

Electronic spin state of ferric iron in Al-bearing perovskite in the lower mantle

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[1] We investigate the effect of pressure on the electronic spin state of ferric iron on Al-bearing MgSiO₃-perovskite using first-principle computations. Ferric iron (6.25 mol%) and Al (6.25 mol%) substitute for Mg and Si respectively. Five substitution models on different atomic position pairs are examined. Our results show that spin state transition from high spin (HS) to low spin (LS) occurs on the Fe³⁺ ions at high pressure, while there is no stability field for the intermediate spin state. Fe³⁺ alone can be responsible for the spin state transition. The five models witness a transition pressure ranging from 97–126 GPa. Differential stress can change the pressure for the spin collapse. The lowest pressure spin state transition occurs where Al³⁺ and Fe³⁺ are in adjacent sites. These results are one explanation to the reported experimental observations that the spin transition occurs over a wide pressure range. This finding may have important implications for the dynamics and seismic signature of the lower mantle. **Citation:** Li, L., J. P. Brodholt, S. Stackhouse, D. J. Weidner, M. Alfredsson, and G. D. Price (2005), Electronic spin state of ferric iron in Al-bearing perovskite in the lower mantle, *Geophys. Res. Lett.*, *32*, L17307, doi:10.1029/2005GL023045.

1. Introduction

[2] Iron is the most abundant transition metal in the Earth's lower mantle and, therefore, its spin state may significantly affect the physical properties of the minerals in which iron is incorporated [Burns, 1993; Gaffney and Anderson, 1973]. For instance it has been suggested that a high spin to low spin transition on iron species (Fe²⁺ and Fe³⁺) in the mantle may result in a non-convecting layer above the core-mantle boundary due to changes in the thermal conductivity [Badro et al., 2004], and a seismic discontinuity caused by changes in the elastic properties [Cohen et al., 1997]. There is considerable evidence that a high to low spin transition occurs in perovskite structured MgSiO₃ (often refereed to as only perovskite in the text) at pressures and conditions appropriate to the lower mantle, and that the spin collapse occurs in discreet steps over a range of pressures [Badro et al., 2004; Jackson et al., 2005; Li et al., 2004]. However, the details of which iron species (Fe²⁺ or Fe³⁺) and which sites in perovskite (A or B) are responsible for the observed transitions, are not clear, and

the different investigations interpret their results in different ways.

[3] This has motivated us to investigate spin transitions of Fe³⁺ in aluminous bearing MgSiO₃ using ab initio methods. In particular, we are able to focus on specific crystallographic sites, spin and valence state of iron in the perovskite, something that is difficult to achieve in experiments. We show that the spin collapse of Fe³⁺ in the A site occurs within the pressure range of the experiments. In addition we show that the different ways of mixing Al³⁺ and Fe³⁺ in perovskites causes this transition to occur over a range of pressures. This also provides insight into understanding the experimental results.

2. Calculations

[4] Computations are performed using the density functional theory (DFT) based VASP code, using the generalized gradient approximation (GGA-PW91) [Perdew et al., 1993, 1992] to describe the electron exchange and correlation. All calculations are spin polarized. To describe the interactions between the valence electrons and the core, the projector augmented wave (PAW) implementation [Blöchl, 1994; Kresse and Joubert, 1999] were used, which is a frozen core approach where the exact valence is used as opposed to the traditional pseudopotential methods. A plane wave basis set with kinetic energy cutoff of 800 eV is used for plane wave expansion. We use a 2 × 2 × 1 super-cell with *P6mm* symmetry containing 80 atoms, motivating us to use the Γ -point for the Brillouin zone sampling. To justify the choice of computational settings we compared the results with calculations on an Al-bearing cell using a cutoff energy of 800 eV and a 2 × 2 × 2 Monkhorst-Pack *k*-point grid [Monkhorst and Pack, 1976]; the total energies for the Γ -point is converged within 1.5 meV/atom. The energy was converged to 10⁻⁷ eV. Calculations were performed with iron in high spin (*j* = 5/2), intermediate spin (*j* = 3/2) and low spin (*j* = 1/2) at seven different pressures: 0, 25, 50, 75, 100, 125, and 150 GPa, in which all the atomic positions and cell parameters were allowed to relax at static conditions (0K).

[5] Transition metals (including Fe) remain a computational challenge. DFT falsely predicts the B1-structure of FeO [Alfredsson et al., 2004; Mazin and Anisimov, 1997], fayalite Fe₂SiO₄ [Matteo et al., 2003] as metallic, suggesting that other approaches should be sought to describe the electronic structure of iron-bearing phase [Alfredsson et al., 2004]. Other studies have used the GGA approximation to study magnetic properties for iron-bearing minerals [Cohen et al., 1997] as well as the elastic properties [Kiefer et al., 2002] for iron-bearing perovskite. Our calculations, con-

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Table 1. Initial Fractional Atom Positions of Substituted Ions for (Mg, Fe)(Si, Al)O₃ Perovskite and Fe-Al Atom Distances for High Spin (at 0 GPa) and Low Spin (at 150 GPa)

	Al ³⁺		Fe ³⁺		d(Fe-Al), Å	
					0 GPa, Å	150 GPa, Å
CCM1	(0.500, 0.248, 0.497)	(0.508, 0.467, 0.747)	2.80	2.34		
CCM2	(0.496, 0.250, 0.500)	(0.738, 0.219, 0.747)	2.92	2.48		
CCM3	(0.500, 0.249, 0.500)	(0.491, 0.529, 0.253)	3.29	2.99		
CCM4	(0.499, 0.250, 0.500)	(0.241, 0.720, 0.750)	5.59	4.93		
CCM5	(0.499, 0.250, 0.500)	(0.008, 0.790, 0.753)	5.77	5.21		

taining 6.25% Fe³⁺, show that the perovskite structure remains insulating after doping. It is also well known that ferric iron (*d*⁵-ion) is better described in DFT than ferrous iron (*d*⁶-ion), and both the geometrical and electronic properties of Fe₂O₃ have been reproduced [Rollmann *et al.*, 2004]. While these concerns suggest a need for caution, the agreement of the calculations with the observations gives confidence in pursuing this type of calculation for transition metals.

[6] Trivalent cations can be introduced into silicate perovskite as a charge coupled substitution (denoted charged-coupled mechanism (CCM) in the paper) of a Mg²⁺-Si⁴⁺ pair (2M³⁺ → M_{Mg}²⁺ + M'_{Si}⁴⁺) or a replacement of two Si⁴⁺ and an oxygen vacancy (2M³⁺ → 2M'_{Si}⁴⁺ + V_O); referred to as oxygen-vacancy mechanism (OVM). The latter mechanism has been reported to be energetically unfavorable for both Al³⁺ [Brodholt, 2000; Yamamoto *et al.*, 2003] and Fe³⁺. In addition, calculations on Al³⁺ and Fe³⁺ bearing perovskites showed that Fe_{Mg}³⁺ + Al'_{Si} is more stable than Al_{Mg}³⁺ + Fe'_{Si} [Richmond and Brodholt, 1998]. We have, therefore, performed calculations on five perovskite models with Fe³⁺ + Al³⁺ → Fe_{Mg}³⁺ + Al'_{Si}, as listed in Table 1. As shown in Table 2, our DFT calculations are consistent with the reported occupancy mechanisms at low pressure. At 100 GPa the enthalpy difference is rather small, indicating that Fe³⁺ + Al³⁺ will be disordered between the two sites. Furthermore, we calculated that the configuration with ferric iron in the B site and Al in the A site has low spin as the stable state even at 0 GPa. Since this configuration is energetically less stable, than Fe³⁺ in the A site and Al in the B site, we do not further consider this configuration.

3. Results

[7] Table 3 lists the calculated cell volumes for the five models. The cell volume for MgSiO₃ (167.28 Å³) is consistent with other reported calculation [Brodholt, 2000; Yamamoto *et al.*, 2003], but slightly higher than indicated by measurements (162.18 Å³; [Ross and Hazen, 1989]), which is to be expected from GGA calculations. We applied

Table 2. Comparison of Volume, V, and Enthalpies, H, Among Different Types of Substitution Mechanisms at -8 and 92 GPa^a

Type	Pc, GPa	V, Å ³	H, eV
CCM1 Fe ³⁺ + Al ³⁺ → Fe _{Mg} ³⁺ + Al' _{Si}	-8	168.44	-564.01
CCM1 Fe ³⁺ + Al ³⁺ → Al _{Mg} ³⁺ + Fe' _{Si}	-8	168.14	-562.83
OVM1 Fe ³⁺ + Al ³⁺ → Fe' _{Si} + Al' _{Si} + V _O	-8	169.64	-551.15
CCM1 Fe ³⁺ + Al ³⁺ → Fe _{Mg} ³⁺ + Al' _{Si}	92	129.82	-200.43
CCM1 Fe ³⁺ + Al ³⁺ → Al _{Mg} ³⁺ + Fe' _{Si}	92	129.71	-200.21
OVM1 Fe ³⁺ + Al ³⁺ → Fe' _{Si} + Al' _{Si} + V _O	92	129.65	-187.38

^aPc is the corrected pressure.

a constant pressure correction (-8 GPa) was done by Oganov *et al.* [2001]. We expect the precision on the pressure is small (1 GPa) while systematic errors arising from choice of model variables are less enumerable. As shown in the Table 3, the coupled substitution of Fe-Al for Mg-Si increases the volume by 0.9%. Throughout the pressure range studied, the CCM1 model has the lowest enthalpy and the shortest Fe-Al atom distance (see Table 1).

[8] Figures 1a–1e shows the relative stability of the three possible spin states for the five models as a function of pressure. For high spin, CCM1 has the lowest ΔH among the five models up to 97 GPa (Figure 1a). Above 97 GPa, for CCM1, the low spin has the lowest energy indicating a spin state transition. We use, therefore, the enthalpy for the CCM1 high-spin model as the reference for all of these figures. The other models (Figures 1b–1e) have similar behavior with the transition occurring in the range from 122 GPa to 126 GPa. The lower pressure transition of the CCM1 model may reflect a greater interaction between the Fe site and the Al site as they coordinate with three common oxygen atoms, while the other arrangements share two or fewer oxygen atoms. The intermediate spin (3 unpaired electrons) never has the lowest enthalpy, and thus has no stability field.

4. Discussion and Conclusion

[9] Two studies [Badro *et al.*, 2003; Li *et al.*, 2004] use the intensity of a satellite peak in the X-ray emission spectra to quantify the magnetic moment and provide evidence for a spin transition at elevated pressure. One [Li *et al.*, 2004] evaluates both Al-bearing and Al-free MgSiO₃-perovskite, while the other [Badro *et al.*, 2004] reported results for only the Al-free MgSiO₃-perovskite. In the former case [Li *et al.*, 2004] the spin state transition occurred over a wide pressure range. At 100 GPa, both the Al-bearing and the Al-free phase had experienced some spin collapse, while the Al-bearing phase had experienced the smaller amount of transition. In the other study on the Al-free samples [Badro *et al.*, 2004], two distinct transitions are reported, one at 70 GPa and the other at 120 GPa. The main difference in

Table 3. Calculated Unit Cell Parameters, a, b and c, Volume, V, and Enthalpies, H, for CCM1, CCM2, CCM3, CCM4, and CCM5

	Pc, GPa	Fe ³⁺ , Spin		H, eV
		State	V, Å ³	
MgSiO ₃	0	–	167.28	-561.76
MgSiO ₃ [Yamamoto <i>et al.</i> , 2003] ^a	0	–	163.35	–
MgSiO ₃ [Brodholt, 2000] ^a	0	–	162.42	–
MgSiO ₃ [Ross and Hazen, 1989] ^b	0	–	162.18	–
MgSiO ₃ [Horiuchi <i>et al.</i> , 1987] ^b	0	–	162.18	–
MgSiO ₃ [Oganov <i>et al.</i> , 2001] ^a	0	–	168.04	–
CCM1	-8	5	168.44	-564.01
CCM2	-8	5	168.44	-563.99
CCM3	-8	5	168.48	-563.95
CCM4	-8	5	168.55	-563.88
CCM5	-8	5	168.52	-563.91
CCM1	142	1	120.25	-44.70
CCM2	142	1	120.29	-44.44
CCM3	142	1.15	120.25	-44.32
CCM4	142	1	120.28	-44.14
CCM5	142	1	120.28	-44.17

^aTheoretical.^bExperimental.

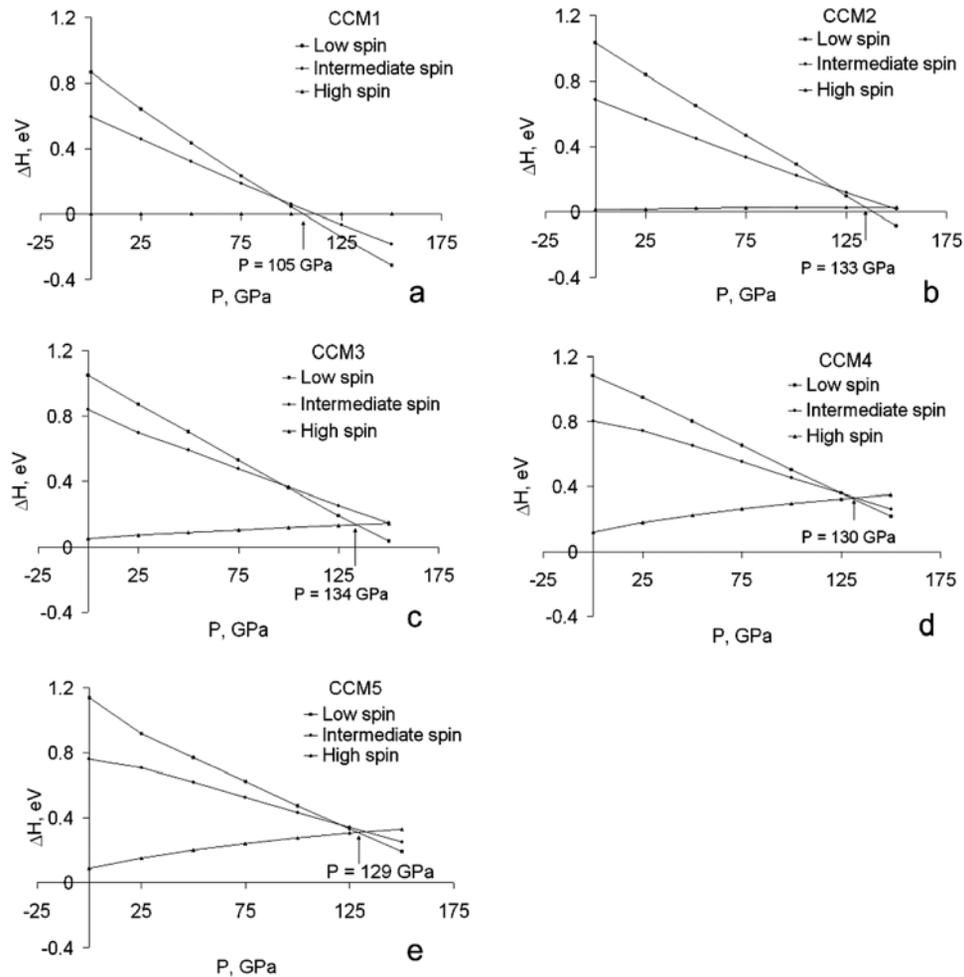


Figure 1. (a)–(e) The Gibbs free energy differences vs. pressure for $(\text{Mg}, \text{Fe})(\text{Si}, \text{Al})\text{O}_3$ perovskite with ferric iron at high spin, intermediate spin and low spin. The five figures represent the CCM1–CCM5 models listed in Table 1. The y axis $\Delta H = H - \langle H \rangle$, where H is the calculated Gibbs free energy; $\langle H \rangle$ is the H for the CCM1 with iron in high spin at each pressure. The pressures indicated here are not corrected for GGA, the corrected pressures $P_c = P - 8$ GPa.

experimental protocol is that the study with the sharp transitions [Badro *et al.*, 2004] annealed the samples at pressure while the other study [Li *et al.*, 2004] did not. A high pressure Mössbauer study [Jackson *et al.*, 2005] indicates evidence of a HS-LS transition over a broad pressure range on the Fe^{3+} ions, terminating at 70 GPa. These studies indicate the common theme that the spin state of iron in perovskite decreases dramatically in a pressure range up to about 120 GPa.

[10] The theoretical calculations presented here are generally consistent with the experimental observations. The calculations predict a two step decay of the spin state, the first at 97 GPa where CCM1 configurations transform from the high spin to the low spin state and the second at about 125 GPa where the other sites transform. The CCM1 site may be relatively more populated since it has the lowest energy of the five models considered, however, the enthalpy difference between CCM1, CCM2 and CCM3 is so small that we would expect a considerable population of all three at high temperatures.

[11] In fact the transitions may be even more complicated since we have not included the effect of Fe^{2+} . While [Cohen *et al.*, 1997] predicted Fe^{2+} in the A site will not have spin

state transition in the reported experimental pressure range, this issue warrants further study in light of experimental data.

[12] The experimental data also have some inconsistencies relative to each other. Some report a smooth transition over a wide pressure range [Jackson *et al.*, 2005; Li *et al.*, 2004], while others indicate multiple sharp transitions [Badro *et al.*, 2004]. The common feature of these three reported experiments [Badro *et al.*, 2004; Jackson *et al.*, 2005; Li *et al.*, 2004] is the diamond anvil cell as the pressurizing device. Compression to such high pressures is usually accommodated with deviatoric stress in the sample. Badro *et al.* [2003] annealed the sample to reduce the deviatoric stress and found sharper transitions compared to the other studies. We investigated the possibility that deviatoric stress is responsible for the broadening of the transition. The strength of silicate perovskite has been measured in diamond anvil cell [Meade, 1990; Merkel *et al.*, 2003] showing that the stress in the perovskite can be as high as 10 GPa under a pressure of 32 GPa. A deformation experiment performed in large-volume apparatus [Chen *et al.*, 2002] further confirmed that strength of the perovskite is at least above 5 GPa at room temperature.

[13] In order to test this, we impose 1% elastic strain on $\text{Fe}^{3+}\text{-Al}^{3+}$ bearing MgSiO_3 perovskites and recalculate the enthalpy at high spin, intermediate spin and low spin states. We calculated six strain cases (ϵ_{11} , ϵ_{22} , ϵ_{33} , ϵ_{12} , ϵ_{13} , ϵ_{23}) for both the CCM1 and the CCM2 configurations. This level of strain corresponds to 2–4 GPa of shear stress. We find that the deviatoric stress changes the transition pressure by about 1–5 GPa for the CCM1 configuration and by 10–15 GPa for the CCM2 case, the amount of change dependent on the specific deviatoric strain imposed. Therefore, we would conjecture that perovskite in a diamond anvil cell at a stress near its yielding point will have much broader transition pressure than the perovskite which has been annealed creating a more hydrostatic environment. The two-step transition in the annealed samples [Badro *et al.*, 2004] is consistent with the fact the different sites of Fe^{3+} can have different transition pressures. Applying these results to the Earth, it is necessary to account for temperature. Badro *et al.* [2004] points out that electronic transitions generally depend on volume and not the pressure–temperature state that produces the volume. With such an assumption, the estimated pressure correction of the HS-LS transition for the deep mantle (~ 2500 K) is about 18 GPa [Badro *et al.*, 2003; Gillet *et al.*, 1999]. Based on this estimation, such spin state transition could take place in or near the D'' region.

[14] Considering the various experimental and theoretical results related to the HS-LS transition in perovskite, our calculations provide a model where ferric iron undergoes a spin transition in perovskite at pressures of 97–126 GPa at 0 K in the calculation. The intermediate spin has no stability field. The adjacent Fe-Al pair is energetically favored in the substitution suggesting the transition pressure is in the low end of this range. Furthermore, deviatoric stress can significantly alter the transition pressure. We should bear in mind that this calculation only focus on ferric iron, ferrous iron may also play an important role in the spin state transitions in iron-bearing perovskite in the lower mantle.

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