhomogeneous of Fe distributions in the samples. It is also noted that our calculations showed a low transition pressure (about 24 GPa) from the (Mg,Fe)(Si,Fe)O₃ OPv to the OPPv form, which is much higher than the transition range (>90 GPa) for x=12.5% (Mg_{1-x}Fe_x)SiO₃ (Mao *et al.*, 2005). That is partially because that it needs to overcome a high barrier to finish such transitions. It also indicates that Fe ions in MgSiO₃ exist in more complicated forms.

In summary, we have performed theoretical calculations for the behaviors of Fe in MgSiO₃ crystals under pressure up to that in the Earth's lower mantle using the DFT-GGA method. The calculations showed that the transition pressure from the OPv to the OPPv phase decreases as the Fe concentration increases. Electronic transitions have been found for the (Mg,Fe)(Si,Fe)O₃ OPv with Fe²⁺-Fe⁴⁺ pair-like

clusters. In such OPvs multiple magnetic moments may exist in a large pressure range (e.g. 78 to 110 GPa). Based on our calculations, we assume that in the high-pressure and high-temperature prepared Fe-MgSiO₃ crystals, Fe ions are positioned at the Mg sites, as well as at the Si-Mg sites, forming Fe²⁺ and Fe^{(2+δ)+}-Fe^{(4-δ)+} type clusters.

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