Spin transition of Fe$^{3+}$ in Al-bearing phase D: An alternative explanation for small-scale seismic scatterers in the mid-lower mantle

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ABSTRACT

Among dense-hydrus magnesium silicates potentially transporting H$_2$O into Earth's deep interior, phase D (MgSi$_2$H$_2$O$_6$) exhibits the highest P-T stability range, extending into the lower mantle along cold slab geotherms. We have studied the compressibility and spin state of Fe in Al-bearing phase D up to 90 GPa using synchrotron X-ray diffraction and X-ray emission spectroscopy. Fe-Al-bearing phase D was synthesized at 25 GPa and 1400 °C with approximate composition MgSi$_{1.5}$Fe$_{0.15}$Al$_{0.32}$H$_{2.6}$O$_6$, where nearly all of the Fe is ferric (Fe$^{3+}$). Analysis of Fe-K$\alpha$ emission spectra reveals a gradual, pressure-induced high-spin (HS) to low-spin (LS) transition of Fe$^{3+}$ extending from 40 to 65 GPa. The fitted equation of state for high-spin Fe-Al-bearing phase D results in a bulk modulus $K_{T_0}$ = 147(2) GPa with pressure derivative $K' = 6.3(3)$. An equation of state over the entire pressure range was calculated using the observed variation in low-spin fraction with pressure and a low-spin bulk modulus of $K_{T_0}$ = 253(30) GPa, derived from the data above 65 GPa. Pronounced softening in the bulk modulus occurs during the spin transition, reaching a minimum at 50 GPa ($\sim$1500 km) where the bulk modulus of Fe-Al phase D is about 35% lower than Fe-Al-bearing silicate perovskite. Recovery of the bulk modulus at 50–65 GPa results in a structure that has a similar incompressibility as silicate perovskite above 65 GPa. Similarly, the bulk sound velocity of Fe-Al phase D reaches a minimum at $\sim$50 GPa, being about 10% slower than silicate perovskite. The potential association of Fe-Al phase D with subducted slabs entering the lower mantle, along with its elastic properties through the Fe$^{3+}$ spin transition predicted at 1200–1800 km, suggests that phase D may provide an alternative explanation for small-scale mid-lower mantle seismic scatterers and supports the presence of deeply recycled sediments in the lower mantle.

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1. Introduction

Subducted oceanic crust can carry kilometer-thick packages of Fe- and Al-rich pelitic sediments into the upper mantle at convergent margins where the average continental shale contains 5–8 wt.% Fe$_2$O$_3$ + FeO and 15–25 wt.% Al$_2$O$_3$ (e.g. Plank and Langmuir, 1998; Poli and Schmidt, 2002). Dehydration reactions of serpentinite-group minerals can produce a number of different dense hydrous magnesium silicates (DHMS) in the MgO–SiO$_2$–H$_2$O system along cold subduction geotherms (e.g. Angel et al., 2001; Irifune et al., 1998; Ohtani et al., 2001; Ringwood and Major, 1967; Yamamoto and Akimoto, 1977). Fluids from dehydrating crust and sediments also interact with downgoing entrained peridotite from the overlying mantle wedge (Kawakatsu and Watada, 2007). Thus, the contribution of chemical components from subducted sediments (H$_2$O, Fe$_2$O$_3$ and Al$_2$O$_3$) may influence phase relations and physical properties of DHMS in the peridotite system and is relevant to understanding the fate of subducted sediments in the mantle and Earth's deep water cycle.

DHMS occurring along the forsterite–brucite join (Fo, Mg$_2$SiO$_4$; Br, Mg(OH$_2$)) include phase A (2Fo + 3Br, 12 wt.% H$_2$O), OH-chondrodite (2Fo + 1Br, 5 wt.% H$_2$O), and OH-chlinohumite (4Fo + 1Br, 3 wt.% H$_2$O), which are commonly found in dehydration experiments of serpentine below 15 GPa and 1200 °C (e.g. Luth, 1995; Stalder and Ulmer, 2001). At higher pressures of 15–30 GPa,...
phase E (2Br + 15SiO₂, 10 wt.% H₂O), superhydrous phase B (3Fo + 2Br + 2MgO, 3 wt.% H₂O), and phase D (1Br + 2SiO₂, 10 wt.% H₂O) are the stable DHMS formed from serpentinite-group minerals (e.g. Frost and Fei, 1998; Irifune et al., 1998; Ohtani et al., 2001; Shieh et al., 2000). Phase D is the highest-pressure phase among DHMS and has a dense structure (ρ₀ = 3.51 g/cm³) with Si in sixfold coordination similar to silicate perovskite. Phase D has therefore been considered a candidate phase for transport of H₂O into the lower mantle.

A path to phase D in the mantle requires breakdown of serpentinite below the critical condition of ~600 °C at 5 GPa, forming phase A plus enstatite (En, MgSiO₃) and fluid H₂O (e.g. Ulmer and Trommsdorff, 1995). Along cold slab geotherms, the phase A plus En assemblage is stable to ~12 GPa, where it will form phase E plus wadsleyite and further transform to superhydrous phase B plus stishovite above ~15 GPa (Litasov and Ohtani, 2003; Komabayshi and Omori, 2006). If temperatures remain below ~1200 °C, phase D will form at pressures above 15–18 GPa (e.g. Irifune et al., 1998; Kawamoto, 2004; Komabayshi and Omori, 2006). In other bulk compositions, phase D has been synthesized at temperatures as high as 1400 °C at 25 GPa (Frost and Fei, 1998; Saikia et al., 2009). The upper stability limit of pure-Mg phase D was found to be ~44 GPa at 1200 °C in laser-heated diamond-anvil cell experiments of serpentinite bulk compositions (Shieh et al., 1998). Litasov et al. (2008) measured the thermal equation of state of Al–Fe-bearing phase D up to 20 GPa and 1273 K; however, the upper stability limit of Al–Fe-bearing phase D has not been determined in comparison with pure-Mg phase D.

Phase D has a trigonal structure with space group P31m, composed of alternating layers of MgO₆ and SiO₆ octahedra along the c-axis (Yang et al., 1997). The ideal chemical formula of phase D is Mg₂Si₂H₂O₆, although the observed stoichiometry varies in H-content from 2.2 to 3.6 H per formula unit and with Mg/Si ratios from 0.2 to 0.7 (e.g. Boffa Ballaran et al., 2010; Frost and Fei, 1999; Yang et al., 1997). The Mg–Si octahedral framework of the phase D structure contributes to its relatively high density and extended stability field among other DHMS, despite consisting of nearly 10% structure contributes to its relatively high density and extended stability field among other DHMS, despite consisting of nearly 10% H₂O by weight.

Symmetrization of the hydrogen bonds in phase D was predicted to occur at ~40 GPa in a first-principles study (Tsuchiya et al., 2005). Symmetric hydrogen bonds result from a single and symmetric potential well for hydrogen, mid-way between the oxygen pair of a hydrogen bond. In phase D, modified oxygen–oxygen interatomic potentials due to symmetric hydrogen bonding could increase its bulk modulus by ~20% and make the c-axis more incompressible (Tsuchiya et al., 2005). Previous studies have shown a change in the pressure-dependence of the c/a axial ratio of both pure-Mg and Fe-bearing phase D at pressures of ~15 GPa (Litasov et al., 2008), at ~20 GPa (Frost and Fei, 1999), at 25–30 GPa (Litasov et al., 2007), and at ~40 GPa (Shinmei et al., 2008; Hushur et al., 2011). There has been some speculation that the observed changes in c/a may result from symmetrization of the hydrogen bonds. However, a high-pressure FTIR study of phase D by Shieh et al. (2009) up to 42 GPa shows no major changes in the O–H stretching region attributable to hydrogen-bond symmetrization, suggesting that the observed changes in compression mechanism above ~40 GPa are unrelated to changes in hydrogen bonding. Possible symmetrization of the hydrogen bonding in phase D requires further investigation.

The isothermal bulk modulus (Kᵣ) of pure-Mg phase D has been determined experimentally in static compression experiments with results ranging from 130 to 168 GPa (Frost and Fei, 1999; Shinmei et al., 2008; Hushur et al., 2011). The highest pressure reached in previous static compression studies was ~56 GPa by Hushur et al. (2011), who observed a slight discontinuity in the volume–compression curve at 40 GPa, coincident with the pressure predicted for hydrogen-bond symmetrization by Tsuchiya et al. (2005). Brillouin scattering measurements of the adiabatic bulk modulus (K₀) of two different pure-Mg samples give a value of 175(15) GPa for the composition Mg₁₀₂Si₁₁₂H₁₅₂O₆ (Liu et al., 2004) and 155(3) GPa for Mg₁₁₂Si₁₁₂H₄₂O₆ (Rosa et al., 2012). Variable Mg/Si ratios and variable water content may be contributing to differences in measured bulk moduli of pure-Mg phase D, although no systematic trend between Mg/Si or H-content and K is observed in the literature data. Fe–Al-bearing phase D was studied by Litasov et al. (2007) showing a bulk modulus of 137(3) GPa for a sample of composition Mg₀.₉₈Fe₀.₁₄Al₀.₂₅Si₁₅₂H₃₉₉O₆. Litasov et al. (2008) reported a bulk modulus of 141(3) GPa for phase D with composition Mg₀.₉₉Fe₀.₁₂Al₀.₀₉Si₁₅₂H₃₅₁O₆. The elastic properties of phase D with composition Mg₁₀₁Fe₀₁₁Al₀₀₁Si₁₅₂H₃₂O₆ were studied using Brillouin scattering by Rosa et al. (2012), who reported a bulk modulus of 158(4) GPa.

An electronic spin transition of Fe from high spin (HS) to low spin (LS) has been documented in a number of Fe-bearing mantle minerals, including ferropericlas-(Mg,Fe)O (e.g. Badro et al., 2003; Lin et al., 2005, 2007; Speziale et al., 2005; Tsuchiya et al., 2006) and silicate perovskite-(Mg,Fe)SiO₃ (e.g. Badro et al., 2004; Catalli et al., 2011; Grocholski et al., 2009; Hsu et al., 2012; Jackson et al., 2005; Li et al., 2004; Lin et al., 2012). For reviews of Fe spin transitions in mantle minerals, see Li (2007) and Lin and Tsuchiya (2008). In (Mg,Fe)O, where the octahedral site hosts Fe⁺³, the spin transition begins to occur at 40–50 GPa (e.g. Lin and Tsuchiya, 2008). In silicate perovskite, Fe²⁺ and Fe⁴⁺ coexist on different sites and both may have multiple spin states. Fe³⁺ occupies both the A site and B sites of the ABO₃-perovskite structure, whereas Fe²⁺ occurs dominantly on the A site (e.g. Lin et al., 2012). In Al-bearing compositions, the Fe²⁺/ΣFe ratio and Fe³⁺ site occupancies are affected by the amount of aluminum (McCammon, 1997; Frost et al., 2004; Vanpeteghem et al., 2006; Hsu et al., 2012), making interpretation of HS–LS transitions of Fe in silicate perovskite considerably more complicated than in (Mg,Fe)O. The potentially high Al-content of phase D may influence the amount of Fe²⁺ in the structure, as has been shown in silicate perovskite (Frost et al., 2004; Saikia et al., 2009). The phase D sample in this study provides the opportunity to study the high-pressure spin-states of Fe³⁺ isolated on an octahedral site.

Pressure-induced spin transitions of Fe in (Mg,Fe)O and silicate perovskite are known to influence their elastic properties (e.g. Catalli et al., 2010; Crowhurst et al., 2008; Hsu et al., 2011; Mao et al., 2011; Marquardt et al., 2009; Speziale et al., 2007; Wentzcovitch et al., 2009), although the evolution of low-spin state fraction (n) with pressure, i.e. n(P) for different Fe valences (2+, 3+) on different sites remain difficult to isolate (Lin et al., 2012). The maximum pressure of previous studies on Fe-Al-bearing phase D is ~30 GPa, and therefore a potential electronic spin transition of Fe in phase D has not been investigated.

Here we report a spin transition of Fe in dense hydrous magnesium silicate phase D, a potential carrier of H₂O into the lower mantle. Using synchrotron X-ray emission spectroscopy in conjunction with X-ray diffraction up to ~90 GPa, we have determined the equation of state and identified a spin transition of Fe⁴⁺ on the octahedral site in phase D with composition MgSi₁₂Fe₁₂⁺Al₁₂H₃₅₂O₆. This composition facilitates a study of the spin-transition character of Fe³⁺ isolated on the octahedral site of the structure. We observed a gradual HS to LS transition occurring between ~40 and 65 GPa, which results in a significant softening of the bulk modulus through the transition followed by recovery to values comparable to silicate perovskite in the lower mantle. The results are used to discuss phase D as a possible alternative explanation for small-scale seismic scatterers in the mid-lower mantle.
measuring about 50 μm across and 20 μm in thickness. Two XES runs were made in diamond-anvil cells using a heavy mineral oil pressure medium (EMD Chemicals Inc.; CAS# 8012-95-1). The first cell was filled with 300 μm cuvet diamond anvils and a Be gasket. An annealed ruby sphere was used as the pressure calibrant (Mao et al., 1986) and experiments in this first run were carried out up to 60 GPa. In order to reach ~95 GPa, a second diamond-anvil cell was prepared with 200 μm culets, and a cubic boron-nitride (cBN) insert was made to strengthen the Be gasket (Lin et al., 2008). XES spectra were collected at ambient conditions using the same experimental setup as the high-pressure spectra. An XES spectrum of hematite was collected as Fe high-spin state standard, and a spectrum of ferropericlase-(Mg0.75Fe0.25) at 90 GPa was collected as Fe low-spin standard (Mao et al., 2011).

2.3. X-ray diffraction

Two compression experiments were conducted using synchrotron X-ray diffraction at sector 16 (HPCAT) at the APS. In run#1, a diamond-anvil cell with 200 μm culets was prepared with a Be gasket. A tungsten-carbide seat with 1-mm opening was used on the side of the X-ray source, and a cBN seat on the detector side. A single crystal of Fe–Al phase D was polished on both sides down to ~20 μm thickness and loaded along with a ruby sphere for pressure measurements. Helium was used as pressure medium using the COMPRES-GSECARS gas loading system at the APS (Rivers et al., 2008). To control the pressure increment in small and consistent steps of ~0.5 GPa, the four bolts on the diamond-anvil cell were attached to a gearbox. An online ruby fluorescence system was setup to measure the in situ pressure while remotely increasing pressure to ensure small and consistent pressure increments. Run#1 was carried out to ~40 GPa, and lattice parameters were refined using the program UnitCell (Holland and Redfern, 1997).

The setup for compression run#2 was similar to run#1, except two single crystals of phase D in different orientations were double polished and loaded together into the pressure chamber, providing a wider coverage of reflections and therefore better constraints on lattice parameters. The cell was gas loaded with neon as pressure medium by using the same setup as in run#1. X-ray diffraction experiments were carried out up to 82 GPa on the 16-IDB beamline using a CCD detector. At the first pressure, omega step-scans ±30° were performed with a rotation of one degree per step and exposure time 2 s/step. The step-scan images were used to create an orientation matrix for indexing the peak positions in the subsequent pressures. Subsequently, wide angle scans were performed with rotating angle of ±12.5° about the X-ray beam with exposure times of 25 s. The lattice parameters of phase D in run#2 were refined by combining all the reflections from two crystals using the software packages GSE_Adjust (Dera, 2007a) and RSV (Dera, 2007b). For comparison, the lattice parameters were also fitted using the program UnitCell (Holland and Redfern, 1997), and the resulting lattice parameters from these two software packages were identical within reported uncertainty.

3. Results

3.1. Electronic spin transition of Fe$^{3+}$ in phase D

Fig. 2a shows the Fe-Kβ X-ray emission spectra of the Fe–Al phase D at various pressures up to 94 GPa. Presence of the Kβ' peak at ~7045 eV at ambient pressure is indicative of Fe$^{3+}$ in the high spin (HS) state originating from 3p–3d electronic exchange interaction (e.g., Lin et al., 2010). The gradual disappearance of the Kβ' peak signifies a pressure-induced HS to LS transition of Fe$^{3+}$. The intensity of the Kβ' peak begins decreasing at ~40 GPa, and eventually disappears above ~65 GPa. The low-spin fraction (n) as
The observed $\text{Fe}^{3+}$ spin-transition interval in phase D is similar to the HS–LS transition pressure interval of $\text{Fe}^{2+}$ in (Mg,Fe)O at $\approx 40$–70 GPa (e.g. Badro et al., 2003; Lin et al., 2005). Catali et al. (2011) reported a sharper and higher-pressure HS–LS transition of $\text{Fe}^{3+}$ in Fe–Al silicate perovskite at 70–83 GPa, in contrast to what Catali et al. (2010) observed in Al-free Fe-perovskite where $\text{Fe}^{3+}$ in the B site is completely low spin by $\approx 60$ GPa and $\text{Fe}^{3+}$ in the A site remains HS to pressures in excess of 130 GPa. Using synchrotron Mössbauer spectroscopy, Lin et al. (2012) observed a spin transition of $\text{Fe}^{3+}$ on the B site between 13 and 24 GPa and a constant high-spin state of $\text{Fe}^{3+}$ on the A site up to 120 GPa, consistent with theoretical calculations by Hsu et al. (2011). Further calculations by Hsu et al. (2012) reported that Fe–Al perovskite behaves similar to Al-free perovskite, finding that $\text{Fe}^{3+}$ undergoes a spin transition at 40–70 GPa on the B site, whereas $\text{Fe}^{3+}$ on the A site remains high spin throughout the lower-mantle pressure range. Therefore, the pressure interval of the $\text{Fe}^{3+}$ HS–LS transition in phase D is similar to $\text{Fe}^{2+}$ in (Mg,Fe)O and similar to octahedral $\text{Fe}^{3+}$ in silicate perovskite (Catalli et al., 2010; Hsu et al., 2012) but occurs at higher pressure than $\text{Fe}^{3+}$ in silicate perovskite as reported by Lin et al. (2012).

### 3.2. Equation of state of Fe–Al phase D

Compression data for Fe–Al phase D through the HS–LS transition are listed in Table 2 and plotted in Fig. 3. A discontinuity in the compression curve occurs at $\approx 40$ GPa, which coincides...
with the onset of the HS-to-LS transition of Fe\textsuperscript{3+} interpreted by XES, but also at the pressure of a predicted hydrogen-bond symmetrization (Tsuchiya et al., 2005). Therefore, the volume changes in Fe–Al phase D at around 40 GPa are potentially influenced by both hydrogen-bond symmetrization and the Fe-spin transition simultaneously. A second discontinuity in the compression curve occurs at ~65 GPa, likely corresponding to completion of the Fe\textsuperscript{3+} spin transition. To further examine HS–LS transition pressure range in Fe–Al phase D, we calculated the difference between measured unit-cell volumes in this experiment (V\textsubscript{FeAl-phd}) and those calculated from the equation of state of pure-Mg phase D (V\textsubscript{Mg-phd}) from Hushur et al. (2011). The resulting ΔV data, shown in Fig. 4, show discontinuities at around 40 GPa and 65 GPa, corresponding exactly to the HS–LS transition interval interpreted from our XES spectra (Fig. 2).

For the purpose of deriving a spin-transition equation of state covering the entire experimental pressure range, we divided the compression data into three regions: ambient to 40 GPa for the HS state, 40–65 GPa for the mixed-spin state, and above 65 GPa for the LS state. Below 40 GPa, run#1 agrees very well with run#2, indicating that these two datasets are compatible and can be combined into one dataset (Table 1). We obtained a 3rd-order Birch–Murnaghan equation of state for HS Fe–Al phase D yielding K\textsubscript{0,HS} = 147(2) GPa, K\textsuperscript{′}\textsubscript{0,HS} = 6.3(3) and V\textsubscript{0,HS} = 86.14(3) Å\textsuperscript{3}. The fitted V\textsubscript{0,LS} for Fe–Al phase D is equal within error to our experimental value of V\textsubscript{0} = 86.116(7) Å\textsuperscript{3}.

The six volume–pressure data within the LS range were similarly fitted to a 3rd-order Birch–Murnaghan equation of state by minimizing the sum-of-squares misfit over the parameter space, yielding an LS equation of state for Fe–Al phase D with K\textsubscript{0,LS} = 253(30) GPa, K\textsuperscript{′}\textsubscript{0,LS} = 4.2(3) and V\textsubscript{0,LS} = 80(1) Å\textsuperscript{3}. To model the elastic properties of phase D through the spin transition, we followed the method of Wentzcovitch et al. (2009) using the resulting K\textsubscript{0,HS}, V\textsubscript{0,HS}, K\textsubscript{0,LS}, V\textsubscript{0,LS}, and the low-spin fraction as a function of pressure, n(P), to model variation of the volume and bulk modulus as a function of n using Eqs. (1)–(3):

\[
V(n) = V_{LS}(P, T) + (1 - n) V_{HS}(P, T)
\]

\[
\frac{V(n)}{K(n)} = \frac{n V_{LS}}{K_{LS}} + (1 - n) \frac{V_{HS}}{K_{HS}} - \left(\frac{V_{LS} - V_{HS}}{\partial P} \frac{\partial n}{\partial P}\right)_T
\]

In Eqs. (1)–(2), n(P, T) is the LS fraction defined as:

\[
n = \frac{1}{1 + \exp(\Delta G(P, T)*/T)}
\]

where ΔG(P, T)* is the difference of the Gibbs free energy between the LS and HS states (e.g. Mao et al., 2011). This model has been used successfully to derive the low-spin fraction of Fe\textsuperscript{3+} in lower-mantle ferropericlase using experimentally measured thermal equation-of-state data (Mao et al., 2011).

The derived low-spin fraction as a function of pressure is shown fitted to the experimental data in Fig. 2b, which was used to calculate V(n) and K(n) using Eqs. (1)–(2). In Fig. 3, the volume-compression data are plotted along with the HS, LS, and complete spin-transition equations of state. The region of largest misfit occurs right around the transition at ~40 GPa, possibly due to the fact that we are only modeling the volume change as a function of the low-spin fraction and not incorporating possible volume effects due to a proposed hydrogen bond symmetrization. However, the data between 40 and 45 GPa fall slightly below the fitted equation of state, indicating a more abrupt softening than modeled by our spin-transition equation of state in contrast to the stiffening effect of hydrogen-bond symmetrization predicted by Tsuchiya et al. (2005) and the discontinuity observed at ~40 GPa in Mg-phase D by Hushur et al. (2011).

Our results show that the electronic spin transition of Fe\textsuperscript{3+} in phase D causes a similar volume contraction to the HS–LS transition in (Mg,Fe)O (e.g. Lin et al., 2005). Variation of the bulk modulus as a function of LS fraction is plotted in Fig. 5a, showing pronounced elastic softening within the spin-transition region between 40 and 65 GPa. The magnitude of bulk modulus softening reaches ~35% at 50 GPa. The variation of K(n) with pressures shows a recovery of the bulk modulus to values extrapolated from the HS state by about 70 GPa. For comparison, we also plotted the bulk modulus of pure-Mg and Fe–Al-bearing silicate perovskite from Boffa Balaran et al. (2012). Remarkably, above about 65 GPa Fe–Al phase D in the LS state has a similar bulk modulus to silicate perovskite within error, despite containing nearly 10 wt.% H\textsubscript{2}O.

In Fig. 5b, the 300 K bulk sound velocity, V\textsubscript{p} = (K/ρ)^{1/2}, is shown for Fe–Al phase D in comparison with silicate perovskite. The velocity contrast between Fe–Al phase D and Fe–Al silicate perovskite reaches a minimum of about 10% at ~50 GPa in the mid-part of the HS–LS transition, but above ~70 GPa the bulk
sound velocity of Fe–Al phase D is actually higher than silicate perovskite by nearly 10%. Therefore, layers of compositional heterogeneity in slabs containing 10% Fe–Al phase D may be capable of producing bulk sound velocity contrast on the order of 1%. Implications for interpreting small-scale heterogeneities in the mid-lower mantle are further discussed in Section 3.4.

3.3. Effects of Fe and Al on bulk and axial compressibility of phase D

The bulk modulus of HS Fe–Al phase D obtained in this study, \( K_{0} = 147(2) \) GPa, is about 5% lower than a result from Brillouin scattering on Fe–Al phase D by Rosa et al. (2012), who obtained \( K_{0} = 158(4) \) GPa. The iron and hydrogen content of our sample is comparable to the study of Rosa et al. (2012) (Table 3). However, our sample contains about 0.3 Al per formula unit, about one order of magnitude more Al than the sample from Rosa et al. (2012), suggesting that the additional Al may have slightly reduced the bulk modulus. There are other compositional factors to consider; for example, the \((\text{Mg} + \text{Fe})/\text{Si}\) ratio of the sample from Rosa et al. (2012) was about 0.58, compared with 0.76 in our sample (Table 3).

Our results for the bulk modulus of HS Fe–Al phase D are about 7% higher than the sample of Fe–Al phase D studied by Litasov et al. (2007), who reported \( K_{0} = 136.5(3.3) \) GPa and \( K' = 6.3(3) \) GPa (Table 3). Compared with our sample, the composition from Litasov et al. (2007) had more hydrogen, with 2.9 H per formula unit and a lower \((\text{Mg} + \text{Fe})/\text{Si}\) ratio of 0.66, compared with our sample having 2.6 H per formula unit and \((\text{Mg} + \text{Fe})/\text{Si}\) of about 0.76 (Table 3). Litasov et al. (2008) reported \( K_{0} = 141(3) \) GPa with \( K' = 6.2(4) \) for a phase D with 2.5 H, 0.09 Al, and 0.12 Fe (per formula unit) and a \(\text{Mg}/\text{Si}\) ratio of 0.57 (Table 3). The fitted \( K' \) from this study for high-spin Fe–Al phase D, \( K' = 6.3(3) \), is identical to the fitted \( K' \) from Litasov et al. (2007) and Litasov et al. (2008), thus we may directly compare values of the bulk moduli. However, at present there are too few studies and too many compositional factors (including Fe-content, Al-content, H-content, \((\text{Mg} + \text{Fe})/\text{Si}\), and \(\text{Fe}^{3+}/\sum\text{Fe}\) ratios) to draw any definitive crystal chemical trends for variation of phase D elastic properties with composition.

Compared with Mg-phase D (e.g. Hushur et al., 2011), the Fe–Al phase D in this study has a slightly shorter c-axis and slightly longer a-axis. The layered structure of phase D results in anisotropic compression of the a- and c-axes, shown in Fig. 6a. The axial incompressibility of the a-axis (\(\rho_{a}\)) in this Al–Fe-phase D is about half that of \(\rho_{c}\), similar to results on Mg-phase D. The volume discontinuity caused by the spin transition appears to result almost entirely from shortening of the c-axis, as observed at \( \sim 40 \) GPa in Fig. 6a.

On compression, the c/a ratio of pure-Mg and Fe–Al phase D decreases with pressure but eventually becomes constant (Fig. 6b).

![Fig. 5. (a) Variation of the bulk modulus \((K)\) for Fe–Al phase D in the HS state (solid blue curve), and for our model where the fraction of low-spin Fe3+ varies with pressure according to the XES measurements (solid black curve). For comparison, we also plot \( K \) of pure-Mg and Al–Fe-bearing silicate perovskite from Boffa Ballaran et al. (2012). The black bar represents 12% uncertainty in the low-spin bulk modulus of phase D, \( K_{0,LS} = 253(30) \) GPa, and illustrates that perovskite bulk moduli fall within that uncertainty. (b) Plot of the calculated bulk-sound velocity for phase D compared with silicate perovskite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

Table 3

<table>
<thead>
<tr>
<th>Formula</th>
<th>( V_{0} ) (Å(^3))</th>
<th>( \rho_{0} ) (g/cm(^3))(^\dagger)</th>
<th>( K_{0} ) (GPa)</th>
<th>( K' ) (GPa)</th>
<th>( P_{\text{max}} ) (GPa)</th>
<th>Method</th>
<th>Reference</th>
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<td>Mg phase D</td>
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<tr>
<td>( \text{Mg}<em>{6.11} \text{Si}</em>{4.3} \text{H}<em>{5.3} \text{O}</em>{6} )</td>
<td>85.66(1)</td>
<td>3.33</td>
<td>160(3)</td>
<td>4.1(3)</td>
<td>30 GPa</td>
<td>XRD</td>
<td>Frost and Fei (1999)</td>
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<td>85.43</td>
<td>3.34</td>
<td>130(1)</td>
<td>7.4(1)</td>
<td>46 GPa</td>
<td>XRD</td>
<td>Shimmie et al. (2008)</td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.89} \text{Fe}</em>{0.14} \text{Al}<em>{0.25} \text{Si}</em>{1.56} \text{H}<em>{2.93} \text{O}</em>{6} )</td>
<td>85.1(2)</td>
<td>3.34</td>
<td>168(9)</td>
<td>4.3(5)</td>
<td>30 GPa</td>
<td>XRD</td>
<td>Hushur et al. (2011)</td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.89} \text{Fe}</em>{0.14} \text{Al}<em>{0.25} \text{Si}</em>{1.56} \text{H}<em>{2.93} \text{O}</em>{6} )</td>
<td>85.43</td>
<td>3.33</td>
<td>150(9)</td>
<td>5.5(4)</td>
<td>55.8 GPa</td>
<td>XRD</td>
<td>Liu et al. (2004)</td>
</tr>
<tr>
<td>( \text{Mg}<em>{8.05} \text{Si}</em>{14.82} \text{H}<em>{5.82} \text{O}</em>{6} )</td>
<td>85.8(2)</td>
<td>3.46</td>
<td>154.8(3.2)</td>
<td>4.2(3)</td>
<td>65–82 GPa</td>
<td>XRD</td>
<td>Rosa et al. (2012)</td>
</tr>
<tr>
<td>Al–Fe–bearing phase D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.10} \text{Fe}</em>{0.14} \text{Al}<em>{0.25} \text{Si}</em>{1.56} \text{H}<em>{2.93} \text{O}</em>{6} )</td>
<td>86.1(3)</td>
<td>3.51</td>
<td>147(2)</td>
<td>6.3(3)</td>
<td>40 GPa</td>
<td>XRD</td>
<td>This study</td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.09} \text{Fe}</em>{0.12} \text{Al}<em>{0.19} \text{Si}</em>{1.55} \text{H}<em>{2.93} \text{O}</em>{6} )</td>
<td>85.32(2)</td>
<td>3.52</td>
<td>141.5(3.0)</td>
<td>6.2(4)</td>
<td>20.6 GPa</td>
<td>XRD</td>
<td>Litasov et al. (2008)</td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.12} \text{Fe}</em>{0.12} \text{Al}<em>{0.19} \text{Si}</em>{1.55} \text{H}<em>{2.93} \text{O}</em>{6} )</td>
<td>85.32(2)</td>
<td>3.52</td>
<td>158.4(3.9)</td>
<td></td>
<td></td>
<td>Ambient</td>
<td></td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.12} \text{Fe}</em>{0.12} \text{Al}<em>{0.19} \text{Si}</em>{1.55} \text{H}<em>{2.93} \text{O}</em>{6} )</td>
<td>86.1(4)</td>
<td>3.51</td>
<td>147(2)</td>
<td>6.3(3)</td>
<td>40 GPa</td>
<td>XRD</td>
<td>This study</td>
</tr>
<tr>
<td>Low-spin phase D</td>
<td>80.00</td>
<td>3.78</td>
<td>253(30)</td>
<td>4.2(3)</td>
<td>65–82 GPa</td>
<td>XRD</td>
<td>This study</td>
</tr>
</tbody>
</table>

\( \dagger \) XRD: X-ray diffraction; BS: Brillouin scattering.

Density was calculated using the formula weight and \( V_{0} \).
The pressure above which c/a is constant varies drastically between studies, ranging from ~20 GPa (Frost and Fei, 1999) to ~40 GPa (Hushur et al., 2011) for pure-Mg phase D. In the current study, c/a for Fe–Al phase D becomes constant above 40 GPa accompanied by a sharp discontinuity in the trend (Fig. 6b). The cause of this behavior is not agreed upon. Hushur et al. (2011) speculated that c/a becomes constant for the symmetrically hydrogen-bonded phase predicted by Tsuchiya et al. (2005). However, a high-pressure FTIR study up to 42 GPa by Shieh et al. (2009) shows no major changes other than gradual shifts in the OH-stretching modes with pressure. The fact that c/a ceases to decrease above 40 GPa for pure-Mg phase D (Hushur et al., 2011), similar to this study, suggests that the behavior may not be related to the spin transition of Fe. Similar behavior in c/a has been observed for brucite, Mg(OH)$_2$ (e.g., Duffy et al., 1995). Structure refinements of phase D over this pressure range will be required to determine what causes the observed change in compression mechanism.

3.4. Implications for small-scale heterogeneity in the mid-lower mantle

Due to the spin transition of Fe, the presence of Fe–Al-rich phase D in subducted slabs entering the lower mantle may be detected with high-spatial resolution seismic methods. Short-period seismic studies of the mid-lower mantle beneath the Pacific rim have detected kilometer-scale heterogeneities at various depths around 1500 km (e.g., Kaneshima and Helffrich, 1998, 1999, 2009, 2010). Characterized by late arrivals from S-to-P converted phases, the depth of seismic scatterers ranges from about 1100–1800 km, although the most prominent scatterers occur at a depth of 1500 km (Kaneshima and Helffrich, 2010). Scattered wave amplitudes range from 1 to 10% of the direct P waves, and are associated with slow S-wave velocity anomalies on the order of 1–4% (Kaneshima and Helffrich, 2010). In some areas, such anomalies have been modeled as thin, dipping layers <10 km thick and having low S-wave velocity but high density (Kaneshima and Helffrich, 1999; Niu et al., 2003).

Because of their association with subducted oceanic crust, the fine-scale heterogeneities in the mid-lower mantle have been attributed to silica-saturated basalts producing free-silica phases which survive into the mid-lower mantle (e.g., Bina, 2010). Although free-silica phases in MORB would be semistably fast compared with the surrounding basaltic assemblage, the second-order phase transition of SiO$_2$ from stishovite to the CaCl$_2$ structure could produce a softening with S-wave anomalies large enough to be detectible seismically in the lower mantle (e.g., Carpenter et al., 2000; Karki et al., 2001). A minimum in the SiO$_2$ transition soft mode is expected to occur at ~1500 km, which is the depth corresponding to greatest scattering potential, but recovery of velocities to ambient levels would cause the heterogeneities to disappear below about 2000 km, consistent with the observations (e.g., Kaneshima and Helffrich, 2009). Velocity anomalies in eclogite can also be attributed to low S-wave velocities associated with Al-rich stishovite (Lakhtanov et al., 2007). Preservation of free-silica within basaltic layers in the lower mantle could be explained as armored relics, cut off from reaction with the surrounding mantle by very slow diffusion rates (Bina, 2010).

Three lines of evidence establish that the spin-transition interval of Fe$^{3+}$ in phase D at 40–65 GPa overlaps with the depth range of observed mid-lower mantle seismic scatterers: analysis of high-pressure Fe-K$\beta$ X-ray emission spectra, discontinuities in the volume–compression curve, and discontinuities in $\Delta V/P$ between Fe–Al phase D and pure-Mg phase D. Onset of the spin transition occurs at the same pressure as the predicted hydrogen-bond symmetrization (Tsuchiya et al., 2005). However, the pronounced softening of the bulk modulus by 35% at 50 GPa (compared with HS phase D) is not consistent with the predicted increase of 20% in the incompressibility of symmetrically-hydrogen-bonded phase D (Tsuchiya et al., 2005). If both stiffening of the bulk modulus by 20% due to hydrogen-bond symmetrization, and softening due to the spin transition were occurring simultaneously, a less pronounced volume discontinuity might be expected. At present, we believe there is insufficient experimental evidence to suggest that hydrogen-bond symmetrization has occurred in Fe–Al phase D.

Although bulk-elastic softening is observed during the transition, similar to Fe-spin transitions in (Mg,Fe)$_3$O$_4$ (Lin et al., 2005; Crowhurst et al., 2008; Marquardt et al., 2009) and silicate perovskite (Hsu et al., 2011), the recovered low-spin phase D above ~65 GPa exhibits an incompressibility comparable to silicate perovskite at lower-mantle pressures. During the HS–LS transition, the bulk sound velocity of Fe–Al phase D reaches a minimum at ~50 GPa and is nearly 10% slower than silicate perovskite, but recovers and becomes 10% faster than silicate perovskite above 70 GPa. The stability field of Fe–Al rich DHMS requires further study, but if Fe–Al phase D remains stable into the deep lower mantle, its elastic properties suggest that it could provide an alternative explanation for small-scale seismic scatterers observed in subducted slabs at 1100–1800 km depth. As a potential carrier of H$_2$O into the lower mantle, Fe–Al phase D should be considered in geochemical and geodynamic models of Earth’s deep water cycle.
4. Conclusions

Our observations of bulk-elastic softening in Fe–Al phase D from 40–65 GPa provide an alternative explanation for the small-scale seismic scatterers in the mid-lower mantle. The minimum in bulk-sound velocity contrast between Fe–Al phase D and silicate perovskite, occurring at 50 GPa (~1500 km), coincides with the depth of greatest scattering potential from the small-scale heterogeneities beneath the Pacific rim (e.g., Kaneshima and Helffrich, 2009, 2010). Further, recovery of the velocities in Fe-Al phase D to levels equal to silicate perovskite between 50–70 GPa (1500–2100 km) is also consistent with the depth range where the scattering power of observed heterogeneities diminish (e.g., Kaneshima and Helffrich, 2009, 2010). Although we have inferred softening in the bulk sound velocity from compression experiments, further elasticity measurements are required to determine how the spin transition of Fe in phase D affects S-wave velocities and elastic wave anisotropy. The association of mid-lower mantle seismic scatterers with subducted oceanic crust, if explained by the presence of Fe–Al phase D, would imply that components from deeply-subducted hydrous sediments with Fe–Al rich compositions, such as mudstones and shales, are being carried into the lower mantle.

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