



Spin transition of Fe³⁺ 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-hydrous magnesium silicates potentially transporting H₂O into Earth's deep interior, phase D (MgSi₂H₂O₆) 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}O₆, where nearly all of the Fe is ferric (Fe³⁺). Analysis of Fe-Kβ emission spectra reveals a gradual, pressure-induced high-spin (HS) to low-spin (LS) transition of Fe³⁺ extending from 40 to 65 GPa. The fitted equation of state for high-spin Fe–Al-bearing phase D results in a bulk modulus $K_{T0} = 147(2)$ 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 $K_{T0} = 253(30)$ 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 (~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 ~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 Fe³⁺ 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.% Fe₂O₃ + FeO and 15–25 wt.% Al₂O₃ (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–SiO₂–H₂O system along cold subduction geotherms (e.g. Angel et al., 2001;

Irfune 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 (H₂O, Fe₂O₃ and Al₂O₃) 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, Mg₂SiO₄; Br, Mg(OH₂)) include phase A (2Fo + 3Br, 12 wt.% H₂O), OH-chondrodite (2Fo + 1Br, 5 wt.% H₂O), and OH-clinohumite (4Fo + 1Br, 3 wt.% H₂O), 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,

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phase E (2Br + 1SiO₂, 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 serpentine-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 ($\rho_0 = 3.51$ g/cm³) with Si in six-fold 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 serpentine below the critical condition of $\sim 600^\circ\text{C}$ 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 $\sim 1200^\circ\text{C}$, 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 MgSi₂H₂O₆, 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% 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 $\sim 20\%$ 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 (K_{T0}) 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 pres-

sure predicted for hydrogen-bond symmetrization by Tsuchiya et al. (2005). Brillouin scattering measurements of the adiabatic bulk modulus (K_{S0}) of two different pure-Mg samples give a value of 175(15) GPa for the composition Mg_{1.02}Si_{1.71}H_{3.12}O₆ (Liu et al., 2004) and 155(3) GPa for Mg_{1.1}Si_{1.9}H_{2.4}O₆ (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 Mg_{0.89}Fe_{0.14}Al_{0.25}Si_{1.56}H_{2.93}O₆. Litasov et al. (2008) reported a bulk modulus of 141(3) GPa for phase D with composition Mg_{0.99}Fe_{0.12}Al_{0.09}Si_{1.75}H_{2.51}O₆. The elastic properties of phase D with composition Mg_{1.0}Fe_{0.11}Al_{0.03}Si_{1.9}H_{2.5}O₆ 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 ferropervicite-(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 Fe²⁺, the spin transition begins to occur at 40–50 GPa (e.g. Lin and Tsuchiya, 2008). In silicate perovskite, Fe²⁺ and Fe³⁺ 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 Fe³⁺/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 Fe³⁺ 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 Fe³⁺ on the octahedral site in phase D with composition MgSi_{1.5}Fe_{0.15}³⁺Al_{0.3}H_{2.6}O₆. 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.

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