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Spin-state crossover and hyperfine interactions of ferric iron in MgSiO₃ perovskite

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Abstract

Using density functional theory plus Hubbard U calculations, we show that the ground state of 9 (Mg,Fe)(Si,Fe)O₃ perovskite, the major mineral phase in the Earth's lower mantle, has high-spin 10 ferric iron (S = 5/2) at both dodecahedral (A) and octahedral (B) sites. With increasing pressure, 11 the B-site iron undergoes a spin-state crossover to the low-spin state (S = 1/2) between 40 and 12 70 GPa, while the A-site iron remains in the high-spin state. This B-site spin-state crossover is 13 accompanied by a noticeable volume reduction and an increase in quadrupole splitting, consistent 14 with recent X-ray diffraction and Mössbauer spectroscopy measurements. The anomalous volume 15 reduction leads to a significant softening in the bulk modulus during the crossover, suggesting a 16 possible source of seismic-velocity anomalies in the lower mantle. 17

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The total electron spin (S) of a transition-metal ion in a crystalline solid can change with 19 many factors, such as pressure, strain, or temperature, to name a few. This phenomenon, 20 known as spin-state crossover, is of great importance in spintronics, as it allows artificial 21 control of magnetic properties of materials, including coordination complexes with potential 22 for molecular switches [1]. Not as widely known, spin-state crossover also plays a crucial role 23 in geophysics. A well studied example is ferropericlase, (Mg,Fe)O, the second most abundant 24 mineral (~ 20 vol%) in the the largest single region (~ 55 vol%) of the Earth's interior -25 the lower mantle. With increasing pressure, ferrous iron (Fe^{2+}) in this mineral undergoes a 26 crossover from high-spin (HS) state, S = 2, to low-spin (LS) state, S = 0, in the pressure 27 range of 40-55 GPa [2–6]. The intermediate-spin (IS) state, S = 1, is not observed in 28 this mineral. The HS-LS crossover in ferropericlase directly affects the structural, elastic, 29 optical, and conducting properties of this mineral [6-11] and thus affects mantle properties. 30 [10, 12, 13].31

In contrast, the spin-state crossover in iron-bearing magnetium silicate (MgSiO₃) per-32 ovskite (Pv), the most abundant mineral ($\sim 75 \text{ vol}\%$) in the lower mantle, has been a source 33 of controversy for two main reasons. One is the coexisting ferrous and ferric iron (Fe^{3+}) in 34 this mineral with an imprecisely estimated population ratio; the other is the lack of definitive 35 tools to directly probe iron spin state at high pressures. Two techniques, X-ray emission 36 spectroscopy (XES) and Mössbauer spectroscopy, have been widely used, but their inter-37 pretation can be ambiguous. The very similar XES spectra [14, 15] and Mössbauer spectra 38 [16–19] have been interpreted in terms of HS-IS and HS-LS crossover in (Mg,Fe)SiO₃ Pv. 39 Plenty of calculations on (Mg,Fe)SiO₃ Pv have been conducted [20–25], but consistency with 40 experiments was not achieved until very recently [26, 27]. Now the spin state in (Mg,Fe)SiO₃ 41 Pv is better understood: the observed increase of iron nuclear quadrupole splitting (QS) in 42 Mössbauer spectra results from neither HS-IS nor HS-LS crossover, but from the change in 43 the 3d orbital occupancy of the HS iron [27]. As to ferric iron in Pv, possibly more abundant 44 than ferrous iron ($Fe^{3+}/\Sigma Fe$ might be as high as 2/3) [28, 29], its spin-state crossover has 45 remained unclear, as described below. 46

Previous experiments investigating the iron spin state in aluminum-free MgSiO₃ Pv were focused mostly on ferrous iron [16, 18]. Nevertheless, it was still observed that the low concentration of ferric iron in the sample exhibited an increase in QS with pressure, which

suggests a crossover from HS (S = 5/2) to LS (S = 1/2) state in the pressure range of 50 30-70 GPa. In contrast, in Al-bearing samples, where ferric iron occupies the dodecahedral 51 (A) site, the QS remains unchanged up to 100 GPa, which suggests the A-site iron remains 52 in the HS state [17]. These results indicate that the ferric iron at the octahedral (B) site 53 undergoes a spin-state crossover. Such a mechanism was recently confirmed by experiments 54 using $(Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O_3$ Pv (x = 0.1) samples: about half of the HS iron changes to 55 LS state in the 45-60 GPa range while the other half remain in the HS state all the way to 56 150 GPa [30]. So far, the computational studies on $(Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O_3$ Pv have found 57 a ground state with HS iron at the A-site and LS iron at the B-site (A-HS; B-LS) and an 58 A-site HS-LS crossover that leads both A- and B-site iron to a final LS state (A:LS; B-LS) 59 at high pressures [21, 22]. These predictions are inconsistent with experiments in two ways: 60 (1) the predicted transition pressure is too high; (2) the predicted HS iron concentration is 61 too low. 62

To compare with recent experiments [30], we stabilize $(Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O_3$ Pv with 63 x = 0.125 in all possible spin states using a 40-atom supercell shown in Fig. 1. We also 64 calculate the iron nuclear electric field gradient (EFG) associated with each state, as the nu-65 clear hyperfine interaction has proven to be a unique fingerprint to identify the spin states of 66 transition-metal ions [27, 31]. The atomic structures were fully optimized with damped vari-67 able cell shape molecular dynamics [32] implemented in the QUANTUM ESPRESSO code [33], 68 where the plane-wave pseudopotential method is adopted [34]. These states were also inde-69 pendently confirmed via the augmented plane-wave plus local orbitals (APW+lo) method 70 [35] implemented in the WIEN2k code [36], with which the EFGs were calculated. The EFGs 71 were converted to QSs with ⁵⁷Fe nuclear quadrupole moment Q = 0.16 [37] and 0.18 barn for 72 the possible uncertainty. To treat $(Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O_3$ Pv, the density functional the-73 ory plus Hubbard U (DFT+U) method is necessary, as standard DFT exchange-correlation 74 functionals, the local density approximation (LDA) and generalized gradient approximation 75 (GGA), sometimes lead to unwanted metallic states (especially at high pressures), in which 76 the iron spin states are not well defined. Since the Hubbard U of A- and B-site iron in each 77 spin state is unknown, we have to stabilize the desired spin state with a trial U and then 78 extract the self-consistent U, referred to as U_{sc} , using the linear response approach [38] in 79 a recently developed iterative procedure. This procedure is equivalent to, but more efficient 80

than the one published earlier [39], and has been successfully implemented [40]. More details are described in the EPAPS [41].

⁸³ Within DFT+U, several combinations of iron spin states can be stabilized. The A-site ⁸⁴ ferric iron can be stabilized in HS, IS, and LS states. The B-site ferric iron can be stabilized ⁸⁵ not only in LS state, but also in HS state that has not found in previous calculations [21, 22]. ⁸⁶ The spin moments of the A- and B-site iron can be either parallel or anti-parallel. The U_{sc} ⁸⁷ of ferric iron in Pv, listed in Table I, mainly depends on the iron spin state, slightly depends ⁸⁸ on the occupied site, and barely depends on pressure and alignment of spin moments.

The relative enthalpy (ΔH) of each stabilized state is shown in Fig. 2, where the pre-89 viously perceived ground state (A-HS; B-LS) [21, 22] is used as a reference. Remarkably, 90 the actual ground state of $(Mg,Fe)(Si,Fe)O_3$ Pv has HS iron on both sites (A-HS; B-HS), 91 regardless of the choice of exchange-correlation functional (LDA or GGA) and Hubbard U92 $(U_{sc} \text{ or } 4 \text{ eV})$. These choices do not affect the spin-state crossover either: an HS-LS crossover 93 only occurs in the B-site iron, while the A-site iron remains HS. As expected, the predicted 94 transition pressure (P_T) depends on the exchange-correlation functional and Hubbard U: 95 with LDA+ U_{sc} , $P_T = 41$ GPa; with GGA+ U_{sc} , $P_T = 70$ GPa; with GGA+U (U = 4 eV), 96 $P_T = 29$ GPa. (Coordination complexes also show similar dependence [42, 43].) Notably, 97 the alignment of iron spins (parallel or anti-parallel), barely affects P_T , as shown in Fig. 2(c). 98 The P_T predicted by LDA+ U_{sc} and GGA+ U_{sc} best agree with the P_T observed in Mössbauer 99 spectra, 50-60 GPa [30]. The LDA+ U_{sc} electronic density of states (DOS) of the two relevant 100 states (A-HS; B-HS and A-HS; B-LS) can be found in EPAPS [41]. 101

The calculated QSs of ferric iron (A- and B-site) and ferrous iron (A-site) [27] in various 102 spin states, along with the measured QSs [16, 18, 30], are shown in Fig. 3. Clearly, our 103 calculations on ferrous and ferric iron in Pv are consistent with Mössbauer spectra. The 104 HS-LS crossover in the B-site ferric iron also helps to explain the decrease in the XES 105 satellite peak (K β) intensity [14, 15]. Interestingly, the QS of ferrous and ferric iron exhibit 106 exactly the opposite trends with respect to the spin moment. This can be understood via 107 their orbital occupancies. The LS ferrous iron, although occupying the A site, is effectively 108 located near the center of a Fe-O octahedron, as it is vertically displaced from the mirror 109 plane [24]. Its six 3d electrons doubly occupy the three orbitals with t_{2g} character and form 110

a charge density with cubic-like shape [24], which barely contributes to the EFG and leads 111 to a very small QS. The HS ferric iron also has a small EFG (and thus QS), irrespective of 112 A or B site. This is because its five 3d electrons (all spin-up) occupy all 3d orbitals, forming 113 an almost spherically shaped electron charge distribution that leads to a small EFG (and 114 thus QS). Similarly, the spin-up electrons in HS ferrous and LS ferric iron barely contribute 115 to EFG, as their charge distributions are nearly spherical and cubic, respectively. It is their 116 spin-down electrons that contribute to the EFGs and lead to larger QSs. This is why the 117 spin moments of ferrous and ferric iron appear to affect the QSs in an opposite manner. 118

The LDA+ U_{sc} compression curves and bulk modulus ($K \equiv -VdP/dV$) of $(Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O_3$ 119 Pv (x = 0.125) along with the experimental data (x = 0.1) [30] are shown in Fig. 4. At 120 low pressures (< 45 GPa), the experimental data falls on the calculated compression curve 121 corresponding to the (A-HS; B-HS) state. Starting from ~ 45 GPa, the data points deviate 122 from the (A-HS; B-HS) curve and then join the (A-HS; B-LS) curve at ~ 60 GPa. Starting 123 from ~ 100 GPa, the data deviates from the curve again. This, however, is very likely to 124 result from the questionable accuracy of the Au pressure scale used in the experiment, as 125 already discussed in the case of (Mg,Fe)SiO₃ Pv [44]. Notice that the observed volume 126 reduction further confirms the B-site HS-LS crossover, as the previously perceived A-site 127 HS-LS crossover barely leads to a volume reduction, evident from the compression curves 128 (A-HS; B-LS and A-LS; B-LS) shown in Fig. 4(a). The B-site spin-state crossover and the 129 observed volume reduction in the 45-60 GPa range can be qualitatively understood via the 130 Fe^{3+} electronic configurations and Fe-O distances at A and B sites. With all 3d orbitals 131 occupied, HS iron has spherically-shaped electron charge density and the largest radius 132 compared with other spin states, favoring longer Fe-O distances. Residing in the large do-133 decahedral cage, the A-site iron can easily maintain longer Fe-O distances and thus remain 134 in HS state. In contrast, the Fe-O octahedron has smaller size and shorter Fe-O distances. 135 With increasing pressure, the internal octahedron bond lengths can be shortened enough to 136 induce the HS-LS crossover. Since the 3d electrons of the B-site LS iron only occupy the 137 t_{2q} -like orbitals pointing away from oxygen, the associated Fe-O distances are significantly 138 shorter than those of the HS iron at the same pressure. Therefore, the spin change of the 139 B-site iron is accompanied by a noticeable octahedral (and thus unit-cell) volume reduction. 140 Such volume reduction leads to anomalous softening in bulk modulus, as described below. 141

At finite temperatures, the spin-state crossover passes through a mixed-spin (MS) state 142 (namely, HS and LS coexist) within a finite pressure range that increases with temperature. 143 During the crossover, the thermodynamic properties of the MS state exhibit anomalous 144 behavior that may affect mantle properties. One example is the softening in bulk modules 145 and its effect on the compressional wave velocity, as already seen in ferropericlase [7, 10, 11]. 146 To estimate such anomaly in $(Mg,Fe)(Si,Fe)O_3$ Pv, we employ a thermodynamic model 147 similar to that used in Ref. [10]. Here, we do not include vibrational free energy, as it 148 barely affects the magnitude of the anomaly, slightly increases the transition pressure, and 149 uniformly decreases the bulk modulus, as shown in the case of ferropericlase [10, 11]. Indeed, 150 the calculated V(P) curve of (Mg,Fe)(Si,Fe)O₃ Pv in the MS state (using LDA+ U_{sc}) at room 151 temperature (300 K), shown as the dashed line in Fig. 4(a), exhibits a volume reduction 152 $(\sim 1.2\%)$ around the predicted P_T , 41 GPa. This reduction leads to a significant softening 153 in bulk modulus, as shown in Fig. 4(b). The softening is still prominent at 2000 K, the 154 temperature near the top of the lower mantle (~ 660 km deep). Given the abundance of 155 iron-bearing Pv and the possibly high population of ferric iron, this softening may have a 156 noticeable impact on the mantle properties, including possible anomalies in the seismic wave 157 velocities. 158

In summary, with a series of DFT+U calculations, we have shown that the actual ground 159 state of (Mg,Fe)(Si,Fe)O₃ perovskite has high-spin ferric iron on both A and B sites. It 160 is the B-site ferric iron that undergoes a crossover from high-spin to low-spin state with 161 increasing pressure, while the A-site iron remains in the high-spin state. The calculated 162 quadrupole splittings and the compression curves are consistent with experiments. The 163 volume reduction accompanying the B-site HS-LS crossover leads to a significant softening 164 in bulk modulus, which suggests a possible source of seismic-velocity anomalies in the lower 165 mantle. This work, one more time, demonstrates that the nuclear hyperfine interaction, 166 combined with first-principles calculations, can be a useful tool to identify the spin states of 167 transition-metal ions in solids under high pressures. 168

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Table I. U_{sc} , the self-consistent Hubbard U (in eV), of ferric iron on the A and B site in

²²⁰ each spin state.

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	A site	B site
HS $(S = 5/2)$	3.7	3.3
IS $(S = 3/2)$	4.6	_
LS $(S = 1/2)$	5.2	4.9

²²² Figure Captions

Fig. 1. (Color online) Atomic structure of $(Mg_{0.875}Fe_{0.125})(Si_{0.875}Fe_{0.125})O_3$ Pv, configured with the shortest iron-iron distance, viewing along the [001] direction. Large (orange) and small (green) spheres represent Fe and Mg sites, respectively. Si-O and Fe-O octahedra are shown in opaque (blue) and translucent (orange) colors.

Fig. 2. (Color online) Relative enthalpies of $(Mg_{0.875}Fe_{0.125})(Si_{0.875}Fe_{0.125})O_3$ Pv in different spin states obtained using different functionals and Hubbard U. The reference state has HS iron in the A site and LS iron in the B site (A-HS; B-LS). Predicted transition pressures by LDA+ U_{sc} (a), GGA+ U_{sc} (b), and GGA+U with U = 4 eV (c) are 41 and 70, and 29 GPa, respectively. Dashed lines in (c) correspond to anti-parallel spins at A- and B-sites.

Fig. 3. (Color online) Calculated QSs of (a) ferrous iron [27] and (b) ferric iron in MgSiO₃ Pv. Letter A and B in (b) refer to iron-occupying site. Arrows in (c) indicate the measured effect of pressure on QSs [16, 18, 30].

Fig. 4. (Color online) Compression curves (a) and bulk modulus (b) of $(Mg_{1-x}Fe_x)(Si_{1-x}Fe_x)O_3$ Pv computed with LDA+ U_{sc} (x = 0.125) and room-temperature measurements (x = 0.1) [30]. Both the measured and calculated compression curves exhibit a clear reduction accompanying with the B-site HS-LS crossover, which leads to a softening in bulk modulus shown in (b).



FIG. 1.



FIG. 2.



FIG. 3.



FIG. 4.