The Post-Perovskite Transition in Fe- and Al-Bearing Bridgmanite: Effects on Seismic Observables

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Abstract The primary phase of the Earth’s lower mantle, (Al, Fe)-bearing bridgmanite, transitions to the post-perovskite (PPv) phase at Earth’s deep mantle conditions. Despite extensive experimental and ab initio investigations, there are still important aspects of this transformation that need clarification. Here, we address this transition in (Al3+, Fe3+)-, (Al3+)-, (Fe2+)-, and (Fe3+)-bearing bridgmanite using ab initio calculations and validate our results against experiments on similar compositions. Consistent with experiments, our results show that the onset transition pressure and the width of the two-phase region depend distinctly on the chemical composition: (a) Fe3+-, Al3+-, or (Al3+, Fe3+)-alloying increases the transition pressure, while Fe2+-alloying has the opposite effect; (b) in the absence of coexisting phases, the pressure-depth range of the Pv-PPv transition is likely too broad to cause a sharp D" discontinuity (<30 km); (c) the average Clapeyron slope of the two-phase regions are consistent with previous measurements, calculations in MgSiO3, and inferences from seismic data. In addition, (d) we observe a softening of the bulk modulus in the two-phase region. The consistency between our results and experiments gives us the confidence to proceed and examine this transition in aggregates with different compositions computationally, which will be fundamental for resolving the most likely chemical composition of the D" region by analyses of tomographic images.

Plain Language Summary In 2004, it was discovered that the main phase of the Earth’s lower mantle, MgSiO3-perovskite (Pv) or bridgmanite, undergoes a phase transition to a post-perovskite phase (PPv) at conditions similar to those expected at the D" discontinuity at the bottom of the lower mantle. The predicted seismic discontinuity across the Pv-PPv transition suggested that the PPv phase is a major phase in the D" region. This paper presents ab initio predictions of this phase change in Al-, Fe3+-, Fe2+-, and simultaneous (Al3+, Fe3+)-bearing bridgmanite. Results are consistent with experiments but extend the range of temperature, pressure, and compositions investigated. These alloying elements affect the onset transition pressure differently and broaden the pressure range of the phase change with consequences for the thickness of this transition in the mantle. In the absence of co-existing phases, the Pv-PPv transition appears too broad to cause a sharp D" discontinuity (<30 km). The consistency between our results and experiments gives us the confidence to proceed and examine this transition in aggregates with different compositions computationally, which will be fundamental for resolving the most likely chemical composition of the D" region by analyzing tomographic images.

1. Introduction

The extraordinary complexity of the D" region, that is, the layer ~300 km above the core-mantle boundary (CMB), originates in this region’s enigmatic composition and thermal structure. In particular, the thermal boundary layer is essential for understanding the heat flux across the CMB and its implications for the thermal evolution of the core and geodynamo generation (Nakagawa & Tackley, 2004). This region is characterized by abnormal seismic gradients with various seismic features that have been the subject of numerous works and reviews (Cobden et al., 2015; Garnero & Wysession, 2000; Garnero et al., 2016; Jackson & Thomas, 2021; Kendall & Silver, 1998; Lay, 2008, 2015; Nowacki et al., 2011; Romanowicz & Wenk, 2017; Thomas et al., 2022; van der Hilst et al., 2007; Walker et al., 2011; Wysession et al., 1998; S. Yu & Garnero, 2018). These diverse observations are linked with structures of different sizes, ranging from small-scale scatterers and ultra-low velocity...
zones to large-scale seismic velocity anomalies and seismic anisotropy. Given the complexity of this region, one can expect that solid-solid phase transitions, thermal and chemical heterogeneity, complex rheology, lattice or shape-preferred orientation, and melting are all necessary to explain the observed structures.

From early on, synthetic waveforms computed from geodynamic simulations suggested that the D” discontinuity pattern was most consistent with a thermal slab interacting with a phase transition (Sidorin et al., 1998). An early review of over 40 studies summarized by Wysession et al. (1998) pointed out that the shear velocity (V_s) discontinuity varied between \(-2.5\%\) and \(3\%\) while the compressional velocity (V_p) discontinuity was systematically smaller but varied more widely and could, in some cases, even exceed \(\Delta V_p\). Today the range of discontinuity variations is known to be more extensive (Cobden et al., 2015; Jackson & Thomas, 2021; Lay, 2015) and the magnitude and depth of the discontinuity, along with its topography, give clues about the nature of the mineralogy change across it.

In 2004, it was found that the major mineral phase of the lower mantle, MgSiO_3 perovskite (Pv), or bridgmanite (Bdm), transforms into the seemingly layered post-perovskite (PPv) phase at approximately 125 GPa and 2,500 K depth (Murakami et al., 2004; Oganov & Ono, 2004; T. Tsuchiya et al., 2004). Following this discovery, extensive experimental and computational (Akber-Knutson et al., 2005; Andraut et al., 2010; Caracas & Cohen, 2005; Catali et al., 2009; Grocholski et al., 2012; Hirose et al., 2008; Itaka et al., 2004; Kuwayama et al., 2022; Mao et al., 2004; Metz & Tsuchiya, 2012; Murakami et al., 2007; Ono & Oganov, 2005; Shim et al., 2004; Simnyo et al., 2008; Tateno, 2005; Tateno et al., 2007; T. Tsuchiya & Tsuchiya, 2008; Wang et al., 2019; Wentzcovitch et al., 2006) studies have been carried out. Predictions of \(\Delta V_p\) larger than \(\Delta V_s\) across the transition in pure MgSiO_3 (Wentzcovitch et al., 2006) along with frequent similar observations across the D” discontinuity lent impetus to the notion that somehow the PPv transition is behind this discontinuity, at least in some form and in some places.

Despite all these efforts, essential aspects of this transformation still need clarification, particularly the effect of alloying elements such as Fe and Al. These elements’ presence or absence changes the Pv-PPv transition pressure and opens a two-phase coexistence region with a chemistry-dependent pressure range and Clapeyron slopes. For instance, various studies have argued that alloying with Al_2O_3 increases the transition pressure (Akber-Knutson et al., 2005; Caracas & Cohen, 2005; Grocholski et al., 2012; Tateno, 2005), while others observed a moderate decrease in transition pressure (J. Tsuchiya & Tsuchiya, 2008; Wang et al., 2019). Similar disagreement exists with ferrous iron (Fe^{2+}) alloying: some studies have found that Fe^{2+}-Bdm lowers the Pv-PPv transition pressure (Caracas & Cohen, 2005; Mao et al., 2004; Ono & Oganov, 2005; Shieh et al., 2006; Sun et al., 2018), while others (Hirose et al., 2008; Tateno et al., 2007) have found the opposite. Furthermore, Catali et al. (2009) showed that the ferric iron (Fe^{3+}) bearing phase had a somewhat narrow Pv-PPv coexistence pressure range while simultaneous (Fe^{3+}, Al^{3+}) substitution had a coexistence range similar to that displayed by the Fe^{2+}-bearing system. However, both Fe^{3+}- and (Fe^{3+}, Al^{3+})-bearing systems increased the onset transition pressure.

In addition to the equilibrium thermodynamics of the Pv to PPv transition in aggregates, which is an essential first step to investigating the nature of the D” discontinuity, other non-mineralogical issues also affect observations of the D” discontinuity. The topography of the discontinuity can cause focusing and defocusing and influence its seismic properties (e.g., Cobden et al., 2015). Phase transformation kinetics affect the D” discontinuity reflection coefficient, which can vary significantly with seismic wave period (Langrand et al., 2019). The latter is relevant because it provides a mechanism whereby a seemingly broad change can still produce sharp seismic reflections, as does preferred orientations and seismic anisotropy in a weak PPv (Ammann et al., 2010). Careful and detailed mineral physics calculations of this transition in aggregates and joint seismology/mineral physics studies of this discontinuity are still required to shed light on the regional nature of this discontinuity.

Seismic velocity reductions at the bottom of the D” region have also been detected (Thomas et al., 2004; Wysession et al., 1998). Some of these velocity reduction patterns have been interpreted by Hernlund (Hernlund, 2010; Hernlund & Labrosse, 2007; Hernlund et al., 2005) as a “double-crossing” phenomenon, where P wave first transforms to PPPv and then back-transforms to P at greater pressure/depth. This phenomenon depends strongly on the phase boundary but also on the local geotherm: lower temperatures stabilize the PPv phase, steep temperature gradients enhance the chances of double-crossing, and very steep temperature gradients may prevent the occurrence of the P-P-P transition (Hernlund et al., 2005). The seismic signature of the P-P-P transition also depends critically on the rock composition (Grocholski et al., 2012; Kuwayama et al., 2022), and this issue also needs more clarification. In particular, the transition pressure range in a pyrolitic aggregate is still debated. It has also been suggested that the stishovite to seifertite transition in SiO_2 in MORB could provide an alternate
explanation for the deeper discontinuity (Grocholski et al., 2013). However, the seismic features resulting from this transformation are still unclear, and this remains a suggestion.

Here we use ab initio thermodynamic results (Shukla et al., 2015, 2016, 2019) on these Pv and PPv alloys to compute the two-phase boundary regions and test them against experiments. This effort is a fundamental step for methodology validation before computing the phase boundary in aggregates. We address the thickness of the coexistence regions, the Clapeyron slope, and the effect on seismic velocities along two geotherms, an adiabatic one (Brown & Shankland, 1981) and another containing a thermal boundary layer above the CMB (Boehler et al., 2008). We also compute the isentropes throughout the Pv-PPv transition to address the potential effect of this transition on the thermal boundary layer. The Pv-PPv transition in aggregates in thermochemical equilibrium is beyond the scope of this work. We will take this step in follow-up work.

2. Methods and Calculation Details

2.1. Ab Initio Calculations

Ab initio results of static, vibrational, and elastic properties of bridgmanite (Pv) and PPv phases of Mg$_{1-x}$Fe$^{3+}$SiO$_3$, (Mg$_{1-x}$Fe$^{3+}$)$_2$Al$_2$O$_4$ and (Mg$_{1-x}$Fe$^{3+}$)$_2$O$_3$ with the bearing element concentration $x = 0$ and 0.125 are from Shukla et al. (Shukla et al., 2015, 2016, 2019). These DFT $+$ USC (LDA $+$ USC and GGA $+$ USC) calculations used the Quantum ESPRESSO software (Giannozzi et al., 2009, 2017) and were performed on supercells with up to 80 atoms. More computational details are reported in those studies. Fe$^{3+}$ and (Fe$^{3+}$, Al) (Fe$^{3+}$ in the A-site and Al in the B-site) in Pv and PPv are in the high-spin (HS) state, while Fe$^{3+}$ in the B-site is in the LS state (Hsu et al., 2010, 2011, 2012; Y. Yu et al., 2012). The HS to LS state change in iron in these systems occurs only on the A-site of Pv and PPv at pressures considerably lower than the Pv to PPv transition (Hsu et al., 2011; Y. Yu et al., 2012) and is not expected to affect the current results significantly. Thermodynamic and thermoelastic properties are here recalculated using the quasi-harmonic approximation (Wallace, 1972) using the qha (Qin et al., 2019) and cij codes (Luo et al., 2021). The performance of these approaches for thermodynamic and thermoelastic properties have been extensively documented (Wentzcovitch, Wu, & Carrier, 2010; Wentzcovitch, Yu, & Wu, 2010).

2.2. Thermodynamic Modeling

Free energies were computed for Pv and PPv alloys using a “quasi-ideal” solid solution model and the standard state model for binary systems (Gaskell, 2008), where the Gibbs free energy of mixing curves of the Pv and PPv phases in an A-B binary system, at a given as (see Figure S1 in Supporting Information S1):

$$\Delta G_A^{Pv} = x \Delta G_A^{Pv - PPv} + k_B T [x \ln x + (1-x) \ln(1-x)],$$

$$\Delta G_A^{PPv} = -(1-x) \Delta G_A^{Pv - PPv} + k_B T [x \ln x + (1-x) \ln(1-x)],$$

with $k_B$ as the Boltzmann constant, the Gibbs free energy differences as $\Delta G_A^{Pv - PPv} = G_A^{Pv} - G_A^{PPv}$ and, $\Delta G_B^{Pv - PPv} = G_B^{Pv} - G_B^{PPv}$. End-member “A” is MgSiO$_3$. The end-member “B” is either Fe$^{3+}$SiO$_3$, Fe$^{3+}$O$_3$, Al$_2$O$_3$, or Fe$^{3+}$AlO$_3$, while the Gibbs free energies of each end-member B are calculated by linearly extrapolating from $x = 0.125$ to $x = 1$ the free energy difference between MgSiO$_3$ and, one of the following: Mg$_{0.875}$Fe$^{2+}$O$_3$, Mg$_{0.875}$Fe$^{3+}$O$_3$, Mg$_{0.875}$Al$^3$O$_3$, (Mg$_{0.875}$Al$_{0.125}$)$\times$Fe$^{3+}$O$_3$, (Mg$_{0.875}$Fe$^{3+}$)$_{0.125}$)O$_3$, or (Mg$_{0.875}$Fe$^{3+}$)$_{0.125}$)(Si$_{0.875}$Al$_{0.125}$)O$_3$, or (Mg$_{0.875}$Fe$^{3+}$)$_{0.125}$)(Si$_{0.875}$Al$_{0.125}$)O$_3$, or (Mg$_{0.875}$Al$^3$)$_{0.125}$)(Si$_{0.875}$Al$_{0.125}$)O$_3$, respectively. We refer to this solution as “quasi-ideal.” It corresponds to a Henryan solution modeling of an A-B alloy with end-member B being FeSiO$_3$, Fe$_2$O$_3$, Al$_2$O$_3$, or FeAlO$_3$ in the low concentration limit and having a constant activity coefficient but different from 1.0. The compositions of the Pv and PPv solvus lines, $X_A^{Pv}$ and $X_B^{PPv}$, are given by (Gaskell, 2008):

$$X_A^{PPv} = \frac{1 - \exp\left(-\frac{\Delta G_A^{Pv - PPv}}{k_B T}\right)}{\exp\left(-\frac{\Delta G_A^{Pv - PPv}}{k_B T}\right) - \exp\left(-\frac{\Delta G_B^{Pv - PPv}}{k_B T}\right)},$$

$$X_B^{Pv} = X_A^{PPv} \times \exp\left(-\frac{\Delta G_B^{Pv - PPv}}{k_B T}\right).$$

The PPv fraction, $n_{PPv}$, is given by the lever rule:

$$n_{PPv} = \frac{X - X_A^{PPv}}{X_B^{PPv} - X_A^{PPv}}.$$

The isentropes of the two-phase aggregate are computed by integrating the adiabatic gradient
3. Results

3.1. Effects of Fe and Al Alloying on the Pv-PPv Phase Boundary

The effects of Fe and Al alloying on the Pv-PPv phase boundaries are indicated in Figure 1 for (a) Mg$_{1-x}$Fe$_{2+}$SiO$_3$, (b) Mg$_{1-x}$Fe$_{3+}$SiO$_3$, (c) (Mg$_{1-x}$Al$_x$)(Si$_{1-x}$Al$_x$)O$_3$, (d) (Mg$_{1-x}$Fe$_{3+}$)Fe$_{3+}$)(Si$_{1-x}$Al$_x$)O$_3$, for a concentration $x = 0.10$. Solid blue lines are the boundaries. Gray shaded areas are the DFT related uncertainties in the calculations. Blue shaded areas are the experimental data from C09 (Catalli et al., 2009) and T05 (Tateno, 2005) respectively. Geotherm1 and Geotherm2 are those from Brown and Shankland (Brown & Shankland, 1981), and Boehler (Boehler, 2000), respectively. The vertical dashed-dotted line indicates the location of the core-mantle boundary.

The blue-shaded areas are the regions where the Pv and PPv phases coexist. Dashed lines and symbols are the experimental data from C09 (Catalli et al., 2009) and T05 (Tateno, 2005) respectively. Geotherm1 and Geotherm2 are those from Brown and Shankland (Brown & Shankland, 1981), and Boehler (Boehler, 2000), respectively. The vertical dashed-dotted line indicates the location of the core-mantle boundary.

A more detailed depiction of the free energy of mixing (Equations 1 and 2) as a function of concentration $x$, at various temperatures and at 125 and 135 GPa is given in Supporting Information S1 (Figure S3). They shed light...
on the shape of the two-phase regions in Figure 1, for example, on the fact that for Fe$^{3+}$-allowing, in contrast to the other cases, the pressure range of the two-phase region slightly increases with increasing temperature. We also explored how the PPv fraction, $n_{PPv}$, varies (see Figure S4 in Supporting Information S1) and the effect of the different exchange-correlation functionals, namely, LDA($+U_{SC}$) and GGA($+U_{SC}$), on the phase boundary (see Figure S5 in Supporting Information S1). Compared to LDA($+U_{SC}$), GGA($+U_{SC}$) produces narrower two-phase regions and shifts phase boundaries to higher pressures, with the mole fraction of PPv, $n_{PPv}$, changing gradually across the transition.

A fundamental aspect of the Pv-PPv transition in the alloys is the pressure range of the two-phase region along some reasonable geotherm, for example, an adiabatic one (Brown & Shankland, 1981). Our predicted thicknesses in these alloys are shown in Figure 4a. The dark colors are the most likely Pv-PPv coexistence regions (blue areas in Figure 1), and the lighter colors are the uncertainties originating in the choice of exchange-correlation functionals in the DFT calculations (see Figure S6 in Supporting Information S1) for more details in the ab initio uncertainty. Fe$^{2+}$ reduces the transition pressure, while Al$^{3+}$, Fe$^{3+}$, (Fe$^{3+}$, Al$^{3+}$)- increase it. These results obtained by systematic and consistent calculations offer consistent trends compared to measurements by Catalli et al. (2009). However, they contrast with results obtained in previous calculations by Wang et al. (2019) that suggested the onset transition pressure should decrease in all cases.

Figures 4b and 4c show thicknesses inferred from experimental phase boundaries in these alloys (see Figure 4 caption) and previous calculations (Wang et al., 2019), respectively. All measurements and calculations suggest a sizable pressure/depth range for these Pv-PPv transitions. Calculations offer narrower ranges, but DFT uncertainties are equally large. Table 1 summarizes the two-phase regions' thicknesses along the Brown and Shankland
Changes in density ($\rho$), compressional ($V_p$), bulk ($V_B$), and shear ($V_S$) velocities across the phase transition depend on the thickness of the two-phase region, alloy concentration, and geotherm. Inside the Earth, the inferred changes in seismic properties also depend on the phase transformation kinetics (Langrand et al., 2019) and concurrent deformation leading to anisotropy. A relatively weaker Ppv phase is likely to contribute to lattice-preferred orientation and anisotropy in the D" region (Ammann et al., 2010). Discontinuity topography may also change the apparent velocity contrasts. Figure 5 shows these properties' percentage changes with respect to the Ppv property values as a function of pressure along adiabatic (Brown & Shankland, 1981) and superadiabatic (Boehler, 2000) geotherms for different alloys with $x=0.10$. Each color depicts changes for a particular alloy. Shaded areas show the uncertainties that result from using LDA($+U_{SC}$) and GGA($+U_{SC}$) boundaries.

Overall, changes in seismic observables are within the magnitude of previous seismic studies (Sidorin et al., 1998; Wysession et al., 1998). All changes along the adiabatic geotherm are positive except for $\Delta V_B(\%)$, which shows values of $\Delta V_B(\%) \sim -0.8\%$ in most cases (Figures 5b*, 5g*, and 5q*) and $\Delta V_B(\%) \sim -2.5\%$ for the Al$^{3+}$ case (Figure 5l*). These negative values of $\Delta V_B(\%)$ reflect a decrease of the adiabatic bulk modulus ($K_S$) across the transition, in accordance with previous studies (T. Tsuchiya et al., 2004; Wentzcovitch et al., 2006; Wysession et al., 1998). In addition, $\Delta V_B(\%)$ displays a remarkable feature throughout two-phase regions. As a general rule, the high-pressure phase is denser. In the single-phase domains of these phases, smooth compression curves are expected. The two-phase region should have an anomalous compressibility caused by the change in the mole fractions of the phases involved (see Figure S4 in Supporting Information S1), as previously pointed out in the case of the spin-crossover in iron ferropericlase (Fp) (Wentzcovitch et al., 2009). The continuous increase...
in the amount of the denser high-pressure phase produces a softening anomaly in the isothermal, $K_T$, and in the adiabatic bulk modulus, $K_S$. In the particular case of the $P_V-P_PV$ transition, the softening in $V_\phi$ is clearly visible, though the expected increase after the softening is less dramatic because the PPv phase is more compressible than the $P_V$ phase right after the transition (Wentzcovitch et al., 2006). The $P_V-P_PV$ transition is an exception in this regard, but still displays such bulk modulus anomaly. Sometimes this bulk modulus softening might not be so evident, depending on the thicknesses of the two-phase region, the degree of equilibrium achieved in the system, and the differences in $K_S/K_T$ of the phases involved. However, this softening anomaly should be a general feature. Such softening should be expected in some of the elastic coefficients related to the bulk modulus, such as the compressional and off diagonal coefficients, as displayed across the spin crossover in iron in Fp (Wu et al., 2013). A similar phenomenon has been clearly observed experimentally in phase transitions in the olivine system (Li & Weidner, 2008). However, the observed effect was time-dependent, also suggesting a kinetic contribution and the important of the rheological properties of the aggregates. Nevertheless, the observed bulk modulus softening is consistent with a component originating from the variation of phase abundances throughout the two-phase region.

Changes in shear velocity are relatively more significant, with values up to $\Delta V_S(\%) \sim 3.7\%$ for the $Fe^{3+}$- case (Figure 5h*). All other $\Delta V_S(\%)$ values are within $\sim 2.0\%$–$2.4\%$. This increase is consistent with seismic observations in some areas of the deep mantle (Cobden et al., 2015; Jackson & Thomas, 2021; Sidorin et al., 1998; Wysession et al., 1998) and previous calculations in pure MgSiO$_3$ (Wentzcovitch et al., 2006). The changes in compressional velocity, $\Delta V_P(\%)$, are positive in all cases with values varying between $\sim 0.3\%$–$0.9\%$ similar to the change in pure bridgmanite (Wentzcovitch et al., 2006). However, $\Delta V_P(\%)$ for $Fe^{2+}$ (Figure 5a) decreases between 95 and 110 GPa. This distinct feature is caused by the softening in $K_S$ in the two-phase region. Density changes, $\Delta \rho(\%)$, are $\sim 1.6\%$ for all cases.

Positive and negative “jumps,” also known as paired discontinuities, have also been reported (Thomas et al., 2004; Wysession et al., 1998). This phenomenon depends strongly on the geotherm and seems to correspond to a $P_V$-$P_PV$-$P_V$ sequence of transitions referred to as “double-crossing” (Hernlund, 2010; Hernlund et al., 2005). We also computed velocity and density changes along a superadiabatic geotherm (Boehler, 2000) (Figure 5**). In this case, double-crossing occurs with PPv reverting to PV, or almost so, for the $Fe^{3+}$-, $Al^{3+}$- and $Al^{2+}$, $Fe^{3+}$- cases, but not for the $Fe^{2+}$- case. The effect of the double-crossing on seismic velocities is an initial increase in $\Delta V_P$ and $\Delta V_S$ followed by a decrease upon the reduction of $n_{PPV}$ (see, e.g., most of Figure 5**).
3.3. Effects on the Adiabatic Temperature Gradient and on Mantle Aggregates

The nature and magnitude of the thermal boundary layer atop the CMB are still debatable. The Pv-PPv transition being exothermic contributes to the nonadiabatic nature of the temperature gradients in this region, with reported temperatures reaching up to 4,000 K. Conductive and to some extent, radiative heat transport across the CMB is the leading cause of the steep temperature gradient above the CMB; however, the Pv-PPv transition also contributes to the temperature gradient in this region. Figure 6 shows the isentropic temperature profiles across this transition for all the alloys investigated. They are obtained by integrating the isentropic temperatures gradient (Equation 5) starting from the same fixed point of the Brown & Shankland geotherm \( T = 1,873 \) K at 23 GPa. They differ from the latter by \( \sim 80 \) K at the CMB. They are \( \sim 1,300 \) K cooler than the Boehler geotherm (Boehler, 2000) since they do not include the effect of heat conduction across the CMB. None of the isentropes exhibit significant gradient changes across the Pv-PPv transition, as shown in the inset in Figure 6. This is because both phases have very similar thermodynamic properties across the Pv-PPv transition (J. Tsuchiya et al., 2005). The procedure adopted here to compute the isentropic temperature profile is the same as that adopted in a recent study of the effect of the spin crossover in iron in Fe on the mantle geotherm (Valencia-Cardona et al., 2017).

4. Discussion

This study aims to clarify the effect of Fe and Al on the Pv-PPv phase transition and its potential consequences on seismic observables and temperature gradients in the deep mantle. Ultimately, a similar study must be carried out on aggregates in thermochemical equilibrium, but computations and experiments must be consistent first before one attempts to inspect detailed effects of aggregate composition on the Pv-PPv transition and shed light on remaining discrepancies between experiments on aggregates, for example, with pyrolytic composition (Grocholski et al., 2012; Kuwayama et al., 2022).

In this regard, the trends in our results are all consistent with measurements in bridgmanite with similar compositions (Catalli et al., 2009).

First, we verified that Fe\(^{2+}\) decreases the transition pressure, an effect similar to that caused by a decrease in temperature, which increases the height of the D\(^{”}\) discontinuity from the CMB. This behavior is opposite to that of (Al\(^{3+}\)), (Fe\(^{3+}\)) and (Fe\(^{3+}\), Al\(^{3+}\))- substitutions. Still, in all cases, the transition pressure shift is approximately proportional to the alloying element concentrations investigated, representing possible deep mantle bridgmanite compositions. In bridgmanite alone, the transitions are all quite broad and don't seem compatible with D\(^{”}\) discontinuity of <30 km (Lay, 2008). A change in composition across the D\(^{”}\) discontinuity with a predominance of PPv on the high-pressure side seems a plausible scenario (Grocholski et al., 2012; Kuwayama et al., 2022). Phase transformation kinetics (Langrand et al., 2019) and shape-preferred-orientation-induced anisotropy in a weak PPv phase (Ammann et al., 2010) might also sharpen the reflector atop the D\(^{”}\) region. On face value, a superadiabatic geotherm could still produce double-crossing or, depending on the concentration, even prevent the phase transition from happening in (Al\(^{3+}\)), (Fe\(^{3+}\)) and (Fe\(^{3+}\), Al\(^{3+}\))-bearing MgSiO\(_3\), but not in (Fe\(^{2+}\))-bridgmanite in the absence of Fe. “Double-crossing,” as shown in most Figure 5**, might not consist of two sharp transitions but a smooth change and reversal of velocities. It has been argued that in the presence of Fe, the change of iron partitioning throughout the transition increases the onset pressure of this transition and narrows the transition pressure range (Catalli et al., 2009). This effect is yet to be reproduced by ab initio calculations.

Second, it is believed that the exothermic nature of the Pv-PPv transition should contribute to the temperature gradient above the CMB (Nakagawa & Tackley, 2004). Regardless of the alloying element, there are no indications of a steep increase in the adiabatic temperature gradient throughout the two-phase region of the Pv-PPv phase transition. This is because the thermodynamic properties of both phases are very similar at the phase
boundary (J. Tsuchiya et al., 2005). The steep temperature gradients in this region should be caused almost exclusively by conductive, and possibly radiative heat flows across the CMB.

Finally, we have also observed an anomalous softening of the bulk modulus throughout the two-phase coexisting region similar to that which occurs throughout the spin crossover in Fp (Wentzcovitch et al., 2009). This type of bulk modulus anomaly, however subtle it might be, is to be expected throughout two-phase regions since they result from the change in molar fractions of initial and final phases with different densities. A more complex time-dependent version of this phenomenon has been observed experimentally in the olivine system (Li & Weidner, 2008).

5. Conclusions

Using ab initio calculations, we examined the effects of Fe and Al on the Pv-PPv phase boundary and its consequences on the thermal structure of the deep mantle and seismic observables. Overall, the dependence of the phase boundaries on the composition agrees with experiments in bridgmanite with similar compositions (Catalli et al., 2009). The onset pressures and thicknesses of the two-phase regions change proportionally with alloying element concentrations, with Fe$^{2+}$ increasing the onset transition pressure and Al$^{3+}$, and (Fe$^{2+}$, Al$^{3+}$) increasing it. We observe a softening of the bulk modulus in the Pv-PPv coexistence pressure range caused by the variable molar fraction of phases. A “double-crossing” of the phase boundary may cause only smooth changes/reversals in velocities, but not sharp “lenses” for compositions in the range investigated here. In bridgmanite alone, the composition-dependent two-phase regions might be too broad (see Figure 4a) to cause $a < 30$ km thick D" discontinuity (Lay, 2008). A change in composition across the D" discontinuity or throughout “double-crossings” with a predominance of PPv on the high-pressure side or inside the lenses seem a plausible scenario to be investigated in aggregates and compare with tomographic images. Finally, the changes in the adiabatic temperature gradients across the transition are minor in all cases. This transition should not contribute significantly to the thermal boundary layer in the D" region.

Data Availability Statement

The authors comply with the AGU’s data policy, and the data sets of this paper are available at https://doi.org/10.6084/m9.figshare.21895608.

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