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*Probing the role of MgSiO_3 polymorphs
in deep mantle processes*

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Despite everything, it's still you.

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List of acronyms

AO *Atomic Orbital*

B3LYP *Becke 3 Lee, Yang and Parr*

BM3-EOS *3rd order (isothermal) Birch-Murnaghan Equation of State*

CO *Crystalline Orbital*

DFT *Density Functional Theory*

EOS *Equation of State*

GGA *Generalized Gradient Approximation*

GTF *Gaussian-Type Function*

GTO *Gaussian-Type Orbitals*

HA *Harmonic Approximation*

HP *High Pressure*

HPA *Hybrid Polymeric Approach*

HP-CEn *High Pressure Clinoenstatite*

HT *High Temperature*

HT-CEn *High Temperature Clinoenstatite*

HT-BM3-EOS *High-Temperature 3rd order Birch-Murnaghan Equation of State*

IBZ *Irreducible Brillouin Zone*

IR *Infra-Red*

LCAO *Linear Combination of Atomic Orbitals*

LDA *Local Density Approximation*

LP *Low Pressure*

LP-CEn *Low Pressure Clinoenstatite*

LT *Low Temperature*

MD *Molecular Dynamics*

MG-EOS *Mie-Grüneisen Equation of State*

MTZ *Mantle Transition Zone*

NF *Network Formers*

NM *Network Modifiers*

OEn *Orthoenstatite*

PCM *Polarized Continuum Model*

PEn *Protoenstatite*

PES *Potential Energy Surface*

QHA *Quasi-Harmonic Approximation*

RMS *Root Mean Square*

SCF *Self-Consistent Field method*

vDOS *Vibrational Density of States*

VRH *Voigt-Reuss-Hill*

ZPC *Zero-Point Correction*

Abstract

This Ph.D. Thesis presents a completely theoretical study, based on state-of-the-art hybrid DFT calculations, on the thermodynamics and phase stability of candidate minerals that have been selected due to their relevant role in determining the mineralogical composition and physico-chemical properties of the Earth's mantle. Such minerals are the polymorphs of MgSiO_3 , in particular the MgSiO_3 pyroxenes. The choice of these minerals derives from their large stability field that spans the shallower portions of the Earth's mantle, down to the mantle transition zone. In fact, pyroxenes make up as much as 30% vol of the Earth's upper mantle and are involved in several processes that take place in the interior of our planet that are of great interest from a geochemical, petrological and geophysical point of view, such as partial melting and the occurrence of global seismic discontinuities. Moreover, stable and metastable pyroxenes are strongly involved in the dynamics of subducting slabs. In fact, the presence of metastable pyroxenes in subducting slabs directly affects the density of the down-going plate, modifying its buoyancy and favouring slab stagnation at the mantle transition zone.

Despite their importance, information on physico-chemical and thermodynamic properties of these minerals is lacking and affected by large uncertainties in current databases, hindering the possibility not only to obtain a clearer picture of their phase stability, but also to better comprehend their rheological behaviour at mantle conditions, preventing the interpretation of the global-scale processes in the Earth.

This study focused on the theoretical simulation of thermodynamic and thermoelastic properties of MgSiO_3 pyroxenes [namely, low-pressure clinoenstatite (LP-CEn), orthoenstatite (OEn), protoenstatite (PEn), high-temperature clinoenstatite (HT-CEn), high-pressure clinoenstatite (HP-CEn)], performed by ab initio DFT calculations up to conditions compatible with their stability in the deep mantle. The

ab initio thermodynamic data computed in this work represent the first attempt to build up a complete dataset of both physically- and internally-consistent properties for MgSiO_3 pyroxenes in a broad range of P-T conditions. This first-principles dataset includes all the main thermodynamic properties necessary for the calculation of the Gibbs free energy (i.e.: enthalpy, entropy, heat capacity, volume thermal expansion, bulk modulus and its pressure and temperature derivatives elastic moduli and seismic properties), hence to investigate phase stability relations of pyroxenes from subsolidus to liquidus conditions. The calculation of the Gibbs free energy at high-pressure and high-temperature conditions and its minimisation provides information on the relative stability of MgSiO_3 pyroxenes, hence allows the calculation of phase diagrams. Moreover, thermoelastic properties computed at high pressure and temperature, such as the thermal equation of state and volume thermal expansion, are fundamental to predict volume and density changes at mantle conditions, which in turn allows to constrain the rheological role of pyroxenes in mantle processes. Computed data also include the elastic and seismic properties (i.e. the full elastic constant tensor and longitudinal and transverse wave velocities), that can be used to infer seismic velocity jumps and impedance contrasts, allowing for a direct comparison with seismological observations on mid-mantle global seismic discontinuities and providing thermodynamic constraints on their origin. In particular, the origin of the so-called X-discontinuity in the mantle, between 270 and 330 km depths, has been tentatively interpreted in the literature as closely related to mineralogical phase transitions that include the OEn to HP-CEn phase transformation as a viable candidate.

The main results, implications and open issues that came out from this work can be summarized as follows:

- ❖ An initio hybrid DFT-QHA calculations at the B3LYP level of theory improve the accuracy on the thermodynamic properties of high-pressure magnesium silicates with respect to less sophisticated LDA and GGA density functionals. In order to test the performance of B3LYP, a first stage in the development of

this PhD project has been dedicated to the theoretical simulation of thermodynamic and thermoelastic properties of γ -Mg₂SiO₄ ringwoodite, using this mineral as a sort of beta test for calculations on more complex crystal structures. The obtained results not only show that ab initio B3LYP calculations are able to accurately predict thermodynamic and thermoelastic properties of this fundamental mineral phase up to lowermost mantle transition zone conditions, but clearly demonstrate that empirical extrapolation of thermoelastic data to deep mantle conditions should be taken with care to avoid inaccurate or spurious predictions in phase equilibrium modelling (cf. Belmonte et al., 2022).

- ❖ Ab initio B3LYP thermodynamic properties of all the pyroxene polymorphs of MgSiO₃ (i.e. PEn, OEn, LP-CEn, HP-CEn and HT-CEn) allow to obtain the full phase diagram of MgSiO₃, hence to provide original insights on the thermodynamic behaviour of such phases at P-T conditions compatible with their stability in the Earth's mantle. Despite the lack of experimental results, B3LYP calculations compare favourably with the few experiments available in the literature. Thermodynamic properties of most of the investigated phases have been determined for the very first time. For instance, the first comprehensive ab initio thermodynamic dataset for high-temperature clinoenstatite (HT-CEn) has been defined in this work, considering that no experimental data exist on this phase and the only information currently available come from thermodynamic assessments. Thermoelastic properties of protoenstatite (PEn), like volume thermal expansivity and thermal equation of state parameters, were previously almost unknown due to experimental difficulties in the synthesis and characterization of this phase. Ab initio calculations performed in this work on high-pressure clinoenstatite (HP-CEn) help to fill the gap in terms of thermodynamic information about this unquechable phase.

- ❖ All the pyroxene phase transitions occurring in the MgSiO_3 system have been investigated and calculated by employing the thermodynamic dataset obtained via first principles in this work. The following univariant equilibria have been determined: MgSiO_3 (low-pressure clinoenstatite) = MgSiO_3 (orthoenstatite), MgSiO_3 (orthoenstatite) = MgSiO_3 (protoenstatite), MgSiO_3 (protoenstatite) = MgSiO_3 (high-temperature clinoenstatite), MgSiO_3 (orthoenstatite) = MgSiO_3 (high-pressure clinoenstatite), MgSiO_3 (low-pressure clinoenstatite) = MgSiO_3 (high-pressure clinoenstatite). The investigation of these phase equilibria allowed to obtain novel information on the stability of pyroxenes at mantle conditions. Moreover, ab initio Clapeyron slopes and density contrasts calculated at high temperature and pressure conditions provide physical constraints to numerical modelling of subduction processes. The computational study shows how some of the phase equilibria involving pyroxenes are extremely sensible to small variations in the Gibbs free energy, thus difficult to reproduce even employing modern DFT-QHA calculations. In particular, some uncertainties still remain in some portions of the MgSiO_3 phase diagram, such as the location of the LP-CEn - OEn phase transition boundary at ambient pressure and that of the triple point between PEn, OEn and liquid. These uncertainties seem to be related to a limitation of the DFT-QHA theory in accurately predicting the thermodynamic properties of orthoenstatite (OEn), which can be explained by the presence of relevant anharmonic effects in this phase (Zucker & Shim, 2009).
- ❖ High-temperature clinoenstatite (HT-CEn) turns out to be unstable in the whole T(-P) range according to our investigation. This result strongly questions the role of this mineral as stable phase on the liquidus of MgSiO_3 system at low pressures, as claimed by some Authors in the literature on the basis of unphysical thermodynamic data (e.g. Shi et al., 1994 and 1996; Gasparik, 2014).
- ❖ The predicted melting curve of the MgSiO_3 system, as determined by assessing thermodynamic properties for the liquid phase that are thermodynamically-

consistent with those determined ab initio for the solid phases (cf. Belmonte et al., 2017), is in excellent agreement with experimental results in the pressure range 0 -10 GPa (Boyd et al., 1964; Presnall & Gasparik, 1990; Dalton and Presnall, 1997). Subsolidus and melting phase relations of pyroxenes in the theoretical phase diagram of MgSiO_3 are thus fully consistent with each other.

- ❖ Predicted P-T stability fields of orthoenstatite and high-pressure clinoenstatite in the MgSiO_3 phase diagram are compatible with the observed depth range of the seismic X-discontinuity in the mantle (i.e. 250-350 km depths). Nevertheless, the theoretical seismic velocity jumps and impedance contrasts calculated for OEn and HP-CEn at mantle conditions turn out to be much higher than those inferred by global seismological studies, thus disregarding the OEn to HP-CEn phase transition as the only responsible for the origin of the X-discontinuity.

1. Introduction

1.1. Structure and composition of the Earth's deep interior

Since the deepest portions of the Earth's mantle remain inaccessible to direct investigation, the most reliable information about its physical and chemical properties currently derives from seismic data analyses, laboratory experiments performed at HP-HT conditions, and thermodynamic simulations (Dziewonski and Anderson, 1981; Akaogi et al., 1989; Katsura & Ito 1989; Yu & Wentzcovitch, 2006). High-pressure experiments aim to reproduce the extreme pressure – temperature conditions of the deep Earth, and to measure the physical properties of minerals under these conditions (Bass and Parise, 2008). Despite the outstanding progress in experimental technology, laboratory experiments simulating the deep Earth's conditions are still challenging and affected by large uncertainties (see for example Shen & Lazor, 1995), linked for the most part to the nature of samples, often simplified or synthetic, and to the limited number of properties that can be measured. Mineral phase relations as inferred from experiments can be misleading due to metastability problems and are mostly valid on a local scale. On the other hand, seismological observations provide global evidence on the nature of the Earth's mantle, but they are based on indirect inversion methods and thus need to be complemented by mineral physics data to really understand the origin of seismic discontinuities and chemical heterogeneities in the mantle. Thermodynamic modelling is able to reconcile the global-scale seismic structure of the mantle with physico-chemical properties of its constituent phases without any limitation of P-T conditions, thus providing original constraints on mantle dynamics and geochemistry.

Figure 1.1.1 shows the variation in mineral proportions of an average mantle composition (pyrolite) as a function of depth along a model mantle geotherm, as deduced by the combination of laboratory experiments, seismic and thermodynamic data. The upper mantle, from the Moho discontinuity to 410 km depth, is composed

of olivine + orthopyroxene + clinopyroxene + an aluminous phase (plagioclase below 30 km, spinel between 30 and 70 km and garnet above 70 km). At depths greater than 410 km, olivine undergoes a phase transition and transforms into wadsleyite, which is a denser polymorph with a modified spinel structure (Ringwood, 1991). The actual cubic structure of spinel is adopted by olivine at 520 km depth, where wadsleyite transforms into ringwoodite, leading to a discontinuity in density. Going down from the upper mantle and mantle transition zone to the lower mantle, beyond 660 km depth, ringwoodite breaks down into ferropericlase and a perovskite-structured magnesium silicate (named bridgmanite in honour of Percy Williams Bridgman, who received the Nobel Prize for his work on the physics of high-pressures) (Tschauner et al., 2014). Concerning magnesium-rich ortho- and clinopyroxenes, with increasing pressure they are both incorporated into garnet, as a result of the chemical substitution in the garnet octahedral site, which is normally occupied by Al, but could exceptionally accept Si under extreme pressure and temperature conditions. This mineral phase is named majorite (Akaogi and Akimoto, 1977; Irifune, 1987). Garnet also incorporates Mg and Fe into the octahedral site but not Ca, so that the majorite substitution initially decreases the proportion of orthopyroxene, while clinopyroxene is still stable up to about 15-16 GPa (and ~400 km depth) with a monoclinic $C2/c$ structure. The transition from an orthopyroxene + clinopyroxene + garnet paragenesis to majoritic garnet is witnessed by field evidence: for instance, the peridotite body of Otrøy Island (Norway) displays evidence for exsolution of orthopyroxene in coarse garnet, implying a “supersilicic” majoritic precursor garnet stable at ultra-high pressure ($P > 6$ GPa) (van Roermund and Drury, 1998; Chopin, 2003; Chopin and Ferraris, 2003). At pressures higher than 18 GPa, calcium perovskite (CaSiO_3) begins to exsolve from garnet. Once entered the lower mantle, majorite starts to transform into perovskite as well. Just above the core-mantle boundary, in the so-called D'' layer between 2700 and 2900 km depths, $(\text{Mg,Fe})\text{SiO}_3$ perovskite transforms into the recently discovered “post-perovskite” phase (Hirose et al., 2007), which allowed to decipher the unusual seismic structure of the deepest part of the mantle, although

there is still no general consensus on the origin of the D'' discontinuity, and other possible explanations include an isochemical thermal boundary (Wyssession et al., 1992), a thermo-chemical boundary (Davies & Gurnis, 1986), or a break-down of the constituent mantle minerals (Stixrude & Cohen, 1993). All the mineralogical changes occurring in the mantle are reflected by discontinuities in the velocity profiles obtained through the inversion of seismic wave travel time data, thus supporting a close link between geophysics and geochemistry, on one side, and mineral physics and thermodynamics on the other side. In particular, global seismic profiles of the Earth's interior (like the Preliminary Reference Earth Model, PREM; Dziewonski and Anderson, 1981) reveal as both longitudinal- and shear-wave velocities increase extremely rapidly with depth in the mantle transition zone, with sudden increases near the 410-km and 660-km seismic discontinuities (which corresponds to the mineralogical phase transition cited above). Smoothly and slowly varying velocities are observed throughout the lower mantle instead (where ferropericlase and bridgmanite are thermodynamically stable phases without any phase transformations), at least up to the D'' layer where another discontinuity clearly occurs due to the post-perovskite phase transition (Figure 1.1.2).

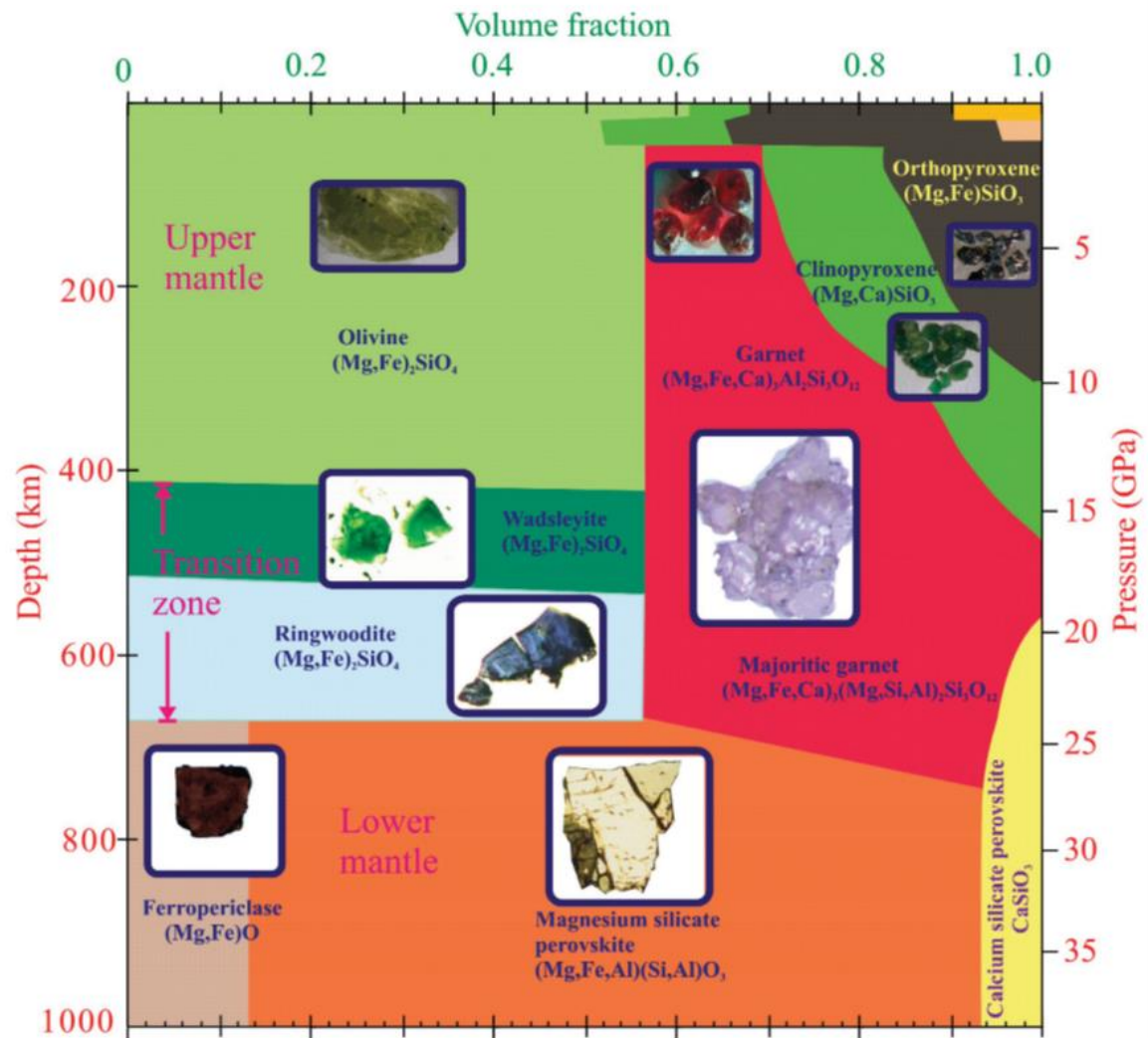


Figure 1.1.1. Mineral volume fractions for the top 1000 km of a pyrolitic mantle. Small orange and pink regions in the top right-hand corner denote the stabilities of plagioclase and spinel, respectively (after Ringwood, 1991; figure taken from Frost, 2008).

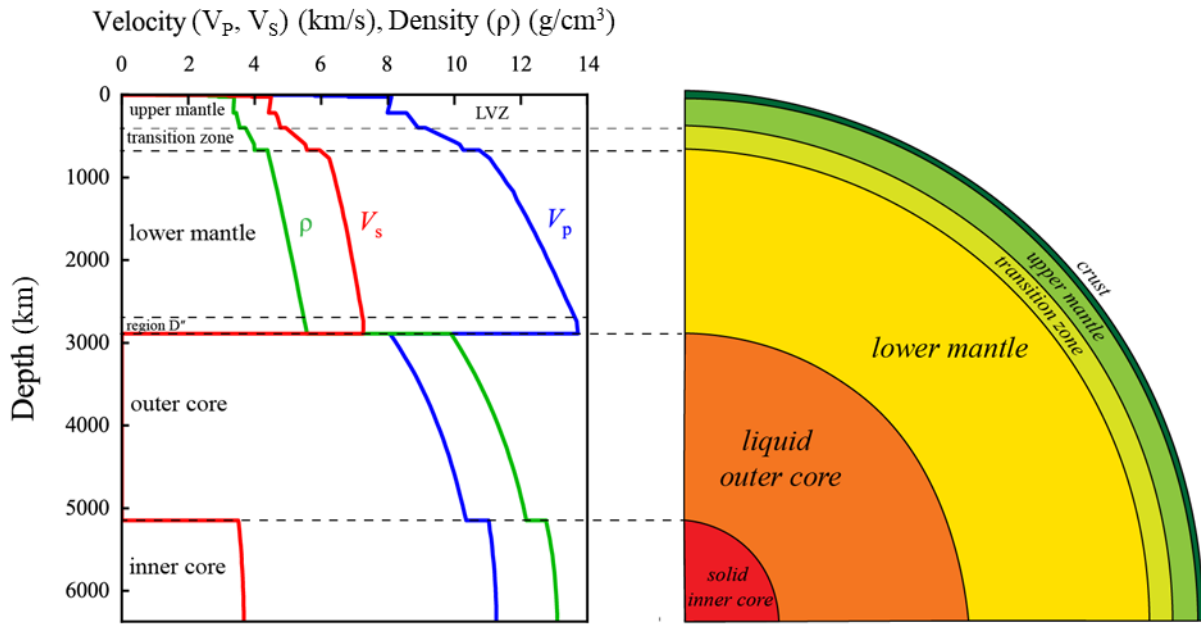


Figure 1.1.2. Density and velocity profile of the Earth (according to PREM model; Dziewonski and Anderson, 1981).

Previous geochemical and geophysical investigations focused mostly on the role of olivine, since it is the most abundant mineral phase, at least in the upper mantle. However, it is widely accepted that MgSiO_3 polymorphs, like Mg-rich pyroxenes, play a fundamental role, determining both chemical and physical heterogeneities in the mantle due to their large stability field that extends up to the uppermost transition zone. In fact, according to the more recent mineralogical models they occupy up to 30% in volume of the Earth's mantle (Irifune and Tsuchiya, 2007; Frost, 2008). Moreover, pyroxenes are important mineral phases since they govern melting processes, seismic anisotropy, and distribution of rheologically weak layers within the mantle. Despite their importance, there is a general lack of studies on pyroxenes thermodynamics because of their complex polymorphism, which is difficult to reproduce experimentally. There are only a few calorimetric investigations on mantle pyroxenes, and their physical properties are still poorly constrained (Ross and Navrotsky, 1988), in particular at high-pressure and temperature conditions (HP-HT).

Moreover, the full details of the MgSiO_3 phase diagram still remain unclear, as will be discussed in the next section.

1.2. Thermodynamic stability of MgSiO_3 pyroxene polymorphs

The thermodynamic stability of the different pyroxene polymorphs depends upon pressure, temperature, and chemical composition. Pyroxenes with MgSiO_3 composition are known to exist in at least five different structures and undergo structural phase transitions with increasing P-T conditions (as summarized by Figure 1.2.1). At low T and P, monoclinic low-clinoenstatite with space group $P21/c$ is the stable phase. A displacive phase transition occurs at high pressure (i.e. $P > 6\text{--}7$ GPa) resulting in high-pressure clinoenstatite with space group $C2/c$ (Angel et al., 1992). Orthoenstatite ($Pbca$) occurs at high T and pressures up to about 7 GPa, whereas protoenstatite ($Pbcn$) and high-T clinoenstatite ($C2/c$) have small stability fields at high T and low P according to current phase diagrams in the literature (e.g. Presnall, 1995; Gasparik, 2014). The polymorphism and stability relations of magnesium pyroxene phases are thus a masterpiece of complexity. This is further complicated by the fact that several additional pyroxene phases have been suggested to exist in the Earth's mantle (Thompson and Downs, 2003), some of which may be preserved as metastable phases. Concerning the question as to whether a detailed knowledge of pyroxene thermodynamics could help to understand their relevance in mantle processes, it should be noted that the experimental thermodynamic investigation of those phases at deep mantle conditions is hindered by problems related to their synthesis in the laboratory as well as to the unquenchable nature of some of the most widespread polymorphs. In other words, pyroxenes stable at deep mantle conditions could be synthesized in-situ by high-pressure experiments but mineral samples cannot be quenched to ambient conditions because they spontaneously change and easily revert to different polymorphic structures. This change happens for instance to protoenstatite and high-pressure clinoenstatite, which always reverts to low-

clinoenstatite or orthoenstatite, at ambient conditions (Smyth, 1974; Thieblot et al., 1999; Ulmer & Stadler, 2001). To further complicate this picture, the existence of high-temperature clinoenstatite has never been confirmed by any experimental investigation, as its stability has only been determined via theoretical simulations and assessments that often rely on thermodynamic properties which clearly suffer from physical unsoundness. This is why physicochemical properties of pyroxenes are still poorly constrained and theoretical calculations currently represent the most effective way (sometimes the only one, indeed) to investigate their thermodynamic properties and thus to assess their effective geodynamic role in the Earth's deep mantle.

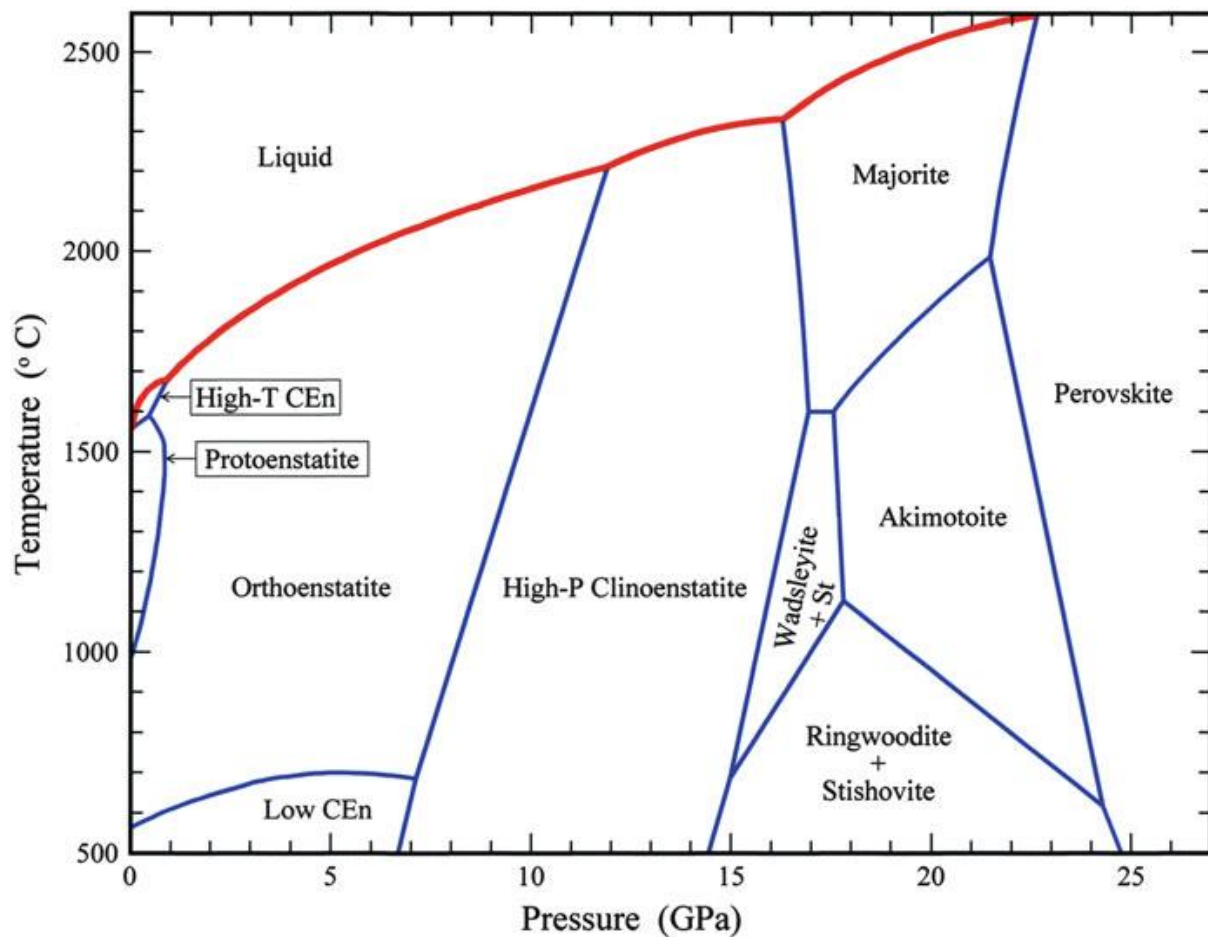


Figure 1.2.1. Temperature – pressure phase diagram for the MgSiO_3 system (according to Gasparik, 2014).

1.3. Metastable pyroxenes and subducting slab dynamics

One of the fundamental debates in the geophysical community deals with the fate of subducting slabs in the Earth's deep interior (Karason & van der Hilst, 2000). Important insights onto this topic come from global seismic tomography, which showed that some subducting slabs can be tracked down to the core-mantle boundary, whereas there are cases where slabs seem to rest in correspondence of the mantle transition zone (Figure 1.3.1).

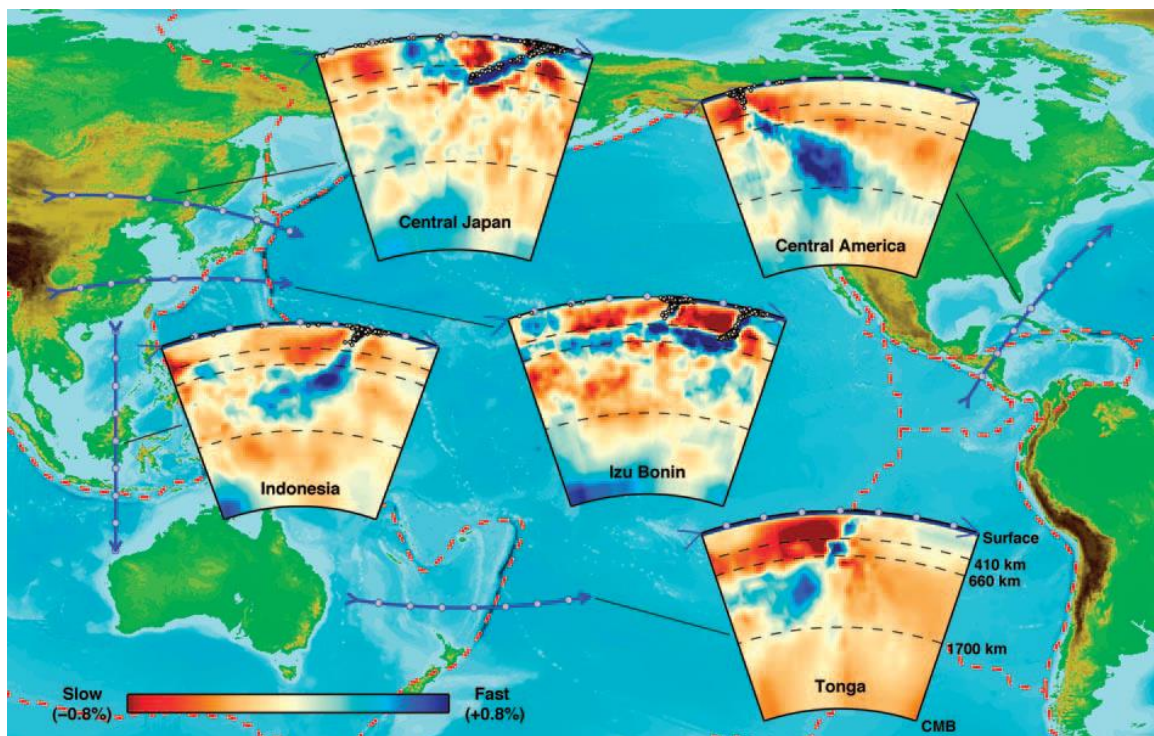


Figure 1.3.1. Seismic tomography of subducted slabs (from Bass & Parise, 2008).

Seismic data provided by mineral physics studies give a rationale to global seismic wave velocities propagation and seismic discontinuities in different subduction environments (as briefly discussed in Section 1.1) but cannot account for the mechanisms of slab dynamics. Thermodynamics of mineral phase transformations is key to understanding the physical behaviour of slabs in the deep mantle and allows to understand why some slabs stagnate near the 660-km discontinuity, whereas other slabs penetrate across the mantle transition zone reaching several thousands of kilometers depths. It is widely accepted that endothermic mineral reactions with a

negative Clapeyron slopes (i.e. reactions occurring at progressively lower temperatures with increasing pressures) may favour slab stagnation, like the breakdown reaction of ringwoodite into bridgmanite + ferropericlase (the so-called post-spinel phase transformation) (e.g. Christensen, 1995). On the other hand, exothermic mineral reactions displaying a positive Clapeyron slopes, like the majorite to bridgmanite phase transition, may hinder slab stagnation and favour their penetration across the mantle transition zone. Only a reliable mineralogical model for the mantle transition zone can therefore constrain relative mineral abundances (i.e. olivine vs. pyroxene vs. garnet), allowing slab dynamics to be interpreted and fully understood (Bina et al., 2001). A reliable mineralogical model for the Earth's deep interior requires in turn an accurate knowledge of thermodynamic properties of the constituent mineral phases at extreme P-T conditions, which is currently far to be defined due to the problems and limitations briefly outlined in Sections 1.1 and 1.2.

Specifically concerning the role of MgSiO_3 pyroxenes in the dynamics of subducting slabs, it is widely accepted that low-density metastable pyroxenes may persist into the transition zone in cold slabs due to extremely low transformational diffusion rates (van Mierlo et al., 2013). In fact, under increasing pressure pyroxenes dissolve progressively into the denser garnet, forming majorite garnet; however, at cold slab temperatures, this dissolution of pyroxene is kinetically inhibited, hence pyroxenes may also survive as metastable phase (Hogrefe et al., 1994; Nishi et al., 2008, 2013). The dissolution rate is controlled by how fast the majorite component can diffuse through the garnet structure, which has been found to be one of the slowest diffusion processes in the Earth's mantle (van Mierlo et al., 2013). The slow diffusion can promote the presence of low-density pyroxenes even at relatively high temperatures in the slab and can thus contribute to the deceleration and potential stagnation of slabs in the transition zone. On the other hand, phase transition of pyroxene to akimotoite (i.e. the MgSiO_3 polymorph with ilmenite-type structure) may account for the eventual descent of slabs in the lower mantle (e.g. Kirby et al., 1996; Bina and Kawakatsu, 2010).

Agrusta et al. (2014) analysed the effect of the metastable persistence of pyroxene on slab stagnation in the mantle transition zone using a dynamically fully self-consistent subduction model (Fig. 1.3.2). They showed that pyroxene can survive as a metastable phase in cold slabs and, due to its low density, favours slab deceleration and stagnation in the transition zone, as was proposed by Van Mierlo et al. (2013). Unlike metastable olivine, which can inhibit slab penetration in the lower mantle only for cold, old, and fast slabs (Tetzlaff and Schmeling, 2000; Bina et al., 2001), metastable pyroxene is likely to also affect sinking of relatively young and slow slabs (rows 3 and 4 in Fig. 1.3.2). Old slabs are normally associated with more negative buoyancy than young slabs and from a dynamical perspective are therefore expected to sink faster and deeper into the mantle. However, observations suggest that many slabs, including old ones such as Izu-Bonin, Tonga, and Japan, stagnate in the transition zone (Fukao and Obayashi, 2013). Agrusta et al. (2014) showed that the combined effects of the pyroxene and olivine metastability can lead to the stagnation of both young and old slabs.

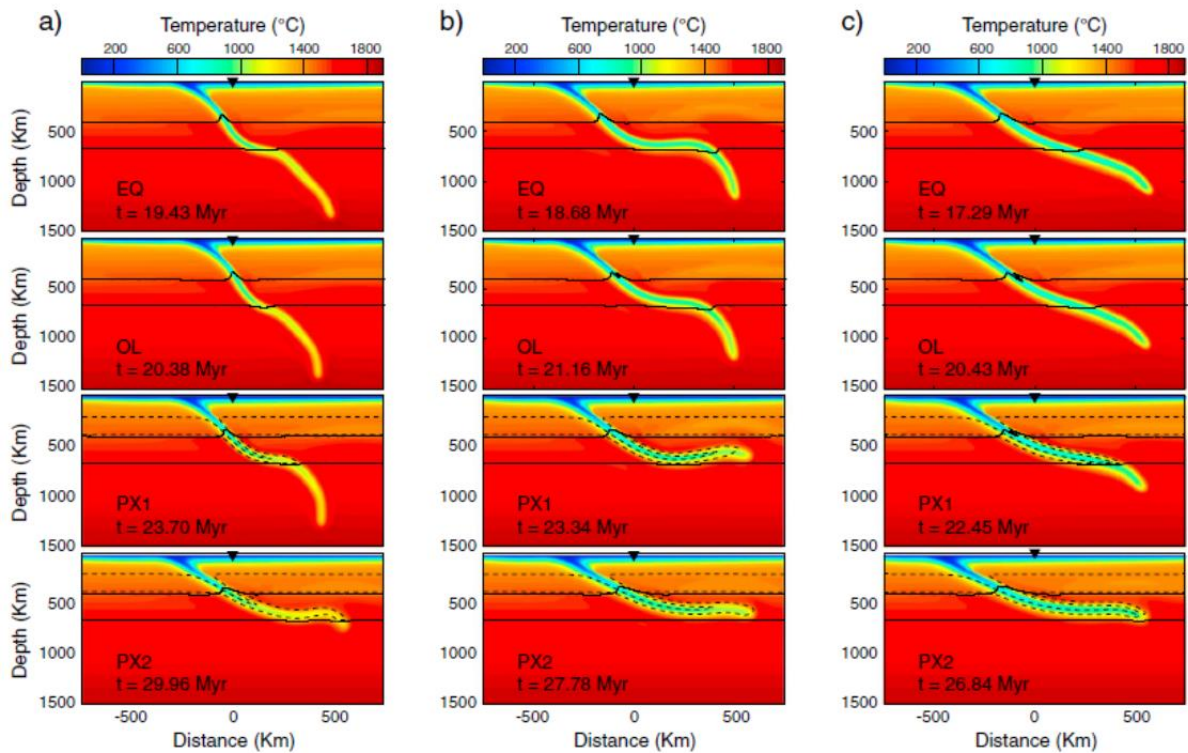


Figure 1.3.2. Temperature fields calculated by numerical simulations of subducting slabs. In the first and second row the starting composition consists of olivine only, the difference being that in the second row the transition between olivine and wadsleyite is considered having a slower kinetic. In the third and fourth row, 10% and 20% of pyroxene are added to the starting composition. The three columns differentiate for the starting age at trench: 50, 100 and 150 Myr from column 1 to 3 respectively (from Agrusta et al., 2014).

1.4. Aim of this study

The main goal of this Thesis is the theoretical simulation of physically-consistent vibrational, elastic and thermodynamic properties of MgSiO_3 pyroxene polymorphs up to HT-HP conditions via state-of-the-art first principles DFT calculations, aimed at predicting a large portion of the MgSiO_3 phase diagram (including the melting curve) exclusively thorough ab initio methods. The chemico-physical properties, as computed in this work, are tested in a broad range of P-T conditions to get original insights on the phase transformations and stability relations of pyroxene phases from upper mantle to mantle transition zone and from melting to subsolidus conditions in the MgO-SiO_2 system which, although simplified, can be considered a good proxy of the real composition of the Earth's mantle. The MgSiO_3 pyroxene phases investigated in this work are:

- ❖ Low-pressure clinoenstatite (LP-CEn)
- ❖ Orthoenstatite (OEn)
- ❖ High-pressure clinoenstatite (HP-CEn)
- ❖ Protoenstatite (PEn)
- ❖ High-temperature clinoenstatite (HT-CEn)

The thermodynamic investigation carried out in this work required several steps, which can be summarized as follows:

- 1) use of the quantum-mechanical computer code CRYSTAL to define structure – energy, elastic and vibrational properties of the investigated mineral phases,

preceded by a “beta test” to check the performance of the level of theory employed in this work (B3LYP) on high-pressure magnesium silicates (see Chapter 3 for further details);

- 2) calculation of theoretical vibrational spectra at ambient and non-ambient conditions and comparison with experimental IR or Raman spectra (when available);
- 3) calculation of the full phonon dispersion of vibrational modes to obtain the vibrational density of states (vDOS) (see section 2 for further details);
- 4) calculation of thermodynamic and thermoelastic properties (e.g. volume thermal expansion and thermal equation of state) of all the investigated pyroxene phases, and comparison with experimental results, either adopting the supercell approach or by employing a semiclassical model to approximate the phonon dispersion (modified Kieffer model) (see section 2 for further details);
- 5) definition of single-crystal and aggregate seismic properties of the mineral phases of interest along with their seismic anisotropy;
- 6) construction of a physically- and internally-consistent thermodynamic dataset, based on first principles, which can be directly employed to calculate phase equilibrium boundaries at planetary interior conditions. The dataset contains all the thermodynamic properties required to calculate Gibbs free energy values at HP-HT for all the phases potentially stable in the MgO-SiO₂ system, namely: standard state enthalpy of formation from the elements (H^0_f), standard state entropy (S^0), molar volume at the athermal limit (V_0), the numerical coefficients of the $C_P(T)$ polynomial function, the bulk modulus (K_0) and its pressure (K'_0) and temperature $(dK/dT)_P$ derivatives, the coefficients of the $\alpha_V(T)$ polynomial function.
- 7) calculation of relevant phase equilibrium boundaries, from subsolidus up to melting conditions and comparison with those experimentally-defined and/or assessed at HT-HP conditions

Possible implications of the computed thermodynamic properties and of the theoretical phase equilibria from a geophysical, geochemical, petrological, and geodynamic point of view are then discussed in detail, for example:

- ❖ Clapeyron slopes of phase equilibrium boundaries and density of pyroxenes in the MgSiO_3 phase diagram as provided by ab initio DFT-QHA calculations performed in this work are key parameters necessary to perform numerical modelling of global-scale processes such as the subduction of slabs (Agrusta et al., 2014). Thermodynamic constraints on the P-T conditions of pyroxene phase stability relations (and metastability as well) can thus be crucial for Earth's mantle dynamics, since the (meta)stability of pyroxenes directly affects the buoyancy of subducting slabs;
- ❖ Calculated density changes, longitudinal- and shear-wave seismic velocity jumps and seismic impedance contrasts associated with phase reaction boundaries involving pyroxenes can provide information on the still nowadays debated origin of some globally detected seismic discontinuities (like the X-discontinuity);
- ❖ Understanding phase relations in the MgSiO_3 system, particularly at high pressure and high temperature conditions, might help to unravel the details of the early melting and crystallization history of the Earth (Ohtani, 1985; Agee & Walker, 1988) by considering this simplified, yet representative, chemical system. Constraints on the origin of melts in the deep mantle environment can also be drawn from the knowledge of melting behaviour of pyroxenes at high-pressure.

This Thesis is structured in 7 chapters (including this brief introduction). The content of each chapter will be very briefly described here in the following text:

- ❖ CHAPTER 2: this chapter will deal with the more technical aspects of the methodology adopted to perform thermodynamical investigation on MgSiO_3 pyroxenes. Details on the most relevant computational aspects, such as the

software used to perform ab initio DFT calculations, the level of theory chosen, the most relevant computational parameters will be provided. The chapter will explain in detail how to calculate thermodynamic properties of crystalline compounds starting from the calculation and the statistical analysis of phonon modes in the framework of the Quasi-Harmonic Approximation (QHA), as well as how to calculate the Gibbs free energy of a given phase once its thermodynamics is known and how phase equilibria is modelled by means of the Gibbs free energy minimisation procedure. Instructions on how to calculate phase equilibria that involve the liquid phase are also provided.

- ❖ CHAPTER 3: this chapter will present the results of ab initio calculations that have been performed on Mg_2SiO_4 ringwoodite, which has been chosen as “beta test” for DFT-QHA based calculation. Its entire set of thermodynamic and thermoelastic properties has been determined by adopting two different approximations of its vibrational density of states (vDOS). The performance of the two method is compared and discussed. Comparison with literature data is also provided and the behaviour of ringwoodite at deep mantle conditions as inferred by its thermodynamics is discussed.
- ❖ CHAPTER 4: this chapter will deal with the calculation of MgSiO_3 protoenstatite thermodynamic and thermoelastic properties. The methodology based on the statistical analysis of phonon modes is here completely presented in detail using protoenstatite as case study. Its complete thermodynamic dataset has been determined for the first time and is here reported showing in detail all the most relevant thermodynamic and thermoelastic properties, which have been tested in reproducing the orthoenstatite-protoenstatite transformation at mantle conditions.
- ❖ CHAPTER 5: this chapter reports the result of the phase equilibria investigation conducted in the MgSiO_3 system. The complete set of thermodynamic properties has been calculated not only for protoenstatite, but also for all other pyroxenes that nucleate in the MgSiO_3 system. All relevant phase boundaries

and phase relations between pyroxene polymorphs not only at *subsolidus*, but up to melting conditions, are here presented and the theoretical version of the MgSiO_3 phase diagram as compared with available experiments is reported. Relevant thermodynamic parameters such as enthalpy, entropy and volume changes across all transformations, as well as the Clapeyron slope of each phase boundary, is reported as well.

- ❖ CHAPTER 6: this chapter will treat in more detail the theoretical melting curve of the MgSiO_3 system, as well as the thermodynamic parameters of the MgSiO_3 liquid as assessed by this study. The melting behaviour of MgSiO_3 pyroxenes up to high-pressure conditions is discussed as inferred by our results.
- ❖ CHAPTER 7: this final chapter will present a systematics of all MgSiO_3 pyroxenes elastic and seismic properties, which for the most part represents data obtained for the very first time in a fully, both physically and internally, consistent way. The elastic and seismic properties of orthoenstatite and high pressure clinoenstatite in particular have been extrapolated at HP-HT conditions and tested to reproduce seismological observations at conditions compatible with the occurrence of the X-discontinuity in the mantle. Eventual implications concerning its origin are discussed.

2. Computational Method

All calculations in this work have been performed using the CRYSTAL computer code (CRYSTAL14 and 17 releases; Dovesi et al., 2014, 2020), which allows for the ab initio calculation of the total energy (the ground state energy) of a crystalline solid, as well as of the first and second derivatives of the total energy, which are relevant to define its physical properties (i.e. elastic, vibrational, etc.) (Dovesi et al., 2020). The code can perform calculations at different levels of theory, with either Hartree-Fock (HF) or Density Functional Theory (DFT) based Hamiltonians, according to the Kohn-Sham formalism for the definition of the exchange – correlation contributions to the total energy (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). Different types of solid can be modelled, with either 0 (molecules), 1 (polymers or chains), 2 (slabs) or 3 (crystals) dimensions. The fundamental theoretical assumption is the expansion of the single particle wave functions (“Crystalline Orbital”, CO) as a linear combination of localized functions (the “Atomic Orbitals”, AOs) which are, in turn, linear combinations of Gaussian-type functions (GTFs), whose coefficients and exponents (defining the so-called basis set) are given in input, along with symmetry constraints and other computational details. The whole procedure is known as LCAO (= Linear Combination of Atomic Orbitals). Coefficients and exponents of the GTFs defining the basis set of Mg, Si and O atoms are reported in section 2.9.

2.1. Geometry optimization

A given molecular compound can exist with different structural configurations, according to the different statistical positions of the nuclei. At each of these configurations corresponds a different energy value, and the structures obtained from experiments are not necessarily representative of the best atomic arrangement (i.e.: don’t correspond to the fully relaxed structure) and can’t be adopted to derive energy-

related properties. In CRYSTAL, the fully-relaxed structural configuration of the compound of interest can be obtained from the *geometry optimization* procedure, which is an iterative procedure that allows to determine the structural parameters of a compound on a local minimum of the potential energy surface (PES) by deriving the total energy with respect to the nuclear coordinates R_i , starting from an initially imposed geometry. The initial geometry is usually chosen from high-quality structural refinements taken from a crystallographic database (e.g. <http://rruff.geo.arizona.edu/AMS/amcsd.php>). In the Born-Oppenheimer approximation, the static potential $V(R_i)$ depends only on the nuclear positions. Following the *geometry optimization* procedure, CRYSTAL not only calculates punctual values of $V(R_i)$, but also its derivatives, defining thus the gradient of the function, which becomes equal to zero at a local minimum. The points of the PES that satisfy $\nabla V = 0$ are called *critical* (or *stationary*) points. There's a chance that a given point for which $\nabla V = 0$ holds is not a local minimum, but a *saddle* point instead. In this case, the only way to test the nature of a *critical* point is to calculate the vibrational frequencies (see section 2.2) for that particular structure: the presence of an imaginary phonon frequency is indicative of a *saddle* point. CRYSTAL operates different types of geometry optimization: it is possible to perform a complete optimization of the structure, involving thus both cell parameters and atomic coordinates, or optimizing volume and cell parameters only while keeping the atomic positions constants, or even optimize the atomic positions only while keeping constant the volume of the unit cell. The instructions to perform a geometry optimization are simply added in the input block. It is also possible to perform constant-volume geometry optimization on compressed or expanded structures, which is a step required to calculate the (static) equation of state parameters (i.e.: K_0 and K'_0) by either applying an external hydrostatic pressure, or by imposing a volume range (expressed as V/V_0 ratio) and the number of E-V points in the considered range. Moreover, the optimization of structures at different volume (or pressure) conditions is a step required to determine

the volume dependence of vibrational modes, hence the mode Grüneisen parameters, within the so-called quasi-harmonic approximation (QHA) (see Section 2.3).

2.2. Vibrational frequencies calculation

The crystal lattice is never rigid. Atoms move about their equilibrium positions inside the crystalline structure. Lattice dynamics provides the key to understand many physical phenomena mainly related to thermal effects, phase transitions, transport properties, and so forth. Theoretical calculation of atom vibrations then gives access to several properties such as the calculation of vibrational spectra, the prediction of structure stability or instability of a crystalline phase and the computation of thermodynamical properties (e.g.: entropy, isobaric heat capacity, internal energy, volume thermal expansion and expansivity, etc.). These properties are in turn fundamental since they allow to derive the Gibbs free energy of a solid, which is the main ingredient for phase equilibrium calculations, as a function of both pressure and temperature (see section 2.7). CRYSTAL calculates vibrational frequencies at the Γ point (i.e.: at the center of the Brillouin zone) and in the framework of the *harmonic approximation* (HA), that is the vibrational frequencies are computed neglecting terms of order higher than 2 in the potential energy surface $V(x)$, where x is the vector of the $3N$ coordinates of the atoms in the system. The PES is defined as:

$$V_{(0)} = \frac{1}{2} \sum_{ij} u_i H_{ij} u_j \quad (2.2.1)$$

where:

u_i = displacement of the i -th cartesian atomic coordinate from its equilibrium value.

H_{ij} = Hessian matrix of the second derivatives of $V_{(x)}$ evaluated with respect to the displacement coordinates, i.e.:

$$H_{ij} = \frac{1}{2} \left[\frac{\partial^2 V(x)}{\partial u_i \partial u_j} \right]_0 \quad (2.2.2)$$

Where the summation in eq. (2.2.1) is performed for all the i and j atomic coordinates. By defining the mass - weighted Hessian matrix as:

$$W_{ij} = \frac{H_{ij}}{\sqrt{M_i M_j}} \quad (2.2.3)$$

where M_i and M_j are the atomic masses at the i -th and j -th position, phonon frequencies are calculated at point Γ ($\mathbf{q}=0$) as eigenvalues of the Hessian by diagonalizing the mass – weighted matrix. CRYSTAL obtains the matrix of the force constants (hence the Hessian H_{ij} in equation 2.2.2) by numerically deriving the analytical atomic gradients. To summarize, these are the steps which lead to the calculation of vibrational frequencies at Γ point of the IBZ (i.e. for $\mathbf{q} = 0$, being $\mathbf{q}$ the wave vector):

- ❖ first of all, a local minimum on the PES is localized through a geometry optimization procedure, hence by the analytical calculation of energy gradients;
- ❖ then atoms are displaced from their equilibrium position within the limits of the harmonic approximation (finite displacement method), calculating the numerical second derivatives of the total energy with respect to the displacement coordinates, so the Hessian;
- ❖ finally, phonon frequencies are evaluated as the eigenvalues of the weighted Hessian matrix by diagonalization.

Since at the centre of the first Brillouin zone the first three solutions of the dispersion relation:

$$\nu = \nu_i(\mathbf{q}) \quad 1 \leq i \leq 3n \quad (2.2.4)$$

vanish (ν_i is the vibrational frequency of the i -th mode, n is the number of atoms in the primitive cell), this type of calculation does not allow to define the frequency value

of the three acoustic branches which need to be defined in a different way (see below). One way is to employ supercells, allowing to take into account the dispersion of phonons. Phonon dispersion arises because the interaction between atomic vibrations is not confined inside the volume of the primitive cell. This means that as the phase difference of the motions of atoms in different cell varies, so do the energy and the frequency. The calculation of phonon dispersion can be performed by means of the supercell approach. The construction of a supercell by linear combination of primitive unit cell vectors implies the partial breaking of the translational symmetry, thus allowing a certain set of phase differences, that is $\mathbf{q}$ points in the first BZ, to be sampled. The sampling depends on the size and shape of the supercell: the reciprocal lattice of the supercell defines the sampling grid on the primitive BZ. Given the low symmetry of the chemical compounds studied in this work (mostly belonging either to orthorhombic or monoclinic systems), both isotropic and anisotropic supercells were employed to perform phonon dispersion calculation while at the same time speed up the computational time. If the calculation on supercells is prevented by high computational costs, an alternative approach based on the modification of the Debye model (Debye, 1912) by Kieffer (Kieffer, 1979a) can be adopted instead to simulate the dispersion of the acoustic branches across the BZ. The Debye-Kieffer approach simplify the first BZ by assimilating the reciprocal unit cell to a sphere of equal volume centered at Γ point and having a radius equal to $q_{\max}$. The volume of the first BZ thus becomes:

$$V_R = \frac{4}{3}\pi(q_{\max})^3 = \frac{(2\pi)^3}{V_L} \quad (2.2.5)$$

where V_R and V_L are the volumes of the reciprocal and direct unit cell, respectively. Kieffer's model assumes a sinusoidal dispersion relation for the acoustic modes, instead of the perfectly linear dispersion assumed by Debye in its original model (fig. 2.2.1). Acoustic mode frequencies (ν_1 , ν_2 and ν_3) are then calculated by inversion of the

single-crystal longitudinal and shear seismic velocities (V_P , $V_{S1} = V_{S,\max}$ and $V_{S2} = V_{S,\min}$), averaged according to the following relations (see Kieffer, 1979a for details):

$$u_3 = V_{P,VRH} \quad (2.2.6)$$

$$\frac{2}{u_2^3} = \frac{1}{(V_{S,VRH})^3} + \frac{1}{(V_{S,\max})^3} \quad (2.2.7)$$

$$\frac{1}{u_1^3} = \frac{2}{(V_{S,VRH})^3} - \frac{1}{u_2^3} \quad (2.2.8)$$

where $V_{P,VRH}$ and $V_{S,VRH}$ are the aggregate longitudinal and shear seismic velocities obtained by a Voigt-Reuss-Hill averaging scheme (Hill, 1952); $V_{S1} = V_{S,\max}$ and $V_{S2} = V_{S,\min}$ are the maximum and minimum single-crystal shear velocities calculated by solving the Christoffel equation along a fixed direction of propagation of the seismic wave in the crystal (e.g. Musgrave, 1970); u_1 , u_2 and u_3 are the directionally-averaged acoustic velocities.

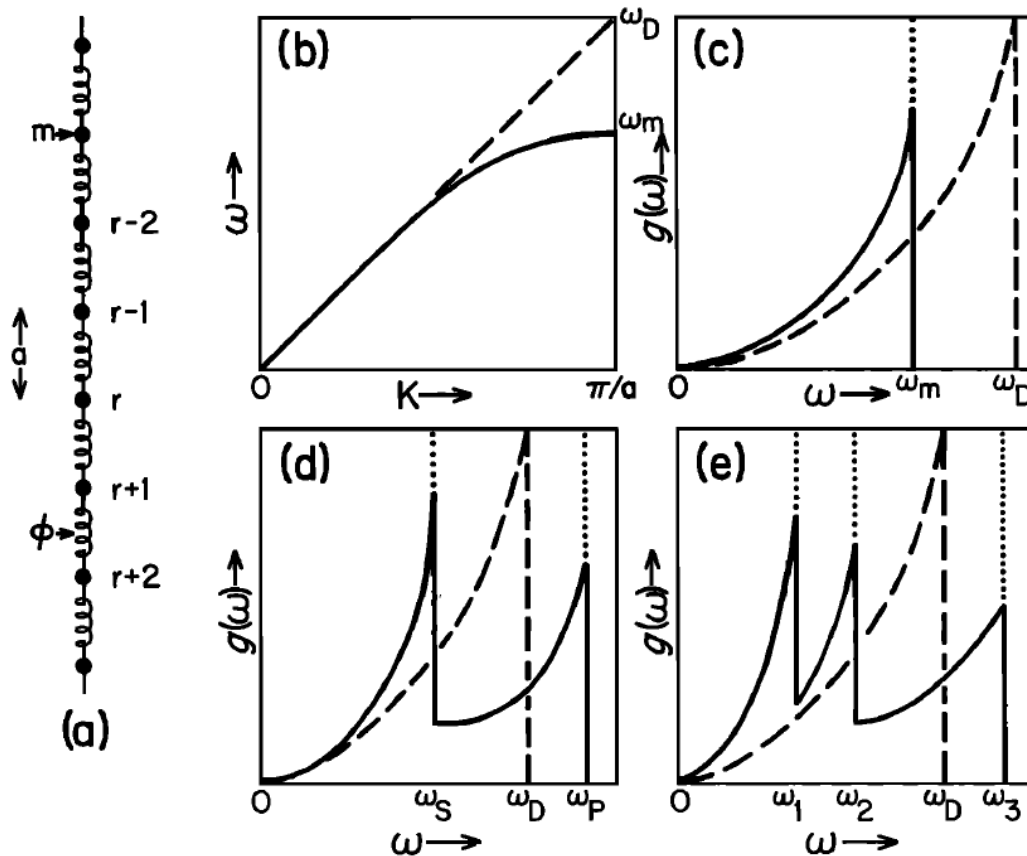


Fig. 2.2.1. (a) Linear monatomic chain. (b) Dispersion relation for monatomic chain (solid curve) compared to dispersion relation for Debye solid (dashed curve). (c) Vibrational spectrum of monatomic chain (solid curve) compared to Debye spectrum (dashed curve). (d) Vibrational spectrum of isotropic monatomic substance (solid curve), with separate P and S velocities, compared to Debye spectrum (dashed curve). (e) Vibrational spectrum of monatomic anisotropic solid (solid curve) with two shear velocities V_{S1} and V_{S2} , compared to the Debye spectrum (dashed curve). ω symbols for vibrational frequency correspond to ν in the text, $\mathbf{K}$ symbol for wave vector correspond to $\mathbf{q}$ in the text. $g(\omega)$ represents the vibrational density of state (vDOS). Taken from Kieffer (1979a).

The definition of single-crystal and aggregate seismic velocities and single-crystal seismic anisotropy (i.e. $V_{S,max}$ in equation 2.2.7) requires the calculation of the elastic constants tensor (C_{ijkl}). The second-order elastic constants (C_{ijkl}) of an ideally elastic solid can be derived from the relations between the stress (σ_{ij}) and strain tensors (ϵ_{kl}) according to Hooke's law:

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl} \quad (2.2.9)$$

which can be expressed in terms of static energy as:

$$\sigma_{ij} = \frac{1}{V} \left(\frac{\partial E}{\partial \epsilon_{ij}} \right)_0 \quad (2.2.10)$$

The components of the elastic constant tensor (*stiffnesses*) are related to the second derivative of the total energy with respect to strain components:

$$C_{ijkl} = \frac{1}{V} \left(\frac{\partial^2 E}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right)_0 \quad (2.2.11)$$

and can then be derived analytically by fitting the total energy vs. strain curves calculated for different types of deformation of the cell.

Once the full elastic constants tensor has been determined, the single-crystal seismic anisotropy can be defined by means of the well-known Christoffel equation (cf. Musgrave, 1970):

$$\sum_k a_k (T_{ik} - \rho V^2 \delta_{ik}) = 0 \quad (2.2.12)$$

where:

$$T_{ik} = \sum_{j,l} C_{ijkl} n_j n_l \quad (2.2.13)$$

and $\mathbf{a}$ is the polarization vector that defines the direction of displacement, $\mathbf{n}$ is the unit vector defining the direction of propagation, ρ the density of the phase, V the phase velocity of the wave and δ_{ij} a Kronecker delta. The Christoffel equation can be treated as an eigenvalue problem solving a Christoffel determinant:

$$|C_{ijkl} n_j n_l - \rho V^2 \delta_{ik}| = 0 \quad (2.2.14)$$

namely a 3×3 symmetric matrix, which, once the direction of propagation is fixed and the elastic constant tensor defined, has three real roots given by the values of a quasi-longitudinal wave (V_P) and two quasi-shear wave (V_{S1} and V_{S2}), with $V_P > V_{S1} > V_{S2}$.

The elastic (bulk modulus and shear modulus) and seismic properties (V_P and V_S) of homogeneous isotropic polycrystalline aggregates can then be derived from single-crystal elastic constants by means of different empirical averaging schemes derived from material science and engineering, like for example the Voigt-Reuss-Hill scheme (VRH; Hill, 1952). The VRH scheme defines the elastic moduli (bulk modulus, K_{VRH} and shear modulus, μ_{VRH}) of isotropic polycrystalline aggregates as the arithmetic mean value of two bounds, a lower Reuss bound (K_R or μ_R) and an upper Voigt bound (K_V or μ_V), corresponding to the assumption of a condition of isostress (slipping grain boundaries) or isostrain (locked grain boundaries) in the aggregate. The Reuss and Voigt bounds are defined through the following general relations:

$$K_V = \frac{1}{9} \times (c' + 2c'') \quad (2.2.17)$$

$$K_R = (s' + 2s'')^{-1} \quad (2.2.18)$$

$$\mu_V = \frac{1}{15} \times (c' - c'' + 3c''') \quad (2.2.19)$$

$$\mu_R = 15 \times (4s' - 4s'' + 3s''')^{-1} \quad (2.2.20)$$

where c' and s' are the sum of the diagonal stiffnesses c_{11} , c_{22} , c_{33} and compliances s_{11} , s_{22} , s_{33} respectively; c'' and s'' are the sum of the off-diagonal terms c_{12} , c_{13} , c_{23} and s_{12} , s_{13} , s_{23} ; c''' and s''' is the sum of the diagonal terms c_{44} , c_{55} , c_{66} and s_{44} , s_{55} , s_{66} . The average bulk modulus and shear modulus can be finally determined as:

$$K_{VRH} = \frac{1}{2}(K_V + K_R) \quad (2.2.21)$$

$$\mu_{VRH} = \frac{1}{2}(\mu_V + \mu_R) \quad (2.2.22)$$

and the aggregate longitudinal ($V_{P,VRH}$) and shear ($V_{S,VRH}$) seismic velocities as:

$$V_{P,VRH} = \sqrt{\frac{\left(K_{VRH} + \frac{4}{3}\mu_{VRH}\right)}{\rho}} \quad (2.2.23)$$

$$V_{S,VRH} = \sqrt{\frac{\mu_{VRH}}{\rho}} \quad (2.2.23)$$

where ρ is the density of the aggregate.

2.3. Mode Grüneisen parameters in the framework of Quasi-Harmonic Approximation (QHA)

Within the frame of standard quantum-chemical methods, temperature can be modelled by explicitly treating the lattice dynamics. To do so, a harmonic approximation (HA) to the lattice potential is commonly adopted, which proves extremely effective in predicting vibrational properties (such as Infrared and Raman spectroscopic features, for instance) of a variety of materials, particularly so when very light atoms are not involved.

However, when the lattice dynamics of a crystal is solved within the purely HA, vibrational frequencies are described as independent of interatomic distances and the

corresponding vibrational contribution to the internal energy of the crystal turns out to be independent of volume. It follows that, within such an assumption, a variety of physical properties would be wrongly described: if phonons are free to “travel” across the crystal devoid of reciprocal interactions, thermal conductivity, which originates from the phonon-phonon collisions and phonon scattering in the lattice, will be infinite. A significant implication that concerns thermodynamic is that thermal expansion would be null, and hence the isochoric heat capacity (C_V), which is supposed to attain a well-known limit at high temperature corresponding to the Dulong-Petit limit (which is equal to $3nR$, where n is the number of atoms in the unit formula of the substance and R is the gas constant), would coincide with the isobaric heat capacity (C_P), in contrast with theory and experimental results as well.

A simple and powerful approach for correcting most of the above-mentioned deficiencies of the HA is represented by the so-called Quasi-Harmonic Approximation (QHA), which introduces the missing volume dependence of phonon frequencies by assuming that the vibrations are considered harmonic about the new equilibrium positions of the atoms in the new expanded or compressed state. Within this framework, isochoric and isobaric heat capacity do not coincide and are related with each other through an anharmonicity term that depends on the volume, on the isothermal compressibility (β_T) and on the isobaric volume thermal expansion coefficient (α_V):

$$C_P = C_V + TV \frac{\alpha_V^2}{\beta_V} = C_V + TV \alpha_V^2 K_T \quad (2.3.1)$$

where $K_T = \frac{1}{\beta_V}$ is the isothermal bulk modulus of the substance.

Within the framework of the QHA, the volume dependence of vibrational mode is expressed by means of the mode Grüneisen parameter (γ_i), which is defined as:

$$\gamma_i = - \frac{\partial \ln \nu_i}{\partial \ln V} \quad (2.3.2)$$

where ν_i is the frequency of the i^{th} vibrational mode of the crystal. The ab initio analysis of mode Grüneisen parameters is carried out in this work by repeating the vibrational frequencies calculation as described in section 2.2 at various compressed/expanded volume states and fitting the results with a 2nd-order polynomial function. The mode-gamma Grüneisen parameters have a crucial role in defining the values of fundamental thermodynamic properties, such as thermal expansivity, thermal EOS, isobaric heat capacity, Gibbs free energy, and so on, as will be described in the next section.

2.4. Partition function and thermodynamic properties calculation

The calculation of the vibrational frequencies (and phonon dispersion) in the harmonic approximation and the mode Grüneisen parameters in the QHA are the main ingredients for the computation of thermodynamic properties. The link between the microscopic and macroscopic view is made possible by a fundamental entity, derived from statistical mechanics, which is the partition function (Q). The partition function gives an atomistic foundation to thermodynamics (like quantum mechanics gives it to classical physics). The general partition function has different contributions (vibrational, rotational, translational, electronic, magnetic, defectual, etc.) and can thus be defined as:

$$Q = Q_{vib} + Q_{trasl} + Q_{rot} + Q_{el} + \dots = \sum_i e^{-\frac{E_i}{kT}} \quad i = 1, 2, \dots, n \quad (2.4.1)$$

where T is the absolute temperature (in Kelvin), k the Boltzmann constant and E_i the eigenvalues of the energy operators defining the n energy levels in the electronic structure (n is an integer expressing the value of the principal quantum number). E_i are thus given by:

$$E_i = \frac{1}{2} \hbar \nu_i, \frac{3}{2} \hbar \nu_i, \frac{5}{2} \hbar \nu_i, \dots (2.4.2)$$

where $\hbar$ is the Plank constant and ν_i is the frequency of the i^{th} vibrational mode of the crystal. If we consider insulating, defect-free and ordered crystalline solids (as all the compounds investigated in this work), the general partition function reduces to its vibrational counterpart. Once the vibrational partition function (Q_{vib}) is defined, the phonon contribution to relevant thermodynamic properties results according to the following equations for the Helmholtz free energy (F_{vib}), internal energy (U_{vib}), isochoric heat capacity (C_V) and entropy (S_{vib}), respectively:

$$F_{\text{vib}} = -kT \ln Q = \frac{1}{2} \sum_{i=1}^{3N} \hbar \nu_i + kT \sum_{i=1}^{3N} \ln \left(1 - e^{-\frac{\hbar \nu_i}{kT}} \right) (2.4.3)$$

$$U_{\text{vib}} = - \left(\frac{\partial \ln Q}{\partial (kT)^{-1}} \right)_V = \frac{1}{2} \sum_{i=1}^{3N} \hbar \nu_i + \sum_{i=1}^{3N} \frac{\hbar \nu_i}{\left(e^{\frac{\hbar \nu_i}{kT}} - 1 \right)} = U_{\text{ZPC}} + U_{\text{th}} (2.4.4)$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = k \sum_{i=1}^{3N} e^{\frac{\hbar \nu_i}{kT}} \left(\frac{e^{\frac{\hbar \nu_i}{kT}}}{e^{\frac{\hbar \nu_i}{kT}} - 1} \right)^2 (2.4.5)$$

$$S_{\text{vib}} = - \left(\frac{\partial F}{\partial T} \right)_V = \frac{1}{T} \sum_{i=1}^{3N} \left(\frac{\hbar \nu_i}{e^{\frac{\hbar \nu_i}{kT}} - 1} \right) - k \sum_{i=1}^{3N} \ln \left(1 - e^{-\frac{\hbar \nu_i}{kT}} \right) (2.4.6)$$

where N represents, in this case, the number of atoms in the unit cell of the crystal and $3N$ the degrees of vibrational freedom (that is, the total number of vibrational modes in the crystal: 3 acoustic and $3N - 3$ optic). In eq. (2.4.4) the term U_{ZPC} is the zero-point correction accounting for the contribution of the zero-point motions to the internal energy at $T=0$ K. If a full phonon dispersion calculation is available, the modal

frequency ν_i in eqs. (2.4.3) - (2.4.6) is replaced with $\nu_i(\mathbf{q})$ and the summations extended to the $\mathbf{q}$ -points grid used to sample the reciprocal space.

Vibrational enthalpy and Gibbs free energy can be derived from the fundamental thermodynamic relations:

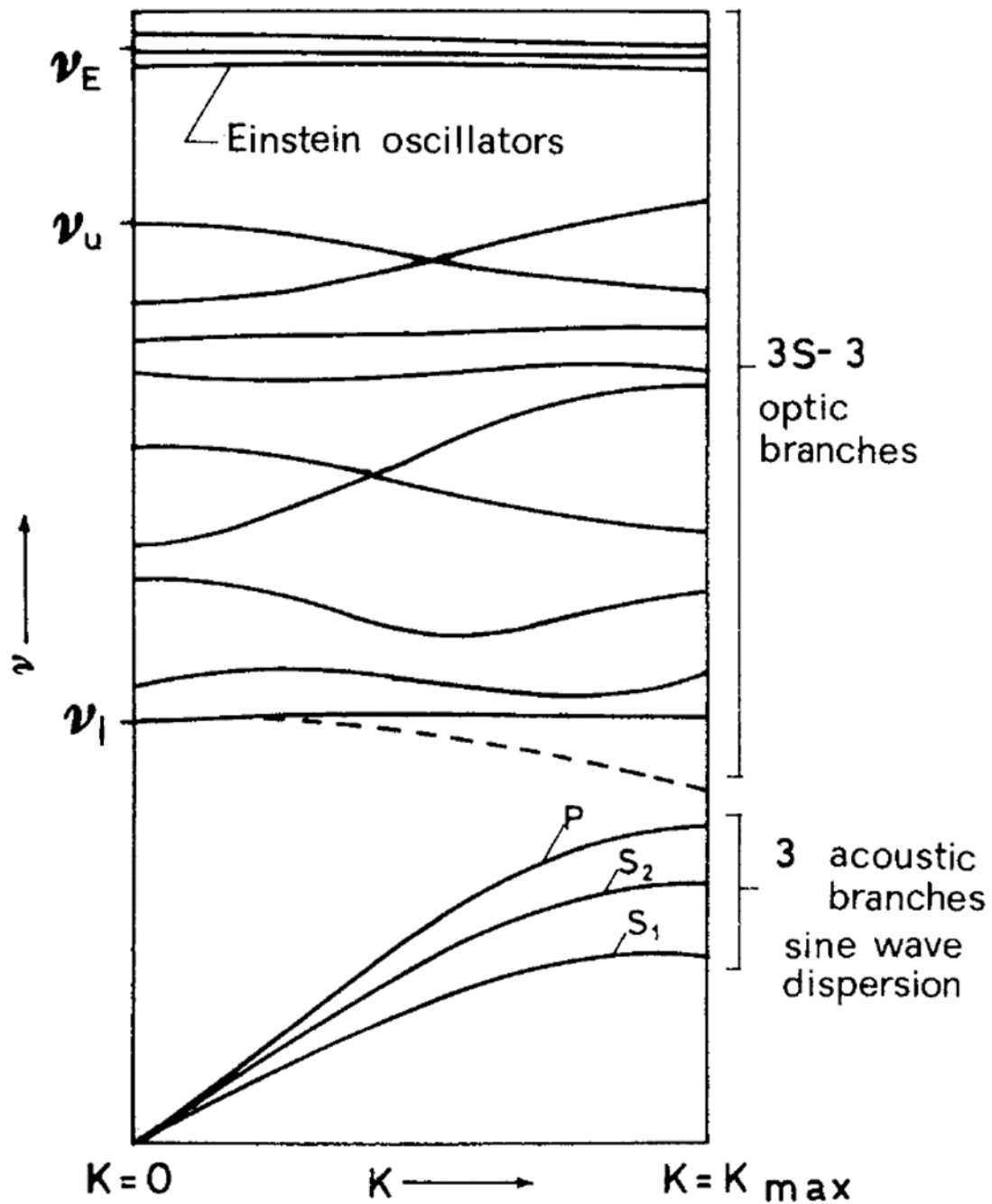
$$H_{vib} = U_{vib} + PV \quad (2.4.7)$$

$$G_{vib} = F_{vib} + PV \quad (2.4.8)$$

The calculation of thermodynamic properties via eq. (2.4.4) – (2.4.6) is possible whenever the full phonon dispersion is available, for example via the supercell approach described in section 2.2. If the computational cost prevents full phonon dispersion calculations, modelling the vDOS (vibrational density of states) in a more or less approximated way is the only way to compute thermodynamic properties. The idea of a simple representation of thermodynamic properties through the frequency distribution of phonons over the entire vibrational spectra of crystalline solids was first proposed by Einstein (1906) and then by Debye (1912). These models rely on the assumption that the thermodynamic properties calculation is roughly independent from the details of the vDOS, which can be then strongly simplified. Although these models work well for certain compounds, their approximation of the vDOS is too rough and oversimplified.

A still approximated, but more rigorous, evolution of the Debye model has been proposed by Susan Kieffer in a series of seminal papers (Kieffer, 1979a, 1979b, 1979c, 1979d). In the Kieffer's model the three acoustic modes obey a sinusoidal (and not linear as in the Debye model) dispersion law and three different vDOS are associated with those modes (Fig. 2.4.1). The phonon dispersion of the $3N - 3$ optic modes (where N represents the number of atoms in the unit cell of the crystal) is described in the low- and medium frequency range by an optical continuum defined at its boundaries by two cut-off frequencies (a lower cut-off, ν_l ; and an upper cut-off,

ν_u). In the high-frequency region, the optic modes are described by non-interacting Einstein oscillators of frequency ν_E , without any kind of dispersion across the first BZ and with a different (relative) weight in the thermodynamic integration.



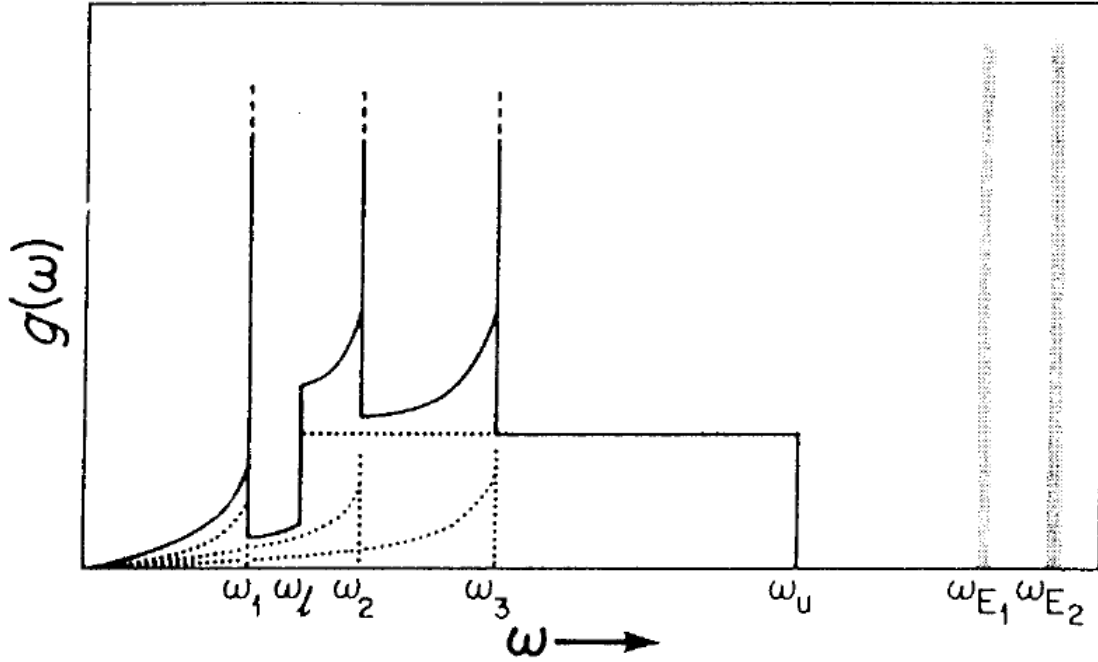


Figure 2.4.1. Phonon dispersion relations (upper figure) and vDOS (lower figure) of acoustic modes, optic modes, and Einstein oscillators according to the Kieffer's model. ω symbols for vibrational frequency in the lower figure correspond to ν in the upper figure and in the text. $\mathbf{K}$ symbol for wave vector correspond to $\mathbf{q}$ in the text. S in the Figure corresponds to N in the text (i.e. the number of atoms in the unit cell). Taken from Kieffer (1979a).

The Kieffer's model is nonetheless affected by some assumptions, mainly related to the empirical definition of some parameters, in particular:

- ❖ The cut-off limits of the optical continuum are defined as the lowest and the highest optical frequency measured via IR and Raman spectroscopy, thus assuming that all IR-active and Raman-active modes can be detected by experimental studies (even those with a low intensity).
- ❖ The silent modes (inactive to both Raman and IR) are disregarded, as well as the possibility they could define the cut-off frequencies of the optical continuum.
- ❖ The relative weight assigned to the Einstein oscillators in the thermodynamic integration which defines the vDOS is a purely adjustable parameter.

- ❖ More generally, the Kieffer's model lacks a detailed description of the full phonon spectrum of crystalline solids, which can be important to define the model parameters, although the definition of thermodynamic properties is often roughly independent from the finest details of the vDOS.

For these reasons, a modified Kieffer's model based on the *ab initio* calculation of the vibrational frequencies of all the modes of a crystalline solids at Γ point has been developed and employed with success on a variety of crystalline compounds (Ottonello et al., 2009a; Ottonello et al., 2009b; Belmonte et al., 2014; Belmonte et al., 2016) as a valid and “low-cost” alternative to rather expensive full phonon dispersion calculations employing supercells. The main resemblance with the Kieffer's model is that the sinusoidal dispersion relation for the three acoustic modes is retained. The main difference is that even the optic modes in the low- and medium frequency range of the phonon spectrum are considered as non-interacting Einstein oscillators without any kind of dispersion across the BZ and can be obtained directly from a routine calculation of vibrational frequencies at Γ point that, together with the quasi-harmonic analysis of vibrational modes, allows for the calculation of thermodynamic properties. The statistical mechanics equations (2.4.4) – (2.4.6) to calculate thermodynamic properties can be restated in the modified Kieffer's model formalism as:

$$U_{vib} = \frac{3RT}{Z} \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \int_0^{X_i} \frac{\left[\arcsin\left(\frac{X}{X_i}\right)^2\right] X dX}{(X_i^2 - X)^{\frac{1}{2}}(e^X - 1)} + \frac{RT}{Z} \sum_{i=4}^{3N} X_i \left(\frac{1}{2} + \frac{1}{(e^{X_i} - 1)}\right) \quad (2.4.9)$$

$$C_V = \frac{3R}{Z} \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \int_0^{X_i} \frac{\left[\arcsin\left(\frac{X}{X_i}\right)^2\right] X^2 e^X dX}{(X_i^2 - X)^{\frac{1}{2}}(e^X - 1)} + \frac{R}{Z} \sum_{i=4}^{3N} e^{X_i} \left(\frac{X_i}{e^{X_i} - 1}\right)^2 \quad (2.4.10)$$

$$\begin{aligned}
S_{vib} = & \frac{3R}{Z} \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \int_0^{X_i} \frac{\left[\arcsin\left(\frac{X}{X_i}\right)\right]^2}{(X_i^2 - X)^{\frac{1}{2}}(e^X - 1)} X dX \\
& - \frac{3R}{Z} \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \int_0^{X_i} \frac{\left[\arcsin\left(\frac{X}{X_i}\right)\right]}{(X_i^2 - X)^{\frac{1}{2}}} \ln(1 - e^{-X}) dX \\
& + \frac{R}{Z} \sum_{i=4}^{3N} \left(\frac{X_i}{e^{X_i} - 1} - \ln(1 - e^{-X_i}) \right) \quad (2.4.11)
\end{aligned}$$

where R is the gas constant, n is the number of atoms in the unit cell, Z is the number of formula units in the unit cell and:

$$X_i = \frac{\hbar \omega_i}{kT} \quad (2.4.12)$$

are the adimensionalized vibrational frequencies. In equations (2.4.9) – (2.4.11) the first summation on the right-hand side refers to the three sinewave dispersed acoustic modes ($i = 1, 2, 3$), defining thus the acoustic contribution to thermodynamic properties; the second summation to the non-dispersed optic modes, defining the optical contribution to thermodynamic properties.

2.5. Calculation of thermoelastic properties

Thermoelastic properties of solids can be derived by the quasi-harmonic analysis of the vibrational modes of the atoms in a crystal lattice. The key quantity is represented by the αK_T product, which is defined as:

$$\alpha K_T = \left(\frac{\partial P}{\partial T} \right)_V = - \frac{\partial}{\partial V} \left[\left(\frac{\partial F}{\partial T} \right)_V \right]_T \quad (2.5.1)$$

By considering eq. (2.4.3) we obtain the following expression:

$$\alpha K_T = \frac{R}{ZV} \sum_{i=1}^{3n} \gamma_i e^{X_i} \left(\frac{X_i}{e^{X_i} - 1} \right)^2 \quad (2.5.2)$$

where R is the universal gas constant; Z is the number of unit formula in the (primitive) unit cell; V is the molar volume expressed in J/bar; γ_i is the mode Grüneisen parameter of the i^{th} vibrational mode as already defined in section 2.3. X_i is, again, the adimensionalized frequency of the i^{th} vibrational mode:

$$X_i = \frac{\hbar \omega_i}{kT} \quad (2.5.3)$$

where $\hbar$ and k represent Planck and Boltzmann constants, respectively, ω_i is the radial frequency and T is temperature. The summation in (2.5.2) should be done for each of the vibrational modes sampled at discrete $\mathbf{q}$ points in the BZ in such a way as to take into account the effect of phonon dispersion. Namely, equation (2.5.2) should be written as:

$$\alpha K_T = \frac{R}{ZV} \sum_{i=1}^{3n} \gamma_i(\mathbf{q}, V) e^{X_i(\mathbf{q}, V)} \left(\frac{X_i(\mathbf{q}, V)}{e^{X_i(\mathbf{q}, V)} - 1} \right)^2 \quad (2.5.4)$$

The same procedure can be applied to eqs. (2.4.3) - (2.4.6) if a supercell is adopted and the full phonon dispersion is considered.

If vibrational frequencies are only available at Γ point, the αK_T product can be approximated as in eq. (2.5.2) neglecting the contribution of the first three acoustic modes to the αK_T product. This approximation is more valid the more is the total number of vibrational frequencies (viz. the number of atoms in the unit cell). For example, Belmonte (2017) showed that in the case of MgO periclase, which has two atoms in the primitive unit cell, hence six vibrational modes, disregarding the three acoustic frequencies translates into losing as much as 50% contribution to the

thermodynamic properties. On the other hand, this approximation works well for example on sapphirine (Belmonte et al., 2014), which has 136 atoms in the primitive unit cell, hence $3N = 408$ vibrational modes, with a contribution of the three acoustic modes to thermodynamic properties of less than 1%.

Since there are no explicit statistical mechanics relations for α_V (i.e.: the volume thermal expansion coefficient) or K_T (i.e.: the isothermal bulk modulus), it is necessary to determine discrete values of one of the two parameters, and then employ the αK_T relation to determine the second one. Our approach consists in calculating K_T at discrete temperatures and then divide αK_T by K_T to obtain discrete values of α_V . According to the thermodynamic definition of the bulk modulus, i.e.:

$$K_T = -V_T \left(\frac{\partial P}{\partial V} \right)_T = V_T \left(\frac{\partial^2 F}{\partial V^2} \right)_T \quad (2.5.5)$$

one way to determine K_T is by fitting either F-V-T (Helmholtz free energy – volume – temperature) or P-V-T (pressure – volume – temperature) data with a given isothermal equation of state (like the 3rd-order Birch-Murnaghan EOS, BM3-EOS). If free energies at compressed states are available, one can proceed with the (numerical) finite difference calculation of the second derivatives of the free energy to derive K_T and the other relevant thermodynamic properties: in principle, this should be the best choice from a theoretical point of view, avoiding possible numerical inconsistencies. Nevertheless, the number of F-V-T data to be fitted is usually not so high, especially if a full phono dispersion calculation with supercells is employed, so a more practical method is to perform a P-V fitting at different temperatures with a HT BM3-EOS. One way to determine P-V-T relations for solids from first principles is to employ the Mie-Grüneisen equation of state (MG-EOS), which has the advantage of being firmly grounded on the lattice dynamics theory of crystal lattices. The MG-EOS formalism splits pressure into its different contributions (namely static and vibrational, the latter being in turn split into zero-point correction and thermal contributions):

$$P(V, T) = -\left(\frac{\partial F}{\partial V}\right)_T = P_{static}(V) + P_{ZPC}(V) + P_{th}(V, T) \quad (2.5.6)$$

In the statistical mechanics notation, eq. (2.5.6) can be restated as:

$$P(V, T) = -\left(\frac{\partial U_{st}}{\partial V}\right)_T + \frac{kT}{2V} \sum_{i=1}^{3n} \gamma_i(\mathbf{q}, V) X_i(\mathbf{q}, V) + \frac{kT}{V} \sum_{i=1}^{3n} \gamma_i(\mathbf{q}, V) \left(\frac{X_i(\mathbf{q}, V)}{e^{X_i(\mathbf{q}, V)} - 1} \right) \quad (2.5.7)$$

If vibrational frequencies at different volumes and mode Grüneisen parameters are available from ab initio phonon dispersion calculations, then a first principles Mie–Grüneisen equation of state (FPMG-EOS) will be obtained by plugging in $X_i(\mathbf{q}, V)$ and $\gamma_i(\mathbf{q}, V)$ values in eq. (2.5.7). Computed P-V-T data can then be fitted with an open-source software, like EoSFit (Angel et al., 2014). This not only gives as a result discrete values of K_T at different temperatures, thus providing information also on the temperature derivative of the bulk modulus, i.e. $\left(\frac{\partial K_T}{\partial T}\right)_P$, but also yield K'_T values at discrete temperatures (i.e. the mixed P-T derivative of the bulk modulus, a thermoelastic parameter of great interest in modelling material properties at simultaneous HP-HT conditions, which is quite difficult to constrain by experiments and is often assumed as constant).

Discrete values of α_V can now be obtained by dividing αK_T by K_T and by fitting them with a suitable polynomial function in the form:

$$\alpha_V(P_0, T) = \alpha_0 T + \alpha_1 + \alpha_2 T^{-1} + \alpha_3 T^{-2} + \alpha_4 T^{-3} \quad (2.5.8)$$

The last ingredient required to determine the anharmonic contribution to the thermodynamic properties is the volume of the substance at discrete temperatures, which can be obtained starting from the definition of the volume thermal expansion coefficient, i.e.:

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (2.5.9)$$

from which we have:

$$V_T = V_0 e^{\int_0^T \alpha_V \partial T} \quad (2.5.10)$$

Once values of $\alpha_{V,T}$, K_T and V_T are known, isobaric heat capacity (C_P) and entropy (S) come out by including the anharmonicity contribution (which is equal to $TV\alpha_V^2 K_T$) in eqs. (2.4.5) and (2.4.6):

$$C_P(P_0, T) = C_V(V, T) + TV\alpha_V^2 K_T \quad (2.5.11)$$

$$S(P_0, T) = S_{vib}(V, T) + \frac{R}{Z} \ln(Q_e) + \int_0^T V\alpha_V^2 K_T dT \quad (2.5.12)$$

The second term in eq. (2.5.12) is the electronic contribution arising from spin multiplicity (here identically equal to zero). The first terms in eqs. (2.5.11) and (2.5.12) can be determined either from eqs. (2.4.5) and (2.4.6), or from eq. (2.4.10) and (2.4.11), depending on whether the full phonon dispersion is available or a modified Kieffer's model is employed in the thermodynamic calculation. Discrete values of C_P are then fitted with a suitable polynomial function, like the Haas-Fisher polynomial function (Haas and Fisher, 1976):

$$C_P = a + bT + cT^{-2} + dT^2 + eT^{-\frac{1}{2}} \quad (2.5.13)$$

or, alternatively, the Shomate equation for C_P (Shomate, 1954), adopted by the National Institute of Standards and Technology (NIST):

$$C_p = a + bT + cT^{-2} + dT^{-\frac{1}{2}} + eT^{-3} + fT^2 + gT^3 \quad (2.5.14)$$

2.6. Calculation of standard state enthalpy

Calculation of the ab initio enthalpy of formation from the elements of a substance requires the assessment of a thermochemical cycle of the type (cf. Belmonte et al., 2014 for details):

$$\bar{H}_{f,298.15}^0 = (\Delta U_{298.15-0} + P\Delta V_{298.15-0}) - D_0 + \sum_{i=1}^{\frac{n}{Z}} n_i H_{f,A_i,0} - \sum_{i=1}^{\frac{n}{Z}} n_i \Delta H_{element_i,0 \rightarrow 298.15} \quad (2.6.1)$$

where the term within brackets is the thermal correction to the enthalpy at 298.15 K, $H_{f,A_i,0}$ is the enthalpy of formation of the i -th gaseous atom from the stable element at $T = 0$ K, $P = 1$ bar (with the summation extended to the n/Z atoms in the molecule), $\Delta H_{element_i,0 \rightarrow 298.15}$ is the enthalpy difference between $T = 298.15$ K and $T = 0$ K for the monatomic elements and D_0 is the zero-point dissociation energy of the gaseous molecule into gaseous atoms at 0 K, i.e.:

$$D_0 = \sum_{i=1}^{n/Z} n_i E_{A_i} - (E_{0,DFT,crystal} + E_{ZPE,crystal}) \quad (2.6.2)$$

This energy term corresponds to the sum of the electronic energies of the gaseous atoms at 0 K minus the electronic + zero-point energy of the crystal. E_{A_i} , $H_{f,A_i,0}$ and $\Delta H_{element_i,0 \rightarrow 298.15}$ values are taken from Table 6 in Belmonte et al. (2014). As a rule of thumb, the procedure allows to reproduce enthalpies of formation within 1–2% of uncertainty with respect to experimental data, essentially due to the difficulty in estimating appropriate electronic energies for the isolated gaseous atoms (E_{A_i} terms in eq. 2.6.2).

2.7. Gibbs free energy minimization and phase equilibria calculation

The coexistence of pure solid phases at equilibrium conditions can be adequately described by reversible chemical reactions between the phases major components. Mineralogical phases with fixed composition and end-members phases of solid mixtures fall within the definition of “pure phases”. From a thermodynamic point of view, at any given P , T conditions a univariant phase equilibrium between pure solid phases depends solely on the pressure and temperature conditions at which the Gibbs free energy (G) of the system is minimized, i.e.:

$$\Delta G_{reaction}(P, T) = 0 \quad (2.7.1)$$

Considering a generic reaction where a reactant phase (a) transforms into a product phase (b), eq. (2.7.1) at equilibrium can be rewritten as:

$$G_{prod,b}(P, T) - G_{react,a}(P, T) = 0 \quad (2.7.2)$$

The theoretical approach to phase equilibria calculation is to calculate the values of the Gibbs free energy of all the phases involved in the reaction of interest at any given P , T conditions and then to minimize the Gibbs free energy of the reaction at those P and T (cf. eqs. 2.7.1-2.7.2). The main ingredients that allow for the calculation of the Gibbs free energy are represented by the thermodynamic functions for all the phases of interest, which are calculated by first principles following the guidelines described in the sections above. In the following passages, the link between the Gibbs free energy and the other thermodynamic properties is shown in detail. Starting from the state functions H and S , their exact differentials lead to the Gibbs equations:

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \quad (2.7.3)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad (2.7.4)$$

Since:

$$\left(\frac{\partial H}{\partial T} \right)_P = C_P \quad (2.7.5)$$

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P \quad (2.7.6)$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T} \quad (2.7.7)$$

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad (2.7.8)$$

substituting eqs. (2.7.5)-(2.7.8) in (2.7.3) and (2.7.4) yields:

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (2.7.9)$$

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP \quad (2.7.10)$$

By considering the following definite integrals:

$$\int_{T_r, P_r}^{T, P} dH = H_{T, P} - H_{T_r, P_r}^0 = \int_{T_r}^T C_P dT + \int_{P_r}^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (2.7.11)$$

$$\int_{T_r, P_r}^{T, P} dS = S_{T, P} - S_{T_r, P_r}^0 = \int_{T_r}^T \frac{C_P}{T} dT - \int_{P_r}^P \left(\frac{\partial V}{\partial T} \right)_P dP \quad (2.7.12)$$

where T_r is the reference ambient temperature (i.e. 298.15 K) and P_r is the reference ambient pressure (i.e. 1 bar), the enthalpy and entropy of the phase at any given T and P can thus be written as:

$$H_{T,P} = H_{T_r,P_r}^0 + \int_{T_r}^T C_P dT + \int_{P_r}^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (2.7.13)$$

$$S_{T,P} = S_{T_r,P_r}^0 + \int_{T_r}^T \frac{C_P}{T} dT - \int_{P_r}^P \left(\frac{\partial V}{\partial T} \right)_P dP \quad (2.7.14)$$

The integrals in dT can be solved by adopting a polynomial function able to reproduce the ab initio values of C_P (see for instance eq. 2.5.14 or eq. 2.5.15).

The Gibbs free energy of a pure phase at whatever pressure and temperature conditions can finally be written as:

$$G_{T,P} = H_{T,P} - TS_{T,P} = H_{T_r,P_r}^0 - TS_{T_r,P_r}^0 + \int_{T_r}^T C_P dT - \int_{T_r}^T \frac{C_P}{T} dT + \int_{P_r}^P V dP \quad (2.7.15)$$

The last integral in eq. (2.7.15) represents the contribution of pressure to the Gibbs free energy, which can have a determinant role in the case of phase equilibria occurring at very HT-HP conditions. To solve it, we adopt a procedure developed by Ganguly (2020). We first split it into two contributions:

$$\int_{P_r}^P V dP = \int_{P_r V(P_r)}^{PV(P)} d(PV) - \int_{V_r}^V P dV = [PV(P) - P_r V(P_r)] - \int_{V_r}^V P dV \quad (2.7.16)$$

The remaining PdV integral can be solved by adopting an equation of state like the 3rd order Birch-Murnaghan EOS already mentioned in the previous sections, i.e.:

$$P(V) = \frac{3}{2}K_0 \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4}(K'_0 - 4) \left[\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\} \quad (2.7.17)$$

By expanding in Taylor series and integrating we have:

$$\int_{V_r}^V P dV = \frac{9}{4}K_0V_0^{\frac{5}{3}} \left[\frac{1}{V^{\frac{2}{3}}} - \frac{1}{2V^{\frac{4}{3}}} \right]_{V_r}^V + \frac{9}{16}K_0(K'_0 - 4) \left[\frac{1}{V^2} + \frac{3}{2V_0^{\frac{2}{3}}V^{\frac{4}{3}}} - \frac{1}{3V_0^{\frac{4}{3}}V^{\frac{2}{3}}} \right]_{V_r}^V \quad (2.7.18)$$

where:

K_0 = bulk modulus at $P=0$

K'_0 = bulk modulus pressure derivative at $P=0$

V_0 = molar volume at $P=0$

V = molar volume at P,T

The effect of temperature on the volume, on the other hand, is added by considering the volume thermal expansion as expressed by eqs. (2.5.8) and (2.5.10).

Up to this point, all the main entities that come into play to define the molar Gibbs free energy of a pure phase according to eq. (2.7.15) at any given P and T are provided by following the guidelines described above. By minimizing the ΔG of reaction at a given pressure, it is possible to calculate the equilibrium temperature and vice versa:

$$\Delta G_{reaction}(P, T) = \sum_i \nu_i G_{prod}(P, T) - \sum_i \nu_i G_{react}(P, T) \quad (2.7.19)$$

If $\Delta G_{reaction}(P, T) < 0$, the reaction occurs spontaneously at those P - T conditions and the products are stable. If $\Delta G_{reaction}(P, T) > 0$, the reaction is not spontaneous at those P - T conditions and the reactants will remain stable. If $\Delta G_{reaction}(P, T) = 0$, we have the phase equilibrium at those P - T conditions.

2.8. Computational approach to melting phase relations at HP-HT

An integrated theoretical and computational approach based on first principles calculations, polymer chemistry and equilibrium thermodynamics has been developed to obtain melting phase relations in multicomponent systems at HP-HT. This method has been already tested on binary (e.g. MgO-SiO₂, Al₂O₃-SiO₂, MgO-Al₂O₃, CaO-SiO₂ and CaO-Al₂O₃) and ternary (i.e. MAS, CAS) silicate systems (Ottonello et al., 2013; Belmonte et al., 2017a and 2017b). Phase diagram topology is computed in a wide range of P-T conditions by a Gibbs free energy minimisation algorithm which employs the convex-hull method to analyse equipotential surfaces in multi-component systems (see Attene and Ottonello, 2011; Natali et al., 2013; Ottonello et al., 2013; Belmonte et al., 2017a for details). Heat capacity (C_P), standard-state entropy ($S^{0}_{298.15}$) and enthalpy of formation from the elements ($H^{0}_{f,298.15}$) of the pure liquid components (i.e.: MgO and SiO₂) have been obtained from ab initio structure-energy and vibrational calculations performed with the Polarized Continuum Model (PCM) (Tomasi and Persico, 1994; Ottonello et al., 2010a; Belmonte et al., 2013). Thermophysical properties and equation-of-state parameters of the pure liquid components have been assessed in order to be consistent with the observed melting curves at HP-HT conditions. The Gibbs free energy of mixing (G_{mixing}) of the multi-component liquid phase is obtained via the Hybrid Polymeric Approach (HPA; see for instance Ottonello, 2005) as a sum of discrete contributions arising from different kinds of interaction among chemical species in the structure of a polymeric substance. The different energy terms are represented by a dominant chemical interaction taking place among polymeric units (structons), a subordinated interaction taking place in the cation matrix and a strain energy contribution arising from medium-range disorder of the various structons within the anion matrix, i.e.:

$$G_{\text{mixing}} = G_{\text{chemical}} + G_{\text{cat.mix-id}} + G_{\text{cat.mix-exc}} + G_{\text{strain}} \quad (2.8.1)$$

Since the liquid compositions investigated in this study have only one basic oxide in the cation matrix (i.e. MgO), the second and third terms on the right-hand side of eq. (2.8.1) are equal to zero and can be disregarded in the following. The chemical interaction between network formers (NF) and network modifiers (NM) constitutes by far the main form of energy gained (or lost) by the liquid in the mixing process. This energy can be expressed according to the Toop-Samis model (Toop & Samis, 1962a, 1962b) as:

$$G_{chemical} = \frac{(O^-)}{2} RT \ln K_P \quad (2.8.2)$$

Where $\frac{(O^-)}{2}$ (i.e. half the concentration of non-bridging oxygens in the melt structure) defines the number of contacts among the functionals of the polymeric units and K_P is the polymerization constant that describes the chemical energy acquired by the melt in a single interaction among different types of oxygen, i.e.:

$$K_P = \frac{(O^{2-}) \times (O^0)}{(O^-)^2} \quad (2.8.3)$$

where O^{2-} are free oxygens, O^0 bridging oxygens and O^- non-bridging oxygens. In the HPA model the polymerization constant can be expressed as:

$$\ln K_P = \frac{A}{T} + B \quad (2.8.4)$$

The A and B coefficients in eq. (2.8.4) acquire a precise thermodynamic meaning since they represent the enthalpic and entropic contributions to the chemical interaction energy between NF and NM per unit mole of contacts. If the effects of the direct interaction between network formers in the anion matrix (weighted on their fractional amount in the system) are added to the NF-NM chemical interaction along with an

excess energy term related to the electrostatic interactions of the NM sub-lattice, we have:

$$G_{chemical} = \frac{(O^-)}{2} RT \ln K_P + \left[\frac{(O^-)^*}{2} RT \ln K_{IJ} \right] \left(\frac{X_{NF}}{X_{NF} + X_{NM}} \right) + G_{excess} \quad (2.8.5)$$

Where X_{NF} and X_{NM} are the molar fractions of network formers and modifiers, respectively, $(O^-)^*$ is the molar amount of non-bridging oxygen involved in NF-NF interactions and K_{IJ} is the equilibrium constant defined for the I^{th} and J^{th} network-forming oxide species (i.e. Al_2O_3 and SiO_2 in the MAS system; just SiO_2 in the MgO- SiO_2 system).

The Hookean strain energy contribution to G_{mixing} (i.e. G_{strain} in eq. 2.8.1) represents the energy spent (or gained) in conforming the relative arrangement of the various polymers in the anion sub-lattice. This term is defined by following the same combinatorial rules for network formers and network modifiers (Ottonello, 2005), i.e.:

$$G_{strain} = \frac{(O^-)}{2} T \eta + \left[\frac{(O^-)^*}{2} T \eta^* \right] \left(\frac{X_{NF}}{X_{NF} + X_{NM}} \right) \quad (2.8.6)$$

$$\eta = \sum_{k=0}^{\eta} \eta_k \cdot (2X_{NF} - 1)^k \quad (2.8.7)$$

$$\eta_0 = \eta_{0,H} - \eta_{0,S} \times T + \eta_{0,V} \times P \quad (2.8.8)$$

The procedure to obtain the strain coefficients (η and η^* in eqs. 2.8.6–2.8.8) can be defined as an asymmetric Toop deconvolution (see Ottonello et al., 2013 for details). Moreover, the interactions within the cation and anion sub-lattices are mutually unaffected with respect to each other. As concerning the definition of the Gibbs free energy of mixing in the liquid aggregation state (along with its enthalpic, entropic and

volumetric components), the advantage of polymeric models is that the chemical interaction assumes a precise significance in terms of energy, based on the Lux-Flood acid-base reaction formalism (Lux, 1939; Flood and Förland, 1947). The number of contacts among polymer functionals [corresponding to half the molar amount of non-bridging singly-bonded oxygens, i.e. $(O^-)/2$] depends explicitly on the contrast in the donor and acceptor properties of the basic (MgO in our case) and acidic (i.e. SiO₂) oxides in the liquid mixture, expressed in terms of Pauling's electronegativity differences (cf. Ottonello, 2005). These assessments are however qualitative at best, and indirect estimates of the enthalpy of mixing per unit mole of melt or optical basicity contrast ($\bar{H}_{\text{mixing};T_f}$) may be obtained from the experimental values of the heat of fusion (ΔH_{fusion}) of solids nucleating in the binary system of interest by applying:

$$\bar{H}_{\text{mixing};T_f} = \frac{H_{\text{solid};T_f} + \Delta H_{\text{fusion}} - \sum_i \eta_i \mu_{i,\text{liquid};T_f}^0}{\sum_i \eta_i} \quad (2.8.9)$$

where μ_i and η_i are the chemical potential and the number of moles per formula unit of the i^{th} oxide in the liquid and the corresponding solid, respectively. By combining eqs. (2.8.4) and (2.8.9) with the topological features of the liquidus inferred from the T-X projection of binary phase diagrams, one acquires the decoupling between (chemical) enthalpic and entropic contributions to the Gibbs free energy of mixing (Belmonte et al., 2017a).

2.9. Computational details

In this section some details concerning the computational parameters adopted in this work for ab initio calculations will be addressed and discussed. All calculations presented in this thesis have been performed adopting the B3LYP hybrid functional, which contains a 20% of exact Hartree-Fock exchange mixed to GGA exchange-correlation (Lee et al., 1988; Becke, 1993). We employed this functional due to its corroborated performances in predicting vibrational, elastic and thermodynamic

properties of a wide variety of magnesium silicates of relevant geophysical and geochemical interest (e.g. Ottonello et al., 2009a, and 2010b; De La Pierre et al., 2011; Többsens and Kahlenberg, 2011; Prencipe et al., 2009 and 2012; Belmonte et al., 2014; De La Pierre and Belmonte, 2016; Belmonte, 2017; see also Section 3 of this Thesis). Basis set for Mg, Si and O atoms and computational parameters are the same as those used in previous investigations on dense magnesium silicates and oxides and consist of an 88-31G(d) contraction for silicon and an 8-411(d) set for oxygen, as proposed by Nada et al. (1996). For Mg we adopted the full re-optimization of the basis set proposed by Harrison et al. (1992) and McCarthy and Harrison (1994). Core electrons were described using atomic like orbitals resulting from a combination of 8 GTOs (Gaussian Type Orbitals). A combination of 5 GTOs described the valence region closer to the nuclei and two individual GTOs described the outer valence electrons in a split-valence basis set arrangement. A diffuse *d*-type function was added to better reproduce the anisotropic distortion of the valence shells. Both coefficients and exponents of the various GTOs were further reoptimized to better account for the periodicity of the investigated systems (cf. Ottonello et al., 2010b). The adopted basis set is shown in Table 2.9.1.

Tab 2.9.1. Basis set adopted in this work for Mg, Si and O		
Mg	Si	O
12 5	14 5	8 5
0 0 8 2. 1.	0 0 8 2.0 1.0	0 0 8 2.0 1.0
68371.875 0.0002226	149866.0 0.0001215	8966.29 0.0010
9699.34009 0.0018982	22080.6 0.0009770	1240.17 0.0091
2041.176786 0.0110451	4817.5 0.0055181	252.114 0.0513
529.862906 0.0500627	1273.5 0.0252000	70.359 0.1702
159.186000 0.169123	385.11 0.0926563	23.9025 0.3662
54.6848 0.367031	128.429 0.2608729	9.2075 0.3859
21.2357 0.400410	45.4475 0.4637538	3.9847 0.1471
8.74604 0.14987	16.2589 0.2952000	1.2266 0.0695
0 1 5 8. 1.	0 1 8 8.0 1.0	0 1 4 6.0 1.00
156.795 -0.00624	881.111 -0.0003	
0.00772	0.0006809	44.9344 -0.0098 0.0107

31.0339 -0.07882		
0.06427	205.84 -0.0050 0.0059446	10.3978 -0.0893 0.0670
	64.8552 -0.0368	
9.6453 -0.07992 0.2104	0.0312000	3.2970 -0.0373 0.2100
3.7109 0.29063 0.34314	23.9 -0.1079 0.1084000	1.2340 0.3730 0.3542
1.61164 0.57164 0.3735	10.001 0.0134 0.2378000	0 1 1 0.0 1.00
0 1 1 2. 1.	4.4722 0.3675 0.3560066	0.4536 1.0 1.0
0.68 1. 1.	2.034 0.5685 0.3410000	0 1 1 0.0 1.00
0 1 1 0. 1.	0.9079 0.2065 0.1326000	0.1810 1.0 1.0
0.224516 1. 1.	0 1 3 4.0 1.0	0 3 1 0. 1.
	2.6668 -0.0491	
0 3 1 0. 1.0	0.0465000	0.60 1.0
0.5 1.	1.0780 -0.1167 -0.1005000	
	0.3682 0.2300 -1.0329000	
	0 1 1 0.0 1.0	
	0.193 1.0 1.0	
	0 3 1 0. 1.	
	0.610 1.0	

Cut-off limits in the evaluation of Coulomb and exchange series appearing in the SCF equation for periodic systems (see Dovesi et al., 2014) have been set namely to 10^{-8} for coulomb overlap tolerance, 10^{-8} for coulomb penetration tolerance, 10^{-8} for exchange overlap tolerance, 10^{-8} for exchange pseudo-overlap in the direct space and 10^{-16} for exchange pseudo overlap in the reciprocal space for all MgSiO_3 pyroxenes (8 8 8 8 16, as written in the CRYSTAL input file). For beta-test Mg_2SiO_4 ringwoodite (see Chapter 3) a slightly tighter 8 8 8 9 18 has been employed instead. Convergence thresholds on total energy change between SCF cycles have been set to 10^{-8} Hartree for geometry optimization, static equation of state and elastic constants calculation, to 10^{-10} Hartree for vibrational frequency calculation.

Full geometry optimization (cell-edges and internal coordinates) was carried out with a symmetry-preserving relaxation procedure fully automatized in the CRYSTAL14 code. Convergence in the geometry optimization process was tested on the root-mean-square (RMS) and the absolute value of the largest component of both the gradients and nuclear displacements. The thresholds for the maximum and the RMS forces were set to 0.00012 and 0.00006 for all phases.

The reciprocal space is sampled according to a regular sublattice of $\mathbf{q}$ points according to the Monkhorst-Pack scheme (Monkhorst and Pack, 1976). The sampling of electronic states in the reciprocal space is defined by a shrinking factor IS corresponding to a certain number of $\mathbf{q}$ points in the IBZ. The $\mathbf{q}$ points mesh used to sample the reciprocal space in phonon dispersion calculation is different from that defined by the shrinking factor, inasmuch as it depends on the size of the (isotropic) supercell adopted in the calculation. As a rule of thumb, the bigger is the cell in the direct space, the smallest is the IS. The IS was set to 6 for all MgSiO_3 pyroxenes and to 4 for Mg_2SiO_4 ringwoodite.

Calculation of thermodynamic properties and Gibbs free energy has been performed by using in-house FORTRAN codes in which the statistical and thermodynamic relations presented in the previous sections are implemented.

3. Mg_2SiO_4 ringwoodite as beta test for hybrid DFT calculations

Part of this Chapter has been published in a paper to which I contributed as a co-author: Belmonte, D., La Fortezza, M. and Menescardi, F. (2022) Ab initio thermal expansion and thermoelastic properties of ringwoodite ($\gamma\text{-Mg}_2\text{SiO}_4$) at mantle transition zone conditions. *European Journal of Mineralogy*, **34**, 167-182, <https://doi.org/10.5194/ejm-34-167-2022>

3.1. Introduction

In order to test the performance of DFT calculations carried out with the most advanced exchange-correlation schemes, the initial part of this work is focused on the theoretical simulation of the vibrational, thermoelastic and thermodynamic properties of Mg_2SiO_4 ringwoodite which, due to its relatively simple spinel-type cubic structure, represents a “beta test” of our calculations. Ringwoodite, although quite different from MgSiO_3 phases, represents nonetheless a major constituent of the lowermost mantle transition zone, between 520 and 660 km depths, where its relative amount is estimated to be between ~40%vol and ~60%vol according to different compositional models of the Earth’s mantle (Ringwood, 1975; Bass and Anderson, 1984). Moreover, it is generally accepted that spinel and post-spinel phase transformations of olivine play a key role in determining global mantle discontinuities in the middle and bottom part of the transition zone (Bina and Helffrich, 1994; Sinogeikin et al., 2003; Ishii et al., 2019). Despite its importance and its abundance in the Earth’s interior, there are still large uncertainties on its thermodynamic and thermoelastic properties, especially at high pressure and temperature conditions. From a crystallographic point of view, ringwoodite is characterized by a simple cubic structure (space group $Fd\bar{3}m$) with a relatively low number of atoms in the primitive unit cell ($Z = 14$). This feature, along

with the uncertainties that currently affect its thermodynamic properties (especially the volume thermal expansivity, α_V) make ringwoodite an interesting candidate for testing a theoretical methodology based on state-of-the-art ab initio DFT calculations with hybrid functionals (i.e. B3LYP). DFT-QHA calculations on Mg_2SiO_4 ringwoodite thermodynamics were performed adopting both approaches described in Chapter 2, that is the vDOS was approximated either by calculating the full phonon dispersion of vibrational modes by the supercell method, or by a modified Kieffer's model starting from the ab initio calculation of phonon modes at Γ point only. Results are presented in this chapter and compared with available literature data, to check the performance of both methods in predicting thermodynamic properties of ringwoodite.

3.2. Computational method

DFT-QHA calculations performed on thermodynamic properties of Mg_2SiO_4 ringwoodite will be described in this chapter taking into account only the more relevant computational parameters, since a comprehensive guide on how to obtain thermodynamic properties from ab initio DFT-QHA calculations has been provided in Chapter 2. Cut-off limits in the evaluation of the Coulomb and Hartree-Fock exchange series are controlled by five parameters that were set to 8 8 8 9 18 to improve the numerical accuracy. The threshold on the self-consistent field (SCF) energy was set to 10^{-8} Hartree for the geometry optimization, and to 10^{-10} Hartree for the vibrational frequencies calculation. The reciprocal space was sampled according to a regular sublattice with shrinking factor (IS) = 4.

Vibrational frequencies of ringwoodite have been computed on the fully relaxed crystal structure performing the calculation both at Γ point, as well as on a large supercell ($2 \times 2 \times 2$), sampling $8 \vec{q}$ points in the reciprocal space. The volume dependence of vibrational frequencies has been defined in the framework of the quasi-harmonic

approximation (QHA) by repeating the vibrational frequencies calculations at the following volume conditions: $V/V_0 = 0.75, 0.78, 0.82, 0.86, 0.89, 0.93, 0.97, 1.00, 1.01, 1.06, 1.10$ (at Γ point) and $V/V_0 = 0.89, 0.92, 0.96, 0.98, 1.00$ (employing a supercell). Least-square fitting of vibrational frequencies computed at the volume conditions described above gives the values of γ_i for all modes (where γ_i is the mode gamma Grüneisen parameter as defined in section 2.3). Thermodynamic properties that depend on vibrational frequencies (i.e., heat capacities, volume thermal expansion, isothermal bulk modulus and its pressure and temperature derivatives, entropy) have then been computed in the framework of the quasi-harmonic approximation (QHA) using vibrational frequencies obtained at Γ point and with the $2 \times 2 \times 2$ supercell, applying mechanical-statistic relations as described in sections 2.4, 2.5, 2.6 and 2.7. P-V-T relations for ringwoodite were obtained applying the Mie-Grüneisen formalism at the same volume conditions described above. P-V-T data acquired in such way were then fitted by a high-temperature, 3rd order Birch-Murnaghan equation of state (HT-BM3-EOS), to derive P-T derivatives of the bulk modulus.

3.3. Seismic and elastic properties

Computed results on elastic and seismic properties of Mg_2SiO_4 ringwoodite will be briefly described in this section.

Table 3.3.1 shows our theoretical calculation for Mg_2SiO_4 ringwoodite elastic properties (elastic constant tensor [i.e. C_{11}, C_{12}, C_{44}], Voigt-Reuss-Hill bulk [K_{VRH}] and shear [μ_{VRH}] moduli, aggregate longitudinal-wave [$V_P(\text{km/s})$] and shear-wave seismic velocities [$V_S(\text{km/s})$]) at $P = 0$ and $T = 0$, as compared with reference data.

Table. 3.3.1. Ab initio B3LYP elastic properties of Mg₂SiO₄ ringwoodite as compared with molecular dynamics results (Li et al., 2006), DFT-LDA calculations performed with plane waves pseudopotentials (Kiefer et al., 1997) and experimental measurements by Brillouin spectroscopy (at T = 298.15 K) (Weidner et al., 1984; Jackson et al., 2000).

	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)	K _{V_{RH}} (GPa)	μ _{V_{RH}} (GPa)	V _P (km/s)	V _S (km/s)	ρ (g/cm ³)
This work (B3LYP)	327	116	138	186.38	123.8	10.03	5.95	3.49
Li et al. (2006)	315	106	127	176	118	9.83	5.85	3.45
Kiefer et al. (1997)	361	118	134	199	129	10.08	5.94	3.65
Weidner et al. (1984)	327±4	112±3	126±2	184	119	9.79	5.77	3.57
Jackson et al. (2000)	327(3)	114(2)	131(2)	185(3)	120(2)	9.85(6)	5.82(3)	3.56

As can be seen, B3LYP calculations performed in this work are able to predict the elastic properties of Mg₂SiO₄ ringwoodite with great accuracy. The theoretical value of the C₁₁ component of the elastic tensor is identical to the experimental result obtained with Brillouin spectroscopy of Weidner et al. (1984), performing better than MD calculations (Li et al., 2006) and DFT-LDA calculations (Kiefer et al., 1997). The same can be seen for the aggregate bulk modulus, whereas the aggregate longitudinal and shear velocities are basically identical to those predicted with plane waves pseudopotentials after Kiefer et al. (1997). Our theoretical seismic velocities are slightly higher with respect to Weidner et al. (1984) due to a well-known effect of the B3LYP hybrid functional, that overestimates the cell volume (hence, underestimates density), thus affecting predicted seismic velocities. Finally, all theoretical elastic and seismic properties of ringwoodite compare exceptionally well with the Brillouin spectroscopy measurements performed by Jackson et al. (2000).

Single-crystal seismic velocities and seismic anisotropy are then calculated from the elastic constant tensor (cf. section 2.2). Figs. 3.3.1 and 3.3.2 show pole figures plotted on contoured stereograms for Mg₂SiO₄ ringwoodite.

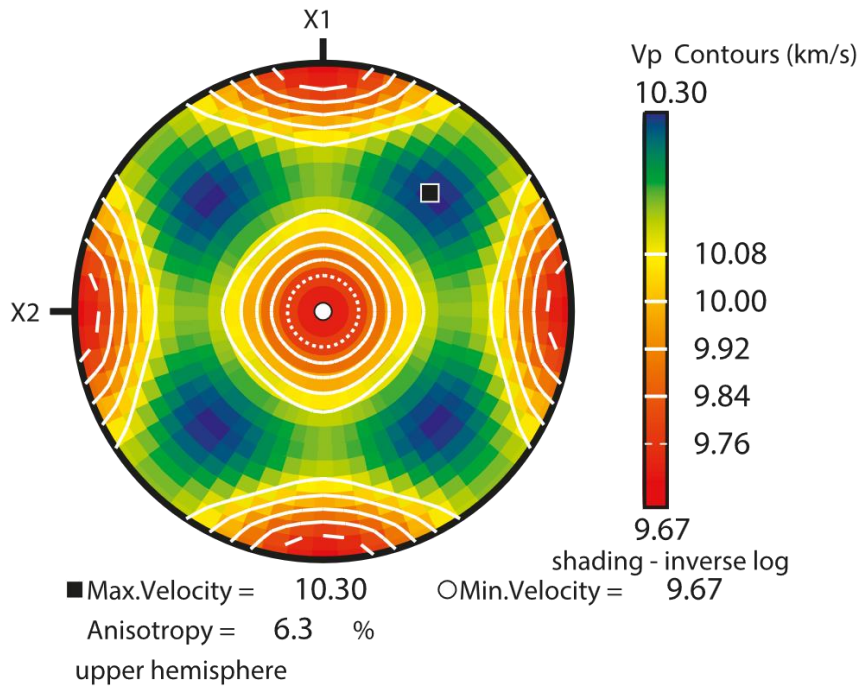


Fig. 3.3.1. Single-crystal seismic anisotropy calculated for V_P longitudinal seismic velocities of Mg_2SiO_4 ringwoodite at $P=0$ GPa and $T=0$ K by ab-initio B3LYP (this work). All the stereograms are obtained with the CAREWARE package (Mainprice, 1990). X1, X2 and X3 are the reference axes, with X1 along [100], X2 along [010] and X3 along [001] crystallographic directions. Contour lines are in km/s.

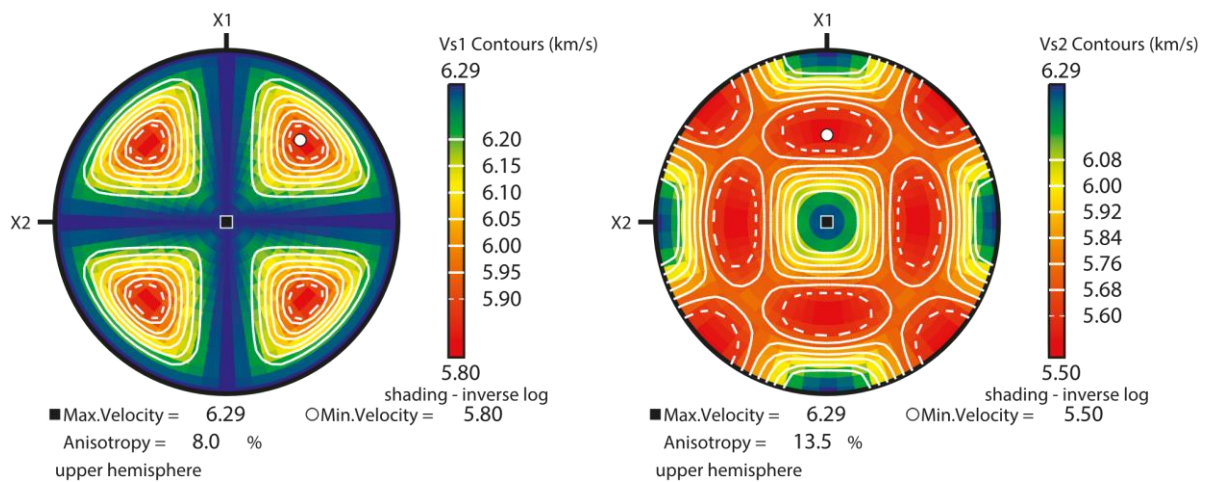


Fig. 3.3.2. Single-crystal seismic anisotropy calculated for V_{S1} (left) and V_{S2} (right) shear-wave seismic velocities of Mg_2SiO_4 ringwoodite at $P=0$ GPa and $T=0$ K by ab-initio B3LYP (this work). X1, X2 and X3 are the reference axes, with X1 along [100], X2 along [010] and X3 along [001] crystallographic directions.

In figures 3.3.1 and 3.3.2 seismic anisotropy for P- and S-waves (A_P and A_S) is defined as follows:

$$A_P = \left(\frac{V_{P,max} - V_{P,min}}{\langle V_P \rangle} \right) \times 100 \quad (3.3.1)$$

$$A_S = \left(\frac{V_{S,max} - V_{S,min}}{\langle V_S \rangle} \right) \times 100 \quad (3.3.2)$$

Mg₂SiO₄ ringwoodite displays a moderate, but non-negligible, seismic anisotropy at P=0 (6.3% for V_P , 8% and 13.5% for V_{S1} and V_{S2} , respectively). Nevertheless, P-T effects sensibly reduce A_P and A_S values of this phase in the lowermost mantle transition zone (Mainprice, 2007). Concerning seismic velocities, the [111] and [001] crystallographic directions are those of fastest and slowest propagation for longitudinal waves (V_P), respectively; [001] and [101] crystallographic directions are those of fastest and slowest propagation for shear waves (V_S).

3.4. Equation of state and thermoelastic properties

Figure 3.4.1 shows the result of the ab initio B3LYP calculation of K_T of Mg₂SiO₄ ringwoodite.

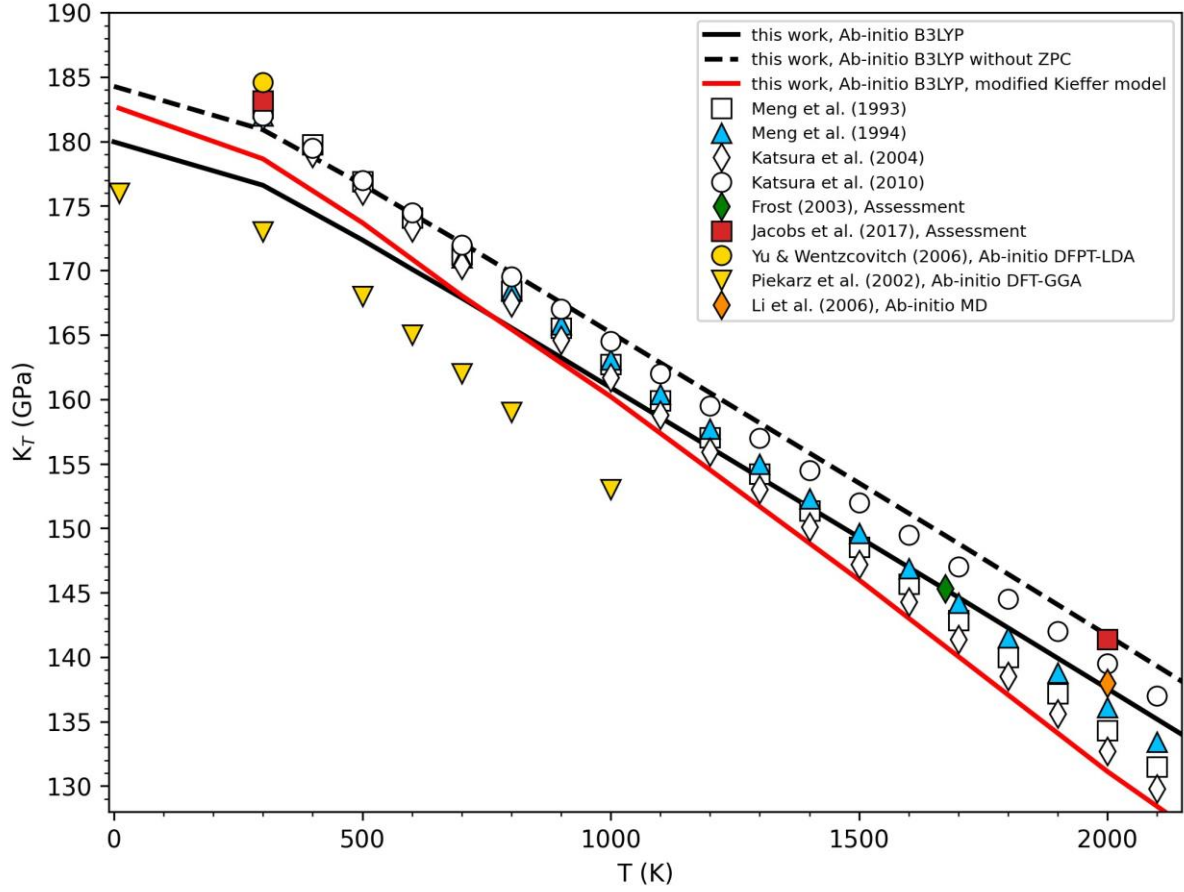


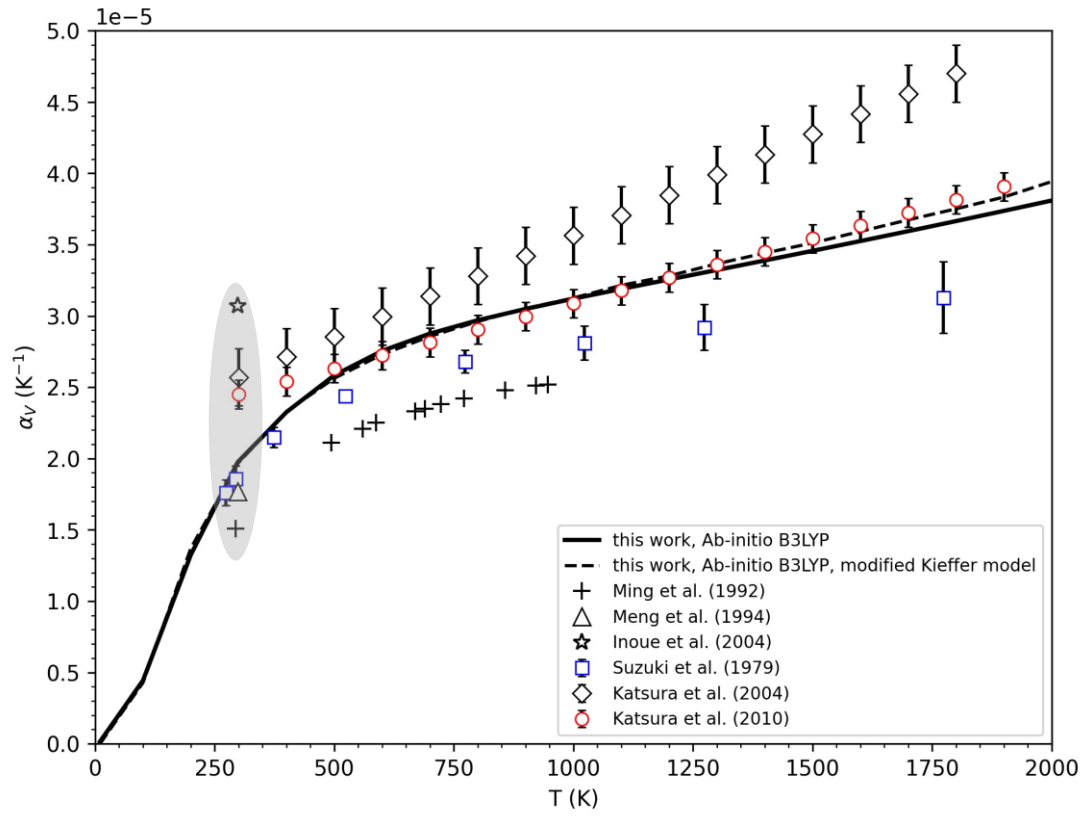
Figure 3.4.1. Temperature dependence of the isothermal bulk modulus (K_T) of Mg_2SiO_4 ringwoodite at zero or ambient pressure. Ab initio B3LYP results are compared with available experimental data (Meng et al., 1993, 1994; Katsura et al., 2004, 2010), thermodynamic assessments (Frost, 2003; Jacobs et al., 2017) and previous ab initio DFT or MD simulations (Piekarz et al., 2002; Yu and Wentzcovitch, 2006; Li et al., 2006).

Static values calculated in this work for bulk modulus (i.e., $K_0 = 180.0$ GPa with full phonon dispersion and zero-point correction; $K_0 = 184.3$ GPa with full phonon dispersion and without zero-point correction; $K_0 = 183.0$ GPa applying a modified Kieffer model with zero-point correction) are in remarkable agreement with experimental results, with the observed isothermal values being around 182–185 GPa at ambient conditions (Meng et al., 1994; Katsura et al., 2004, 2010). Our calculated values for the bulk modulus pressure derivative (i.e., $K'_0 = 4.13$ at the static level), which is close to the vibrationally constrained thermodynamic assessments of Jacobs et al., (2017) (i.e.: $K'_0 = 4.21$). The effect of zero-point motions alone decreases the bulk

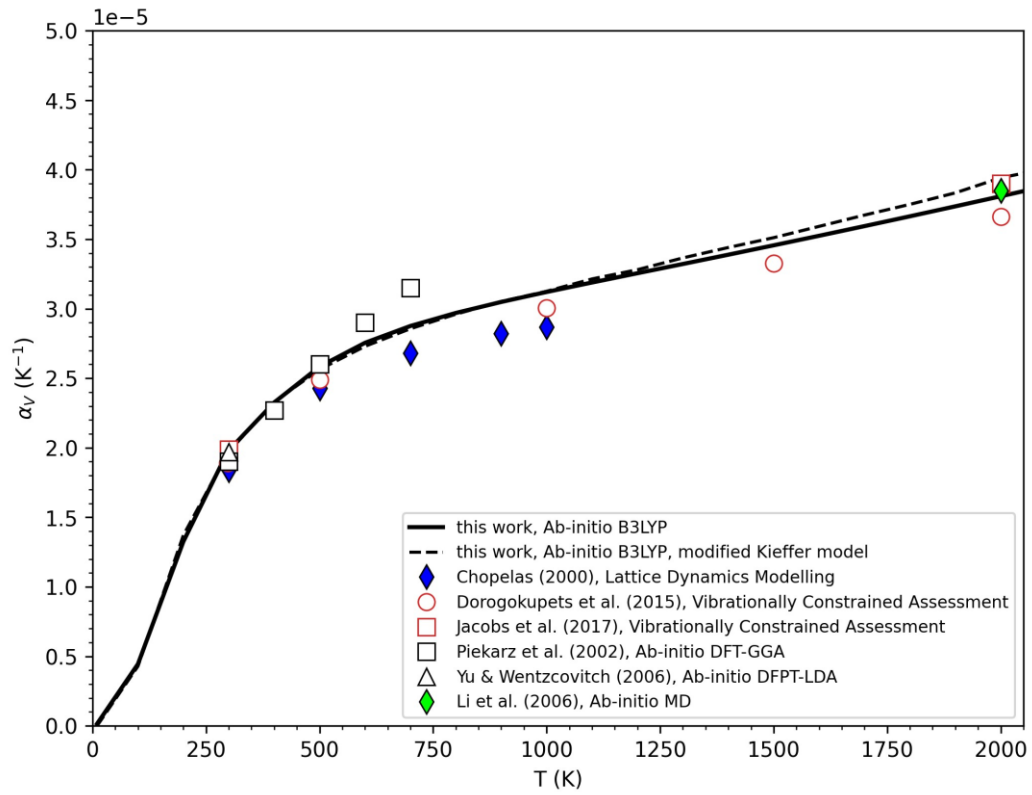
modulus by ~2.5% over the entire temperature range, suggesting that vibrational effects on thermoelastic properties cannot be disregarded in DFT simulations even at ambient P–T conditions (Belmonte, 2017). The temperature dependence of the isothermal bulk modulus of Mg₂SiO₄ ringwoodite at P = 0 GPa is shown in Figure 3.4.1. Ab initio B3LYP results compare favourably with literature values, especially in the medium- to high-temperature range. The value inferred for $\left(\frac{\partial K_T}{\partial T}\right)_P$ by linear fitting of ab initio P–V–T data obtained from full phonon dispersion is -0.0233 GPa K⁻¹, which is not far from the available experimental results (Meng et al., 1993, 1994; Katsura et al., 2010). The only exception is represented by the markedly negative value given by Katsura et al. (2004) [i.e.: $\left(\frac{\partial K_T}{\partial T}\right)_P = -0.029$ GPa K⁻¹], which is on the other hand closer to the value obtained by fitting P–V–T data calculated by applying a modified Kieffer's model [i.e.: $\left(\frac{\partial K_T}{\partial T}\right)_P = -0.0278$ GPa K⁻¹]. Interestingly, the computed $\left(\frac{\partial K_T}{\partial T}\right)_P$ is in excellent agreement with that obtained by some thermodynamic assessments based on the Helmholtz free energy, hence constrained by vibrational theory (Dorogokupets et al., 2015; Jacobs et al., 2017). Furthermore, the isothermal bulk modulus values computed by ab initio B3LYP at HT conditions are nearly coincident with those predicted by Frost, (2003) at T = 1673K and by the ab initio MD simulation of Li et al., (2006) at T = 2000K (see Fig. 2.5.1). For instance, Li et al. (2006) obtain K_T = 138 ± 6 GPa at T = 2000K, compared to our value of 137.6 GPa at the same temperature. This remarkable agreement supports the evidence that QHA performs well for Mg₂SiO₄ ringwoodite in the whole P–T range of the mantle transition zone (Belmonte et al., 2022).

Figures 3.4.2 a – c and 3.4.3 report as an example the result for the calculation of Mg₂SiO₄ ringwoodite volume thermal expansion coefficient (α_V) and volume thermal expansion (expressed as V/V₀, where V₀= molar volume at the athermal limit) respectively.

(a)



(b)



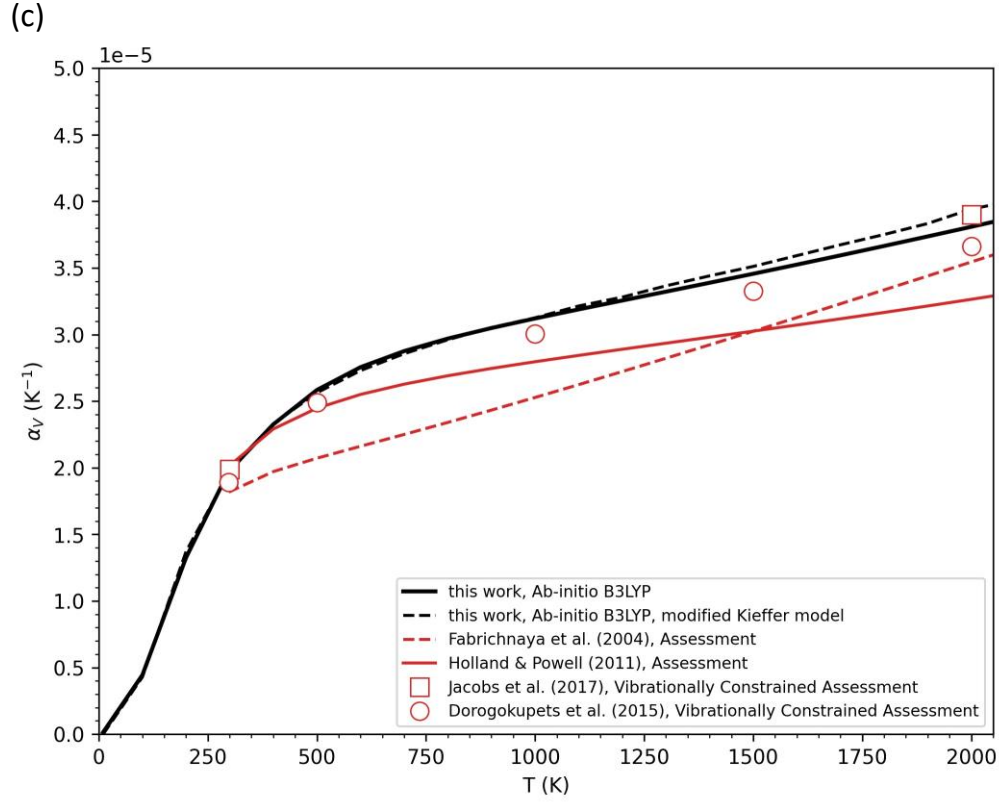


Figure 3.4.2. Ab initio B3LYP volume thermal expansivity (α_v) of Mg_2SiO_4 ringwoodite at zero pressure, compared with (a) experimental data (grey shaded area highlights scattering of values at ambient conditions), (b) different theoretical simulations and (c) thermodynamic assessments.

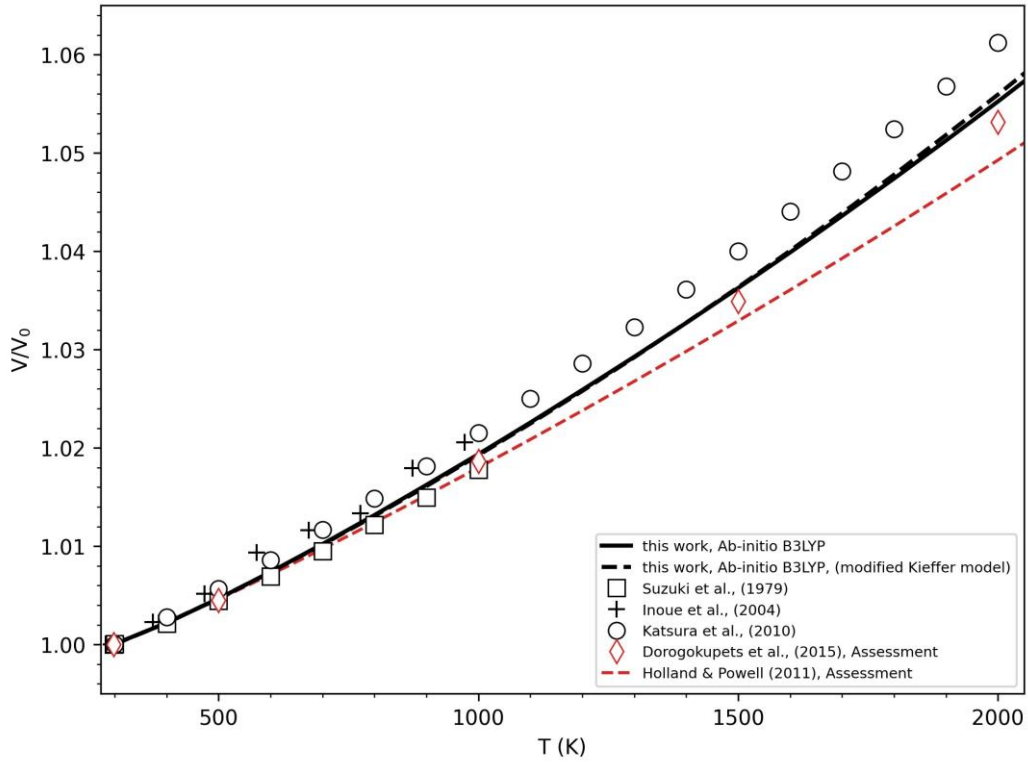


Figure 3.4.3. Ab initio B3LYP volume thermal expansion (V/V_0) of Mg_2SiO_4 ringwoodite at zero pressure, compared with experimental data and thermodynamic assessments.

Fitted numerical coefficients of the polynomial function (eq. 2.5.8 in Chapter 2) at $P = 0$ are $\alpha_0 = 8.839 \times 10^{-9} \text{ K}^{-2}$, $\alpha_1 = 1.6033 \times 10^{-5} \text{ K}^{-1}$, $\alpha_2 = 11.586 \times 10^{-3}$, $\alpha_3 = -6.055 \text{ K}$ and $\alpha_4 = 804.31 \text{ K}^2$ for the full phonon dispersion calculation (black curves in figures 3.4.2a, b and c), whereas regarding the calculation performed with the modified Kieffer's model, numerical coefficients are $\alpha_0 = 9.440015 \times 10^{-9} \text{ K}^{-2}$, $\alpha_1 = 1.869143 \times 10^{-5} \text{ K}^{-1}$, $\alpha_2 = 5.434824 \times 10^{-3}$, $\alpha_3 = -2.663163 \text{ K}$ and $\alpha_4 = 260.2974 \text{ K}^2$ (black, dashed curves in figures 3.4.2a, b and c).

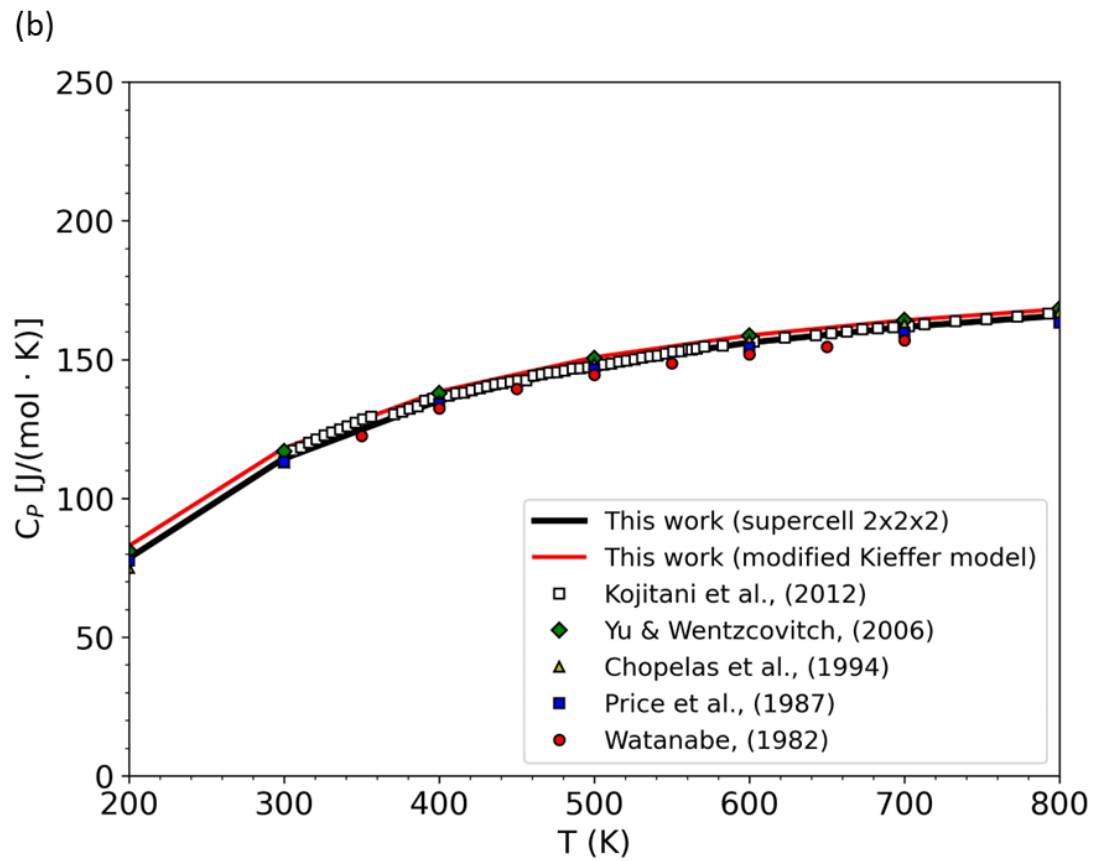
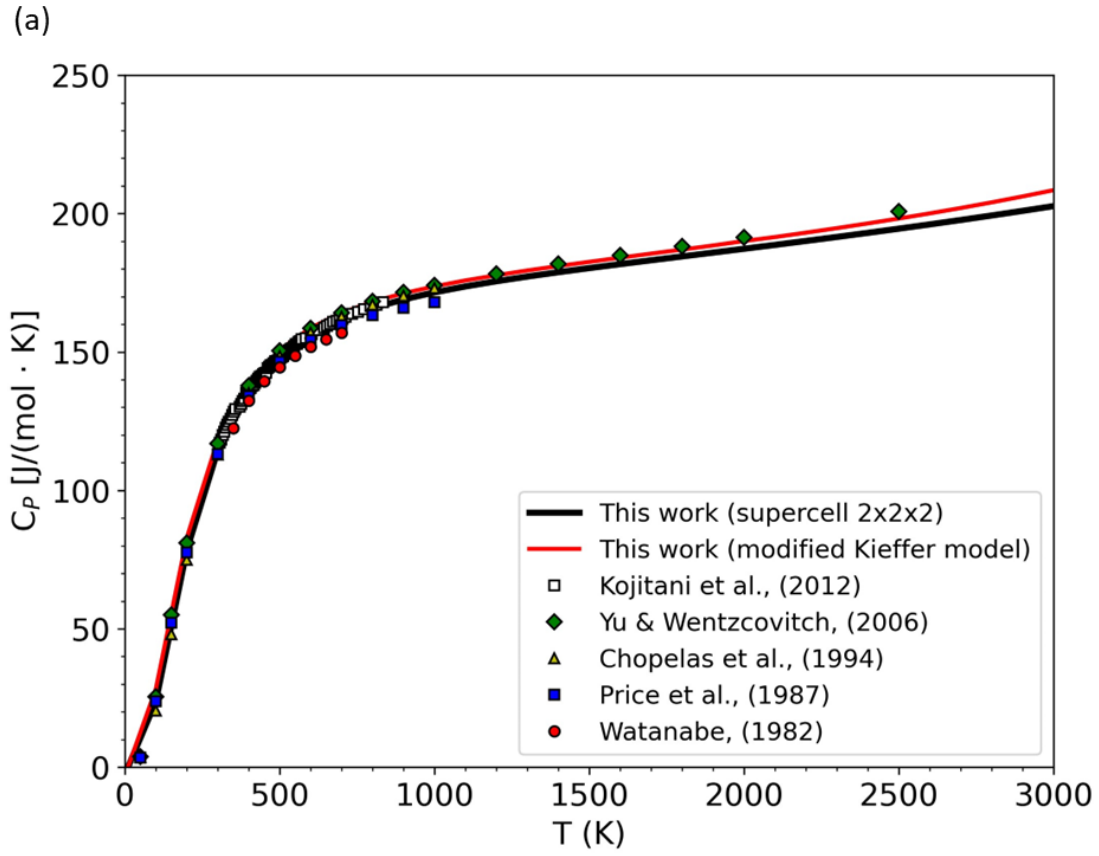
Thermal expansivity is a key parameter to predict density and volume changes of constituent mineral phases in the Earth interior. It follows that an accurate knowledge of thermal expansivity at pressure and temperature conditions compatible with those of the Earth mantle is essential to correctly simulate mantle processes such as thermal convection (Tosi et al., 2013). Nevertheless, a huge uncertainty exists even on the ambient value of volume thermal expansion coefficient of Mg_2SiO_4 ringwoodite

(shaded area in figure 3.4.2a), with experimental values ranging from $\alpha_{V0} = 1.51 \times 10^{-5} \text{ K}^{-1}$ (Ming et al., 1992) to $\alpha_{V0} = 3.07 \times 10^{-5} \text{ K}^{-1}$ (Inoue et al., 2004), implying thus a 100% variation in α_{V0} according to different experimental investigations. The computed value in this work, i.e., $\alpha_{V0} = 1.98 \times 10^{-5} \text{ K}^{-1}$ as results from the full phonon dispersion calculation ($\alpha_{V0} = 1.98 \times 10^{-5} \text{ K}^{-1}$ according to the calculation performed with the modified Kieffer model), is not far from the experimental value $\alpha_{V0} = (1.86 \pm 0.09) \times 10^{-5} \text{ K}^{-1}$ obtained by Suzuki et al., (1979). Both values are quite different from those determined by other experimental works (Meng et al., 1994; Katsura et al., 2004). On the other hand, ambient thermal expansion coefficients calculated by lattice dynamics modelling or other vibrationally constrained assessments are in remarkable agreement with our result (i.e., $\alpha_{V0} = 1.84 \pm 0.10 \times 10^{-5} \text{ K}^{-1}$ according to Chopelas, 2000; $\alpha_{V0} = 1.89 \times 10^{-5} \text{ K}^{-1}$, Dorogokupets et al., 2015; $\alpha_{V0} = 1.99 \times 10^{-5} \text{ K}^{-1}$, Jacobs et al., 2017), marking the physical soundness of our calculations. The evidence that different DFT and QHA simulations give quite similar values of α_{V0} (see Piekarz et al., 2002; Yu and Wentzcovitch, 2006; Hernández et al., 2015) strengthens the ability of ab initio calculations to identify and select accurate experimental results for thermal expansivity (figure 3.4.2b). α_{V0} as calculated from full phonon dispersion does not display any inflection point in the entire T range investigated in this work, thus confirming that (i) QHA performs exceptionally well for Mg_2SiO_4 ringwoodite up to deep mantle temperatures and (ii) ringwoodite can be considered a “quasi-harmonic” solid in the Earth’s mantle transition zone. Further supporting evidence is that the thermal expansivity predicted at $T = 2000\text{K}$ and room pressure by the first-principle molecular dynamics of Li et al. (2006) are almost identical to that predicted by this work, with the former being equal to $3.85 \times 10^{-5} \text{ K}^{-1}$ and the latter around $3.81 \times 10^{-5} \text{ K}^{-1}$ (green diamond in figure 3.4.2b). On the other hand, the dashed black curve in figure 3.4.2b, that corresponds to the result obtained by applying a modified Kieffer model, shows a slight inflection at high temperature, leading to a quite higher $\alpha_{V,2000\text{K}} = 3.94 \times 10^{-5} \text{ K}^{-1}$, which could be a sign of the onset of quasi-harmonic effects. This might point out that in the case of Mg_2SiO_4 ringwoodite the full phonon dispersion calculation is a

preferable approach since it assures a better approximation of the vDOS, improving this way the accuracy in predicting thermoelastic properties. The comparison between ab initio calculations and internally consistent thermodynamic assessments deserves special attention. Figure 3.4.2c shows that thermal expansivity assessed via mathematical procedures able to reproduce selected phase equilibria of Mg_2SiO_4 ringwoodite (e.g., Fabrichnaya et al., 2004; Holland and Powell, 2011) turns out to be inaccurate at mantle temperatures. For instance, Holland and Powell, (2011) used a thermal pressure Tait EOS, along with some assumptions on thermoelastic properties, to predict thermal expansion of mantle minerals at HP–HT conditions. α_V values obtained for Mg_2SiO_4 ringwoodite are underestimated by 10 %–15% in the high-temperature range (see fig. 3.4.2c). This is even more evident if thermal expansion data by Fabrichnaya et al. (2004) are considered in fig. 3.4.2c, which basically means that internally consistent thermodynamic datasets currently developed for deep mantle minerals are not necessarily also physically consistent. The same also applies to the relative volume thermal expansion trend depicted in figure 3.4.3. In the case of the calculation of volume thermal expansion performed with the modified Kieffer model, the result is basically coincident with that obtained from the full phonon dispersion. If the reader is interested in a more detailed treatment of Mg_2SiO_4 ringwoodite volume thermal expansivity, more details can be found in Belmonte et al. (2022).

3.5. Thermodynamic properties

The isobaric heat capacity of Mg_2SiO_4 ringwoodite is reported in Figures 3.5.1a – 3.5.1d, as calculated both with full phonon dispersion obtained on a $2\times 2\times 2$ supercell, as well as by applying a modified Kieffer’s model based on vibrational frequencies calculate at the Γ point only (black and red curves, respectively).



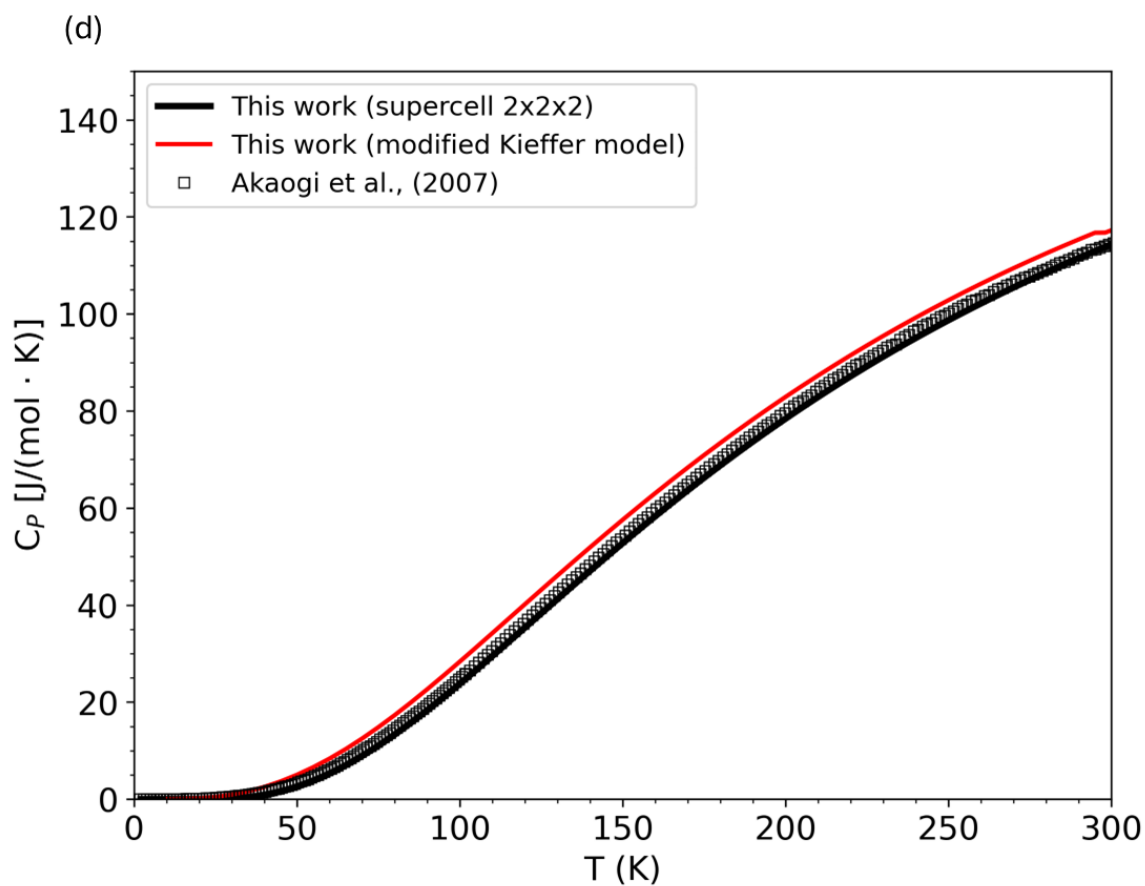
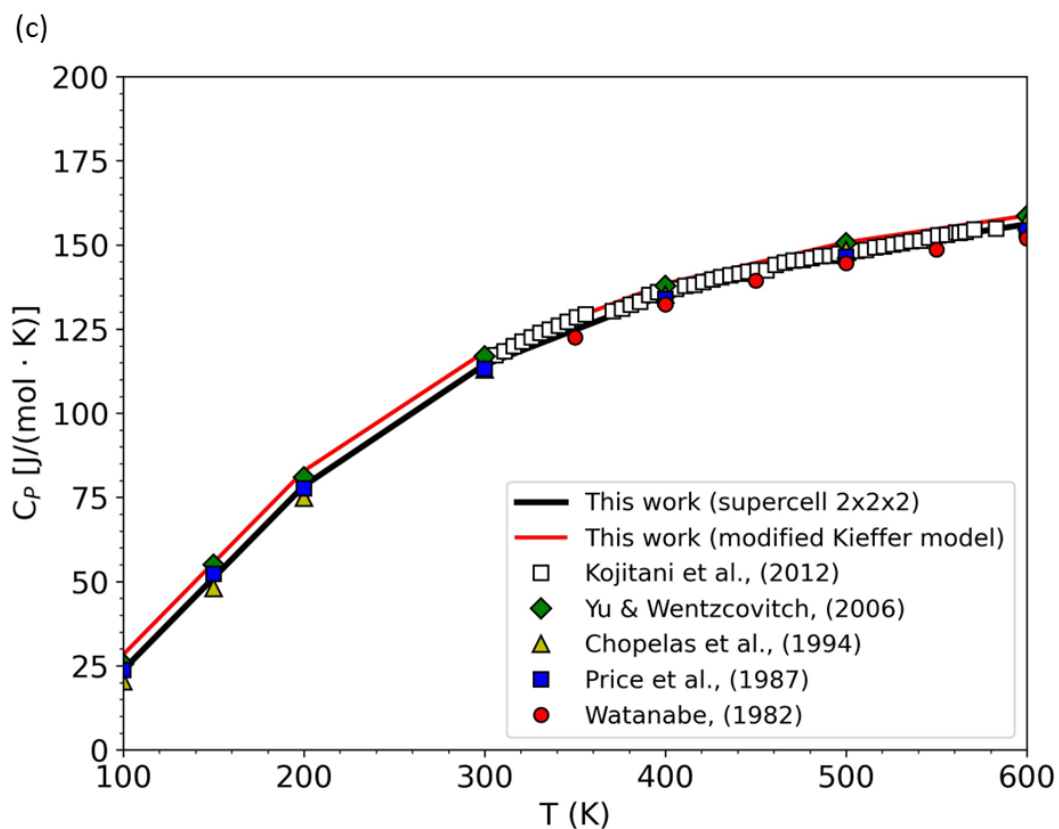


Figure 3.5.1. Ab initio B3LYP isobaric heat capacity (C_P) of Mg_2SiO_4 ringwoodite at zero pressure, compared with calorimetric measurements (Watanabe, 1982; Kojitani et al., 2012) and theoretical calculations (Price et al., 1987; Chopelas et al., 1994; Yu & Wentzcovitch, 2006). Figures (a) – (c) display calculated results in three different temperature ranges, to better appreciate the comparison with reference data, whereas figure (d) shows a comparison with the low-T calorimetry of Akaogi et al. (2007).

In the case of Mg_2SiO_4 ringwoodite isobaric heat capacity, whether calculated via full phonon dispersion or with the modified Kieffer's model, the discrete values can be fitted with the polynomial function corresponding to eq. (2.5.14) in Chapter 2. Numerical coefficients are $a = 150.75$, $b = 6.6962 \times 10^{-3}$, $c = -1.3652 \times 10^7$, $d = 724.08$, $e = 1.9233 \times 10^9$, $f = 3.2448 \times 10^{-6}$, $g = -3.4909 \times 10^{-10}$ and $a = 191.01$, $b = 1.2419 \times 10^{-2}$, $c = -4.0403 \times 10^6$, $d = -690.75$, $e = 2.31 \times 10^8$, $f = -5.7243 \times 10^{-6}$, $g = 1.6737 \times 10^{-9}$ respectively. As can be seen in figure 3.5.1, the calculation performed with the supercell method reproduces very well both the calorimetry results (Watanabe, 1982; Kojitani et al., 2012) and the theoretical calculations (Price et al., 1987; Chopelas et al., 1994). The values obtained with the modified Kieffer's model (red curves in figure 3.5.1) appear to be overestimated of about 1 – 2%, especially at high temperature where a slight inflection is observed in the C_P curve, probably due to the onset of anharmonic effects related to volume thermal expansivity and isothermal bulk modulus. A striking feature that arises from the analysis figure 3.5.1d is the excellent agreement between B3LYP calculation performed in this work with the supercell method and the accurate low-temperature calorimetric study of Akaogi et al. (2007). The importance of a detailed description of the isobaric heat capacity of a compound in the low temperature range comes from the fact that it allows to constrain the value of the standard state entropy (S_0), which is obtained as the definite integral of C_P from 0 K to 298.15 K. As discussed in section 2.7, an analytical function that describes the isobaric heat capacity from 298.15 K up to high temperature conditions is required to calculate the effect of temperature on enthalpy (H), entropy (S) and, ultimately, Gibbs

free energy (G), which is the main thermodynamic quantity that comes into play when investigating phase equilibria at deep interior conditions.

As a final example, Figure 3.5.2 reports the theoretical values of Mg_2SiO_4 ringwoodite entropy (S) obtained via full phonon dispersion, as well as with the modified Kieffer's model, as compared with calorimetric results and other theoretical calculations.

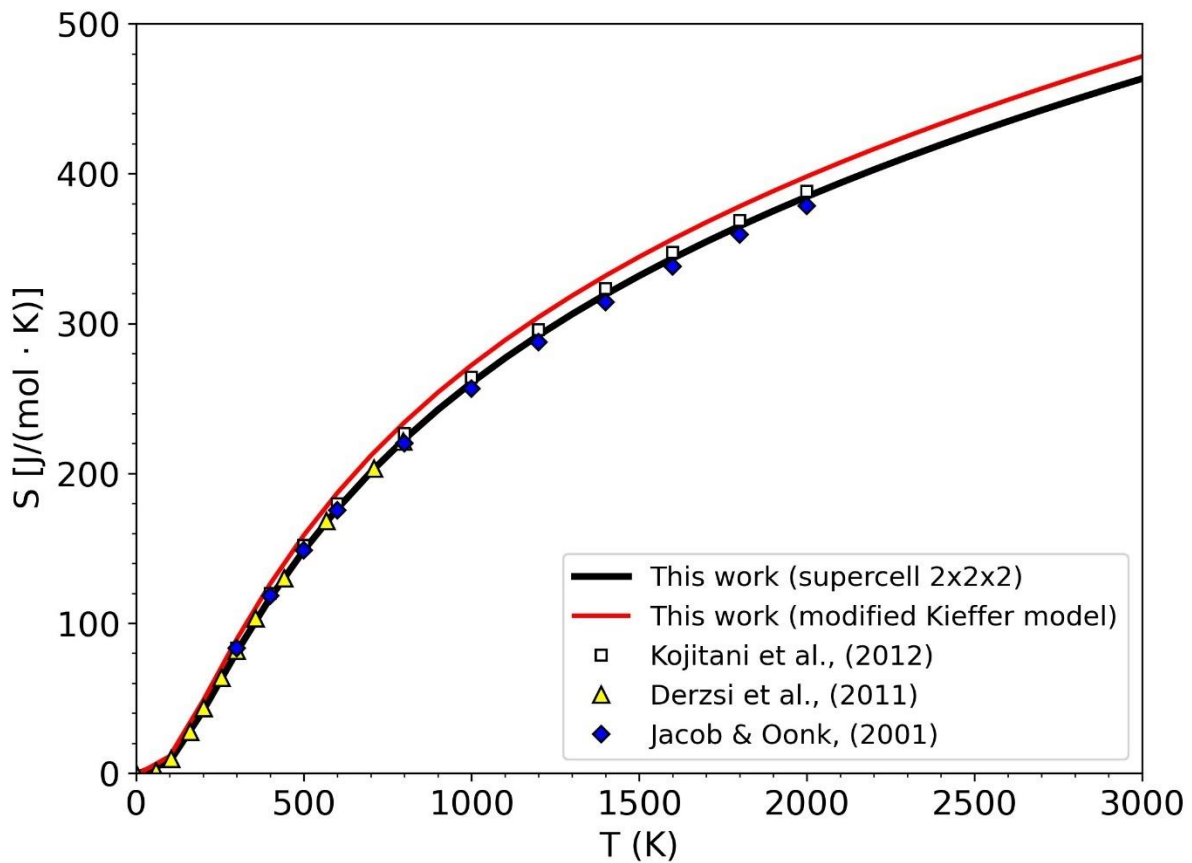


Figure 3.5.2. Ab initio B3LYP entropy (S) of Mg_2SiO_4 ringwoodite at zero pressure, compared with assessments (Jacobs & Oonk, 2001; Kojitani et al., 2012) and theoretical calculations (Derzsi et al., 2011).

Once again, the theoretical values of Mg_2SiO_4 ringwoodite total entropy as obtained from full phonon dispersion B3LYP calculations are in good agreement with the reference data reported in Figure 3.5.2, whereas the modified Kieffer's model results appear to overestimate entropy between 10% (at low temperature conditions) and 3%

(at high temperatures). The standard state entropy value attained at 298.15 K is equal to 80.31 J/(mol×K) (full phonon dispersion) and 88.681 J/(mol×K) (modified Kieffer's model), respectively, which compare favourably with the calorimetric result of Akaogi et al. (2007) [i.e.: $S_0 = 82.7 \pm 0.5$ J/(mol×K)] as well as with the assessed value by Jacobs & Oonk, (2001). As a brief sum up, given the favourable comparison with both the experimental and theoretical data, the full phonon dispersion calculation performed with the supercell method seems to be the recommended approach to obtain accurate results on thermodynamic properties of Mg₂SiO₄ ringwoodite.

3.5. Conclusions

In this chapter, Mg₂SiO₄ has been adopted as preliminary case study to test the performances of ab initio DFT-B3LYP calculations in predicting thermodynamic properties of stable magnesium silicates in the deep mantle, adopting two different approaches to approximate the vDOS: the calculation at Γ point combined with a modified Kieffer model, and a full phonon dispersion calculation performed by means of a 2×2×2 supercell. Despite both approaches proves viable when comparing the result of ringwoodite thermodynamic properties with experimental and theoretical data, the latter gave more satisfactory results, probably due to the low number of atoms in ringwoodite primitive unit cell (viz. the relatively low number of vibrational modes), which prevent an accurate description of the vDOS when approximated with a modified Kieffer model. Ringwoodite not only served as a perfect beta test for hybrid DFT calculations, but our results allowed to obtain insights on its behaviour at deep mantle conditions. In fact, ab initio thermal expansivity and isothermal bulk modulus calculated in this work support the evidence of a quasi-harmonic behaviour of ringwoodite in the Earth's mantle transition zone. This seems to be supported by the evidence that high-temperature values of α_V and K_T predicted in this work by DFT-QHA calculations turn out to be nearly coincident with the results of the first

principles molecular dynamics simulation by Li et al. (2006), stressing that intrinsic anharmonic effects are virtually absent for ringwoodite at MTZ conditions.

4. Thermodynamics and phase stability of MgSiO_3 protoenstatite by first principles calculations

The content of this chapter has been adapted from a manuscript draft to be submitted to *ACS – Earth and Space Chemistry*

4.1. Introduction

Protoenstatite is one of the high temperature forms of MgSiO_3 pyroxene minerals, displaying a stability range from 1200 to 1700 K at ambient pressure (Presnall, 1995). Despite being a somewhat elusive and poorly characterized mineral, protoenstatite is involved in a variety of geological and cosmochemical processes. For instance, it has been recognized as the first *liquidus* phase to form in some Mg-rich basalts, at least at low pressure conditions, subsequently reverting to clino- or orthoenstatite with decreasing temperature (Dallwitz et al., 1966; Shiraki et al., 1980). Experimental studies performed in different model compositional systems support the evidence that protoenstatite is the liquidus phase for the MgSiO_3 metasilicate composition (Schairer, 1954; Schreyer and Schairer, 1961; Chen and Presnall, 1975; Smart and Glasser, 1976). In the MgO-SiO_2 binary system, protoenstatite display incongruent melting at $P = 1$ bar and $T = 1830$ K and is formed by peritectic reaction of Mg_2SiO_4 forsterite with a liquid of composition $X_{\text{SiO}_2} \cong 0.51$ (Bowen and Andersen, 1914; Chen and Presnall, 1975). However, clino-enstatite instead of protoenstatite is often found in the run products of melting experiments performed by the quenching technique because protoenstatite reverts to clinoenstatite during rapid cooling (Atlas, 1952; Muan and Osborn, 1956). Nevertheless, the exact temperature of this inversion is still an open question due to the sluggish nature of the phase transition. Previous experimental investigations locate the enstatite-protoenstatite inversion in a broad temperature range between 1258 K and 1413 K (Atlas, 1952; Yoder, 1952; Bowen and Schairer, 1935; Schairer, 1954), but also in this case it's difficult to characterize the

phase transition at 1-bar pressure due to kinetic reasons. High-pressure studies constrained the phase stability field of protoenstatite at HP-HT (Boyd et al., 1964; Kushiro et al., 1968; Anastasiou and Seifert, 1972; Chen and Presnall, 1975) but gave quite different results on the Clapeyron slope of the protoenstatite-orthoenstatite phase boundary, hence on the P-T location of the protoenstatite-orthoenstatite-liquid triple point in the MgSiO_3 phase diagram ($P = 0.8 \text{ GPa}$ and $T = 1923 \text{ K}$ according to Boyd et al., 1964; 1.52 GPa and $T = 1973 \text{ K}$ according to Chen and Presnall, 1975).

Protoenstatite also plays an important role as a precursor phase in the solar system. First of all, its stability field is compatible with P-T conditions inferred for the typical condensation sequence of the gas solar nebula, where orthoenstatite (originally protoenstatite before inversion) is predicted to be one of the most abundant phase in the mid-temperature region (i.e. $T = 800 \div 1400 \text{ K}$) for total pressures of 10^{-4} - 10^{-3} bar by thermodynamic calculations (Grossman, 1972; Grossman and Larimer, 1974; Ebel, 2006; Pignatale et al., 2011; Nagahara, 2018). This is consistent with condensation experiments performed in vacuum (i.e. $P_{\text{tot}} = 10^{-9}$ - 10^{-10} bar) by Tachibana et al. (2002) and Nagahara (2018), who showed that, starting from a gas of solar composition, protoenstatite/orthoenstatite may form by incongruent condensation of forsterite and a Si-rich gas phase in a temperature range between 1473 K and 1773 K. Therefore, the incongruent evaporation of enstatite is able to produce Mg/Si variations in the residual solid (Mg-rich) and gas phase (Si-rich), which can explain Mg/Si fractionation that occurred in the primitive solar nebula and that is currently recorded in chondritic meteorites composition (Tachibana et al, 2002).

The finding of protoenstatite pyroxene in cometary material sampled in the coma of the comet Wild 2 during NASA Stardust mission (Schmitz and Brenker, 2008) further support the importance of this phase from a cosmochemical and astrophysical point of view. In that case the stability of a protoenstatite precursor phase is supported by microstructural evidences on samples of cometary pyroxenes: the intense stacking disorder and twinning with alternating low-clinoenstatite and orthoenstatite lamellae and (100) twins, along with the widespread occurrence of $4.5 \text{ \AA}$ wide (100) half-planes

are both interpreted as indicative of a direct transformation from a protoenstatite precursor (Schmitz and Brenker, 2008). The same transformation mechanism from a PEn precursor is clearly shown by TEM observations carried out on low-CEn/OEn intergrowths in fine-grained calcium-aluminum-rich inclusions (CAIs) from CV3 chondrites (Che and Brearly, 2021).

Despite its well-established stability field at high-temperatures, protoenstatite is found very rarely in natural occurrences. Indeed, as the only occurrence in natural samples is that reported by Xu et al. (2017), who found Al,Fe-bearing protoenstatite as metastable nanophase inclusions in gem-quality labradorite phenocrysts (Oregon “watermelon” sunstones). The reason for the metastable preservation of protoenstatite as quenched nanocrystals seems to be linked to surface effects triggered by the reduced dimensions of the crystals that inhibit the usual inversion to ortho- or clinoenstatite (Jones et al., 1999; Xu et al., 2017).

Finally, synthetic protoenstatite also finds relevant applications in material sciences, especially with respect to the production of high temperature steatite-based ceramics (Reynard et al., 2008). In this context, the phase transition of protoenstatite to orthoenstatite during cooling assumes a relevant role since this reaction is often accompanied by the formation of cracks induced by the phase change, which in turn affect the stiffness of the ceramic.

For a better understanding of all the processes described above, which involve protoenstatite as a key phase, the knowledge of accurate thermodynamic properties of this pyroxene polymorph is crucial. Unfortunately, the unquenchable nature of this mineral has always hindered a reliable and comprehensive thermodynamic characterization (e.g. Smyth, 1974). Even though pyroxenes have been extensively studied during the last 70 years, their thermodynamics is still affected by evident shortcomings, and this is especially true for protoenstatite. For instance, its thermoelastic parameters are often unknown or assumed in current thermodynamic databases (e.g. Berman, 1988; Holland and Powell, 2011). The isobaric heat capacity is

also poorly constrained, since the only calorimetric measurement made so far on protoenstatite by Thieblot et al. (1999) allowed to determine its isobaric heat capacity in its narrow temperature range of stability (i.e. between 1400 and 1600 K) at ambient pressure. Although some authors managed to quench metastable protoenstatite crystals in the laboratory, these samples were often obtained either by doping pure MgSiO_3 protoenstatite with Li and Sc (Smyth and Ito, 1977) or by treating glass or melt of MgSiO_3 composition. For example, Lee & Heuer (1987) and Reynard et al. (2008) obtained quenched protoenstatite by dropping MgSiO_3 melt into water. Only in a more recent study by Kanzaki & Xue (2017) a more reliable procedure for synthesizing protoenstatite via conventional solid-state reaction has been developed. However, all these methods seem to work only for the production of crystal powders, whereas a single crystal of protoenstatite is far more difficult (if not impossible) to stabilize due to inversion. With the exception of few experimental studies that will be discussed in the following, the majority of the information on protoenstatite thermodynamics come from assessments adopted in current thermodynamic databases (Berman, 1988; Fabrichnaya, 2004; Holland and Powell, 2011). Although those mathematical procedures are internally consistent and allow to reproduce experimental phase boundaries, the inferred thermodynamic properties might be affected by uncertainties and physical unsoundness, especially when extrapolated at high temperature and/or high-pressure conditions. All these issues contribute to the general lack of information on protoenstatite thermodynamics which in turn hinders the possibility to investigate phase equilibria involving this mineral.

This chapter deals with the computational investigation of the thermodynamic and thermophysical properties of MgSiO_3 protoenstatite at mantle conditions by ab initio density functional theory (DFT) calculations performed at the B3LYP level of theory. All the relevant thermodynamic properties of protoenstatite (namely heat capacity, vibrational entropy, volume thermal expansion, thermal equation of state parameters) were calculated in the framework of the quasi-harmonic approximation (QHA) via

first principles phonon dispersion calculations. This allowed to obtain original insights into protoenstatite thermodynamics and enabled to determine a complete set of physically-consistent thermodynamic properties, that are compared with the few available reference data. Computed thermodynamic properties have been used to calculate phase equilibria of interest in geological and planetary sciences (and material science as well) and tested against experimental observations by taking the orthoenstatite – protoenstatite phase transition as relevant example.

4.2. Computational method

Ab initio DFT calculations have been performed using the CRYSTAL14 computer code (Dovesi et al., 2014), according to the methodology described in section 2. Hereon in, only the more relevant computational parameters will be reported. Cut-off limits in the evaluation of the Coulomb and Hartree-Fock exchange series are controlled by five parameters that were set to 8 8 8 8 16 to improve the numerical accuracy. The threshold on the self-consistent field (SCF) energy was set to 10^{-8} Hartree for the geometry optimization, and to 10^{-10} Hartree for the vibrational frequencies calculation. The reciprocal space was sampled according to a regular sublattice with shrinking factor (IS) = 6.

Vibrational frequencies of protoenstatite have been computed on the fully relaxed crystal structure performing a full phonon dispersion on a large supercell ($2 \times 2 \times 2$), sampling this way 8 $\vec{q}$ points in the reciprocal space. The volume dependence of vibrational frequencies has been defined in the framework of the quasi-harmonic approximation (QHA).

Since numerical convergence on quasi-harmonic thermodynamic properties is usually reached by a coarser sampling of the reciprocal space (cf. Belmonte, 2017), vibrational frequencies for supercells at four different volume conditions ($V/V_0 = 0.94, 0.97, 1.00, 1.02$) have been computed exploiting anisotropic supercells (in particular: $1 \times 1 \times 2$, $1 \times 2 \times 1$, $2 \times 1 \times 1$), sampling four $\vec{q}$ points in total in order to compensate for the high

computational cost. Least-square fitting of vibrational frequencies computed at volume conditions described above gives the values of the mode Grüneisen parameters (γ_i) for all modes, as described in section 2.3. Thermodynamic properties that depend on vibrational frequencies (i.e., heat capacities, thermal expansion, bulk modulus and its pressure and temperature derivatives, entropy, enthalpy, Gibbs free energy) have then been computed applying statistical mechanics relations as described in sections 2.4, 2.5, 2.6 and 2.7. P-V-T relations for protoenstatite were obtained at the following volume conditions: $V/V_0 = 0.94, 0.96, 0.97, 0.99, 1.00, 1.01, 1.02, 1.04$ applying the Mie-Grüneisen formalism and then fitting with a high-temperature, 3rd order Birch Murnaghan equation of state. The ortho – protoenstatite phase transition has been investigated via equilibrium thermodynamic modelling employing Gibbs free energy minimization.

4.3. Structure – energy properties and equation of state

Protoenstatite is an orthorhombic polymorph (space group *Pbcn*) of the pyroxenes group of minerals with general formula $M_2T_2O_6$ (where T sites are tetrahedral sites while M sites display six-fold or eight-fold coordination in the orthopyroxene and clinopyroxene structures, respectively). The crystal structure of protoenstatite is composed of single silicate chains and double octahedral bands running parallel to the *c* axis. The octahedral bands and tetrahedral chains form interrupted layers alternately along the *a* direction. Protoenstatite is distinguished from the other polymorphs by the various stacking sequences depending on the orientation of the MgO_6 octahedra with respect to the silicate chains, which is ABAB in this case. There are two distinct MgO_6 octahedra, M1 and M2, both with point symmetry $2(C_2)$; they are slightly irregular with average Mg-O distances of 2.121 and 2.191 Å, respectively. There is a single distinct SiO_4 tetrahedron, and hence, a single distinct tetrahedral chain. In contrast, orthoenstatite (*Pbca*) and clinoenstatite ($P2_1/c$) both contain two distinct silicate tetrahedra, A and B, and two distinct silicate chains

(Smyth, 1971; Ghose et al., 1994). In protoenstatite at 1353 K, the silicate tetrahedron with point symmetry $1(C1)$ is slightly irregular with average Si-O distance of 1.626 Å (Murakami et al., 1982).

Full geometry optimization of both cell-edges and internal coordinates was carried out with a symmetry-preserving relaxation procedure implemented in the CRYSTAL14 computer code. Computed equilibrium volume for the fully – relaxed structure attains a value of 442.87 Å³, having cell parameters $a = 9.333$ Å; $b = 8.834$ Å; $c = 5.372$ Å. The B3LYP volumes are slightly overestimated with respect to experiments due to the well-known effect of exchange-correlation functionals based on the generalized gradient approximation (GGA), which show an underbinding trend in predicted Mg-O and Si-O bond lengths (Kohanoff, 2006; Ottonello et al., 2009a; Belmonte et al., 2014). The volume overestimation may be expected within 2–3%. On the other hand, the inclusion of some fraction (20%) of non-local exact Hartree-Fock exchange in the hybrid density functional improves the quality of the calculated vibrational spectra of insulating magnesium silicates, hence the thermodynamic accuracy, as pointed out by several computational works in the literature (e.g. Demichelis et al., 2010; De La Pierre et al., 2011; Prencipe et al., 2012; Ulian et al., 2013; Belmonte et al., 2014).

Figure 4.3.1 shows the crystal structure of MgSiO₃ protoenstatite as from the fully relaxed B3LYP geometry with the VESTA software (Momma and Izumi, 2011).

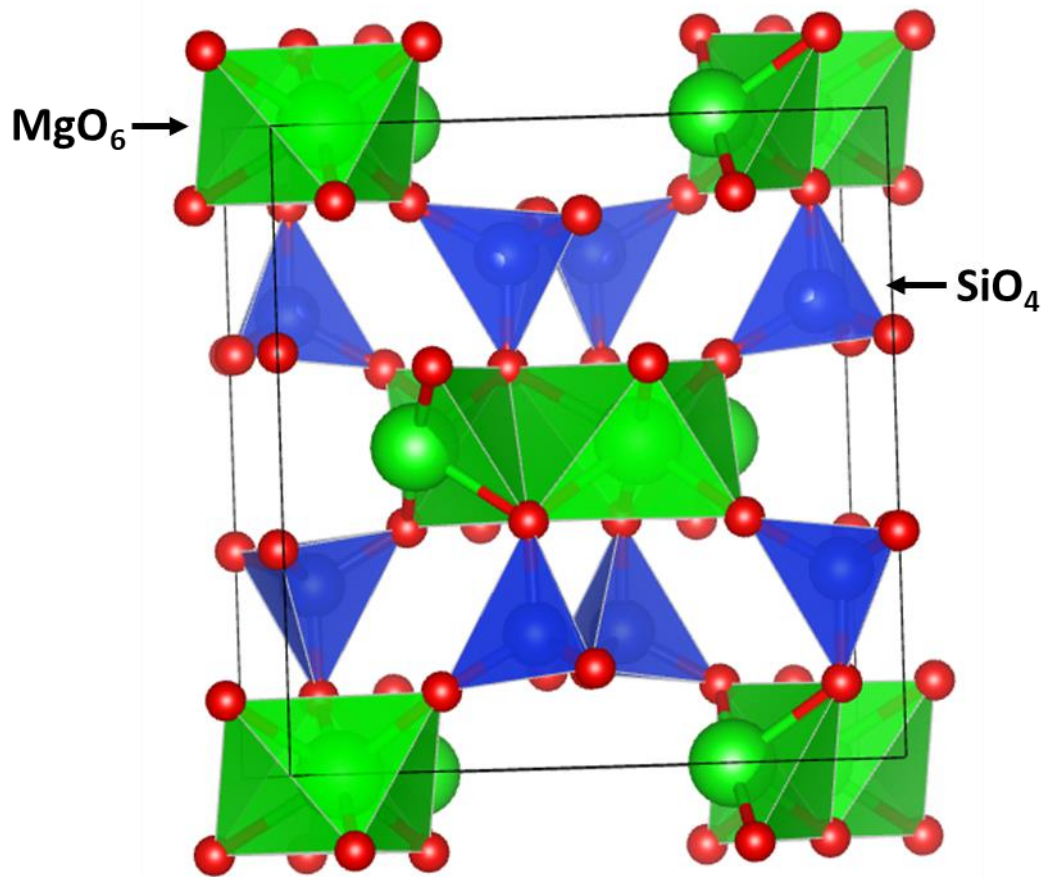


Figure 4.3.1. Crystal structure of MgSiO_3 orthorhombic (*Pbcn*) protoenstatite. The green octahedra and blue tetrahedra represent $[\text{MgO}_6]$ and $[\text{SiO}_4]$ groups, respectively.

Static bulk modulus and its pressure derivative were obtained by fitting ab initio static energy – volume curves determined at 8 volume conditions ($V/V_0 = 0.94, 0.96, 0.97, 0.99, 1.00, 1.01, 1.02, 1.04$, corresponding to a pressure range from 7.8 to -3.5 GPa) with a third-order finite strain Birch-Murnaghan equation of state (BM3-EOS) (Figures 4.3.2 and 4.3.3). The analytical fitting yields a static bulk modulus $K_0 = 101.88$ GPa and a pressure derivative $K'_0 = 6.59$. Our results on protoenstatite bulk modulus can be compared with other ab initio calculations, like those performed by Chibisov, (2013) and Philipps et al. (2017), which yield $K_0 = 106$ GPa and 103.8 GPa respectively, in excellent agreement with our value. On the contrary, the experimental value obtained by Yang et al., 1999 on a protoenstatite doped with Li^+ and Sc^+ yields $K_0 = 130 \pm 3$ GPa, which is considerably higher. As regards K'_0 , this is its first determination made so far

(at least to our knowledge) and there are no experimental or computational data to compare with. As a further check for the internal consistency of our calculations, we compared K_0 as obtained from fitting E-V values with the theoretical aggregate bulk modulus (K_{VRH}) computed from the elastic constant tensor by applying the Voigt – Reuss – Hill averaging procedure (Table 4.3.1). The result yields $K_{VRH} = 105.39$ GPa, which is not so far from $K_0 = 101.88$ GPa, hence strengthening the quality of our static EoS calculation. Fitting static energy – strain curves also provides the components of the elastic constants tensor C_{ij} , which are reported in Table 4.3.1 as well.

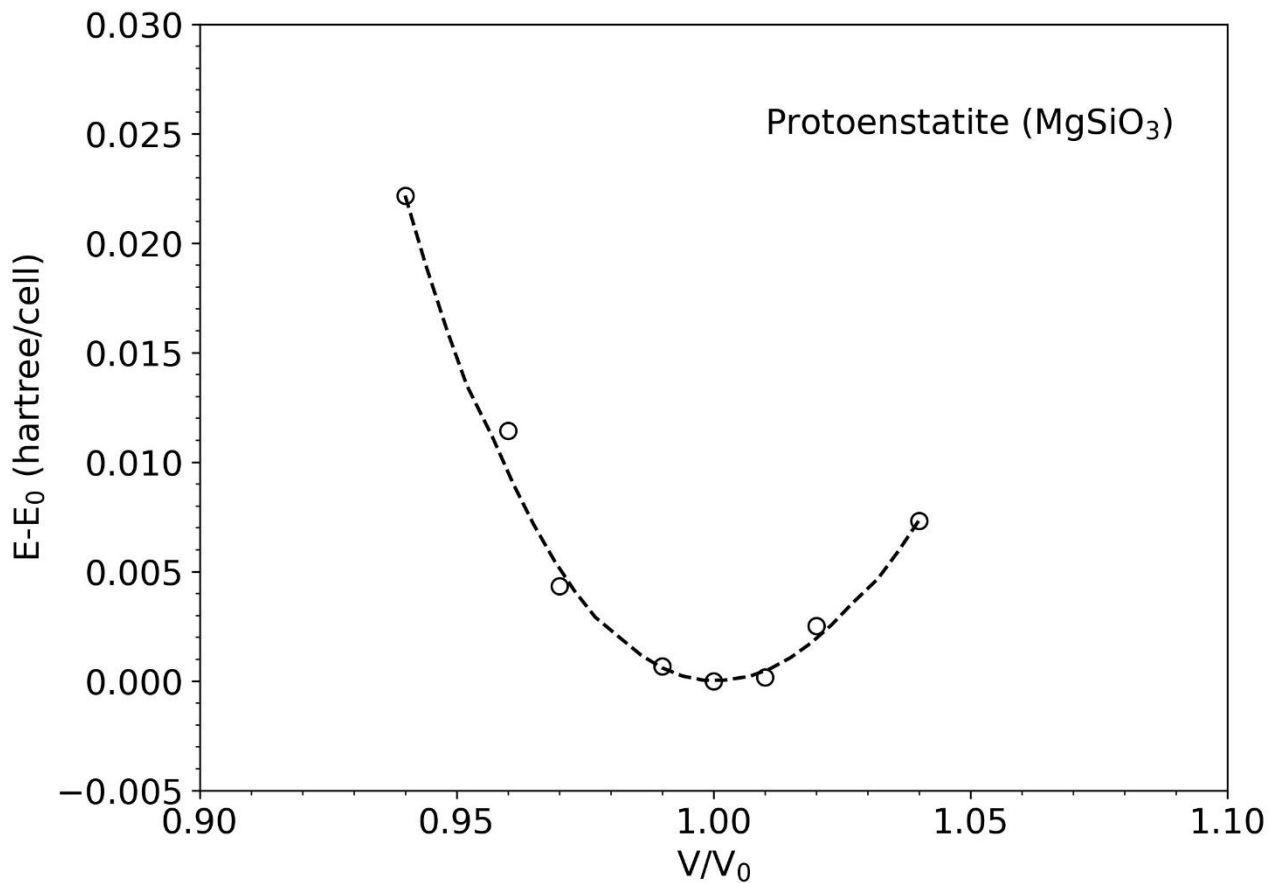


Figure 4.3.2. Ab initio B3LYP potential well of MgSiO_3 protoenstatite. The dashed line is an interpolation of the calculated energy-volume points.

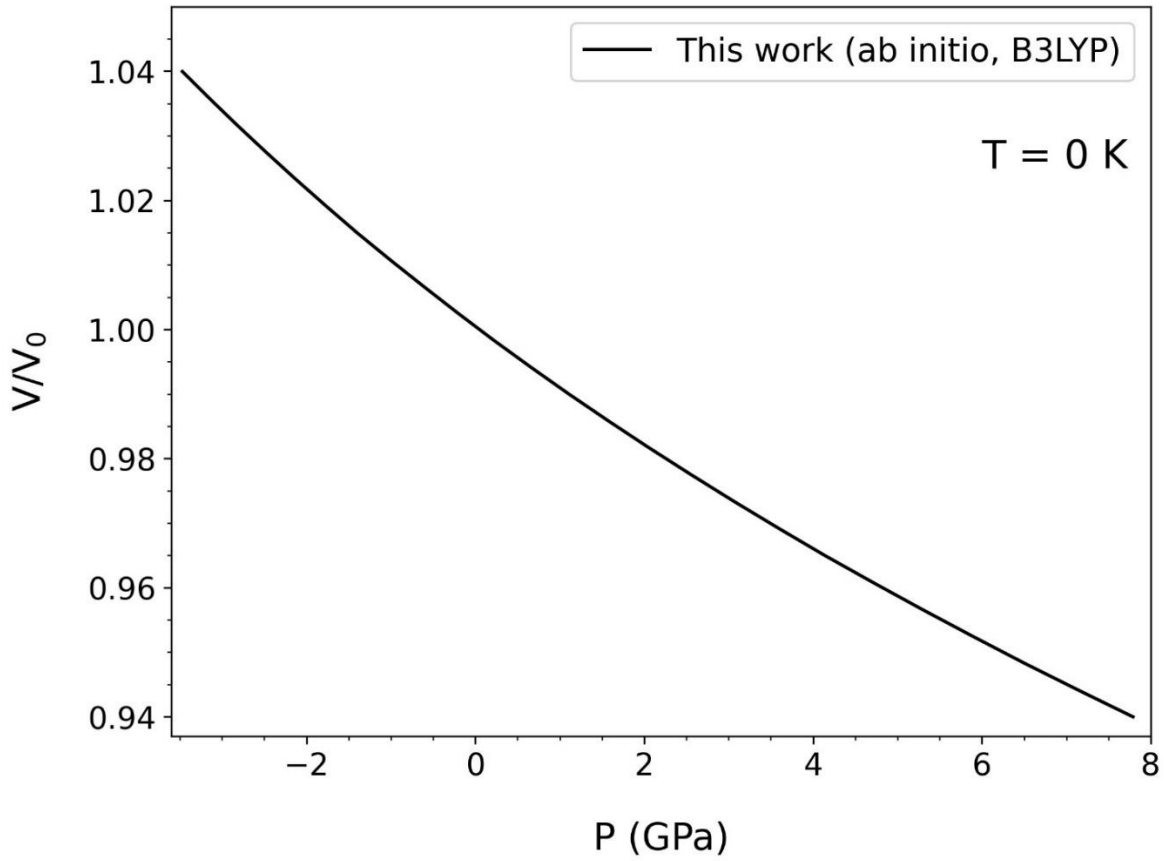


Figure 4.3.3. Static P-V curve of MgSiO₃ protoenstatite (expressed as V/V_0) at T = 0 K.

Table 4.3.1 Elastic constants (C_{ij}) and aggregate bulk (K_{voigt} , K_{reuss} , K_{VRH}) and shear (μ_{voigt} , μ_{reuss} , μ_{VRH}) moduli of MgSiO₃ protoenstatite, as compared with Brillouin scattering experimental measurements by Vaughan & Bass (1983) (VB (1983)).

Elastic constants (Mbar)	This work	VB (1983)
C_{11}	2.25	2.13
C_{22}	1.45	1.52
C_{33}	2.38	2.46
C_{44}	0.80	0.81
C_{55}	0.54	0.44
C_{66}	0.57	0.67
C_{12}	0.67	0.76
C_{13}	0.48	0.59
C_{23}	0.61	0.70
K_{voigt} (GPa)	107.17	113.5
K_{reuss} (GPa)	103.62	110.5

K_{VRH} (GPa)	105.39	112
μ_{Voigt} (GPa)	67.31	65.6
μ_{Reuss} (GPa)	63.36	60.7
μ_{VRH} (GPa)	65.34	63

Comparison of the calculated values with experimental results obtained by Brillouin spectroscopy by (Vaughan and Bass, 1983) show the high performance of ab initio B3LYP calculations in predicting elastic properties of protoenstatite, considering also the fact that experimental measurements by Vaughan and Bass (1983) have been obtained on a protoenstatite sample of formula $[(Mg_{1.6}Li_{0.2}Sc_{0.2})SiO_3]$, hence stabilized by doping with Li and Sc. However, it is not clear how the addition of such elements in the crystal structure might really impact on its elastic properties.

4.4. Lattice dynamics and vibrational spectra

The orthorhombic primitive unit cell of protoenstatite (space group $Pbcn$) contains 40 atoms, each having 3 degrees of freedom, which makes a total of 120 (40×3) vibrational modes. The zone-center ($\vec{q} = 0$) vibrational modes at Γ point can be classified by symmetry analysis as follows:

$$\Gamma = 14A_g + 16B_{1g} + 16B_{2g} + 14B_{3g} + 16B_{1u} + 16B_{2u} + 14B_{3u} + 14A_u \quad (4.4.1)$$

where A_g , B_{1g} , B_{2g} , B_{3g} modes are Raman-active, B_{1u} , B_{2u} , B_{3u} modes are IR-active, and A_u are silent modes. Ab initio B3LYP phonon frequencies of $MgSiO_3$ protoenstatite at Γ point are reported in Table 4.4.1, as compared with experimental and theoretical results. Our calculations allowed to obtain also IR intensities (see De La Pierre and Belmonte, 2016 for details about the method), hence the first IR spectrum of this mineral, which is reported in Figure 4.4.1. According to our calculations, the most intense infrared-active modes occur at the following frequencies: 335.44 cm^{-1} , 452.98 cm^{-1} , 465.75 cm^{-1} , 493.10 cm^{-1} , 931.14 cm^{-1} , 938.21 cm^{-1} , 943.75 cm^{-1} , 946.84 cm^{-1} , 1016.17 cm^{-1} , 1049.89 cm^{-1} , and 1068.49 cm^{-1} .

Table 4.4.1. Ab initio B3LYP vibrational frequencies computed at Γ point (ν_i , wavenumbers in cm^{-1}) as compared to experimental results obtained by Raman spectroscopy (Exp.1 - Mao et al., 1987; Exp. 2 – Kanzaki & Xue, 2017; Exp. 3a – Reynard et al., 2008, Raman spectroscopy on quenched PEn from melt; Exp. 3b - Reynard et al., 2008, Raman spectroscopy on PEn doped with Li and Sc; Exp 4 – Ghose et al., 1994, Raman spectroscopy on PEn doped with Li and Sc). Other DFT calculations are also shown for comparison (Calc. – Ghose et al., 1994, semiempirical potentials). The statistical index $|\bar{\Delta}| = M^{-1} \sum_{i=1}^M |\nu_i^{calc} - \nu_i^{exp}|$ is the mean absolute difference between our results and reference values.

No	Mode	Activity	ν_i (cm^{-1}) (B3LYP, this work)	Exp 1 (Raman)	Exp 2 (Raman)	Exp 3a (Raman)	Exp 3b (Raman)	Exp 4 (Raman)	Calc. (semi- empirical)
1	B _{3u}	IR	0						
2	B _{1u}	IR	0						
3	B _{2u}	IR	0						
4	B _{2g}	Raman	73.57						85
5	A _g	Raman	111.74	99	107	102	102	107	111
6	B _{2u}	IR	114.38						
7	B _{1u}	IR	120.99						
8	B _{3g}	Raman	126.21		120			132	132
9	B _{1g}	Raman	142.68						167
10	A _u	Silent	145.36						
11	B _{2u}	IR	147.62						
12	B _{1u}	IR	164.22						
13	B _{2g}	Raman	180.58					173	179
14	B _{1g}	Raman	180.61					184	190
15	A _g	Raman	190.66	192	195	191		187	195

16	B _{1u}	IR	198.31						
17	A _u	Silent	198.64						
18	B _{1g}	Raman	204.55					203	204
19	B _{3u}	IR	206.92						
20	B _{3g}	Raman	207.74			209		206	208
21	B _{2u}	IR	208.42						
22	A _g	Raman	212.93					209	212
23	B _{2g}	Raman	213.0						
24	B _{3g}	Raman	248.35				250	251	249
25	B _{2g}	Raman	255.37		252			256	
26	B _{1g}	Raman	257.22						
27	B _{1u}	IR	265.35						
28	A _u	Silent	266.92						
29	B _{3g}	Raman	270.64					270	266
30	A _g	Raman	275.04						275
31	B _{3u}	IR	275.64						
32	B _{2u}	IR	279.47						
33	B _{3g}	Raman	285.36						
34	B _{1g}	Raman	287.91					297	
35	A _g	Raman	295.82					300	292
36	B _{2u}	IR	297.09						
37	B _{2g}	Raman	305.68		307		300	309	302
38	B _{3g}	Raman	312.31	311				310	311
39	A _u	Silent	316.31						

40	B _{1u}	IR	318.55						
41	B _{3u}	IR	322.65						
42	B _{1g}	Raman	325.39				323	321	316
43	A _u	Silent	327.0						
44	B _{3u}	IR	327.92						
45	B _{1u}	IR	332.96		332	330			
46	A _g	Raman	333.42						333
47	B _{2u}	IR	335.44						
48	B _{2g}	Raman	345.51					341	337
49	B _{2u}	IR	357.15						
50	A _g	Raman	371.79					375	368
51	A _u	Silent	372.33						
52	B _{1g}	Raman	374.93	377			375	379	374
53	B _{1u}	IR	382.24						
54	B _{3g}	Raman	386.74						
55	B _{1g}	Raman	390.11						394
56	B _{2g}	Raman	391.57						412
57	B _{3u}	IR	398.87						
58	B _{2u}	IR	404.91						
59	A _u	Silent	415.43						
60	B _{3u}	IR	419.64						
61	B _{2g}	Raman	427.27					431	421
62	B _{1u}	IR	429.34						
63	B _{2u}	IR	435.96						

64	A _g	Raman	440.34					438	
65	B _{1g}	Raman	445.39						
66	B _{2g}	Raman	450.85						
67	B _{3g}	Raman	450.87						456
68	B _{1u}	IR	452.98						
69	B _{3u}	IR	465.75						
70	B _{2g}	Raman	469.38					460	460
71	A _u	Silent	472.14						
72	A _g	Raman	476.38					476	476
73	B _{2g}	Raman	489.45						480
74	B _{1u}	IR	493.10						
75	B _{3u}	IR	493.61						
76	B _{1g}	Raman	497.45					509	504
77	B _{1g}	Raman	517.77					521	519
78	A _u	Silent	526.30						
79	B _{2u}	IR	530.98						
80	B _{2g}	Raman	535.96						534
81	B _{3g}	Raman	541.06						
82	B _{3g}	Raman	548.11						
83	B _{3u}	IR	549.15						
84	B _{2u}	IR	549.57						
85	B _{1u}	IR	551.77						
86	A _g	Raman	558.37					569	561
87	A _u	Silent	587.11						

88	B _{1g}	Raman	594.41					620	624
89	B _{2u}	IR	640.98						
90	B _{1u}	IR	673.89						
91	B _{3g}	Raman	675.09	673	675	673	669	671	678
92	A _g	Raman	680.98						
93	B _{1g}	Raman	718.33						724
94	B _{2g}	Raman	737.81					738	743
95	A _u	Silent	751.25						758
96	B _{3u}	IR	769.69						764
97	B _{3u}	IR	884.82						
98	B _{1g}	Raman	885.36					883	812
99	B _{2g}	Raman	910.82						
100	A _u	Silent	920.06						
101	B _{1u}	IR	931.14						
102	A _g	Raman	936.91					936	930
103	B _{2u}	IR	938.20						
104	B _{3g}	Raman	941.72					947	960
105	B _{2u}	IR	943.74						
106	B _{1u}	IR	946.84						
107	B _{2g}	Raman	1003.70	989				990	974
108	A _g	Raman	1006.75					997	995
109	B _{3g}	Raman	1011.50		1017	1013	1011	1009	996
110	B _{3u}	IR	1016.17						
111	A _u	Silent	1024.81						

112	B _{2g}	Raman	1027.66					1023	
113	A _g	Raman	1030.55						1030
114	B _{1g}	Raman	1034.45	1034		1036	1033	1032	
115	B _{1u}	IR	1036.43						
116	B _{1g}	Raman	1045.26		1041				1043
117	B _{2u}	IR	1049.89						
118	A _u	Silent	1064.79						
119	B _{3u}	IR	1068.49						
120	B _{3g}	Raman	1157.41						1173
			$ \bar{\Delta} $ (cm ⁻¹)	5	3	3	3	5	8

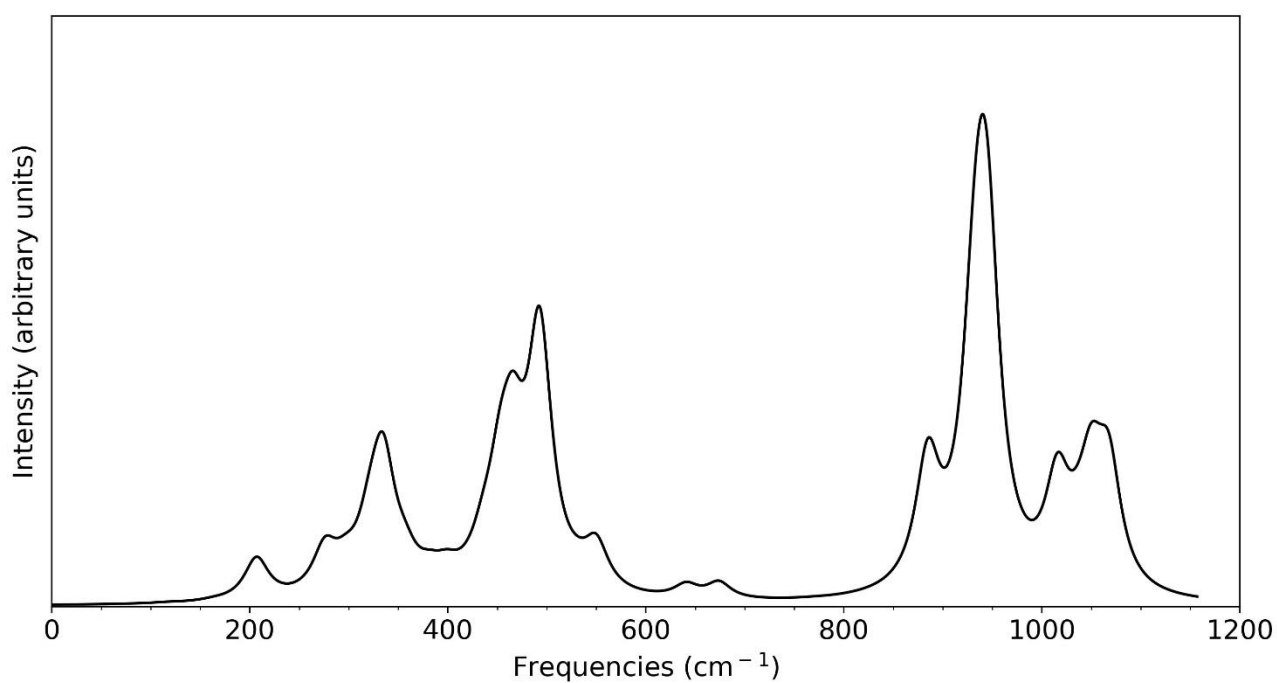


Figure 4.4.1. Computed IR spectra of MgSiO₃ protoenstatite (ab initio B3LYP) at P = 0 GPa and T = 0 K.

According to Reynard et al. (2008), a quick way to identify protoenstatite using Raman spectroscopy consists in the identification of a single peak at around 673 cm⁻¹, which can be used as diagnostic feature, whereas clinoenstatite and orthoenstatite both exhibit a doublet in the same frequency region. Our B3LYP calculation correctly predict the position of the most intense vibration at 675 cm⁻¹, with a maximum deviation of a few cm⁻¹ from literature results. The other most intense vibration according to experimental investigations consists of a single peak at 1034 cm⁻¹, which is once again correctly predicted by our calculations and in good agreement with literature works, except for Kanzaki & Xue (2017), where it is absent. Raman bands with weaker intensity are also accurately predicted, with a maximum deviation of 30 cm⁻¹, which occurs only in one B_{1g} vibrational mode at 594 cm⁻¹, that is recognized at 624 cm⁻¹ according to Ghose et al. (1994). However, it should be noted that theoretical calculations by semi-empirical potentials rarely provide accurate results on vibrational spectra. The correct mode assignment according to the group theory can be rather complex. The only work that provides a complete symmetry analysis of the protoenstatite vibrational spectrum is that of Ghose et al. (1994), employing semi-empirical potentials. Matching mode assignment made by Ghose et al. (1994) can be nonetheless quite difficult. For example, the most intense and diagnostic peak at 675 cm⁻¹ is assigned to a B_{3g} mode according to our calculations, whereas Ghose et al. (1994) assign it to a A_g mode. Furthermore, while Ghose et al. (1994) recognize 14 B_{2g} modes and 16 B_{3g} modes, our ab initio investigation found 16 B_{2g} modes and 14 B_{3g} modes. In order to test the performance of ab initio B3LYP calculations, theoretical and experimental frequencies are compared by means of a global statistical index, which is defined as follows (see De La Pierre and Belmonte, 2016):

$$|\bar{\Delta}| = M^{-1} \sum_{i=1}^M |v_i^{calc} - v_i^{exp}| \quad (4.4.2)$$

where M is the number of data considered in the statistics and $|\bar{\Delta}|$ is the mean absolute difference between calculated (ν_i^{calc}) and experimentally observed frequencies (ν_i^{exp}). Despite considering only the most intense Raman active modes identified in literature works, the agreement with our calculations is excellent, with $|\bar{\Delta}|$ varying between 3 cm^{-1} (when our data are compared with Kanzaki & Xue, 2017 or Reynard et al., 2008) and 8 cm^{-1} (when our data are compared with Ghose et al., 1994). So, as expected, the highest value of $|\bar{\Delta}|$ is observed when our data are compared with the semi-empirical calculations performed by Ghose et al. (1994).

4.5. Thermoelastic and thermodynamic properties

Full phonon dispersion calculations directly provide the total vibrational density of state (vDOS) which, combined with the quasi-harmonic analysis of vibrational modes by the mode gamma Grüneisen parameters (γ_i), allows for the calculation of all thermodynamic properties of a given crystalline solid, as illustrated in Chapter 2. Table 4.5.1 and Figure 4.5.1 report the vibrational modes of MgSiO_3 protoenstatite coupled with their relative mode Grüneisen parameters (γ_i). Figure 4.5.1 also shows the mean mode Grüneisen parameter, which attains a value of $\bar{\gamma}_i = 0.75$.

Table 4.5.1. Ab initio B3LYP vibrational frequencies (ν_i , cm^{-1}) and their relative mode Grüneisen parameters (γ) calculated for MgSiO_3 protoenstatite.

Mode	ν_i (cm^{-1}) (B3LYP)	γ (B3LYP)
B_{2g}	73.57	2.02
A_g	111.74	0.08

B _{2u}	114.38	0.04
B _{1u}	120.99	0.55
B _{3g}	126.21	0.75
B _{1g}	142.68	0.31
A _u	145.36	0.58
B _{2u}	147.62	0.38
B _{1u}	164.22	2.35
B _{2g}	180.58	3.46
B _{1g}	180.61	0.33
A _g	190.66	2.71
B _{1u}	198.31	1.21
A _u	198.64	2.62
B _{1g}	204.55	1.45
B _{3u}	206.92	1.82
B _{3g}	207.74	1.86
B _{2u}	208.42	0.32
A _g	212.93	1.22
B _{2g}	213.0	1.04
B _{3g}	248.35	2.69
B _{2g}	255.37	0.59
B _{1g}	257.22	1.62
B _{1u}	265.35	1.34
A _u	266.92	0.94
B _{3g}	270.64	1.57
A _g	275.04	1.03
B _{3u}	275.64	1.70
B _{2u}	279.47	1.18
B _{3g}	285.36	1.20
B _{1g}	287.91	0.66
A _g	295.82	2.47

B _{2u}	297.09	0.79
B _{2g}	305.68	0.61
B _{3g}	312.31	0.89
A _u	316.31	1.08
B _{1u}	318.55	0.83
B _{3u}	322.65	2.22
B _{1g}	325.39	1.64
A _u	327.0	1.71
B _{3u}	327.92	1.27
B _{1u}	332.96	0.51
A _g	333.42	1.07
B _{2u}	335.44	0.48
B _{2g}	345.51	0.77
B _{2u}	357.15	1.95
A _g	371.79	1.17
A _u	372.33	0.87
B _{1g}	374.93	0.32
B _{1u}	382.24	0.08
B _{3g}	386.74	0.21
B _{1g}	390.11	0.81
B _{2g}	391.57	0.86
B _{3u}	398.87	0.06
B _{2u}	404.91	0.05
A _u	415.43	0.32
B _{3u}	419.64	0.35
B _{2g}	427.27	0.32
B _{1u}	429.34	0.46
B _{2u}	435.96	-0.08
A _g	440.34	0.22
B _{1g}	445.39	-0.14

B _{2g}	450.85	0.30
B _{3g}	450.87	0.31
B _{1u}	452.98	0.27
B _{3u}	465.75	0.51
B _{2g}	469.38	0.12
A _u	472.14	0.32
A _g	476.38	-0.16
B _{2g}	489.45	0.08
B _{1u}	493.10	-0.15
B _{3u}	493.61	0.39
B _{1g}	497.45	0.42
B _{1g}	517.77	0.36
A _u	526.30	0.45
B _{2u}	530.98	-0.01
B _{2g}	535.96	0.36
B _{3g}	541.06	0.36
B _{3g}	548.11	0.36
B _{3u}	549.15	0.53
B _{2u}	549.57	0.40
B _{1u}	551.77	0.30
A _g	558.37	0.36
A _u	587.11	0.51
B _{1g}	594.41	0.08
B _{2u}	640.98	0.47
B _{1u}	673.89	0.51
B _{3g}	675.09	0.66
A _g	680.98	0.59
B _{1g}	718.33	0.18
B _{2g}	737.81	0.17
A _u	751.25	0.28

B _{3u}	769.69	0.25
B _{3u}	884.82	0.86
B _{1g}	885.36	0.79
B _{2g}	910.82	0.75
A _u	920.06	0.71
B _{1u}	931.14	0.49
A _g	936.91	0.34
B _{2u}	938.20	0.55
B _{3g}	941.72	0.32
B _{2u}	943.74	0.47
B _{1u}	946.84	0.51
B _{2g}	1003.70	0.69
A _g	1006.75	0.70
B _{3g}	1011.50	0.66
B _{3u}	1016.17	0.30
A _u	1024.81	0.70
B _{2g}	1027.66	0.41
A _g	1030.55	0.71
B _{1g}	1034.45	0.44
B _{1u}	1036.43	0.72
B _{1g}	1045.26	0.63
B _{2u}	1049.89	0.73
A _u	1064.79	0.39
B _{3u}	1068.49	0.68
B _{3g}	1157.41	0.65

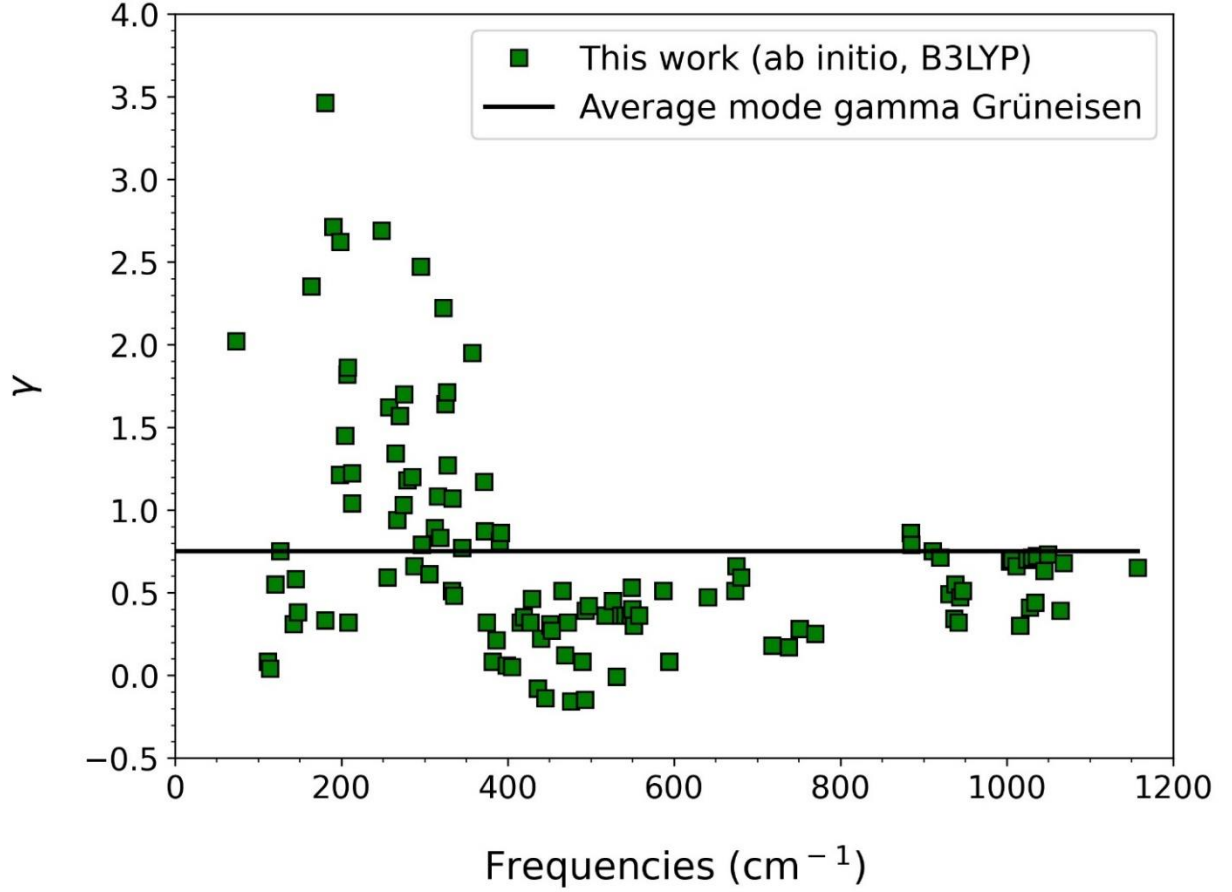


Figure 4.5.1. Distribution of theoretical mode Grüneisen parameters as computed for MgSiO₃ protoenstatite. Mean mode gamma Grüneisen is represented by the black horizontal line and attains a value of $\bar{\gamma}_l = 0.75$.

As described in Chapter 2, once the quasi-harmonic analysis of the vibrational modes is performed and the phonon dispersion is available, the first step to determine thermodynamic properties of a crystalline compound is the calculation of the αK_T product which, in the case of MgSiO₃ protoenstatite, attains a fairly constant value of 0.0028 GPa/K in the temperature range between 1400 and 3000 K (figure 4.5.2). Fitting P-V-T relations of MgSiO₃ protoenstatite, as obtained from the Mie-Grüneisen formalism (see section 2.5), with a 3rd order, high-temperature, Birch-Murnaghan equation of state (HT-BM3 EOS) yields $\left(\frac{\partial K_T}{\partial T}\right)_p = -278 \text{ bar /K}$. This is the first determination of the bulk modulus temperature derivative of protoenstatite, and as such there are no data available for comparison.

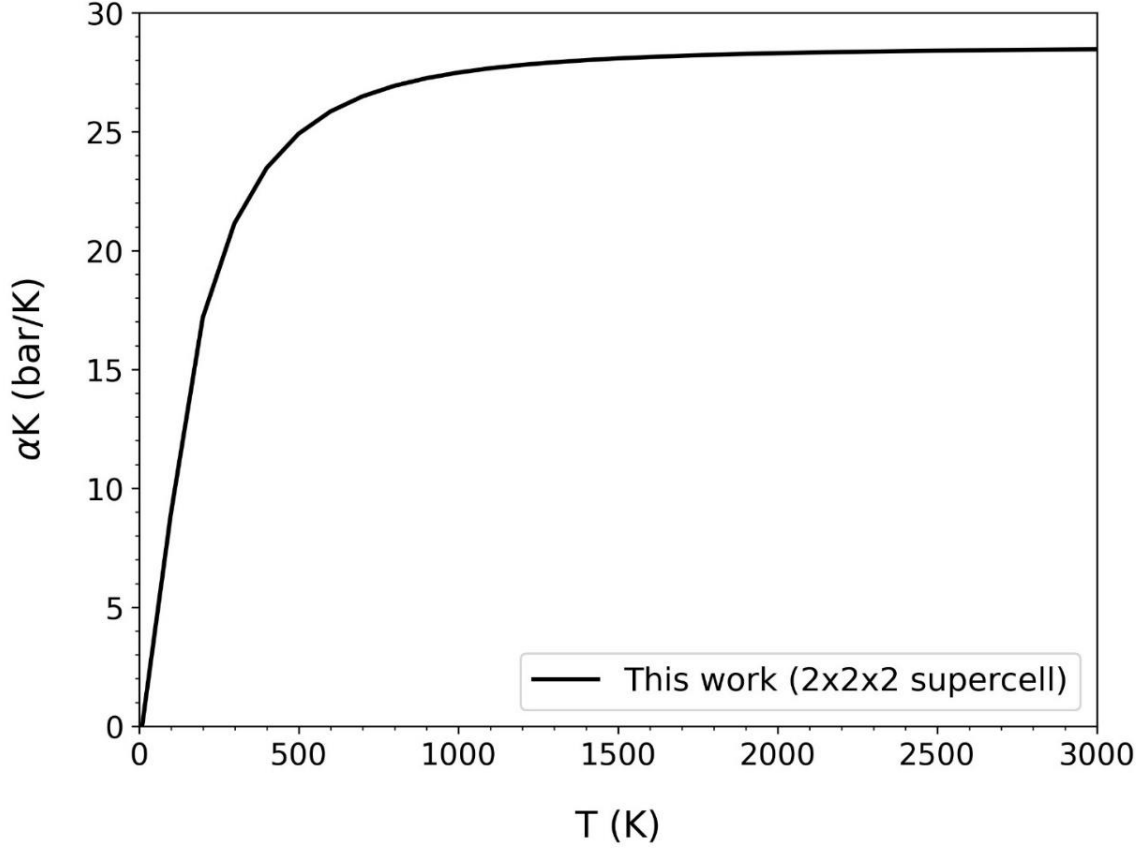


Figure 4.5.2. αK_T product as calculated in this work for MgSiO_3 protoenstatite by ab initio B3LYP.

Thermal expansion coefficient (α_v) of protoenstatite was calculated in the framework of the quasi-harmonic approximation at zero pressure and discrete temperatures. Discrete values of α_v were fitted with a suitable polynomial function in the temperature range from $T = 298.15\text{K}$ to $T = 2000\text{K}$ as follows:

$$\alpha_v(P_0, T) = \alpha_0 T + \alpha_1 + \alpha_2 T^{-1} + \alpha_3 T^{-2} + \alpha_4 T^{-3} \quad (4.5.1)$$

Fitted numerical coefficients of the polynomial function at $P = 0$ are $\alpha_0 = 3.1574 \cdot 10^{-8}$, $\alpha_1 = -2.03221 \cdot 10^{-5}$, $\alpha_2 = 3.679 \cdot 10^{-2}$, $\alpha_3 = -13.5445$ and $\alpha_4 = 1646.0216$. The results of our ab initio B3LYP calculations for protoenstatite volume thermal expansion (i.e. V/V_0 vs. T) and volume thermal expansion coefficient or volume thermal expansivity (α_v) are reported in Figures 4.5.3 and 4.5.4, respectively, as compared with the available

experimental results from Murakami et al. (1984), Schrader et al. (1990), Yang & Ghose, (1995) and Jiang et al. (2002).

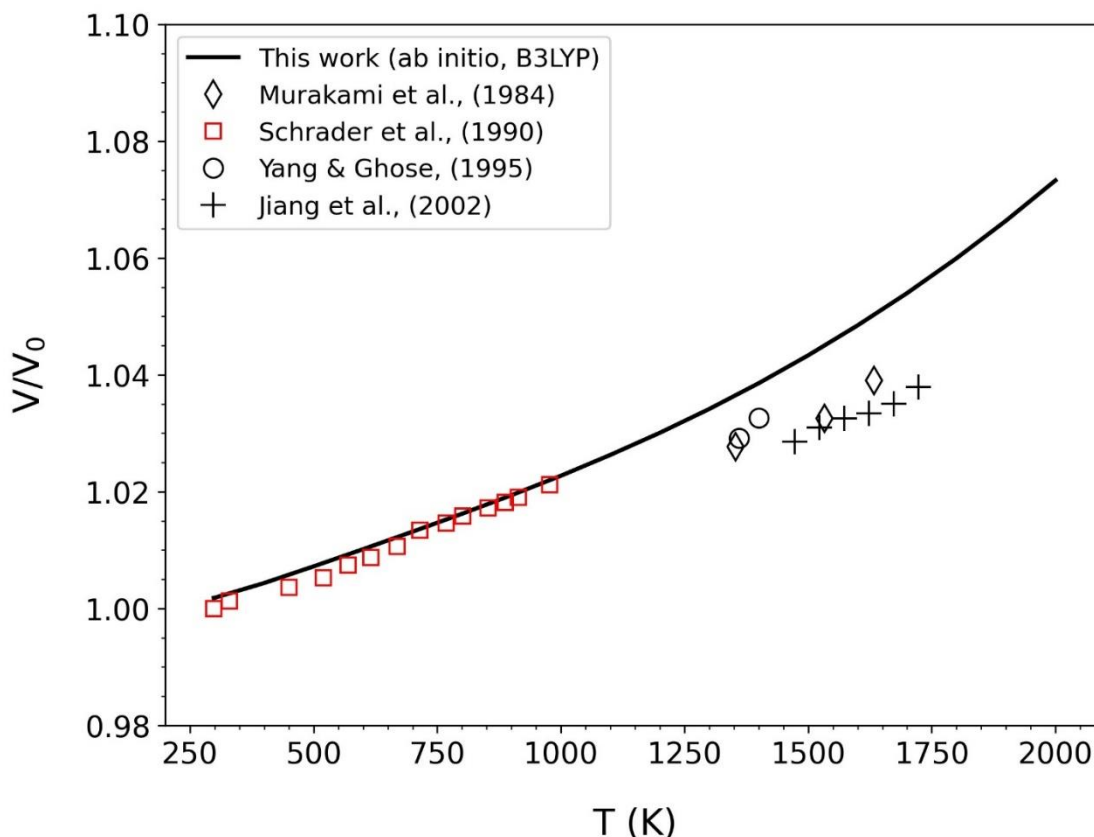


Figure 4.5.3. Ab initio B3LYP volume thermal expansion of MgSiO₃ protoenstatite at zero pressure, as compared with experimental measurements at ambient pressure [V(T) values for Murakami et al., 1984, Yang & Ghose, 1995 and Jiang et al., 2002 are normalized to V₀ = 3.242 J/bar as reported in Berman, 1988].

Calculated result for the volume thermal expansion of protoenstatite reproduces extremely well the low temperature data of Schrader et al. (1990). On the contrary, the high temperature measurements of Yang & Ghose (1995), Murakami et al. (1984) and Jiang et al. (2002) are sensibly lower and quite different from our results. Nevertheless, once fitted to derive the volume thermal expansion coefficient as $\alpha_V = (\partial V/\partial T)_P$, only the experimental data by Schrader et al. (1990) give sensible results, while inaccurate or unphysical results seem to come out by fitting the other ones (see below). Computed values for volume thermal expansivity of protoenstatite are reported in

Figure 4.5.4. Due to the lack of experimental data to use as comparison, we fitted volume – temperature relations according to Schrader et al. (1990) and Jiang et al. (2002) to obtain volume thermal expansivity values that could be compared with our ab initio data. The comparison with the fitted data from Schrader et al. (1990) turns out to be acceptable, with the exception of a slight overestimation of the fitted data in the temperature range between 300 and 500 K. On the contrary, fitted data according to Jiang et al. (2002) are sensibly underestimated with respect to computed data and display a steeper increase with temperature. This might be due to the low number of points used for fitting or to inaccurate results.

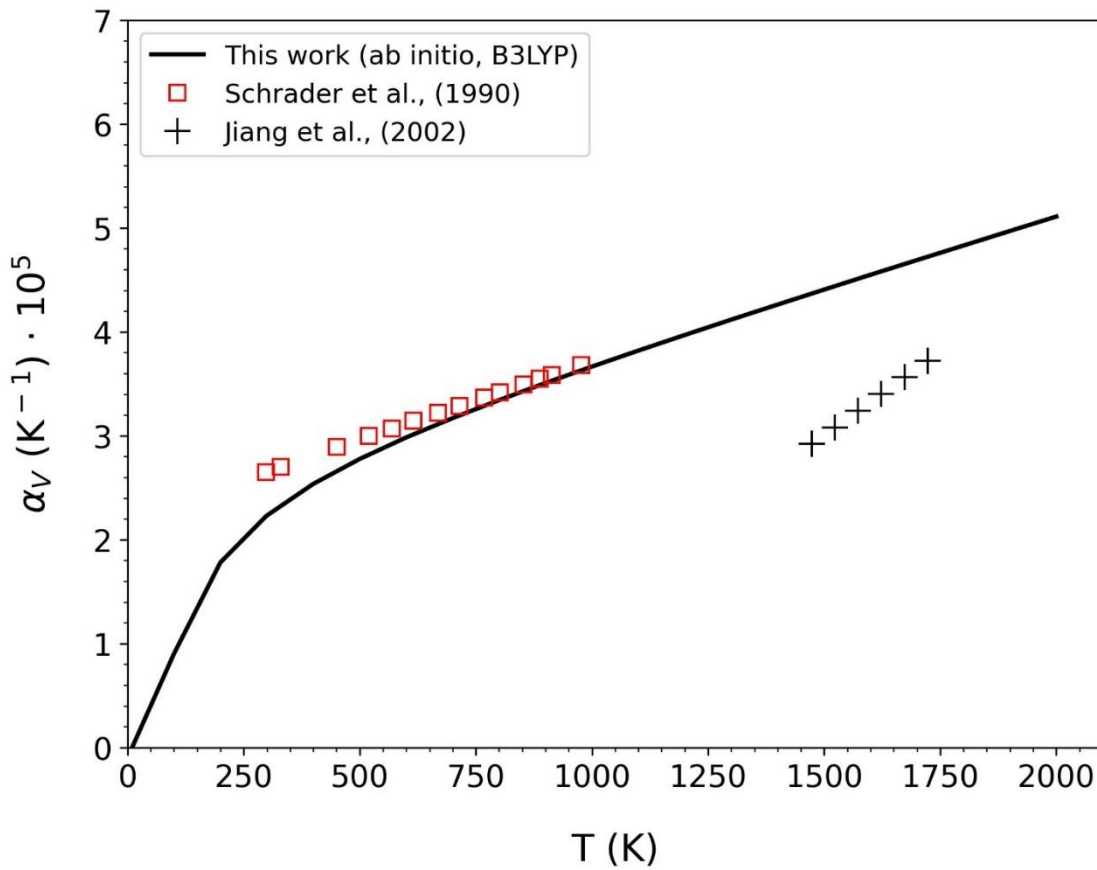


Figure 4.5.4. Ab initio B3LYP volume thermal expansivity (α_V) of MgSiO₃ protoenstatite at zero pressure, as compared with fitted experimental data according to Schrader et al. (1990) and Jiang et al. (2002).

Isobaric heat capacity (C_P) and molar entropy (S) can then be computed according to equations presented in section 2.5. Discrete values obtained for C_P were fitted in the temperature range between 298.15 and 2000 K using a Shomate polynomial function:

$$C_P = a + bT + cT^{-2} + dT^{-\frac{1}{2}} + eT^{-3} + fT^2 + gT^3 \quad (4.5.2)$$

where $a = 106.9$, $b = 1.6761 \times 10^{-2}$, $c = -2.8123 \times 10^5$, $d = -135.1$, $e = -5.6979 \times 10^8$, $f = 3.8461 \times 10^{-6}$, $g = -2.3662 \times 10^{-9}$.

Calculated results are compared with the only calorimetric investigation available so far for protoenstatite (Thieblot et al., 1999), and with the thermodynamic assessment of Berman (1988) in Fig. 4.5.5.

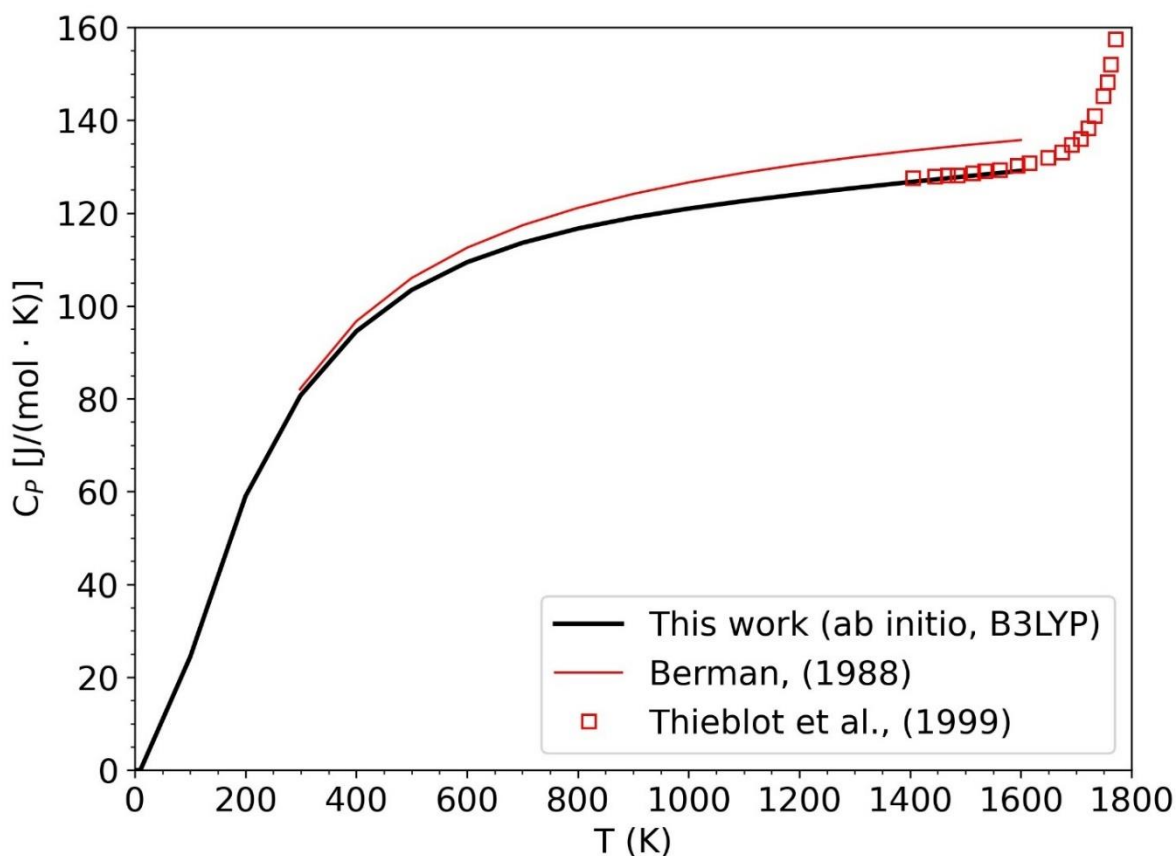


Figure 4.5.5. Ab initio isobaric heat capacity (C_P) for protoenstatite as compared with experimental results and thermodynamic assessment.

Ab initio values of isobaric heat capacity perfectly reproduce the available experimental data in the temperature range between 1400 and 1600 K, with a deviation from the measured values of less than 1%. One noteworthy feature in Figure 4.5.5 is the anomalous C_P increase observed by calorimetric measurements, which has been interpreted by Thieblot et al. (1999) with the onset of premelting effects, that take place about 130 K below the incongruent melting point of protoenstatite. This behavior, which is likely related to the partial collapse of the crystalline structure before reaching the melting point (Richet and Fiquet, 1991), cannot be modelled by QHA calculations. It should also be noted that experimental measurements of the heat capacity performed by Thieblot et al. (1999) are performed only within the stability limits of protoenstatite, since $T < 1400$ K protoenstatite was observed to revert into orthoenstatite. To obtain a reliable C_P function it is then necessary to extrapolate the experimentally measured values of C_P in the medium to low-temperature range, which might strongly affect numerical accuracy at those conditions. The polynomial function fitted from ab initio data, on the contrary, reproduces heat capacity values in the whole temperature range, which is important for the calculation of the Gibbs free energy which requires an integrable analytical function for C_P from low to high temperature conditions. The comparison with the C_P function proposed by Berman (1988) shows that isobaric heat capacity assessed via mathematical procedures is able to reproduce selected phase equilibria but is severely overestimated in almost the entire temperature range (up to 5% at high temperature conditions, where the C_P values assessed by Berman, 1988 turn out to be sensibly different from calorimetric values and ab initio results as well).

Concerning the total entropy of protoenstatite, our calculation yields $S^0 = 67.692$ J/(mol $\times$ K), which is consistent with assumed values in the literature (Table 4.5.2). In the absence of any experimental data, we compared our results with thermodynamic assessments (Berman, 1988; Fabrichnaya et al., 2004; Holland & Powell, 2011).

Table 4.5.2. Computed standard state entropy as compared with assessed values in thermochemical tables (1 = Berman, 1988; 2 = Holland & Powell, 2011; 3 = Fabrichnaya et al., 2004).

	This work	1	2	3
S^0 [J/(mol $\times$ K)]	67.692	67.438	68.5	66.96

Computed standard-state enthalpy of formation from the elements (H_f^0) of protoenstatite attains a value of -1546.039 kJ/mol, which is in good agreement with other thermochemical tabulations reported in Table 4.5.3. The thermochemical cycle that allows to assess the value of H_f^0 has been described in detail in section 2.6.

Table 4.5.3. Computed standard state enthalpy of formation as compared with thermochemical tables (1 = Berman, 1988; 2 = Holland&Powell, 2011; 3 = Fabrichnaya et al., 2004).

	This work	1	2	3
H_f^0 (kJ/mol)	-1546.039	-1543.959	-1542.285	-1545.790

4.6. Ab initio thermodynamic dataset

A summary of the most relevant thermodynamic properties of MgSiO_3 protoenstatite as obtained in this study by ab initio B3LYP is reported in Table 4.6.1, whereas a detailed thermodynamic tabulation in the temperature range from 298.15 K to 2000 K is reported in Table 4.6.2.

Table 4.6.1. Summary of the most relevant thermodynamic properties of MgSiO_3 protoenstatite, as computed in this work. H_f^0 = standard-state enthalpy of formation from the elements; S^0 = standard state entropy; a, b, c, d, e, f, g = numerical coefficients of the polynomial function for isobaric heat capacity (C_p), fitted in the T range 298.15 – 2000 K (Eq. 3.5.2); V_0 = molar volume at the athermal limit (T = 0 K; P = 0 GPa); K_0 = static bulk modulus; K'_0 = pressure derivative of bulk modulus; dK_T/dT =

isobaric temperature derivative of isothermal bulk modulus; $\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4$ = numerical coefficients of the polynomial function for volume thermal expansivity, fitted in the T range 200 – 2000 K (Eq. 3.5.1).

H^0_f (kJ/mol)	-1546.039	V_0 (cm ³ /mol)	33.337
S^0 [J/(mol × K)]	67.692	K_0 (GPa)	101.88
a	106.90	K'_0	6.59
$b \times 10^3$	16.761	dK_T/dT (bar/K)	-278
$c \times 10^{-5}$	-2.812	$\alpha_0 \times 10^7$	0.31574
d	-135.1	$\alpha_1 \times 10^7$	-203.221
$e \times 10^{-8}$	-5.6979	$\alpha_2 \times 10^3$	36.79
$f \times 10^6$	3.8461	α_3	-13.5445
$g \times 10^9$	-2.3662	α_4	1646.0216

Table 4.6.2. Ab initio B3LYP thermodynamic and thermophysical functions of MgSiO₃ protoenstatite. C_P = isobaric heat capacity; S = molar entropy; V = molar volume; U_{vib} , H_{vib} , G_{vib} = vibrational contribution to internal energy, enthalpy and Gibbs free energy, respectively; K_T = isothermal bulk modulus; α_v = thermal expansion coefficient; $P_{thermal}$ = thermal pressure.

T(K)	C_P [J/(mol × K)]	S [J/(mol × K)]	V (cm ³ /mol)	U_{vib} (kJ/mol)	H_{vib} (kJ/mol)	G_{vib} (kJ/mol)	K_T (GPa)	$\alpha_v \times 10^5$ (K ⁻¹)	$P_{thermal}$ (GPa)
298.15	80.510	67.692	33.420	56.504	56.538	36.407	94.45	2.220	0.318
300	80.825	68.192	33.421	56.653	56.687	36.282	94.40	2.227	0.321
400	94.547	93.465	33.500	65.410	65.444	28.207	92.24	2.544	0.535
500	103.459	115.591	33.59	75.245	75.279	17.786	89.41	2.785	0.77
600	109.431	135.022	33.688	85.773	85.807	5.313	86.68	2.982	1.019
700	113.611	152.217	33.791	96.763	96.797	-8.961	84.27	3.156	1.277
800	116.683	167.595	33.901	108.071	108.105	-24.833	81.12	3.319	1.542
900	119.057	181.485	34.015	119.605	119.639	-42.138	78.34	3.478	1.811
1000	120.986	194.131	34.135	131.306	131.341	-60.735	76.30	3.637	2.083
1100	122.629	205.743	34.262	143.131	143.166	-80.511	72.78	3.801	2.358
1200	124.088	216.476	34.395	155.051	155.086	-101.368	70.81	3.972	2.635
1300	125.429	226.463	34.536	167.047	167.082	-123.223	67.22	4.153	2.913
1400	126.697	235.803	34.684	179.103	179.138	-146.004	64.44	4.346	3.192
1500	127.922	244.590	34.84	191.208	191.243	-169.647	62.16	4.554	3.473
1600	129.119	252.876	35.005	203.352	203.387	-194.101	58.88	4.779	3.754
1700	130.299	260.747	35.178	215.530	215.566	-219.314	56.15	5.025	4.035

1800	131.462	268.230	35.361	227.735	227.771	-245.246	53.32	5.294	4.318
1900	132.608	275.366	35.554	239.964	240.000	-271.855	50.54	5.593	4.601
2000	133.726	282.193	35.756	252.212	252.248	-299.111	46.49	5.925	4.884

4.7. Phase stability of protoenstatite at mantle conditions

Computed thermodynamic properties for protoenstatite have been tested by predicting the orthoenstatite – protoenstatite P-T phase boundary via Gibbs free energy minimization, coupling our theoretical data for protoenstatite with an optimized set of thermodynamic properties for orthoenstatite (input data are provided in the supplementary section in Tables S.6.1a,b). The phase boundary in Figure 4.7.1 (black curve) represents the result of the calculation. Some ab initio-assisted assessment on the thermodynamic properties of orthoenstatite was necessary in order to make them consistent with those calculated for protoenstatite in this work. In order to pinpoint the protoenstatite-orthoenstatite inversion at 1-bar pressure according to the experimental determination by Atlas (1952): i) the enthalpy change of the protoenstatite-orthoenstatite reaction at ambient P-T conditions (i.e. ΔH^0) has been lowered by 1.2 kJ/mol, within the range of experimental uncertainty of the standard-state enthalpy values of the pyroxene phases (estimated to be around 1.5 kJ/mol for orthoenstatite; cf. Robie and Hemingway, 1995) (see Table 4.7.1); ii) the isobaric heat capacity of orthoenstatite have been set equal to that of protoenstatite, as assumed also by other thermodynamic assessments (e.g. Berman, 1988; Holland and Powell, 2011). The latter assumption, which may seem quite rough at first glance, can be justified with the fact that preliminary ab initio B3LYP calculations performed on orthoenstatite yield C_P values for OEn nearly coincident with those of protoenstatite in the whole temperature range [see Fig. 4.7.2a, where C_P values of OEn (the blue curve in the diagram) show a mean difference of ~1.6% from those of PEn (the black curve) in T range between 400 K and 1000 K]. Such a difference is close or within the limits of resolution of the QHA and/or the uncertainty of the fitting procedure of ab initio C_P data with the polynomial function given by Equation (4.5.2). Nevertheless, since heat

capacity data optimized for OEn in this work are different from calorimetric results obtained by Krupka et al. (1985) and Thieblot et al. (1999) (by 2-3%; see Figure 4.7.2a), further theoretical investigation is still needed for orthoenstatite. Alternatively, DFT calculation performed in the QHA might not be able to accurately reproduce thermodynamic properties of orthoenstatite, which in this case could be affected by intrinsic anharmonic effects (Zucker and Shim, 2009).

As to the high-pressure part of the PEn-OEn phase boundary, ab initio results are in reasonable agreement with the experiments of Anastasiou & Seifert (1972) and Chen & Presnall (1975) up until ~ 0.6 GPa, while the phase boundary observed by Boyd et al., (1964) plots at higher temperatures. At higher pressures (i.e.: above ~ 0.7 GPa) a change in the theoretical Clapeyron slope from 2.89 MPa/K to 3.77 MPa/K marks a flattening of the theoretical phase boundary, which moves away from the experiments. The reason for this behaviour seems to be linked to the differences of free energies of these polymorphs at these conditions, that are so small to be at the very resolution limit of the DFT – QHA theory itself. For this reason, Figure 4.7.1 also shows two dashed phase boundaries (in blue), which were obtained by coupling the theoretical properties of protoenstatite with optimized thermodynamic data for orthoenstatite. The upper phase boundary comes from the adoption of the ab initio value for V_0 of orthoenstatite (i.e. 32.504 cc³/mol) and the assessed thermodynamic and thermoelastic properties reported in Belmonte et al. (2017a) (still retaining the assumption made on the isobaric heat capacity). The lower phase boundary was obtained by setting the enthalpy change of the OEn = PEn reaction equal to that of Berman (1988) [i.e. $\Delta H^0_{(\text{OEn} = \text{PEn})} = 1.593$ kJ/mol]. In other words, the upper and lower bounds in Figure 4.7.1 show the effect of small changes in the $\Delta H^0_{(\text{OEn} = \text{PEn})}$ of reaction on the P-T location and Clapeyron slope of the PEn–OEn phase boundary. It's interesting to note that the upper optimized phase boundary [with $\Delta H^0_{(\text{OEn} = \text{PEn})} = 1.892$ kJ/mol] matches both the P – T location as defined by experiments of Atlas (1952), Anastasiou & Seifert (1972) and Chen & Presnall (1975) and the observed Clapeyron slope [i.e.: $dP/dT = 2.016$ MPa/K, in excellent agreement with the values inferred by

Anastasiou & Seifert (1972) (i.e.: $dP/dT = 2.090$ MPa/K) and Chen & Presnall (1975) (i.e.: $dP/dT = 2.114$ MPa/K), respectively]. The lower bound [calculated with an assessed value of $\Delta H^0_{(\text{OEn} = \text{PEn})} = 1.593$ kJ/mol] reproduces well the Clapeyron slope, but not the P-T location of the observed phase boundary. To conclude, a difference of just 0.3 kJ/mol in the $\Delta H^0_{(\text{OEn} = \text{PEn})}$ is reflected by a shift of the univariant curve of about 200 K. This strengthens the fact that this phase boundary is extremely difficult to investigate by theoretical methods, since predicting such small differences of energy is close to the limits of theory. On the other hand, experimental results obtained so far on the same phase boundary are quite contradictory. Therefore, despite the aforementioned technical and computational troubles, the PEn-OEn phase boundary definitely deserves further investigation even though ab initio B3LYP calculations performed in this work seem to support much more the experimental results obtained by Anastasiou & Seifert (1972) and Chen & Presnall (1975), rather than those obtained by Boyd et al. (1964), the latter providing a much steeper Clapeyron slope.

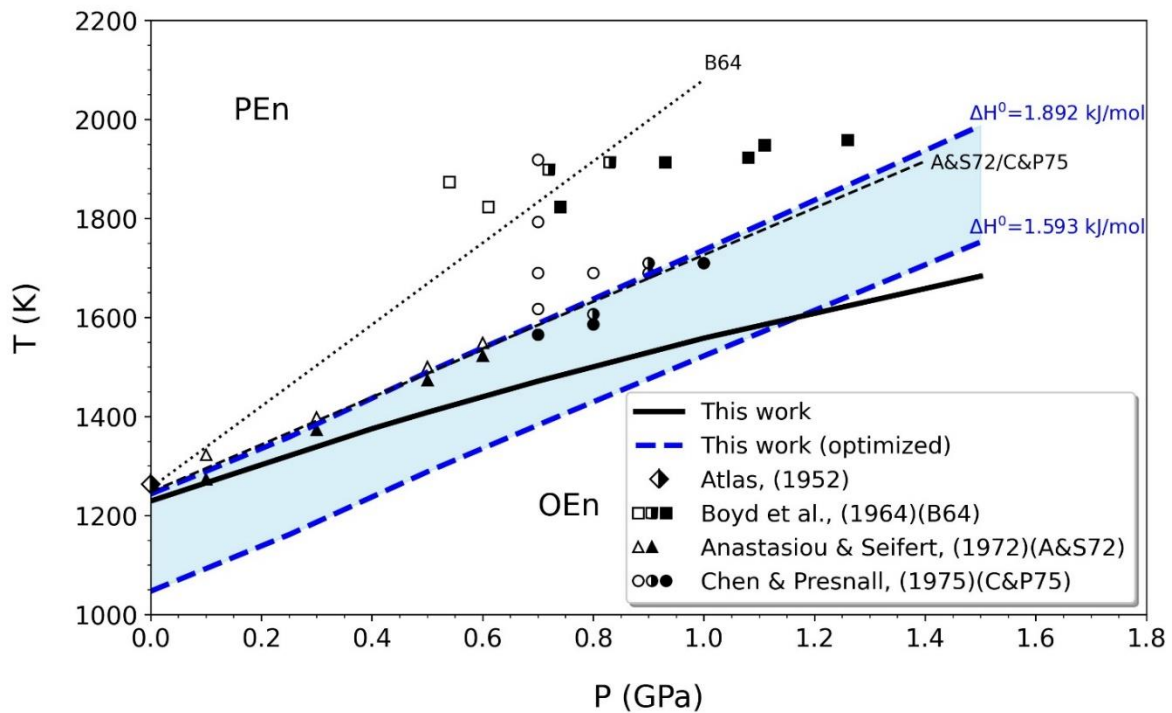


Figure 4.7.1. Orthoenstatite (OEn) – protoenstatite (PEn) phase transition boundary as calculated in this work (black and blue dashed lines; see text for explanation). Experimental

data are shown for comparison. Symbols: empty markers = protoenstatite stable; half-colored markers = orthoenstatite + protoenstatite stable together; black markers = orthoenstatite stable. Thin dotted and dashed lines in black represent best-fits of experimental data, as proposed by the mentioned authors in the caption.

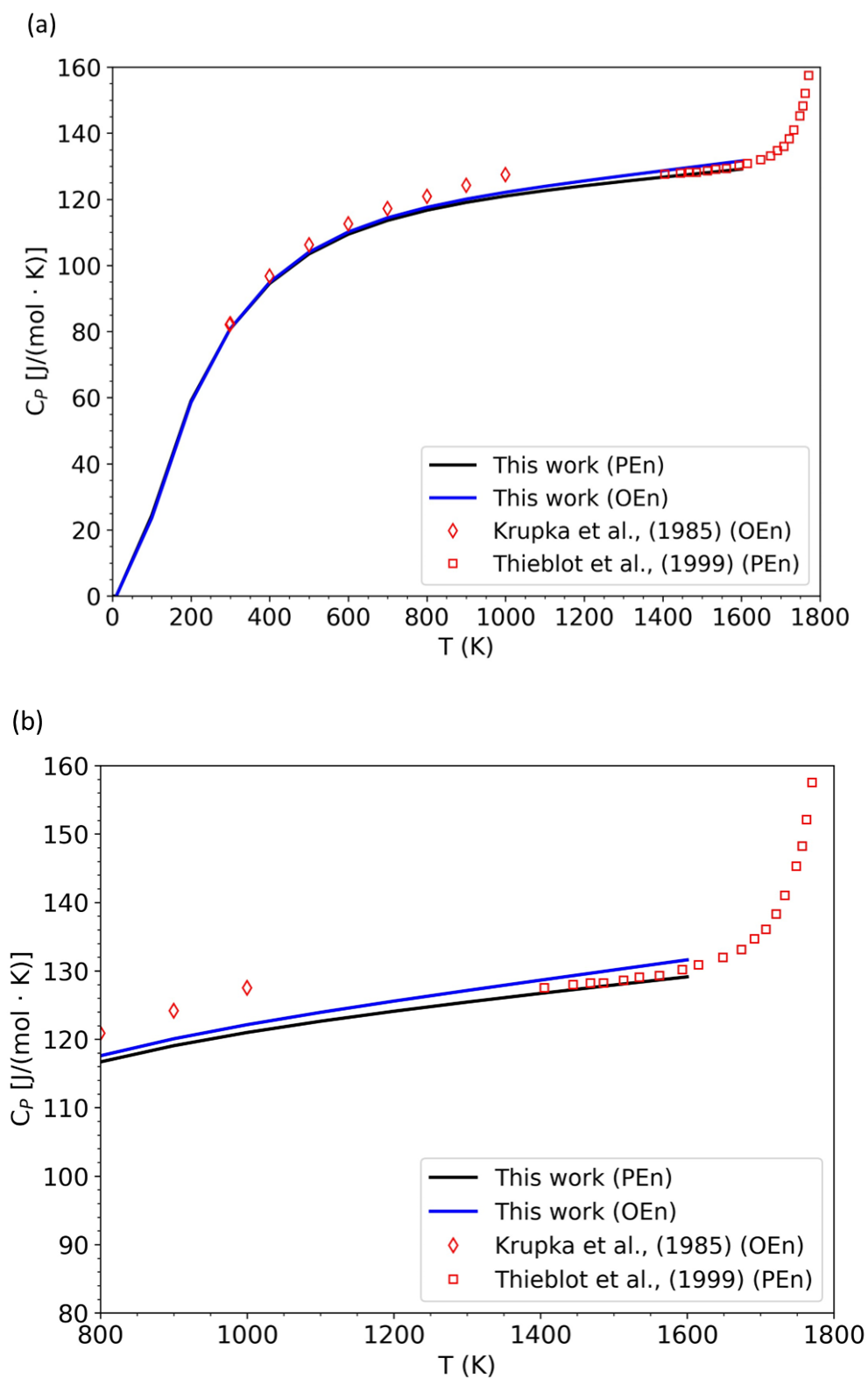


Figure 4.7.2. Comparison between protoenstatite (PEn) and orthoenstatite (OEn) isobaric heat capacities (a). Experimental results of calorimetric investigations are also shown for comparison (Krupka et al., 1985; Thieblot et al., 1999). Panel (b) shows a more detailed view in the high-temperature range.

Table 4.7.1. Thermodynamic dataset used to calculate the ab initio Pen-OEn phase boundary (black curve in Figure 4.7.1).

	MgSiO ₃ protoenstatite	MgSiO ₃ orthoenstatite
H ⁰ _f (kJ/mol)	-1544.860	-1546.485
S ⁰ [J/(mol × K)]	67.692	66.371
a	106.90	106.90
b × 10 ³	16.761	16.761
c × 10 ⁻⁵	-2.812	-2.812
d	-135.10	-135.10
e × 10 ⁻⁸	-5.69790	-5.69790
f × 10 ⁶	3.8461	3.8461
g × 10 ⁹	-2.3662	-2.3662
V ⁰ (cm ³ /mol)	33.337	32.504
K ₀ (GPa)	101.88	76.29
K' ₀	6.59	13.77
dK/dT (bar/K)	-278	-223
α ₀ × 10 ⁷	0.31574	0.4829
α ₁ × 10 ⁷	-203.221	-409.734
α ₂ × 10 ³	36.79	59.37
α ₃	-13.5445	-21.0068
α ₄	1646.0216	2510.7907

4.8. Metastability of protoenstatite polymorphs

X-ray diffraction studies (e.g. Smyth, 1971) has been shown that protoenstatite, whose structure is usually refined in the *Pbcn* space group, may also exist as a polymorph with a different symmetry (i.e. in the *P2₁cn* space group). Yang et al. (1999) performed a single-crystal diffraction study on a Li,Sc-bearing protopyroxene of formula (Mg_{1.54}Li_{0.23}Sc_{0.23})Si₂O₆ and showed that a first-order displacive phase transition occurs from the *Pbcn* polymorph to the *P2₁cn* polymorph, stabilizing the latter at higher pressures. The high-pressure phase stability of the *P2₁cn* polymorph

was also supported by a DFT-LDA study by Jahn & Martonak (2009), who found the $P2_1cn$ as a stable phase already at pressures higher than few kilobars on the basis of static enthalpy calculations performed at $T = 0$ K. According to this study, the $P2_1cn$ polymorph, (and not the $Pbcn$ polymorph) would be the stable phase of protoenstatite in the most part of its P-T stability field inside the $MgSiO_3$ phase diagram. Fig. 4.8.1 shows the results of static enthalpy calculations we performed at the B3LYP level of theory on the $P2_1cn$ and $Pbcn$ protoenstatite polymorphs. Interestingly enough, our calculations predict a phase transition occurring at $T = 0$ K at $P \cong 1.8$ GPa, thus stabilizing the $P2_1cn$ polymorph as the energetically-favoured phase at higher pressures. This outcome could be relevant since the $P2_1cn$ protoenstatite phase may form at P-T conditions compatible with those of the PEn-OEn transition, making the (meta)stability of this phase worth investigating on. Moreover, ab initio static enthalpy calculations performed in this work by B3LYP possibly improve the accuracy of previous LDA calculations by Jahn & Martonak (2009), since the latter would imply a too restricted stability field for the $Pbcn$ phase in contrast with experimental evidences. In a future perspective, full phonon dispersion calculations on the $P2_1cn$ phase could help to solve this still open issue.

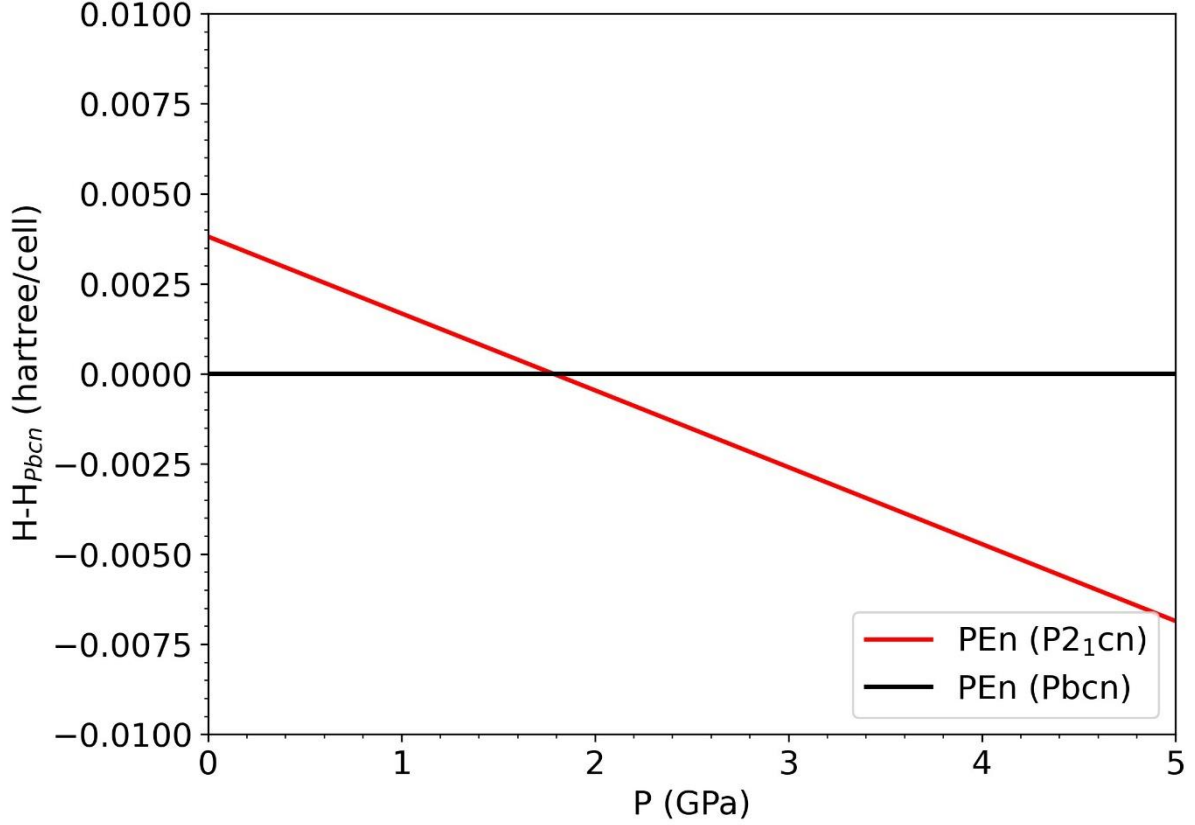


Figure 4.8.1. Relative phase stability of protoenstatite polymorphs ($P2_1cn$ vs. $Pbcn$) from static B3LYP calculations performed in this work at $T = 0$ K. In this diagram, static enthalpy differences are calculated with respect to $Pbcn$ protoenstatite taken as reference.

4.9. Conclusions

Using the hybrid B3LYP density functional, we computed a full set of physically-consistent thermodynamic and thermophysical properties of $MgSiO_3$ protoenstatite. Vibrational properties have been determined by full phonon dispersion calculation exploiting a $2 \times 2 \times 2$ supercell. All thermodynamic properties that depend on vibrational frequencies (heat capacities, enthalpy, entropy, bulk modulus and its pressure and temperature derivatives, volume thermal expansion coefficient) were computed in the framework of the quasi-harmonic approximation (QHA) considering the volume dependence of vibrational frequencies as expressed by the mode Grüneisen parameters (γ_i). Computed thermodynamic properties of protoenstatite are in excellent agreement with the few calorimetric data available in

the literature (i.e. Thieblot et al., 1999) and allow to reproduce the orthoenstatite – protoenstatite phase boundary (both in its P-T location and Clapeyron slope) *once* thermodynamic properties of orthoenstatite are properly assessed. Nevertheless, a full ab initio prediction of the PEn-OEn phase boundary seems to be hindered by the very small Gibbs free energy differences among the polymorphs or, alternatively, to possible shortcomings of the QHA in accurately predicting thermodynamic properties of orthoenstatite due to the fact that intrinsic anharmonic effects may be relevant for this phase (e.g. Zucker & Shim, 2009). Despite those limitations, our results provide a realistic picture of protoenstatite stability at Earth’s mantle conditions, in particular in the high-temperature range. This study is part of a broader project aimed at setting up a comprehensive thermodynamic dataset of ab initio properties for all MgSiO_3 pyroxenes, which will be used to investigate pyroxene phase equilibria in planetary systems. Moreover, other polymorphic structures of protoenstatite (like the $P2_1cn$ phase) would deserve much attention since they may have a real stability field in the pyroxene phase diagram or, alternatively, may play a role as metastable actors in Earth’s mantle dynamics.

5. Stability and metastability of pyroxene polymorphs in the MgSiO₃ system: a comprehensive ab initio study

The content of this chapter has been adapted from a manuscript draft which is currently in preparation.

5.1. Introduction

Phase diagrams of deep mantle minerals are an outstanding source of information to understand stability relations, reaction mechanisms and dynamic processes in this part of the Earth. The MgSiO₃ phase diagram, in particular, is one of the most important tools for understanding the structure, mineralogical composition and rheological properties of the Earth's interior, given the abundance and broad stability range of MgSiO₃ polymorphs (cf. Chapter 1 of this Thesis). Despite having been studied for more than a century (e.g. Wagner, 1932), the thermodynamics of MgSiO₃ mineral phases are far from being well constrained from an experimental point of view, especially in the P-T stability field of pyroxene polymorphs. The reason for this is easily explained by considering: (i) the unquenchable nature of some of these phases (i.e. protoenstatite and high-pressure clinoenstatite), which prevents quenching and characterization of samples at ambient conditions; (ii) the complexity of pyroxenes polymorphism, due to the presence of several metastable phases which are suggested to exist but are rarely taken into account in thermodynamic modelling; (iii) the prediction of a stability phase for high-temperature clinoenstatite, despite not being supported by any experimental evidences; finally, (iv) the often inaccurate (or, in some cases, unphysical) thermodynamic data provided by current thermodynamic databases. In fact, thermodynamic properties currently available for mantle pyroxenes, despite being internally-consistent, are not necessarily also physically-

consistent and their extrapolation to high-temperature and high-pressure conditions might lead to inaccurate predictions in phase equilibrium modelling.

In this chapter, the results of thermodynamic modelling performed on the phase relations between pyroxene polymorphs of MgSiO_3 will be presented. The following MgSiO_3 phases have been taken into account: low-pressure clinoenstatite (LP-CEn), orthoenstatite (OEn), protoenstatite (PEn), high-temperature clinoenstatite (HT-CEn) and high-pressure clinoenstatite (HP-CEn), as well as the MgSiO_3 liquid phase. Thermodynamic properties of the solid phases have been obtained with the same methodology used for protoenstatite (see Chapter 4), hence full details about the procedure will not be provided again, but only the final dataset computed for each pyroxene will be reported. Regarding the liquid phase, it will be treated in more detail in Chapter 6. The theoretical version of the MgSiO_3 phase diagram, as modelled in this study in the pressure range $P = 0 - 12$ GPa and in temperature range $T = 298.15 - 3000$ K, will be presented and discussed in comparison with the available literature results from experimental studies and thermodynamic assessments.

5.2. Computational methods

Ab initio DFT calculations have been carried out at the B3LYP level of theory by using the CRYSTAL14 code, similarly to what described for MgSiO_3 protoenstatite in Chapter 4. Once again, only the most relevant computational parameters will be reported in this section. Cut-off limits in the evaluation of the Coulomb and Hartree-Fock exchange series are controlled by five parameters that were set to 8 8 8 8 16 to improve the numerical accuracy. The threshold on the self-consistent field (SCF) energy was set to 10^{-8} Hartree for the geometry optimization, and to 10^{-10} Hartree for the vibrational frequencies calculation. The reciprocal space was sampled according to a regular sublattice with shrinking factor = 6. These parameters have been set to be the same for all pyroxene polymorphs.

Vibrational frequencies of MgSiO_3 pyroxenes have been computed on the fully relaxed crystal structures by performing full phonon dispersion calculations on large $2 \times 2 \times 2$ supercells. Due to high computational cost, either isotropic or anisotropic supercells have been exploited to perform the quasi-harmonic analysis of phonon frequencies, depending on the investigated polymorph. For HP-clinoenstatite, phonon calculations on $2 \times 2 \times 2$ supercell have been performed on the equilibrium volume and at four different compressed states (by imposing an external pressure on the crystal structure), namely at 0.0, 5.0, 7.93 and 12.5 GPa (which correspond to $V/V_0 = 1.00, 0.95, 0.93$ and 0.91 , respectively, according to the computed static EOS). For LP-clinoenstatite, the following anisotropic supercells have been exploited to determine phonon frequencies at non-equilibrium conditions: $1 \times 1 \times 2$, $1 \times 2 \times 1$ and $2 \times 1 \times 1$ (corresponding to 4 $\mathbf{q}$ points sampled in the BZ). Calculations have been carried out at the following pressures: $-1.3, 0.0, 1.9$ and 4.3 GPa, corresponding to $V/V_0 = 1.02, 1.00, 0.98$ and 0.96 . For HT-clinoenstatite, $1 \times 2 \times 2$, $2 \times 1 \times 2$ and $2 \times 2 \times 1$ anisotropic supercells have been employed for the quasi-harmonic analysis of phonon modes (6 $\mathbf{q}$ points sampled in the BZ), which has been carried out at $P = -0.7, 0.0, 1.0, 2.9$ GPa, corresponding to $V/V_0 = 1.01, 1.00, 0.99, 0.97$. For orthoenstatite, only a $2 \times 2 \times 2$ supercell calculation was available due to the very high computational cost (80 atoms in the primitive unit cell). Quasi-harmonic analysis of phonon modes has been carried out by calculating vibrational frequencies at Γ point at expanded and compressed states ($P = 7.0, 4.6, 2.7, 0.9, 0.0, -0.5, -1.5, -2.3$ GPa, corresponding to $V/V_0 = 0.94, 0.96, 0.97, 0.99, 1.00, 1.01, 1.02, 1.04$, respectively) and by assuming an average mode Grüneisen parameter for all the modes sampled at different $\mathbf{q}$ points by the $2 \times 2 \times 2$ supercell. Least-square fitting of vibrational frequencies computed at different volume conditions gives the values of γ_i for all the modes. Thermodynamic properties that depend on vibrational frequencies (i.e. heat capacities, thermal expansion, bulk modulus and its pressure and temperature derivatives, entropy, enthalpy, Gibbs free energy) have then been computed in the framework of the quasi-harmonic approximation applying statistical mechanics relations presented in Sections 2.4 and 2.5. Thermal EOS for all

pyroxenes have been obtained by fitting pressure – volume – temperature data obtained at the following volume conditions: $V/V_0 = 0.91, 0.93, 0.95, 1.00$ for HP-clinoenstatite; $V/V_0 = 0.920, 0.939, 0.959, 0.979, 0.999, 1.000, 1.019, 1.040$ for LP-clinoenstatite; $V/V_0 = 0.940, 0.956, 0.973, 0.989, 1.000, 1.006, 1.023, 1.040$ for HT-clinoenstatite, $V/V_0 = 0.96, 0.969, 0.979, 0.9897, 0.999, 1.000, 1.0098, 1.02$ for orthoenstatite. P-V-T data have been fitted with a high-temperature 3rd order Birch Murnaghan equation of state (HT-BM3-EOS) to obtain K_T values and its temperature derivative $(dK_T/dT)_P$. Ab initio data calculated for volume thermal expansivity (α_V) and isobaric heat capacity (C_P) have been fitted with the following polynomial functions:

$$\alpha_V(P_0, T) = \alpha_0 T + \alpha_1 + \alpha_2 T^{-1} + \alpha_3 T^{-2} + \alpha_4 T^{-3} \quad (5.2.1)$$

$$C_P = a + bT + cT^{-2} + dT^{-\frac{1}{2}} + eT^{-3} + fT^2 + gT^3 \quad (5.2.2)$$

except for C_P values of orthoenstatite, which have been fitted with a Haas-Fisher polynomial function that better reproduces the computed values:

$$C_P = a + bT + cT^{-2} + dT^2 + eT^{-\frac{1}{2}} \quad (5.2.3)$$

Thermodynamic properties of MgSiO_3 pyroxenes have been used to build a physically- and internally-consistent dataset, that has been tested by reproducing the following univariant phase equilibria:

$$\text{MgSiO}_3 (\text{HP-CEn}) = \text{MgSiO}_3 (\text{LP-CEn}) \quad (5.2.4)$$

$$\text{MgSiO}_3 (\text{HP-CEn}) = \text{MgSiO}_3 (\text{OEn}) \quad (5.2.5)$$

$$\text{MgSiO}_3 (\text{LP-CEn}) = \text{MgSiO}_3 (\text{OEn}) \quad (5.2.6)$$

$$\text{MgSiO}_3 (\text{PEn}) = \text{MgSiO}_3 (\text{HT-CEn}) \quad (5.2.7)$$

The phase equilibrium MgSiO_3 (OEn) = MgSiO_3 (PEn) has been already discussed in detail in Chapter 4. The results of the thermodynamic modelling of all the phase equilibria listed above are presented and discussed in the next section, together with the full MgSiO_3 phase diagram obtained by first principles. The phase diagram defines phase relations of MgSiO_3 pyroxenes from subsolidus up to melting conditions, although the melting curve of the MgSiO_3 system will be treated in detail in Chapter 6.

5.3 Stability of MgSiO_3 pyroxenes at mantle conditions

5.3.1. Low-pressure clinoenstatite (LP-CEn) – high-pressure clinoenstatite (HP-CEn) phase transition boundary

Figure 5.3.1.1 shows the HP-CEn – LP-CEn phase boundary as calculated in this work (solid black curve). The theoretical value of $H^0_{\text{f (HP-CEn)}}$ has been optimized to -1544.593 kJ/mol within the limit of B3LYP theory (cf. Belmonte et al, 2014). Unfortunately, experimental data on the LP-CEn – HP-CEn phase equilibrium are scarce in the literature because of the difficulty in obtaining suitable samples (cf. Angel & Hugh Jones, 1994) and due to the unquenchable nature of HP-CEn, which immediately reverts to LP-CEn upon cooling (Angel et al., 1992; Ulmer & Stadler, 2001). Figure 5.3.1.1 also reports the hysteresis loop of the transition HP-CEn – LP-CEn at room temperature according to Angel et al. (1992), which brackets our room temperature theoretical result. The experimental points by Ulmer & Stadler (2001) are also reported, even though some difficulties in distinguishing between HP- and LP-clinoenstatites are mentioned by the Authors due to, once again, the unquenchable nature of the former. Three different ranges of P – T conditions have been considered to calculate the Clapeyron slope of the phase boundary in order to take account of its curvature (see Tab. 5.3.1.1). In the P – T range $P = 7 - 7.8$ GPa and $T = 640 - 920$ K, the theoretical value of dP/dT (i.e. 2.749 MPa/K) is quite similar to those obtained by Angel et al. (1992) and Gasparik (2003) (2.0 and 2.157 MPa/K, respectively). It is noteworthy

to mention that there is not a general agreement on both the absolute value and the sign of the Clapeyron slope of this univariant phase boundary, since some thermodynamic assessments (e.g. Saxena et al., 1993) even found a negative sign for the Clapeyron slope. Table 5.3.1.2 shows the ab initio values of ΔH^0 , ΔS^0 and ΔV_0 of the LP-CEn – HP-CEn reaction, as compared with the values reported in Angel & Hugh Jones (1994). The molar volume of HP-CEn as obtained by ab initio B3LYP [i.e.: $V_0(\text{HPCEn}) = 31.707 \text{ cm}^3/\text{mol}$] is predicted to increase of $0.683 \text{ cm}^3/\text{mol}$ as HP-CEn transforms into LP-CEn [with $V_0(\text{LPCEn}) = 32.39 \text{ cm}^3/\text{mol}$], a volume change which is quite close to the that observed by Angel & Hugh Jones (1994) [i.e.: $\Delta V_0(\text{HPCEn} = \text{LPCEn}) = 0.838 \text{ cc}^3/\text{mol}$]. Also the ΔS^0 values are quite similar, while ab initio values of ΔH^0 turn out to be less negative (cf. Table 5.3.1.2). Table 5.3.1.3 reports the thermodynamic properties for LP-CEn and HP-CEn used in the calculation.

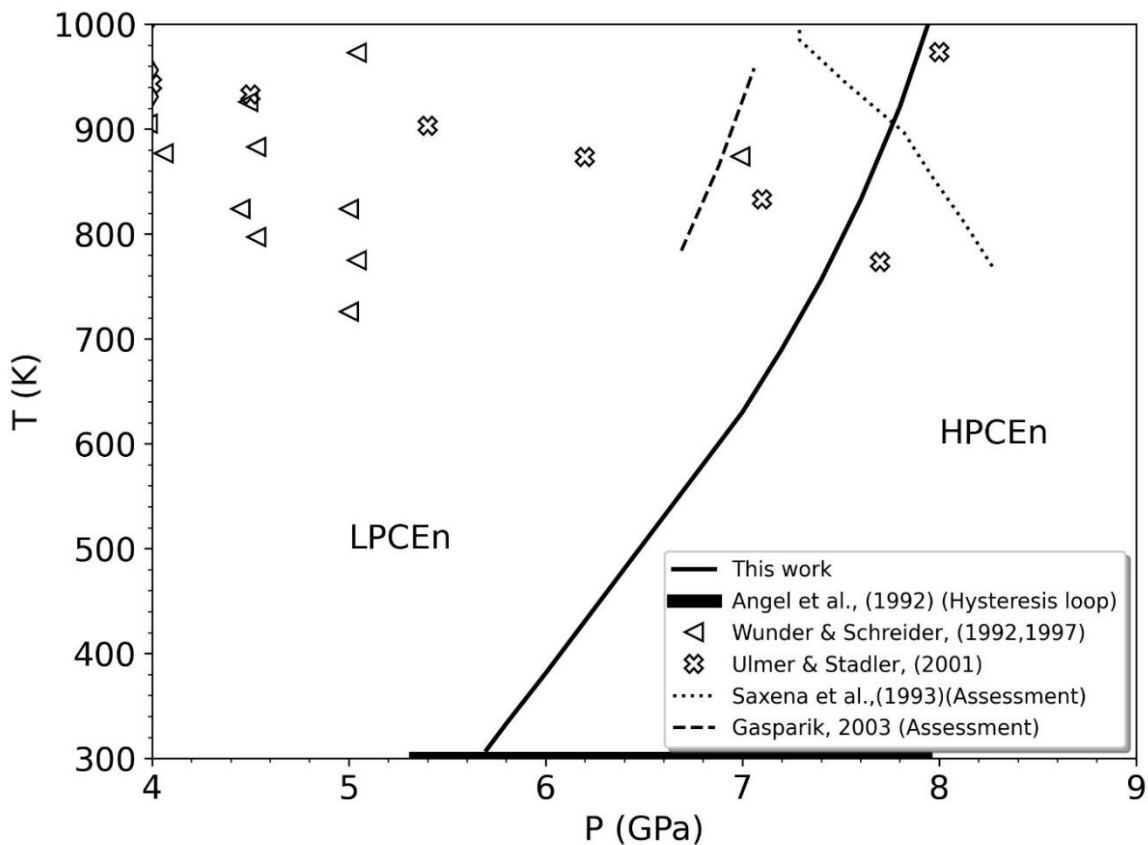


Figure 5.3.1.1. HP-CEn–LP-CEn ab initio phase transition boundary (thin solid black curve) as compared with experiments and assessments. Dotted and dashed lines after

Saxena et al. (1993) and Ulmer & Stadler, (2001) are assessed phase univariant curves for the HP-CEn – LP-CEn transition. White markers are experimental results reported as a reference and consist of LP-CEn.

Table 5.3.1.1. Clapeyron slope of the HP-CEn –LP-CEn phase boundary.

	P range (GPa)	T range (K)	dP/dT (MPa/K)
This work (B3LYP)	5.7 – 7.0 GPa	308 - 630 K	4.037
	7.0 - 7.8 GPa	630 - 921 K	2.749
	7.8 - 8.5 GPa	921 - 1723 K	0.873
Gasparik, (2003)			2.157
Saxena et al. (1993)			–4.483

Table 5.3.1.2. ΔH^0 , ΔS^0 , ΔV_0 of the HP-CEn = LP-CEn reaction.

ΔH^0 (kJ/mol) (this work, ab initio B3LYP)	–2.221
ΔS^0 (J/mol × K) (this work, ab initio B3LYP)	1.670
ΔV_0 (cc ³ /mol) (this work, ab initio B3LYP)	0.683
ΔH^0 (kJ/mol) (Angel & Hugh-Jones, 1994; assessed from Grover, 1972)	–5.5
ΔS^0 (J/mol) (Angel & Hugh-Jones, 1994; assessed from Grover, 1972)	1.4
ΔV_0 (cc ³ /mol) (Angel & Hugh-Jones, 1994)	0.838

Table 5.3.1.3. Thermodynamic dataset used to calculate the HP-clinoenstatite – LP-clinoenstatite phase transition. H_f^0 = standard-state enthalpy of formation from the elements; S^0 = standard-state entropy; a, b, c, d, e, f, g = numerical coefficients of the polynomial function for the isobaric heat capacity (C_p), fitted in the range $T = 298.15 \text{ K} - 2000 \text{ K}$ (cf. Eq. 5.2.2); V_0 = molar volume at the athermal limit ($T = 0 \text{ K}$; $P = 0 \text{ GPa}$); K_0 =

static bulk modulus; K'_0 = pressure derivative of the bulk modulus; dK/dT = isobaric temperature derivative of the bulk modulus; $\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4$ = numerical coefficients of the polynomial function for volume thermal expansivity, fitted in the range $T = 200 \text{ K} - 2000 \text{ K}$ (cf. Eq. 5.2.1).

	MgSiO ₃ LP-CEn	MgSiO ₃ HP-CEn
H^0_f (kJ/mol)	-1546.814	-1544.593
S^0 [J/(mol × K)]	65.764	64.094
a	115.76	116.95
$b \times 10^3$	11.287	5.4872
$c \times 10^{-5}$	-17.796	-78.194
d	-198.40	151.69
$e \times 10^{-8}$	-2.1632	10.755
$f \times 10^6$	3.9542	0.82213
$g \times 10^9$	-1.1141	0.3414
V^0 (cm ³ /mol)	32.39	31.707
K_0 (GPa)	79.95	113.11
K'_0	12.69	5.86
dK/dT (bar/K)	-244	-306
$\alpha_0 \times 10^7$	0.69104	0.42055
$\alpha_1 \times 10^7$	-927.86	-399.45
$\alpha_2 \times 10^3$	106.3709	57.9667
α_3	-38.2307	-20.6994
α_4	4694.409	2515.839

5.3.2. Orthoenstatite (OEn) – high-pressure clinoenstatite (HP-CEn) phase transition boundary

Figure 5.3.2.1 shows the ab initio OEn – HP-CEn phase boundary (solid black curve). The P-T location of the theoretical phase boundary is quite consistent with the experimental results of Pacalo & Gasparik (1990) and Akashi et al. (2009), whereas the HP-CEn – OEn phase boundary would be located at slightly lower pressures according to Yamamoto and Akimoto (1977) and Ulmer & Stadler (2001). The Clapeyron slope of the theoretical phase boundary is also slightly different from those inferred by experimental data best-fits (see Tab. 5.3.2.1), except in the pressure range between 8 and 9 GPa, where the ab initio Clapeyron slope (i.e. $dP/dT = 2.599 \text{ MPa/K}$) compares favourably with both Pacalo & Gasparik (1990) (i.e. $dP/dT = 3.100 \text{ MPa/K}$) and Angel et al. (1992) (i.e. $dP/dT = 3.005 \text{ MPa/K}$). The computed volume change of the OEn – HP-CEn reaction is quite close to that measured by Angel & Hugh Jones

(1994) [i.e.: ΔV_0 (OEn = HPCEn) $\cong -0.8$ vs. -0.9 cc³/mol] (see Tab. 4.3.2.2). The predicted ΔS^0 of reaction is also close the value obtained by Angel & Hugh Jones (1994), whereas Ulmer & Stadler found a slightly lower value (cf. Table 5.3.2.2). Table 5.3.2.3 reports the thermodynamic properties of OEn and HP-CEn used in the calculation. Thermodynamic data for HP-CEn are the same used for the HP-CEn = LP-CEn phase boundary (cf. Tab. 5.3.1.3).

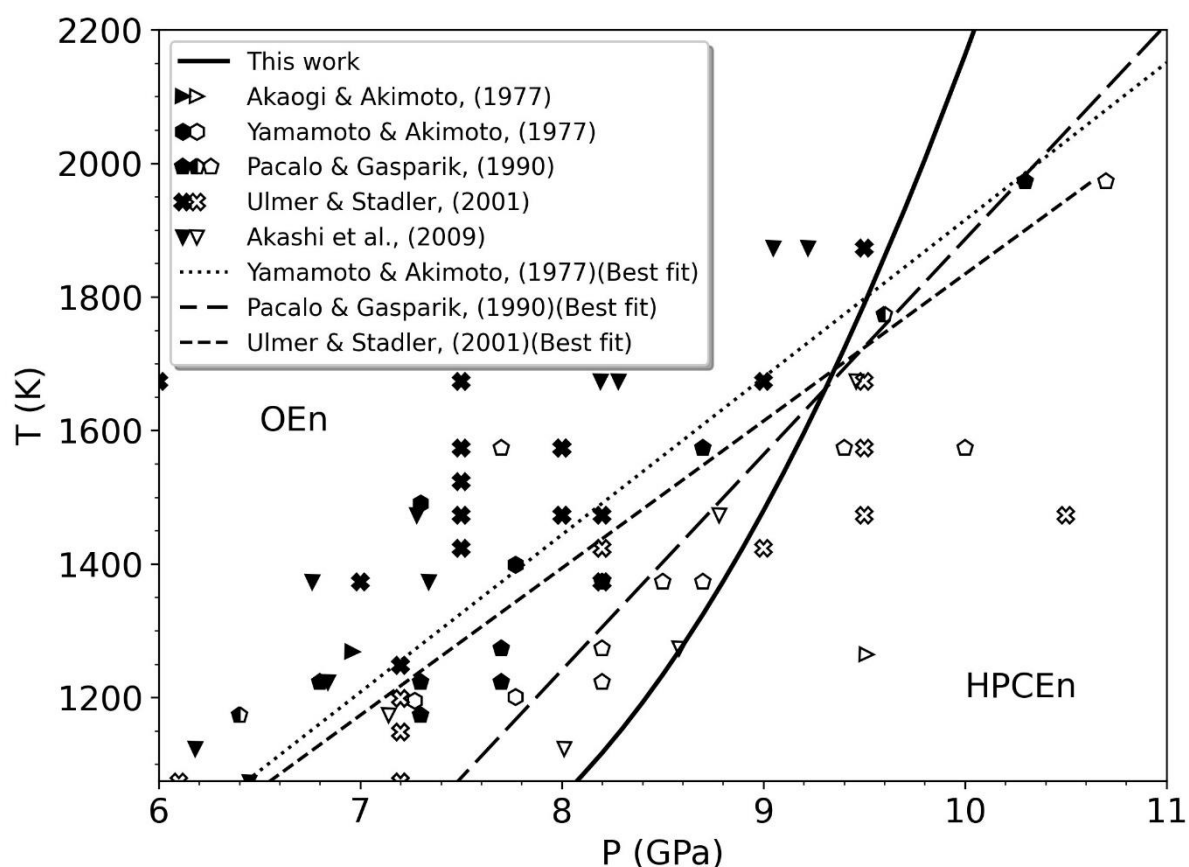


Figure 5.3.2.1. OEn–HP-CEn ab initio phase transition boundary (solid black curve) as compared with experiments (experimental runs represented by symbols, best-fits of experimental data by dotted and dashed curves). Black markers = OEn, white markers = HP-CEn, black + white markers = OEn + HP-CEn.

Table 5.3.2.1. Clapeyron slope of the OEn = HPCEn phase boundary

	P range (GPa)	T range (K)	dP/dT (MPa/K)
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This work	8.08 - 8.8 GPa	1085 - 1362 K	2.60
	8.8 - 9.5 GPa	1365 - 1807 K	1.57
Ulmer & Stadler, (2001)			4.54
Pacalo & Gasparik, (1990)			3.1
Yamamoto & Akimoto (1977)			4.4

Table 5.3.2.2. ΔH^0 , ΔS^0 , ΔV_0 of the OEn = HPCEn reaction.

ΔH^0 (kJ/mol) (this work, ab initio B3LYP)	1.892
ΔS^0 (J/mol $\times$ K) (this work, ab initio B3LYP)	-2.276
ΔV_0 (cc ³ /mol) (this work, ab initio B3LYP)	-0.796
ΔH^0 (kJ/mol) (Angel & Hugh-Jones, 1994; assessed from Grover, 1972)	4.5
ΔS^0 (J/mol $\times$ K) (Angel & Hugh-Jones, 1994; assessed from Grover, 1972)	-2.59
ΔV_0 (cc ³ /mol) (Angel & Hugh-Jones, 1994)	-0.90
ΔH^0 (kJ/mol) (Ulmer & Stadler, 2001)	1.40
ΔS^0 (J/mol) (Ulmer & Stadler, 2001)	-3.80

Table 5.3.2.3. Thermodynamic dataset used to calculate the orthoenstatite – HP-clinoenstatite phase transition. H_f^0 = standard state enthalpy of formation from the elements; S^0 = standard state entropy; a, b, c, d, e, f, g = numerical coefficients of the polynomial function for the isobaric heat capacity (C_p), fitted in the range $T = 298.15$ K – 2000 K (cf. Eq. 5.2.2 for HPCEn; Eq. 5.2.3 for OEn); V_0 = molar volume at the athermal limit ($T = 0$ K; $P = 0$ GPa); K_0 = static bulk modulus; K'_0 = pressure derivative of bulk modulus; dK/dT = isobaric temperature derivative of bulk modulus; $\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4$ = numerical coefficients of

the polynomial function for volume thermal expansivity, fitted in the range $T = 200 \text{ K} - 2000 \text{ K}$ (cf. Eq. 5.2.1).

	MgSiO ₃ HP-clinoenstatite	MgSiO ₃ orthoенstatite
H_f^0 (kJ/mol)	-1544.593	-1546.485
S^0 [J/(mol × K)]	64.094	66.371
a	116.95	103.41
$b \times 10^3$	5.4872	12.573
$c \times 10^{-5}$	-78.194	-37.209
d	151.69	236.06
$e \times 10^{-8}$	10.755	0.0
$f \times 10^6$	0.82213	1.3992
$g \times 10^9$	0.3414	0.0
V^0 (cm ³ /mol)	31.707	32.503
K_0 (GPa)	113.11	76.29
K'_0	5.86	13.77
dK/dT (bar/K)	-306	-223
$\alpha_0 \times 10^7$	0.42055	0.4829
$\alpha_1 \times 10^7$	-399.45	-409.734
$\alpha_2 \times 10^3$	57.9667	59.37
α_3	-20.6994	-21.0068
α_4	2515.839	2510.7907

5.3.3. Low-pressure clinoenstatite (LP-CEn) – orthoenstatite (OEn) phase transition boundary

Figure 5.3.3.1 shows the LP-CEn – OEn ab initio phase boundary (solid black curve) as compared with the experiments of Boyd & England (1995), Wunder & Schreyer (1992, 1997) and Ulmer & Stadler (2001). In this case, the computed univariant curve roughly matches the experiments at high pressure but deviates from experiments at lower pressures. The transition temperature between LP-CEn and OEn at 1 bar seem to differ of as much as 300 – 400 K when our results are compared with those of Sclar et al. (1964) and Boyd & England (1965). Both the Clapeyron slope (14.770 MPa/K) and the ΔH^0 , ΔS^0 and ΔV_0 of reaction (i.e. 0.329 kJ/mol, 0.606 J/mol × K and 0.113 cm³/mol, respectively) differ from the results found in the literature (see Tables 5.3.3.1 and 5.3.3.2). Table 5.3.3.3 reports the thermodynamic data used to compute the univariant curve in Figure 5.3.3.1.

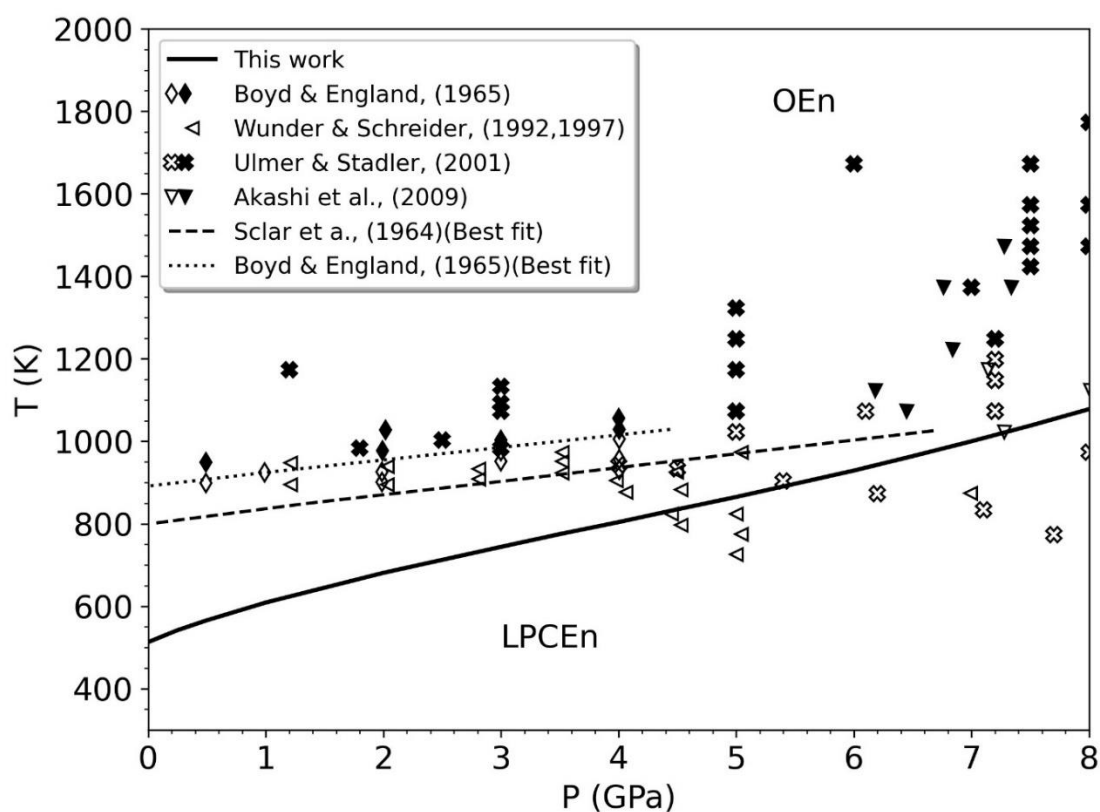


Figure 5.3.3.1. LP-CEn–OEn ab initio phase transition as compared with experiments (both experimental runs and best-fits are reported). White markers = LP-CEn, black markers = OEn.

Table 5.3.3.1. Clapeyron slope of the LP-CEn = OEn phase boundary

	dP/dT (MPa/K)
This work (ab initio B3LYP)	14.770
Boyd & England (1965)	32.397
Sclar et al. (1964)	29.810

Table 5.3.3.2. ΔH^0 , ΔS^0 , ΔV_0 of the LP-CEn = OEn reaction.

ΔH^0 (kJ/mol) (this work, ab initio B3LYP)	0.329
ΔS^0 (J/mol $\times$ K) (this work, ab initio B3LYP)	0.606
ΔV_0 (cc ³ /mol) (this work, ab initio B3LYP)	0.113

ΔH^0 (kJ/mol) (Angel & Hugh-Jones, 1994; assessed from Grover, 1972)	1.0
ΔS^0 (J/mol) (Angel & Hugh-Jones, 1994; assessed from Grover, 1972)	1.2
ΔV_0 (cc ³ /mol) (Angel & Hugh-Jones, 1994)	0.056

Table 5.3.3.3. Thermodynamic dataset used to calculate the LP-clinoenstatite – orthoenstatite phase transition. H_f^0 = standard state enthalpy of formation from the elements; S^0 = standard state entropy; a, b, c, d, e, f, g = numerical coefficients of the polynomial function for the isobaric heat capacity (C_p), fitted in the range $T = 298.15$ K – 2000 K (cf. Eq. 5.2.2 for LP-CEn; Eq. 5.2.3 for OEn); V_0 = molar volume at the athermal limit ($T = 0$ K; $P = 0$ GPa); K_0 = static bulk modulus; K'_0 = pressure derivative of bulk modulus; dK/dT = isobaric temperature derivative of bulk modulus; $\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4$ = numerical coefficients of the polynomial function for volume thermal expansivity, fitted in the range $T = 200$ K – 2000 K (Eq. 5.2.1).

	MgSiO ₃ LP-clinoenstatite	MgSiO ₃ orthoenstatite
H_f^0 (kJ/mol)	–1546.814	–1546.485
S^0 [J/(mol × K)]	65.764	66.371
a	115.76	103.41
$b \times 10^3$	11.287	12.573
$c \times 10^{-5}$	–17.796	–37.209
d	–198.40	236.06
$e \times 10^{-8}$	–2.1632	0.0
$f \times 10^6$	3.9542	1.3992
$g \times 10^9$	–1.1141	0.0
V_0 (cm ³ /mol)	32.39	32.503
K_0 (GPa)	79.95	76.29
K'_0	12.69	13.77
dK/dT (bar/K)	–244	–223
$\alpha_0 \times 10^7$	0.69104	0.4829
$\alpha_1 \times 10^7$	–927.86	–409.734
$\alpha_2 \times 10^3$	106.3709	59.37
α_3	–38.2307	–21.0068
α_4	4694.409	2510.7907

5.3.4. MgSiO_3 phase diagram of pyroxenes

Figure 5.3.4.1 reports our theoretical result for the MgSiO_3 phase diagram up until 11 GPa, obtained combining together all the univariant curves described in the previous paragraphs, along with the OEn – PEn phase boundary discussed in Chapter 4. The phase diagram also reports the melting curve of the MgSiO_3 system, which will be presented in Chapter 6. By considering all the experimental data currently available for pyroxene phase boundaries, it appears evident that several experimental studies tried to constrain the location of the main univariant curves in the MgSiO_3 system. Nevertheless, significant uncertainties still remain both from the experimental and the theoretical side as well. In particular, some uncertainties are evident in the high temperature / low pressure portion of the phase diagram, as already discussed in previous Sections. Specifically, the ab initio LP-CEn – OEn phase transition differs from the position inferred from experiments of about 300 – 400 K at 1-bar pressure; then, the P – T location of the triple point orthoenstatite – protoenstatite – liquid cannot be solved by theory within a reasonable level of confidence (due to thermodynamic reasons highlighted in Chapter 4; see also considerations about melting phase relations in Chapter 6). Concerning the OEn-PEn-liquid triple point, as already discussed in Chapter 4, a change in the Clapeyron slope of the phase boundary marks its progressive flattening at pressures higher than 1.5 GPa, preventing it to reach the melting curve (see dashed line in Fig. 5.3.4.1, where the triple point is expected to be). The reason of this behavior could be related to the very small Gibbs free energy differences between the MgSiO_3 polymorphs at those conditions, which are close to the limits of resolution of the DFT QHA theory or, alternatively, to the shortcomings of QHA in accurately predicting thermodynamic properties of orthoenstatite, whose stability would be influenced in this case by anharmonic effects (see discussion in Chapter 4). If on one side some issues still remain in the low-pressure portion of the phase diagram, the ab initio LP-CEn-OEn-HP-CEn triple point is predicted at $P = 8.08$ GPa and $T = 1085$ K, which is in good agreement with the result of Angel & Hugh

Jones (1994) (i.e. $P = 7.58$ GPa, $T = 1124$ K) and also not so far from that inferred by Ulmer & Stadler (2001) (i.e.: $P = 6.6$ GPa and $T = 1093.25$ K). So, despite the open issues, the full ab initio approach to predict a complex phase diagram like that of the MgSiO_3 system proved to be much more than promising.

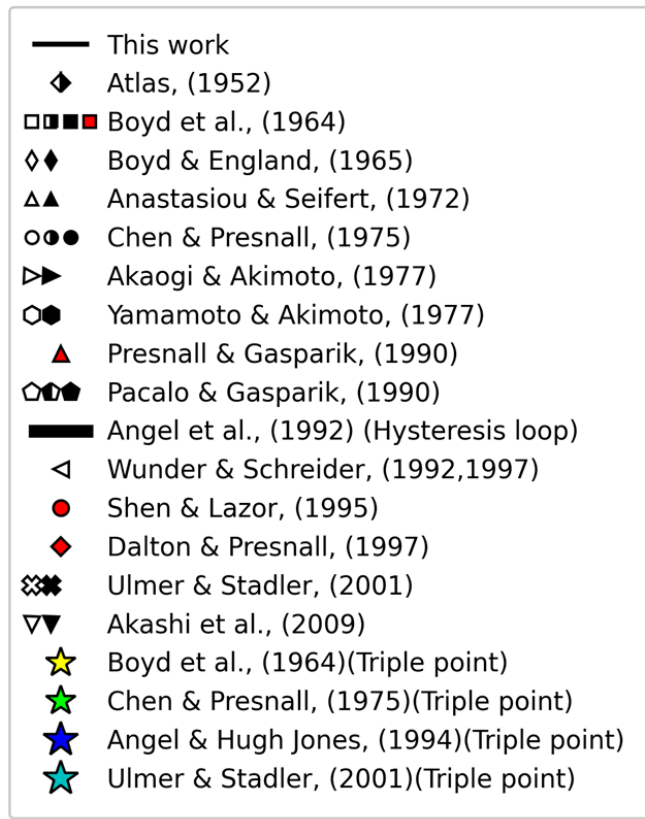
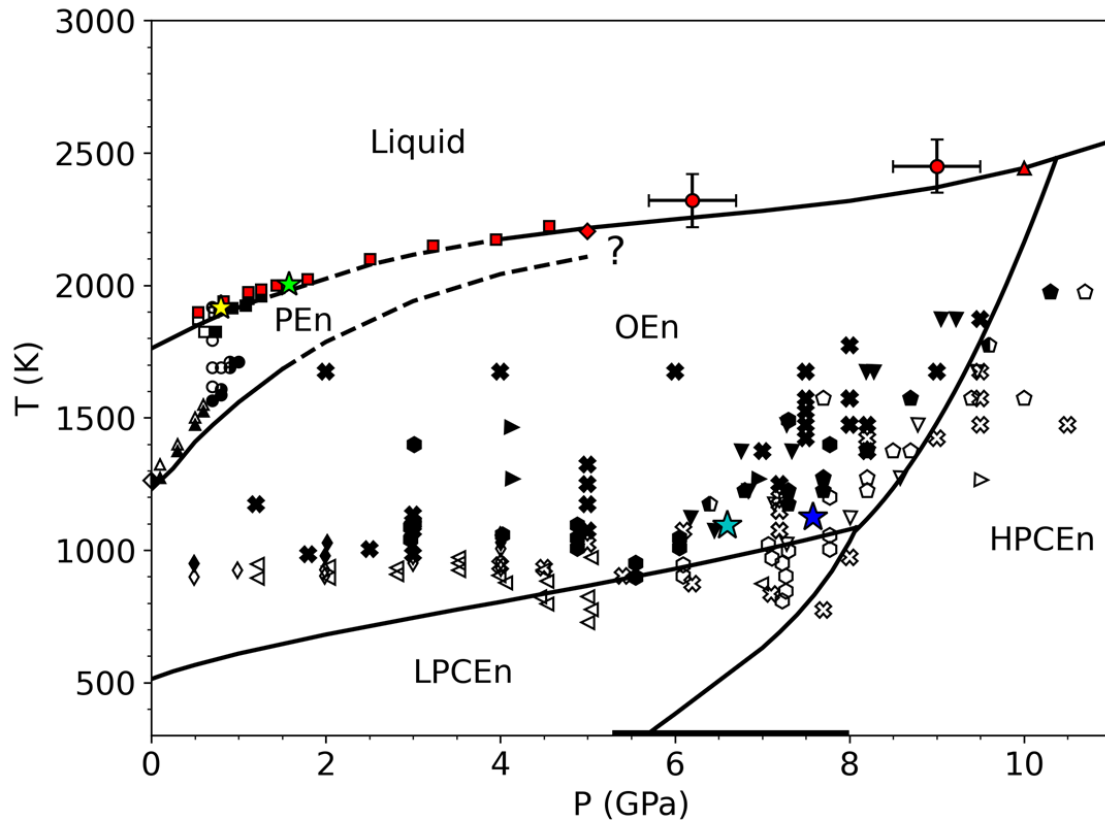


Figure 5.3.4.1. Ab initio phase diagram for the MgSiO_3 system, as compared with literature data. White markers = PEn/LPCEn/HPCEn, black markers = OEn, red markers = liquid.

5.4. Thermodynamics and stability of high-temperature clinoenstatite (HT-CEn)

High-temperature clinoenstatite (HT-CEn) is a monoclinic ($C2/c$) pyroxene polymorph with $MgSiO_3$ composition. Its existence has been suggested by some X-ray diffraction investigations dating back to the 1960s-1970s. Boyd and Schairer (1964) suggest the existence of a high-temperature monoclinic polymorph by quenching $MgSiO_3$ composition from temperatures above 1658 K at ambient pressure, which yields a clinoenstatite phase with anomalous unit cell parameters. Perrotta & Stephenson (1965) found that a metastable displacive transformation from low clinoenstatite to a triclinic high temperature clinoenstatite occurs at around 1268 ± 5 K, with no evidence on the presence of protoenstatite in a Ca-poor system and no inversion of the new phase up to about 1673 K. Smith (1969) reinterpreted the powder X-ray diffraction data obtained by Perrotta & Stephenson (1965) and suggested that HT-CEn should have monoclinic structure, with space group $C2/c$. Smyth (1969) and Sadanaga & Okamura (1971) came to the same conclusion by refining the structure of a $C2/c$ phase transformed from a natural iron-rich orthoenstatite or a natural clinoenstatite heated for 10-60 hours at temperatures between 1323 K and 1373 K. On the other hand, Smyth (1974) found no evidence of a stability field for HT-CEn above that of protoenstatite when a crystal of PEn underwent partial, incongruent melting to forsterite plus liquid. This observation is consistent with the experimental results obtained by Foster (1951) and Atlas (1952). In more recent times, the phase transition from orthoenstatite (OEn, $Pbca$) or low-clinoenstatite (LP-CEn, $P2_1/c$) to HT-CEn was observed by in situ TEM studies performed at high temperatures (Shimobayashi & Kitamura, 1991 and 1993; Iishi & Kitayama, 1995), while a HT-CEn/HP-CEn was simulated by classical molecular dynamics based on empirical potentials (Shimobayashi et al., 1998; Miyake et al., 2002).

Nevertheless, all the above considerations based on experimental observations are affected by kinetic hindrance, since HT-CEn is basically an unquenchable phase, exactly

like PEn (see Chapter 4). As far as we know, only one attempt was successful in quenching a single-crystal of HT-CEn from HP-HT conditions (Yoshiasa et al., 2013).

Due to the above reasons, a comprehensive knowledge of the thermodynamic properties of HT-CEn is almost completely lacking in modern databases. No calorimetric investigations exist so far, nor investigations of its P-V-T relations and elasticity.

We thus performed an ab initio B3LYP study of the thermodynamic, thermoelastic, and equation of state parameters of HT-CEn in a broad range of P-T conditions. As far as we know, this is the first ab initio DFT investigation made so far on HT-CEn. Starting from computed properties for HT-CEn, its stability relations with other MgSiO_3 pyroxenes have been investigated by Gibbs free energy minimization in order to test the stability (or metastability) of HT-CEn in the whole P-T range investigated for the MgSiO_3 system (i.e., $P = 0 - 10$ GPa; $T = 298.15$ K – 2000 K). In fact, as can be seen in Figure 4.3.4.1, the stability field of high-temperature clinoenstatite (HT-CEn) is missing in our theoretical phase diagram, despite some Authors claimed this phase as the 1-bar *liquidus* phase in MgSiO_3 system (e.g. Shi et al., 1994, 1996; Gasparik, 2014).

The calculation of phonon frequencies and their quasi-harmonic analysis yielded the αK_T product for HT-CEn, which attains a fairly constant value of 0.0028 GPa/K in the temperature range between 1100 and 3000 K (Figure 5.4.1).

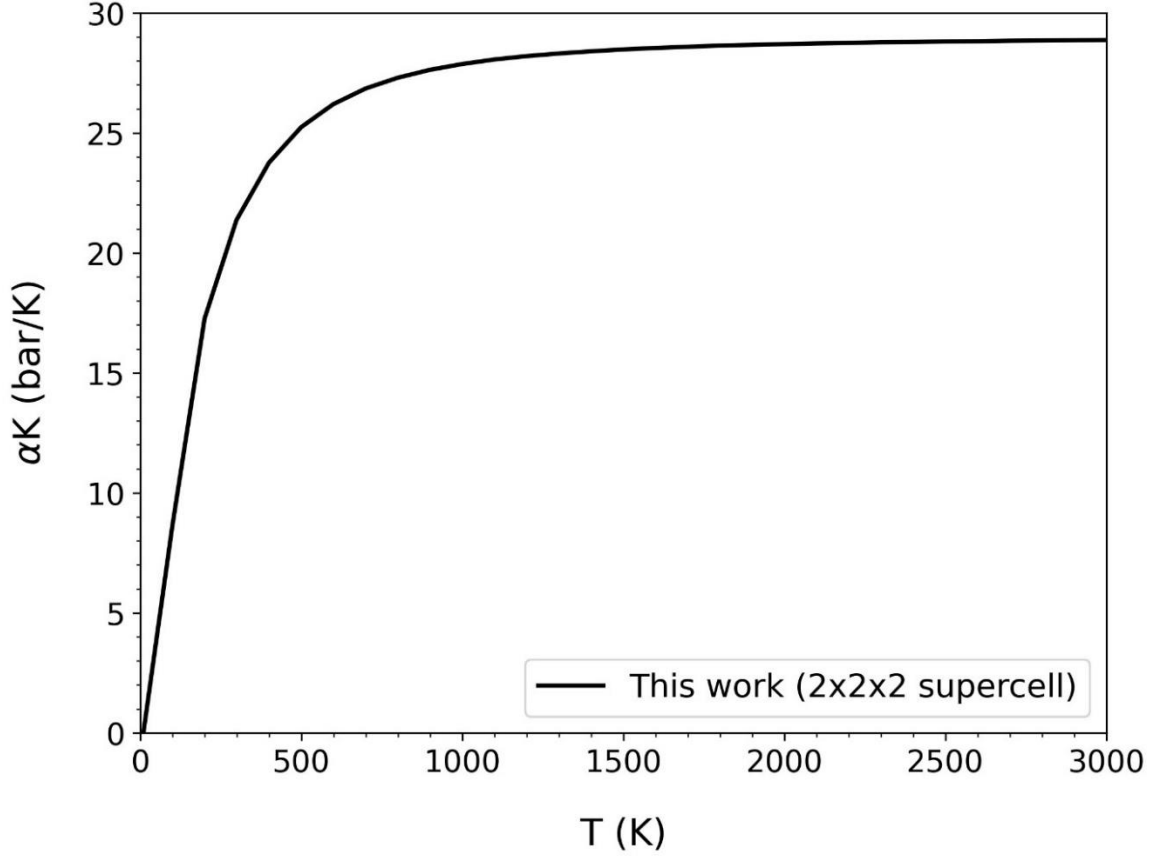


Figure 5.4.1. αK_T product as calculated in this work for MgSiO₃ HTCEn by ab initio B3LYP.

Fitting of static energy – volume curve with a BM3-EOS yields $K_0 = 100.32$ GPa and $K'_0 = 9.63$, while P-V-T data fitting with a HT-BM3-EOS gives $\left(\frac{\partial K_T}{\partial T}\right)_P = -192$ bar /K (see Chapter 2 for details about the method). Since this is the first determination of HT-CEn equation of state, there are no data available for comparison.

Thermal expansion coefficient (α_V) of HT-CEn was calculated in the framework of the quasi-harmonic approximation at zero pressure and discrete temperatures. Discrete values of α_V were then fitted with a suitable polynomial function in the temperature range from $T = 200$ K to $T = 2000$ K, as follows:

$$\alpha_V(P_0, T) = \alpha_0 T + \alpha_1 + \alpha_2 T^{-1} + \alpha_3 T^{-2} + \alpha_4 T^{-3} \quad (5.4.1)$$

Fitted numerical coefficients of the polynomial function at $P = 0$ are $\alpha_0 = 2.12823 \cdot 10^{-8}$, $\alpha_1 = -8.007 \cdot 10^{-6}$, $\alpha_2 = 3.2225 \cdot 10^{-2}$, $\alpha_3 = -13.07843$ and $\alpha_4 = 1680.3809$. The results of our

ab initio B3LYP calculations for HT-CEn volume thermal expansion (expressed as V/V_0 vs. T) and thermal expansivity (α_V) are reported in Figures 5.4.2 and 5.4.3, respectively.

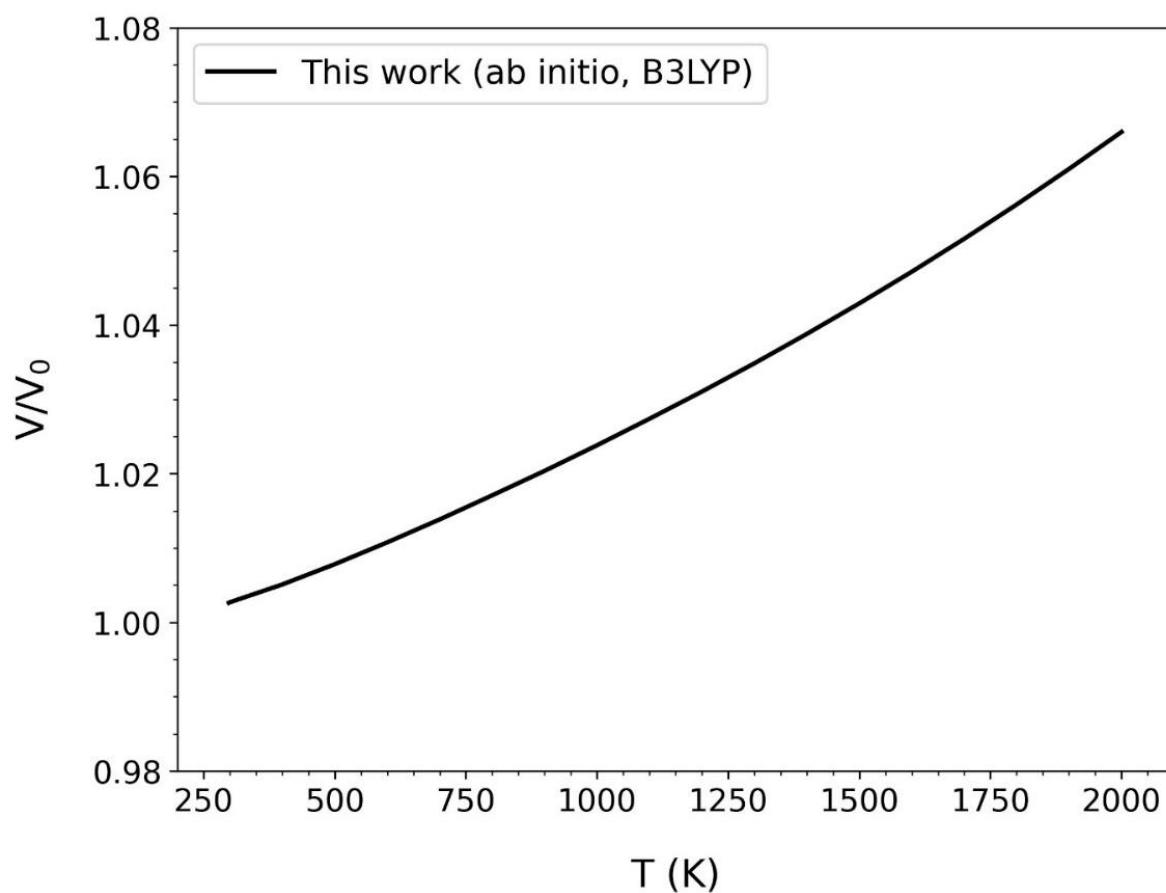


Figure 5.4.2. Ab initio B3LYP volume thermal expansion of MgSiO₃ HT-CEn at $P = 0$.

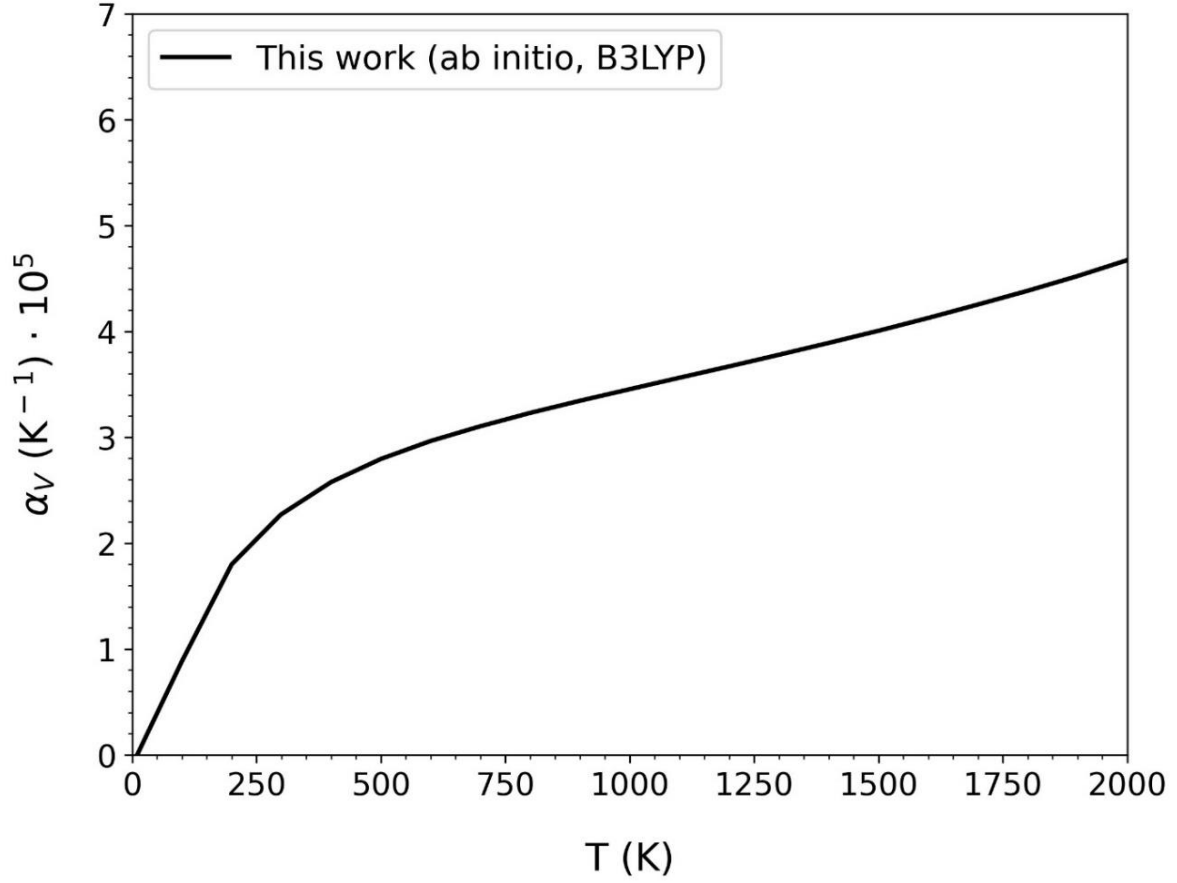


Figure 5.4.3. Ab initio B3LYP volume thermal expansivity of $MgSiO_3$ HT-CEn at $P = 0$.

The calculation of vibrational frequencies (and phonon dispersion) in the harmonic approximation and the mode Grüneisen parameters in the QHA allowed to determine the isobaric heat capacity (C_P) and the bulk molar entropy (S^0) of high-temperature clinoenstatite. The discrete values obtained for C_P were fitted in the temperature range between 298.15 and 2000 K using a polynomial function commonly adopted in metallurgy:

$$C_P = a + bT + cT^{-2} + dT^{-\frac{1}{2}} + eT^{-3} + fT^2 + gT^3 \quad (5.4.2)$$

where $a = 133.63$, $b = 3.911 \times 10^{-3}$, $c = 1.8254 \times 10^6$, $d = -694.48$, $e = -9.6967 \times 10^8$, $f = 3.0491 \times 10^{-6}$, $g = -6.7403 \times 10^{-10}$. Results are reported in Figure 5.4.4.

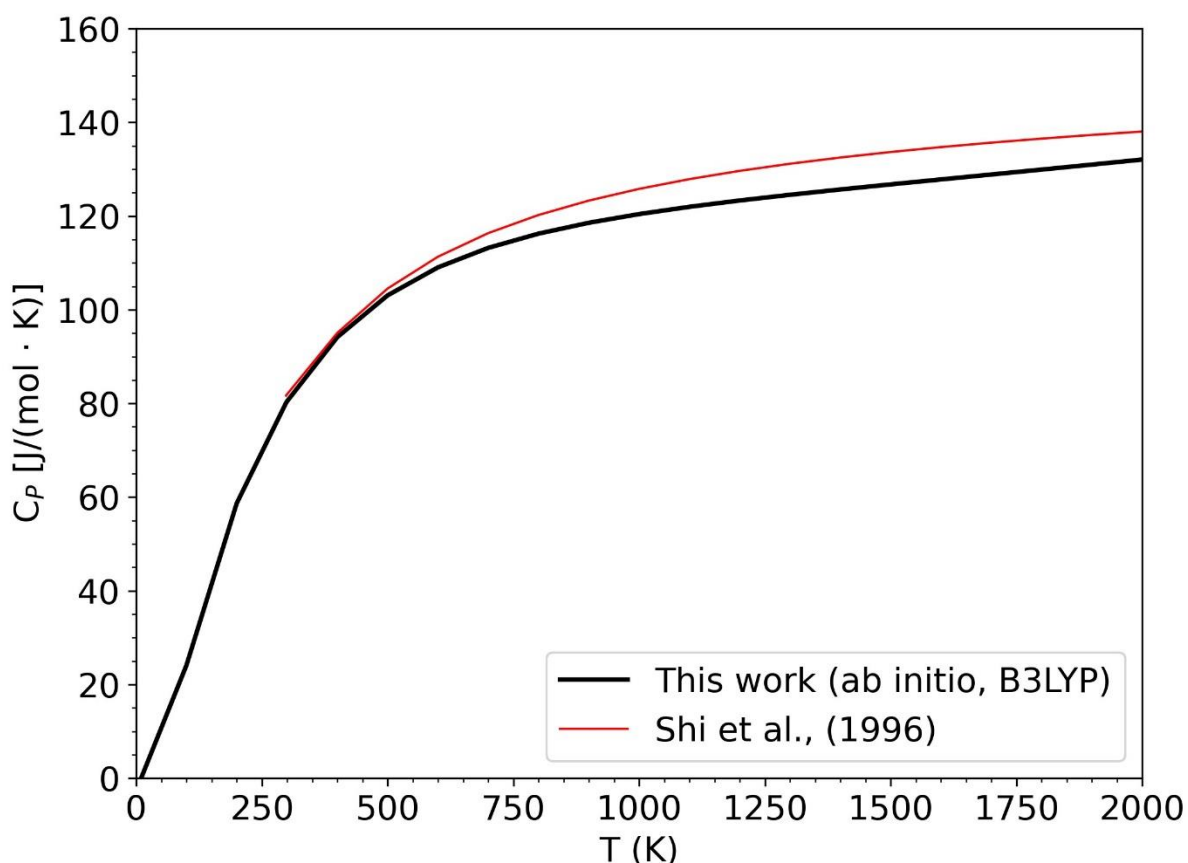


Figure 5.4.4. Ab initio B3LYP isobaric heat capacity (C_P) of MgSiO_3 HT-CEn at $P = 0$.

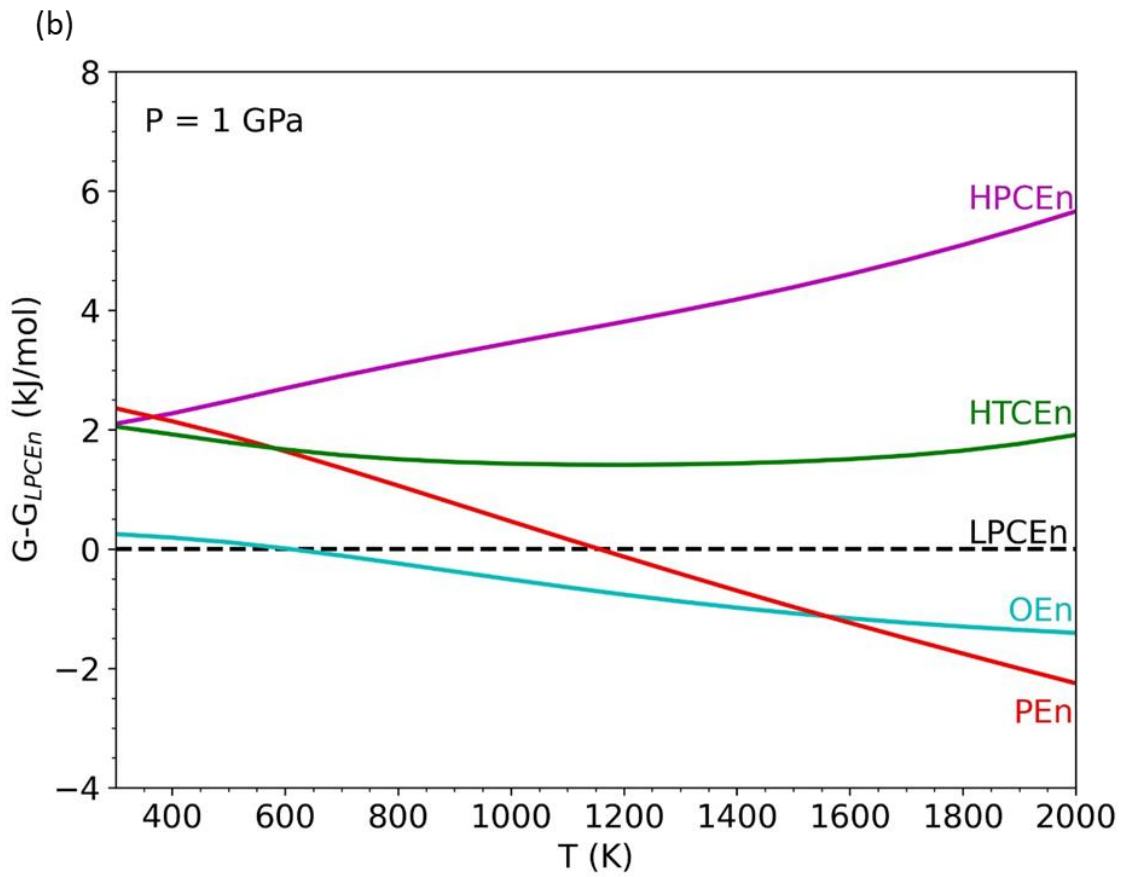
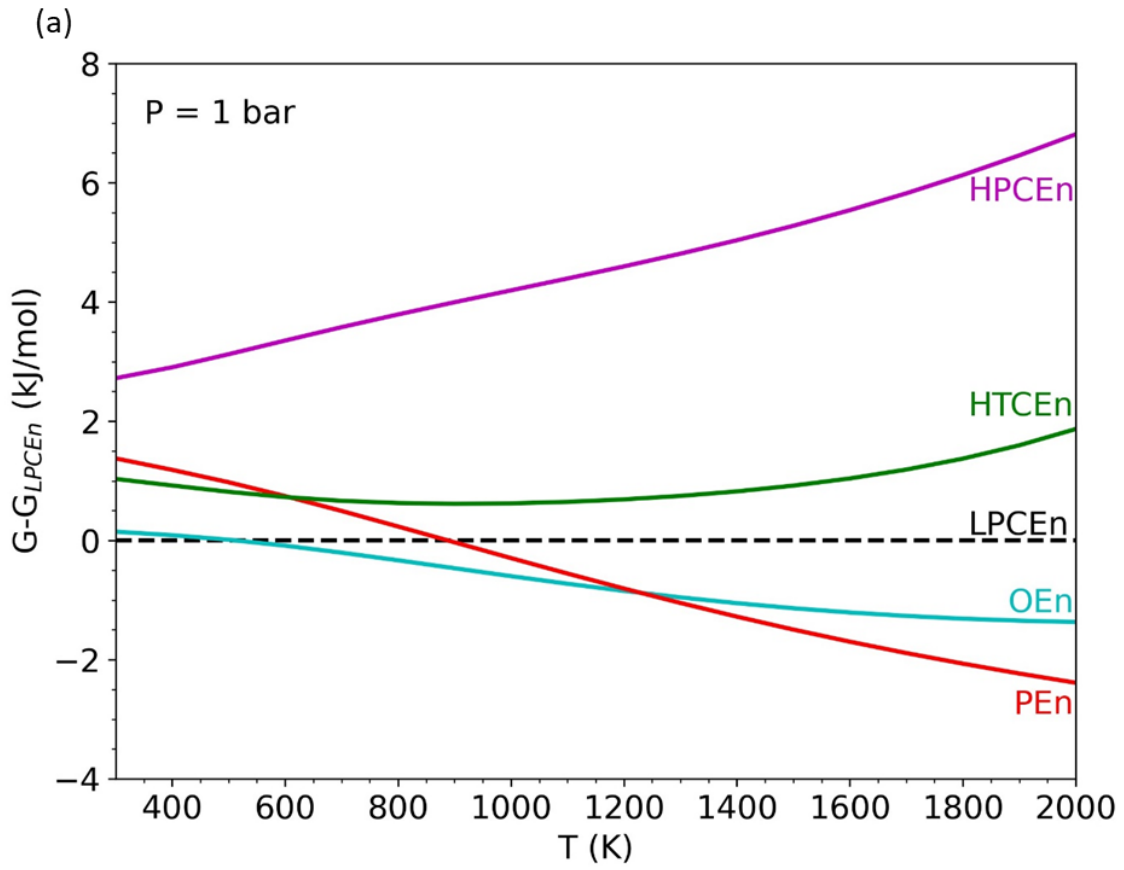
The red curve in Figure 5.4.4 is a polynomial function determined by Shi et al., (1996), who performed a thermodynamic assessment of Ca-Mg-Si-O pyroxene phases. It's quite evident from Figure 5.4.4 that mathematical procedures aimed at assessing thermodynamic properties able to reproduce selected phase equilibria often provide inaccurate or unphysical results, since the isobaric heat capacity assessed by Shi et al. (1996) for HT-CEn is drastically overestimated over the whole temperature range (up to 4.5% at 2000 K). Therefore, the ensuing stability field of HT-CEn in the MgSiO_3 phase diagram as obtained by Shi et al. (1996) is flawed by physical unsoundness of thermodynamic data.

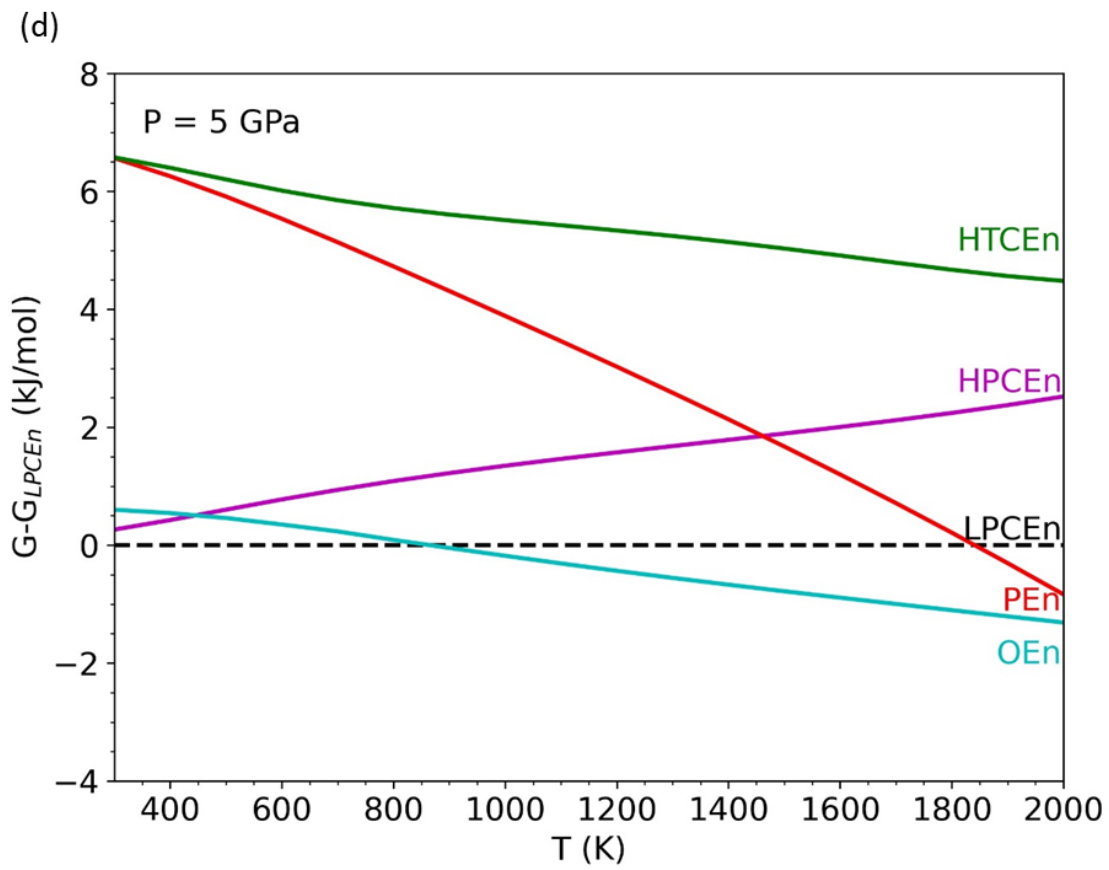
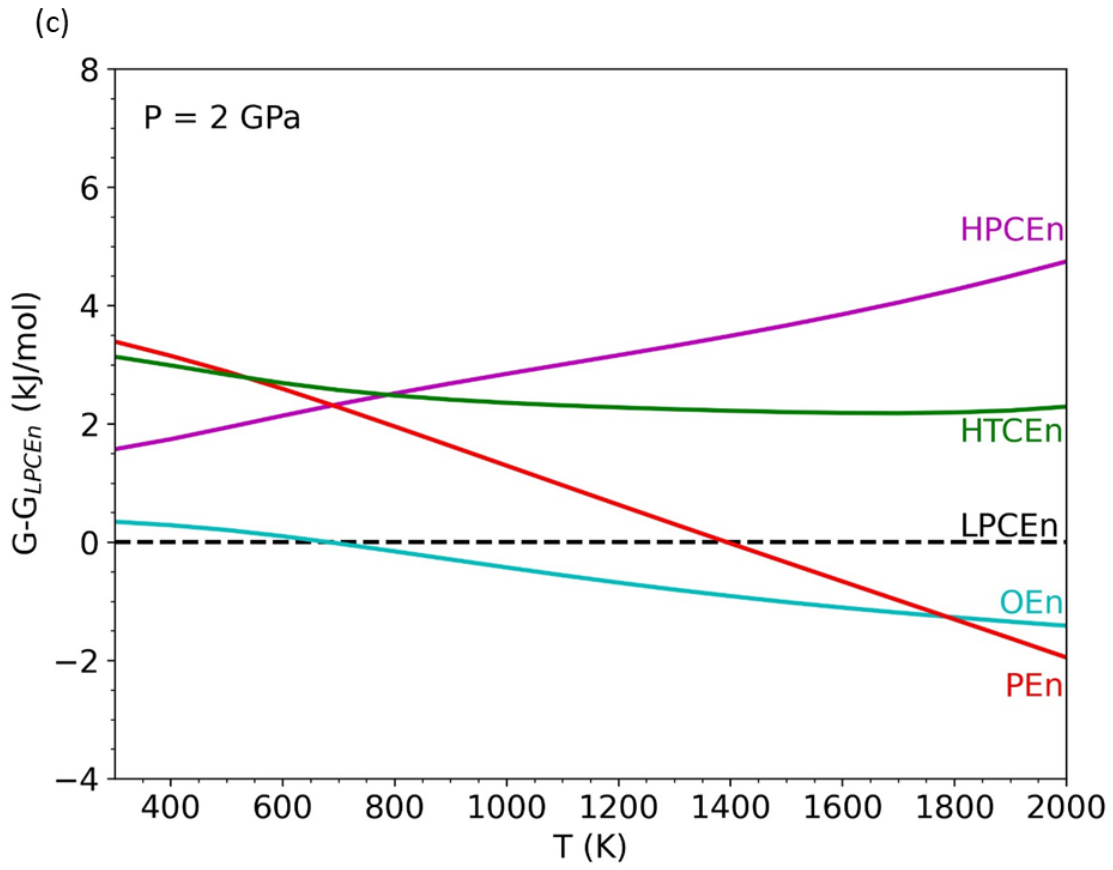
The complete dataset of thermodynamic properties of MgSiO_3 high-temperature clinoenstatite is reported in Table 5.4.1.

Table 5.4.1. Thermodynamic dataset for MgSiO₃ high-temperature clinoenstatite. H_f^0 = standard state enthalpy of formation from the elements; S^0 = standard state entropy; a, b, c, d, e, f, g = numerical coefficients of the polynomial function for the isobaric heat capacity (C_p), fitted in the range $T = 298.15 \text{ K} - 2000 \text{ K}$ (cf. Eq. 5.2.2); V_0 = molar volume at the athermal limit ($T = 0 \text{ K}$; $P = 0 \text{ GPa}$); K_0 = static bulk modulus; K'_0 = pressure derivative of bulk modulus; dK/dT = isobaric temperature derivative of bulk modulus; $\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4$ = numerical coefficients of the polynomial function for thermal expansion, fitted in the range $T = 200 \text{ K} - 2000 \text{ K}$ (cf. Eq. 5.2.1).

H_f^0 (kJ/mol)	-1545.456	V_0 (cm ³ /mol)	33.372
S^0 [J/(mol × K)]	66.951	K_0 (GPa)	100.32
a	133.63	K'_0	9.63
$b \times 10^3$	3.9114	dK/dT (bar/K)	-192
$c \times 10^{-5}$	18.254	$\alpha_0 \times 10^7$	0.21282
d	-694.48	$\alpha_1 \times 10^7$	-80.070
$e \times 10^{-8}$	-9.6967	$\alpha_2 \times 10^3$	32.22
$f \times 10^6$	3.0491	α_3	-13.0784
$g \times 10^9$	-0.67403	α_4	1680.380

The stability of high-temperature clinoenstatite with respect to other MgSiO₃ pyroxenes has been investigated by Gibbs free energy minimization (see Section 2.7 for details). The G-T curves calculated at different pressures (i.e. between 0 and 10 GPa) for all the pyroxene polymorphs investigated in this study are shown in Figures 5.4.5a – 5.4.5e.





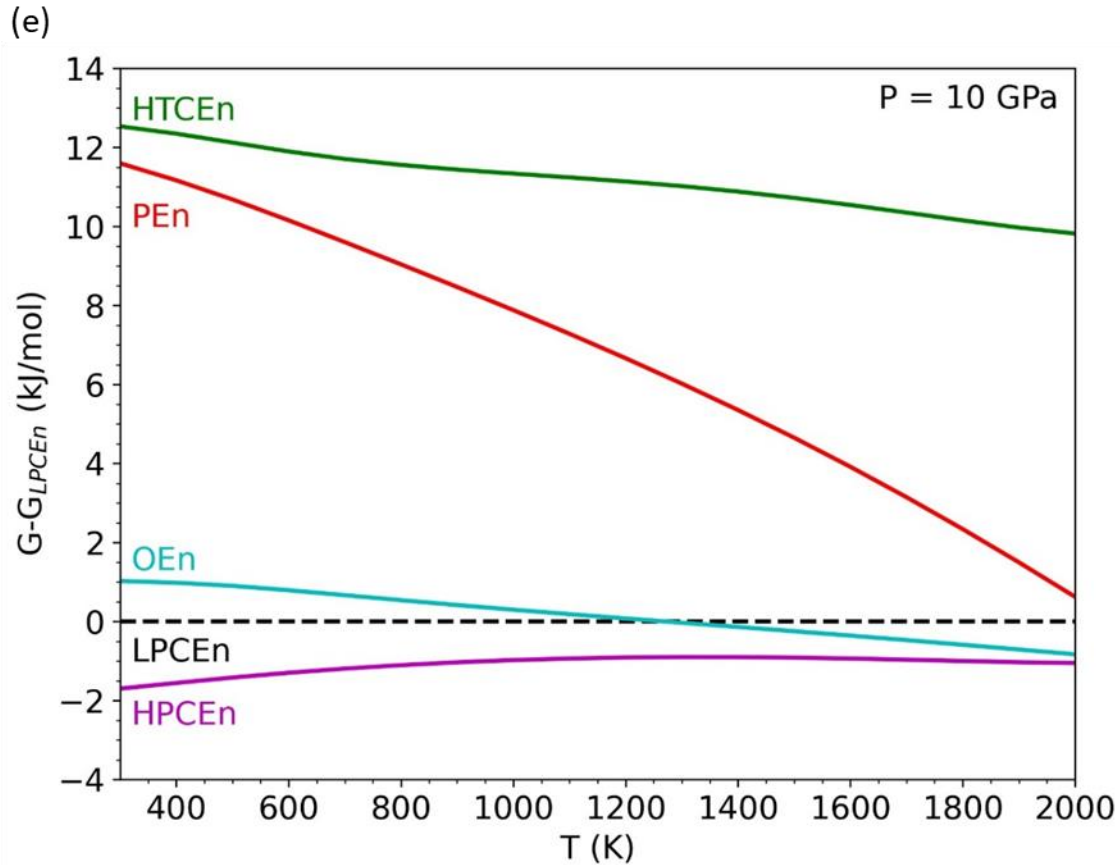


Figure 5.4.5. Ab initio Gibbs free energy vs. temperature curves for MgSiO₃ pyroxenes at 1 bar (a), 1 GPa (b), 2 GPa (c) 5 GPa (d), and 10 GPa (e). HPCEn = high-pressure clinoenstatite, HTCEn = high-temperature clinoenstatite, LPCEn = low-pressure clinoenstatite, OEn = orthoenstatite, PEn = protoenstatite. The Gibbs free energy of all polymorphs is normalised to that of the low-pressure clinoenstatite (i.e. the stable polymorph at T = 0 K and P = 0).

The principle behind the interpretation of the G – T relations reported in Figure 5.4.5 is that the phase with the lowest Gibbs free energy at given P-T conditions is the most stable at those P – T conditions. So, for example, at 1 bar and in the temperature range between 298.15 K and ~513 K, low-pressure clinoenstatite (LP-CEn) is stable, then LP-CEn transforms into orthoenstatite (OEn), which remains stable up to ~1229 K before transforming into protoenstatite (PEn) (cf. Fig. 5.4.5a). This is consistent with what calculated in the theoretical phase diagram of MgSiO₃, where HT-CEn doesn't have any stability field a 1-bar pressure. It's interesting to note that at ambient pressure and

in the high temperature range (i.e. $T > 1200$ K), the Gibbs free energy of PEn is lower than that of HT-CEn by 2 to 4 kJ/mol (hence, well above the level of confidence for this kind of calculations, which is around 1 kJ/mol). Raising the pressure, ab initio $G(T,P)$ calculations show that HT-CEn is always unstable with respect to the other pyroxene polymorphs also at higher pressures and, ultimately, in the whole investigated $P - T$ range (cf. Figures 5.4.5b – 5.4.5e). For instance, at $P = 2$ GPa the Gibbs free energy values of HT-CEn are higher by 3-4 kJ/mol than those of the stable pyroxene polymorph (cf. Fig. 5.4.5c), while at higher pressures this difference sensibly increases (i.e. to around 6 kJ/mol and 12 kJ/mol at $P = 5$ GPa and $P = 10$ GPa, respectively) (cf. Figures 5.4.5d and 5.4.5e). Therefore, at variance with some assessments in the literature (e.g. Shi et al., 1996; Gasparik, 2014), ab initio B3LYP calculations performed in this work support the evidence that: i) HT-CEn doesn't have any P - T stability field occurring between that of protoenstatite and the incongruent melting point of MgSiO_3 ; ii) protoenstatite (and not HT-CEn) is the liquidus phase of MgSiO_3 at low pressure conditions. So, first principles calculations clearly show that HT-CEn is a metastable phase in the MgSiO_3 system, thus proving on a thermodynamic basis some suggestion provided by experimental studies (e.g. Smyth, 1974; Jiang et al., 2002; Yoshiasa et al., 2013). At the same time, this finding does not contradict previous experiments which found a monoclinic polymorph in the HT-range (i.e. Boyd and Schairer, 1964; Perrotta & Stephenson, 1965; Smyth, 1969 and 1974; Sadanaga & Okamura, 1971; Jiang et al., 2002; Yoshiasa et al., 2013), since it's highly probable that HT-CEn is a metastable phase which forms in high-temperature experimental runs. The fact that some thermodynamic assessments (i.e. Shi et al., 1994 and 1996; Gasparik, 2014) predict subsolidus temperatures for the HT-CEn/PEn phase transition that are much higher than those observed in the above cited experiments seems to be a clear sign of their physical unsoundness and support the main outcome of first principles calculations performed in this work.

6. Melting curves and behaviour of MgSiO_3 pyroxene polymorphs at HP-HT conditions

6.1. Introduction

Understanding melting phase relations in complex geological systems is hindered by a still lacking knowledge of the thermodynamic properties of liquid and solid phases at high pressures and temperatures (HP-HT). Laboratory measurements can be applied to complex compositions and roughly constrain the onset of melting processes at HP-HT conditions, but they usually suffer from large uncertainties (mainly due to high thermal gradients) and rarely predict the ultimate nature of melting (i.e.: peritectic or eutectic fusion). In this context, a thermodynamically-consistent computational framework has been recently developed and tested (Ottonello et al., 2013; Belmonte et al., 2017a, 2017b) to predict melting phase relations in multicomponent systems at high pressures and temperatures by using a combination of well-established theoretical methods (i.e. *ab initio* DFT and MD calculations, polymer chemistry and computational thermodynamics). These methods basically provide the Gibbs free energy values of all the solid and liquid phases within a given compositional system on a grid of P-T-X conditions and allow to infer melting phase relations by minimisation algorithms based on the convex-hull method (see Belmonte et al., 2017a for details).

The MgSiO_3 system has been chosen to test our model calculations, as already anticipated in the previous chapter. The main difference with previous investigation by Belmonte et al. (2017a) is the fact that physically-consistent full *ab initio* thermodynamic properties for the MgSiO_3 phases that form at *subsolidus* conditions are adopted in this work, whereas Belmonte et al. (2017a) relied on either assessed or experimental thermodynamic data for the MgSiO_3 pyroxene polymorphs. So, this work represents an improvement toward a completely theoretical description of the MgSiO_3 phase diagram, from *subsolidus* to melting conditions, in a chemically relevant

system for the Earth's interior. In fact, the MS binary system accounts for ~80 - 90% of a pyrolite bulk composition (Irifune, 1987), being so a realistic proxy for a deep mantle system. *Liquidus* curves of the MS system at various pressure conditions have been calculated following the guidelines presented both in section 2.8 and in the following paragraph. Melting curves of the various MgSiO_3 pyroxene polymorphs stable on the liquidus have been predicted by computational theory and are discussed and compared with the available literature data in this chapter.

6.2. Computational method

The procedure adopted to obtain the thermodynamic properties of the binary $\text{MgO} - \text{SiO}_2$ liquid phase and then to compute melting phase relations at HP-HT conditions via first principles has been described in detail in section 2.8, hence only the more relevant aspects will be reported here. Thermodynamic properties for the solid phases (pyroxene polymorphs) have been already presented and discussed in previous chapters (cf. Tables 4.7.1a, 5.3.1.3, 5.3.2.3 and 5.3.3.3). Protoenstatite has been included in the calculation up to 5 GPa and dismissed from the calculation at higher pressures, so that orthoenstatite results as the *liquidus* phase between 5 GPa and 10 GPa at least. *Liquidus* curves have been calculated by reassessing the parameters that define the excess volume of mixing of the MgO-SiO_2 liquid phase according to Belmonte et al. (2017a) (see their Table 3), so as to make some selected melting temperatures found for the MgSiO_3 composition at high pressures consistent with experimental results, in particular Dalton & Presnall (1997) and Presnall & Gasparik (1990). The effects of the new parameters on either the silica-rich side or the magnesium-rich side of the $\text{MgO} - \text{SiO}_2$ binary join have not been considered by taking into account only the $X(\text{SiO}_2) = 0.5$ composition (i.e.: MgSiO_3). Fusion points of either protoenstatite or orthoenstatite have been fitted with Simon-Glatzel equation (Simon and Glatzel, 1929) in the pressure range of stability of the two polymorphs, i.e. 0 – 5 GPa and 5 – 10 GPa, respectively.

6.3. Thermodynamic properties of liquid end-member compositions

A comprehensive description of how the thermodynamic properties of the pure liquid components have been obtained is reported in Belmonte et al. (2017a) and will be dismissed here. Table 6.3.1 reports the thermodynamic parameters of MgO and SiO₂ liquids (i.e. H^0_f , S^0 and C_P function) adopted in this work.

Table 6.3.1. Thermodynamic properties of pure liquid components in the MgO-SiO₂ system as adopted in this work (cf. Belmonte et al., 2017a). H^0_f = enthalpy of formation from the elements at $T_r = 298.15$ K, $P_r = 1$ bar; S^0 = standard-state entropy; C_P = isobaric heat capacity ($C_P = a + bT + cT^{-2} + dT^{-1/2} + eT^{-3} + fT^2 + gT^3$); V^0_{298} = molar volume at $T_r = 298.15$ K and $P_r = 1$ bar; K_0 = bulk modulus at the athermal limit ($T = 0$ K); K'_0 = pressure derivative of the bulk modulus; $(dK/dT)_P$ = temperature derivative of the bulk modulus; α_V = volume thermal expansion coefficient ($\alpha_V = \alpha_0 T + \alpha_1 + \alpha_2 T^{-1}$).

MgO			
H^0_f (J/mol)	-563,716.5	V^0_{298} (cm ³ /mol)	11.41
S^0 [J/(mol × K)]	16.725	K_0 (GPa)	35.3
a	72.708	K'_0	4.81
$b \times 10^3$	18.183	dK/dT (bar/K)	0.0
$c \times 10^{-5}$	-13.124	$\alpha_0 \times 10^7$	-0.05514
d	-257.27	$\alpha_1 \times 10^7$	1088
$e \times 10^{-8}$	30.899	$\alpha_2 \times 10^3$	8.412
$f \times 10^6$	0.379074		
$g \times 10^9$	-0.038084		
SiO ₂			
H^0_f (J/mol)	-911,746.2	V^0_{298} (cm ³ /mol)	27.872
S^0 [J/(mol × K)]	33.887	K_0 (GPa)	5.0
a	88.455	K'_0	15.8
$b \times 10^3$	-3.00137	dK/dT (bar/K)	0.0
$c \times 10^{-5}$	-48.527	$\alpha_0 \times 10^7$	-0.3611
d	-114.33	$\alpha_1 \times 10^7$	843.1
$e \times 10^{-8}$	72.829	$\alpha_2 \times 10^3$	0.0
$f \times 10^6$	0.71332		
$g \times 10^9$	0.0059239		

Interactions in the liquid state have been resolved in terms of the Hybrid Polymeric Approach (Ottonello, 2005), whose details are given in Section 2.8. The topological analysis of the MgO-SiO₂ liquidus at 1-bar and HP conditions according to the experiments of Bowen and Andersen (1914), Hageman and Oonk (1986), Dalton and

Presnall (1997) and Presnall and Gasparik (1990) gives the HPA parameters (i.e. A and B in Equation 2.8.4) and the parameters for the excess volume of mixing (i.e. η_k in Equation 2.8.7) for the liquid phase, as reported in Table 6.3.2.

Tab 6.3.2. Parameters of the Hybrid Polymeric Approach (HPA) for the MgSiO_3 liquid as re-assessed in this work for the HP range.

A	B	$\eta_{1,S}$	$\eta_{6,S}$	$\eta_{0,V}$	$\eta_{1,V}$	$\eta_{2,V}$	$\eta_{6,V}$
-3330	-2.5	3	-10	-0.06 ^a /-0.044 ^b	0.05 ^a /0.16 ^b	0 ^a /-2.7 ^b	-0.35 ^a /-0.83 ^b

In Table 6.3.2 parameters labelled with “a” are used up to $P = 5$ GPa, whereas parameters labelled with “b” are used for pressures between 5 and 16 GPa. The former have been assessed by setting the excess volume of mixing of the liquid so that the resulting melting point for the MgSiO_3 composition at 5 GPa is consistent with that obtained by Dalton & Presnall (1997), whereas the latter have been assessed by setting the excess volume of mixing of the liquid so that the resulting melting point for the MgSiO_3 composition at 10 GPa is consistent with that obtained by Presnall & Gasparik (1990). In order to provide a more straightforward way to reproduce the energy properties of the MgSiO_3 liquid, volume vs. temperature and Gibbs free energy vs. temperature curves are provided in Figures 6.3.1 and 6.3.2 as computed at 1 bar, 3 GPa, 5 GPa, 7 GPa and 10 GPa. V-T and G-T relations have been fitted with either second or third order polynomial functions, as follows:

$$V_{(T,P=1\text{bar})}(T) = -3 \times 10^{-7}T^2 + 0.0019T + 18.799 \quad (6.3.1)$$

$$V_{(T,P=3\text{GPa})}(T) = -2 \times 10^{-7}T^2 + 0.0017T + 16.086 \quad (6.3.2)$$

$$V_{(T,P=5\text{GPa})}(T) = -2 \times 10^{-7}T^2 + 0.0016T + 15.312 \quad (6.3.3)$$

$$V_{(T,P=7\text{GPa})}(T) = -2 \times 10^{-7}T^2 + 0.0016T + 13.534 \quad (6.3.4)$$

$$V_{(T,P=10\text{GPa})}(T) = -2 \times 10^{-7}T^2 + 0.0015T + 12.999 \quad (6.3.5)$$

$$G_{(T,P=1bar)}(T) = 5 \times 10^{-9}T^3 - 5 \times 10^{-5}T^2 - 0.0214T - 749.47 \quad (6.3.6)$$

$$G_{(T,P=3GPa)}(T) = 5 \times 10^{-9}T^3 - 5 \times 10^{-5}T^2 - 0.0161T - 698.24 \quad (6.3.7)$$

$$G_{(T,P=5GPa)}(T) = 5 \times 10^{-9}T^3 - 5 \times 10^{-5}T^2 - 0.0129T - 666.89 \quad (6.3.8)$$

$$G_{(T,P=7GPa)}(T) = 6 \times 10^{-9}T^3 - 5 \times 10^{-5}T^2 - 0.0092T - 645.35 \quad (6.3.9)$$

$$G_{(T,P=10GPa)}(T) = 6 \times 10^{-9}T^3 - 5 \times 10^{-5}T^2 - 0.0046T - 604.58 \quad (6.3.10)$$

The polynomial fits can be used to directly retrieve the Gibbs free energies and thermal EOS parameters of the MgSiO₃ liquid, but some care must be taken in using those functions to derive other thermodynamic properties.

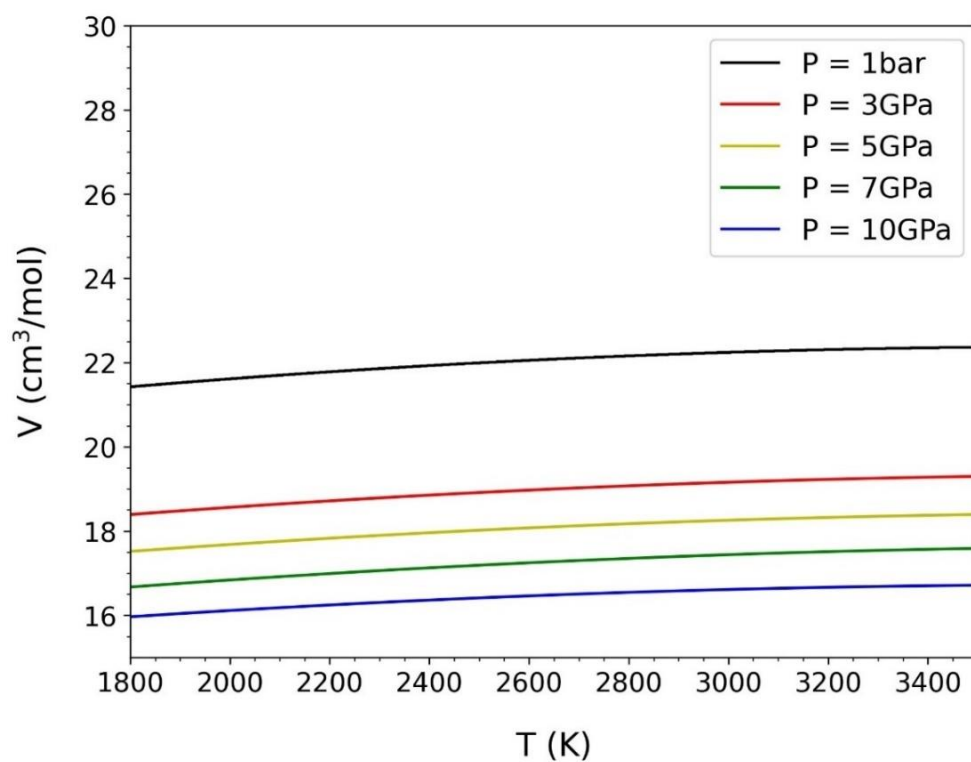


Figure 6.3.1. Volume vs. temperature curves computed for the MgSiO_3 liquid at different pressures.

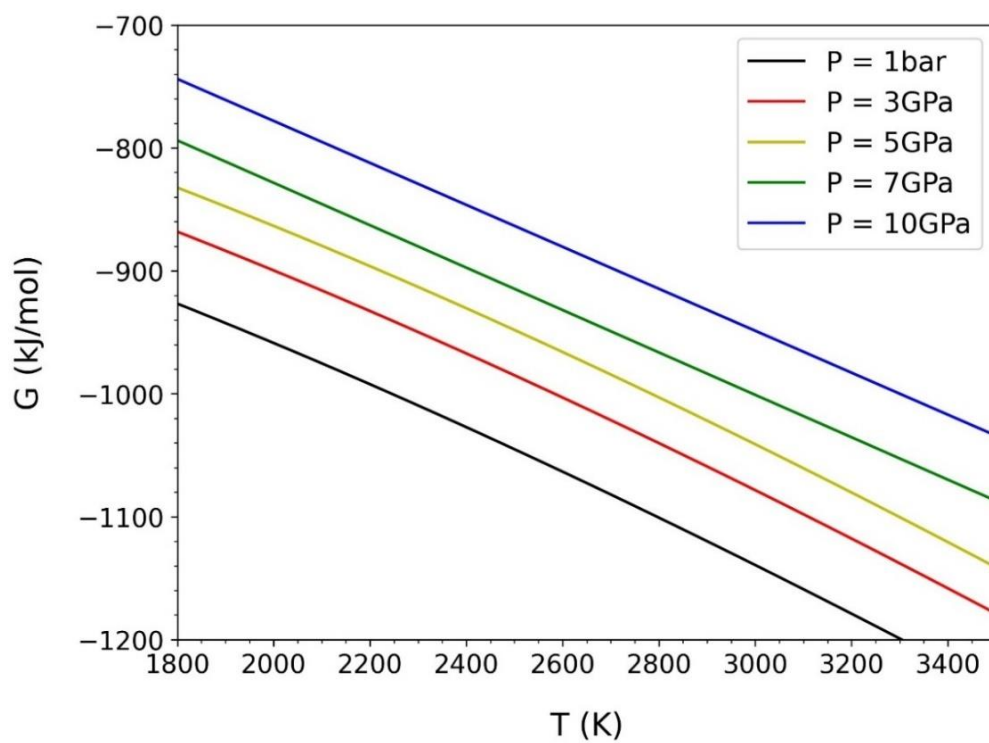


Figure 6.3.2. Gibbs free energy vs. temperature curves computed for the MgSiO_3 liquid at different pressures.

6.4. Melting curve of the MgSiO₃ system

Figure 6.4.1a,b shows a detail of the MgSiO₃ phase diagram already presented and discussed in Chapter 5. The theoretical melting curve as obtained in this work is reported as compared with melting experiments after Boyd et al. (1964); Chen & Presnall (1975), Gasparik & Presnall (1990), Shen & Lazor, (1995), Dalton & Presnall, (1997). The dashed part of the melting curve in the pressure range 1 – 4 GPa corresponds to the portion of the melting curve that has been inferred, due to the impossibility to locate the protoenstatite – orthoenstatite – liquid invariant point, as discussed above. Some experimental results obtained at *subsolidus* conditions are also shown for comparison. Panel (a) shows that our theoretical curve reproduces quite well the experimental data, with just a slightly higher difference that can be observed when comparing our results to those of Boyd et al., (1964) in the lower temperature range. Our results are also consistent with experimental measurements obtained by LH-DAC within their quite large error bars (Shen & Lazor, 1995). The theoretical triple point between orthoenstatite – high pressure clinoenstatite – liquid has been located at $P = 10.4$ GPa and $T = 2479$ K in this work, which is close to that obtained in multi-anvil experiments by Presnall & Gasparik (1990), i.e. $P = 11.9$ GPa and $T = 2503$ K. This slight difference is mostly due to the steeper Clapeyron slope of the theoretical orthoenstatite – high pressure clinoenstatite phase boundary, which leads to the invariant point occurring at lower pressures. Panel (b) shows a further detail of the melting curve in a narrower pressure range (i.e.: $P = 1 - 5$ GPa). The best fit of experimental runs by Boyd et al. (1964), as well as the melting curve determined by Chen & Presnall (1975) are also reported for comparison. The 1-bar melting temperature of protoenstatite, as determined in this study, is located at $T = 1761$ K, which is lower than the results obtained by Boyd et al. (1964) and Chen & Presnall (1975) (i.e.: $T = 1830$ K for both authors). It should be noted that the calculation of the peritectic melting temperature of the MgSiO₃ composition at ambient pressure (actually, at 1 bar the fusion of pyroxene occurs at a peritectic point, which is slightly

more silica rich with respect to the MgSiO_3 composition) was prevented by the subtle differences of free energies between the solids and the liquid phases, which inhibited the correct location of the peritectic point at 1 bar. Our estimate of the protoenstatite peritectic melting point at 1 bar pressure relies on an extrapolation of the melting curve below 0.54 GPa. It is well known that pyroxene undergoes a change in melting behaviour as pressure increases, which leads to a shift from an incongruent, peritectic melting, to a congruent, eutectic one. Different melting experiments roughly constrained the pressure at which this change occurs between 1.3 and 4.1 kbar by extrapolation of experimental data (Boyd et al., 1964; Taylor, 1973; Chen and Presnall, 1975). However, Belmonte et al. (2017) found that pyroxene still melts incongruently until 1 – 2 GPa and showed a congruent melting at 5 GPa, in agreement with that observed for orthoenstatite by Dalton & Presnall (1997). Hence, the change from incongruent to congruent melting for MgSiO_3 should occur between 2 and 5 GPa, which is more than 1 order of magnitude higher than the above cited experimental results and some thermodynamic assessments as well (e.g. Hudon et al., 2005). According to this study, protoenstatite is predicted to shift from incongruent to congruent melting in a pressure range between $P = 2.51 - 3$ GPa, which is in agreement with what found by Belmonte et al. (2017a). However, our result should be taken with care since the stability of protoenstatite with respect to orthoenstatite is affected by the uncertainties already discussed in the previous chapters. As a matter of fact, the correct location of the change in melting behaviour of the MgSiO_3 metasilicate composition is still uncertain.

Finally, the calculated $P - T$ points on the melting curve have been fitted with a Simon-Glatzel equation (cf. equation 6.4.1) in two different pressure ranges, i.e. 0 – 5 GPa for protoenstatite and 5 – 10 GPa for orthoenstatite, i.e.:

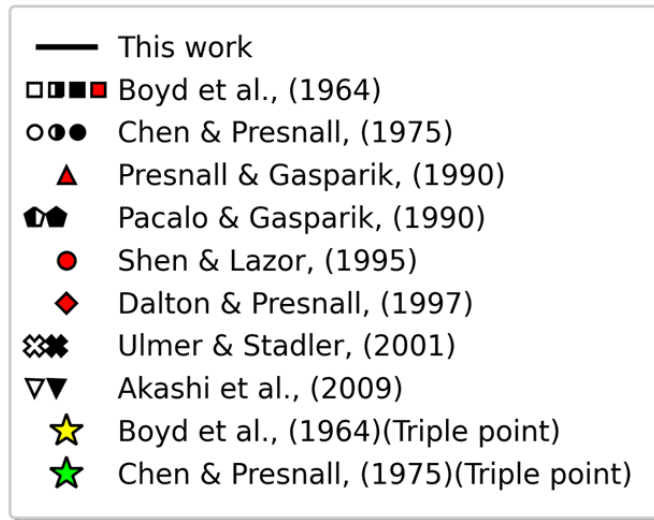
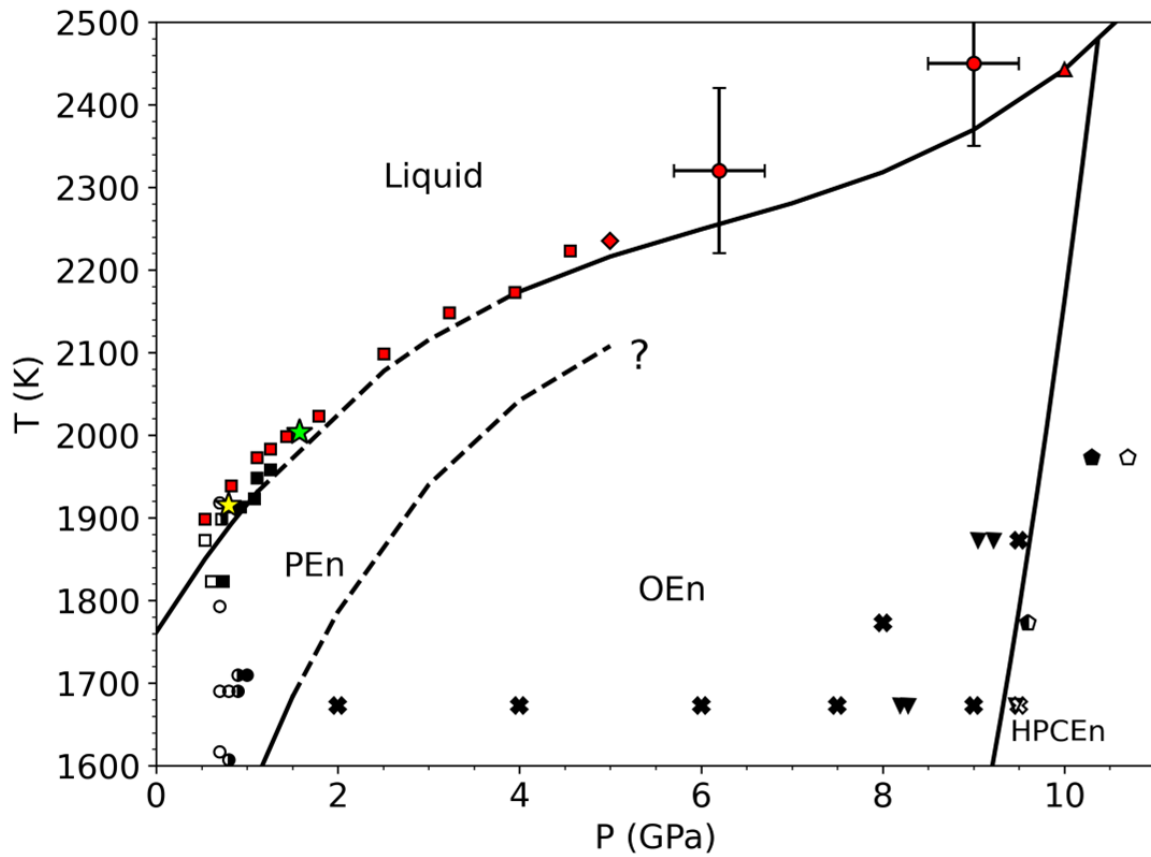
$$T = T_0 \left(\frac{P}{a} + 1 \right)^{\frac{1}{c}} \quad (6.4.1)$$

Fitted parameters of equation 6.4.1 for protoenstatite and orthoenstatite are reported in Table 6.4.1.

Table 6.4.1. Parameters of the Simon-Glatzel equation for the melting curves of protoenstatite (PEn) and orthoenstatite (OEn).

	P range 0 – 5 GPa (PEn)	P range 5 – 10 GPa (OEn)
T_0 (1bar) K	1805	1700
a	6.00	5.00
c	2.75	3.01

(a)



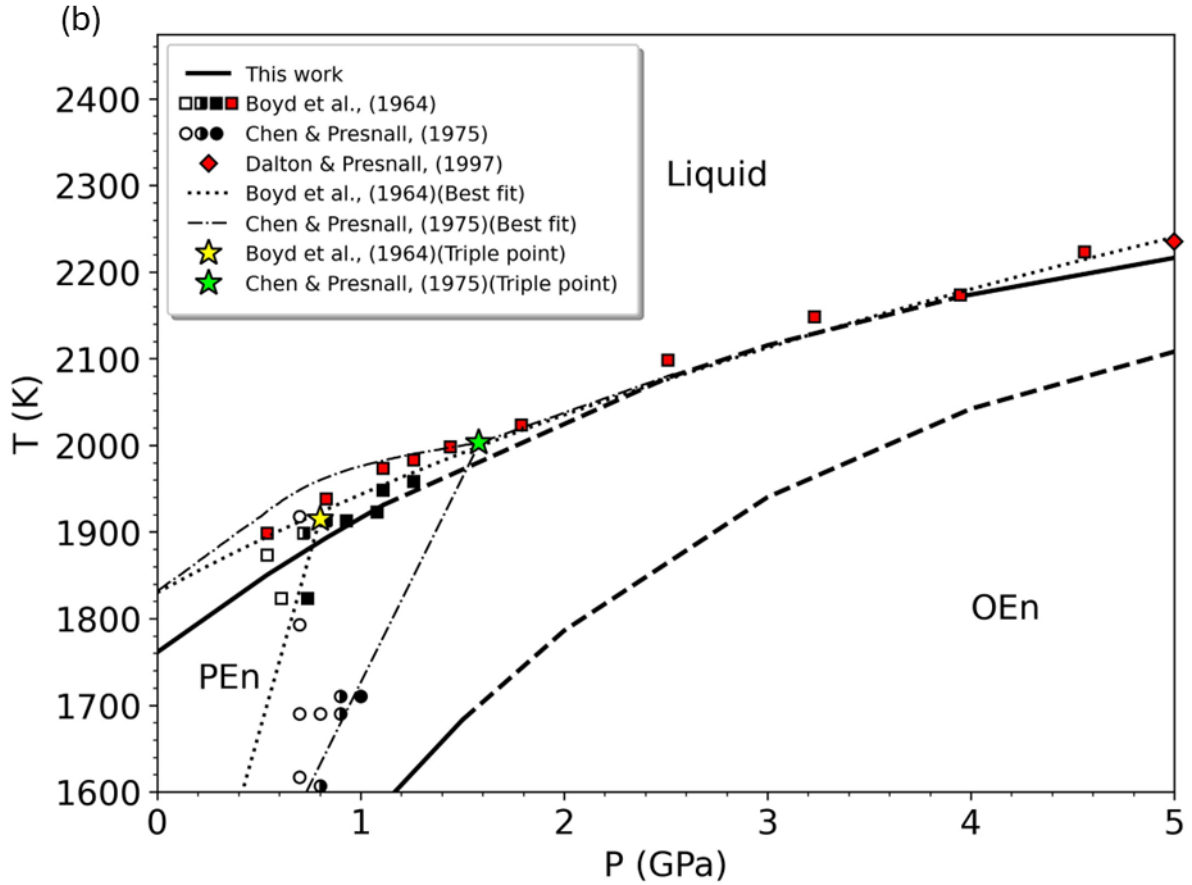


Figure 6.4.1. Melting curve of the MgSiO_3 system calculated (a) in the pressure range between 0 and 10 GPa and in the temperature range between 1600 and 2500 K and (b) in a narrower pressure range (0 – 5 GPa). Best fits of experimental results according to Boyd et al. (1964) and Chen & Presnall (1975) are also shown for comparison. The invariant point between protoenstatite, orthoenstatite and liquid according to different experimental investigations are also indicated by stars. White markers = protoenstatite (PEn) or high pressure clinoenstatite (HPCEn) stable, black markers = orthoenstatite (OEn) stable, black & white markers = protoenstatite + orthoenstatite or orthoenstatite + high pressure clinoenstatite stable, red markers = liquid stable.

6.5. Conclusions

In this chapter we show that melting phase relations in the MgSiO_3 system can be predicted up to HP-HT conditions by an integrated theoretical and computational approach based on first principles calculations, polymer chemistry and equilibrium thermodynamics. Thermodynamically-consistent energy properties of MgSiO_3 liquid have been obtained by a polymeric model according to Belmonte et al. (2017a). The computed melting curve of the MgSiO_3 system is in overall good agreement with the experimental data and shows that pressure effects not only shift liquidus conditions to higher temperatures but also possibly change the nature of melting of solid phases from incongruent to congruent, although some uncertainties still remain on the precise pressure conditions at which this change occurs. Although additional chemical components (like Al_2O_3 , CaO , FeO , H_2O etc.) may have important effects on melting phase relations at HP-HT, the information provided by the analysis of phase diagrams in simplified, but representative, compositional systems like the MS constitute a reference framework to model physico-chemical properties of liquids in deep mantle environments and to extrapolate the overall melting behaviour of deep mantle sources to more complex systems.

7. Elastic and seismic properties of MgSiO_3 pyroxenes by first-principles DFT calculations

7.1. Introduction

In this Chapter of the Thesis, a systematic study of seismic and elastic properties of MgSiO_3 pyroxenes will be presented and results compared to the available literature data. Some implications for the origin of mid-mantle global seismic discontinuities (like the so-called X-discontinuity) will be also discussed.

Seismic and elastic properties are fundamental to model the rheological behavior of constituent mineral phases at Earth's mantle conditions and can provide useful constraints for the interpretation of global seismological observations by mineral physics. The stiffness tensor of all pyroxene polymorphs investigated in this work has been calculated via first principles DFT calculations at the B3LYP level of theory. Aggregate elastic moduli (i.e. bulk and shear moduli, K_{VRH} and μ_{VRH}) and seismic velocities [namely, longitudinal ($V_{\text{P,VRH}}$) and transversal ($V_{\text{S,VRH}}$) seismic velocities] have been computed in a fully consistent way from the ab initio values of density and elastic constants by employing a Voigt-Reuss-Hill averaging scheme (Hill, 1952).

Computed elastic and seismic properties of orthoenstatite and high-pressure clinoenstatite have been extrapolated at high temperature and pressure conditions in such a way as to determine seismic velocity jumps and impedance contrasts associated with the OEn/HP-CEn phase transition at upper mantle depths. The obtained results have been tested against and compared with global seismological observations (e.g. Deuss & Woodhouse, 2004), experimental results (Kung et al., 2004, 2005) and other theoretical calculations (e.g. Song et al., 2023) to provide thermodynamic and thermophysical constraints to the interpretation of the origin of the X-discontinuity, a small seismic discontinuity frequently observed at ~250-350 km depths in the Earth's mantle. Although it cannot be strictly considered as a global discontinuity (at least if compared with the 410-km and 660-km seismic discontinuities of the mantle transition

zone), X-discontinuity has been detected by seismic studies in a range of mantle environments, in particular beneath continental areas and ocean basins as well as near subduction zones, like the Tonga slab (Revenaugh and Jordan, 1991; Williams and Revenaugh, 2005; Bagley and Revenaugh, 2008). The origin of the X-discontinuity has been usually related to mineralogical phase changes in the mantle and the orthoenstatite (OEn) to high-pressure clinoenstatite (HP-CEn) phase transition is often advocated as one of the possible candidate reaction able to account for seismological evidences (Woodland, 1998; Akashi et al., 2009).

7.2. Computational method

As already outlined in Chapter 2, the second-order elastic constants of a crystal can be derived from the relations between the stress and strain tensors defined for an ideally elastic solid, defining the former in terms of the change upon deformation of an appropriate thermodynamic potential (in this case represented by the static internal energy). Following this approach, the components of the elastic constant tensor are related to the second derivative of the total energy with respect to strain components and can then be derived analytically by fitting total energy vs. strain curves calculated for different types of deformation of the unit cell. The computed elastic constants at $P = 0$ (stiffnesses) can be expressed via the Voigt's tensor notation (cf. Nye, 1957):

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ & & & & & C_{66} \end{pmatrix} \quad (7.2.1)$$

The number of independent components in Equation (7.2.1) depends upon the symmetry of the crystalline phase (see for instance Mainprice, 2007).

Aggregate elastic moduli (K_{VRH} and μ_{VRH}) and can then be calculated from the ab initio of elastic constant tensor by employing a Voigt-Reuss-Hill averaging scheme (Hill, 1952) (cf. Equations 2.2.17 - 2.2.22 in Chapter 2). Aggregate seismic velocities ($V_{P,VRH}$ and $V_{S,VRH}$) are finally obtained from the ab initio elastic moduli and density values (cf. Equations 2.2.23 - 2.2.24 in Chapter 2), the latter being available from first principles P-V-T relations.

7.3. Elastic and seismic properties of $MgSiO_3$ pyroxenes

A complete set of first principles seismic and elastic properties of $MgSiO_3$ pyroxenes are presented below. The components of the static elastic constants tensor (C_{ij}), aggregate bulk (K_{voigt} , K_{reuss} , K_{VRH}) and shear (μ_{voigt} , μ_{reuss} , μ_{VRH}) moduli, bulk longitudinal ($V_{P,VRH}$) and shear-wave ($V_{S,VRH}$) seismic velocities have been computed at $T = 0K$, $P = 0$ for orthoenstatite (OEn, Tab. 7.3.1), high-pressure clinoenstatite (HP-CEn, Tab. 7.3.2), low-pressure clinoenstatite (LP-CEn, Tab. 7.3.3) and high-temperature clinoenstatite (HT-CEn, Tab. 7.3.4). The static elastic tensor of protoenstatite (PEn) have been already reported in Chapter 4 (cf. Table 4.3.1). When available, our results are compared with reference data; for some of the pyroxene polymorphs (e.g. HT-CEn) B3LYP data computed in this work represent the first results produced so far.

Table 7.3.1. Elastic constants (C_{ij}), aggregate bulk (K_{voigt} , K_{reuss} , K_{VRH}) and shear (μ_{voigt} , μ_{reuss} , μ_{VRH}) moduli, bulk longitudinal ($V_{P,VRH}$) and transversal ($V_{S,VRH}$) seismic velocities of $MgSiO_3$ orthoenstatite at $T = 0K$, $P = 0$, as compared with various experimental results: Jackson et al. (2007) (J2007), Kung et al. (2011) (K2011), Flesch et al. (1998) (F1998), Weidner et al. (1978) (W1978); and LDA/GGA calculations: Li et al. (2014) (L2014).

Elastic constants (Mbar)	This work	J2007	K2011	F1998	W1978	L2014 (LDA)	L2014 (GGA)
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C ₁₁	2.03	2.36(1)		2.247(23)	2.51	2.00
C ₂₂	1.46	1.73(1)		1.779(22)	1.95	1.46
C ₃₃	1.59	2.16(1)		2.136(36)	2.41	1.47
C ₄₄	0.78	0.84(1)		0.776(19)	0.89	0.76
C ₅₅	0.66	0.79(1)		0.759(11)	0.80	0.63
C ₆₆	0.74	0.80(1)		0.816(16)	0.86	0.70
C ₁₂	0.56	0.74(2)		0.724(42)	0.90	0.59
C ₁₃	0.25	0.57(2)		0.541(110)	0.77	0.38
C ₂₃	0.20	0.50(2)		0.527(46)	0.71	0.29
K _{voigt} (GPa)	78.74	109.5(15)		108		
K _{reuss} (GPa)	76.05	107.4(15)		107		
K _{VRH} (GPa)	77.40	108.5(15)	107	104(2)	107.8	
μ _{Voigt} (GPa)	70.50	78.6(7)		76		
μ _{Reuss} (GPa)	68.97	77.3(7)		75		
μ _{VRH} (GPa)	69.74	77.9(7)	77	74.9(15)	75.7	
ρ (g/cm ³)	3.089	3.196(4)		3.18(3)	3.204	
V _{P,VRH} (km/s)	7.43	8.15(8)	8.03	8.00	8.07	
V _{S,VRH} (km/s)	4.75	4.94(5)	4.88	4.85	4.86	

In Table 7.3.1 a comparison between the results of our calculations on orthoenstatite seismic and elastic properties and various experimental data is provided. Concerning elastic constants, our results show a systematic offset with respect to the references provided, with the main variations being observed in the case of the C₃₃ component (0.57 and 0.546 MPa), the C₁₂ (0.18 and 0.164 MPa), the C₁₃ (0.32 and 0.291 MPa), the C₂₃ component (0.3 and 0.327 MPa) when compared to Jackson et al. (2007) and Weidner et al. (1978) respectively. The comparison with Li et al. (2014) shows how calculations performed with the hybrid B3LYP functional are almost coincident with GGA results, whereas values obtained adopting an LDA functional appear to overestimate both theoretical and experimental investigations. The computed values of aggregate shear moduli appear slightly underestimated of about 7 – 8 GPa when compared to experiment, but the most notable differences are observed when our theoretical aggregate bulk moduli are compared to experimental investigations, since a variation of as much as 30 – 31 GPa occurs. Since our results for orthoenstatite compressibility are consistent with the bulk modulus obtained after fitting static – energy curves (i.e.:

$K_0 = 76.29$ GPa), we conducted a further investigation on orthoenstatite static equation of state and elastic properties by changing the functional adopted in the DFT calculations to check whether there could be any notable effects on the predicted elastic properties. The result is reported in the Supplementary section of the Thesis. Concerning orthoenstatite density, a variation of as much as 3.7% is observed, which is consistent with the well-known overestimation of the predicted volume which affects calculations performed with the hybrid B3LYP functional. Aggregate bulk velocities are overall in good agreement with the experiments, with just a slightly higher difference of 0.72 km/s which is observed in the case of $V_{P,VRH}$ when compared to Jacksons et al. (2007).

Table 7.3.2. Elastic constants (C_{ij}), aggregate bulk (K_{voigt} , K_{reuss} , K_{VRH}) and shear (μ_{voigt} , μ_{reuss} , μ_{VRH}) moduli, bulk longitudinal ($V_{P,VRH}$) and transversal ($V_{S,VRH}$) seismic velocities of MgSiO_3 high-pressure clinoenstatite (HP-CEn) at $T = 0$ K, $P = 0$.

Elastic constants (Mbar)	This work
C_{11}	2.06
C_{22}	1.69
C_{33}	2.82
C_{44}	1.01
C_{55}	0.41
C_{66}	0.58
C_{12}	0.46
C_{13}	0.30
C_{15}	0.61
C_{23}	0.70
C_{25}	0.41
C_{35}	0.54
C_{46}	0.29
K_{voigt} (GPa)	105.65
K_{reuss} (GPa)	35.18
K_{VRH} (GPa)	70.42
μ_{Voigt} (GPa)	73.88

μ_{Reuss} (GPa)	37.61
μ_{VRH} (GPa)	55.74
ρ (g/cm ³)	3.156
$V_{\text{P,VRH}}$ (km/s)	6.67
$V_{\text{S,VRH}}$ (km/s)	4.20

Table 7.3.3. Elastic constants (C_{ij}), aggregate bulk (K_{voigt} , K_{reuss} , K_{VRH}) and shear (μ_{voigt} , μ_{reuss} , μ_{VRH}) moduli, bulk longitudinal ($V_{\text{P,VRH}}$) and transversal ($V_{\text{S,VRH}}$) seismic velocities of MgSiO_3 low-pressure clinoenstatite (LP-CEn) at $T = 0$ K, $P = 0$.

Elastic constants (Mbar)	This work
C_{11}	1.77
C_{22}	1.59
C_{33}	2.59
C_{44}	0.90
C_{55}	0.60
C_{66}	0.63
C_{12}	0.49
C_{13}	0.39
C_{15}	0.35
C_{23}	0.58
C_{25}	0.26
C_{35}	0.30
C_{46}	0.14
K_{voigt} (GPa)	98.83
K_{reuss} (GPa)	79.75
K_{VRH} (GPa)	89.29
μ_{Voigt} (GPa)	72.57
μ_{Reuss} (GPa)	65.08
μ_{VRH} (GPa)	68.83
ρ (g/cm ³)	3.099
$V_{\text{P,VRH}}$ (km/s)	7.64
$V_{\text{S,VRH}}$ (km/s)	4.71

Table 7.3.4. Elastic constants (C_{ij}), aggregate bulk (K_{voigt} , K_{reuss} , K_{VRH}) and shear (μ_{voigt} , μ_{reuss} , μ_{VRH}) moduli, bulk longitudinal ($V_{\text{P,VRH}}$) and transversal ($V_{\text{S,VRH}}$) seismic velocities of MgSiO_3 high-temperature clinoenstatite (HT-CEn) at $T = 0 \text{ K}$, $P = 0$.

Elastic constants (Mbar)	This work
C_{11}	2.05
C_{22}	1.48
C_{33}	2.21
C_{44}	0.80
C_{55}	0.81
C_{66}	0.49
C_{12}	0.73
C_{13}	0.86
C_{15}	0.28
C_{23}	0.64
C_{25}	0.03
C_{35}	-0.55
C_{46}	0.35
K_{voigt} (GPa)	113.11
K_{reuss} (GPa)	108.47
K_{VRH} (GPa)	111.15
μ_{Voigt} (GPa)	65.64
μ_{Reuss} (GPa)	60.44
μ_{VRH} (GPa)	63.04
ρ (g/cm^3)	2.994
$V_{\text{P,VRH}}$ (km/s)	8.07
$V_{\text{S,VRH}}$ (km/s)	4.59

7.4. Selected applications: implications for the origin of the X-discontinuity

Seismic discontinuities with impedance contrasts of 2–8% in depth ranges between 250–350 km were initially designated as the X-discontinuity by Revenaugh & Jordan (1991) and they have been subsequently detected beneath stable continents and hotspots and near subduction zones (Deuss and Woodhouse, 2002; Bagley and Revenaugh, 2008; Schmerr, 2015; Srinu et al., 2021) (Figure 7.4.1). However, the origin of X-discontinuity is still debated. Several mechanisms have been proposed, including the formation of phase A ($\text{Mg}_7\text{Si}_2\text{O}_8(\text{OH})_6$) (Revenaugh and Jordan, 1991), the reaction of forsterite and periclase to form anhydrous phase B ($5\text{Mg}_2\text{SiO}_4 + 4\text{MgO} \rightarrow \text{Mg}_{14}\text{Si}_5\text{O}_{24}$) (Ganguly and Frost, 2006; Ottonello et al., 2010b; Song et al., 2023), the phase transition from coesite to stishovite (Chen et al., 2015; Williams and Revenaugh, 2005), and the phase transition from orthopyroxene to high-pressure clinopyroxene (Woodland, 1998; Akashi et al., 2009); however, none of them can well explain most seismic features of the X-discontinuity, especially the indistinguishable seismological Clapeyron slopes (Deuss and Woodhouse, 2004). Phase A is only stable at P-T conditions compatible with those of hydrated cold slabs (Kawamoto, 1996), indicating that the formation of this phase can only provide an explanation for the origin of the X-discontinuity limited to those environments. The formation of anhydrous phase B requires a local enrichment of periclase in the upper mantle, but the mechanisms for generating substantial amounts of periclase remain unclear. The phase transition from coesite to stishovite generates anomalous impedance contrasts of ~70% and ~78% for P and S seismic waves, respectively, and only 4–8 wt% of free silica would be required to cause the observed X-discontinuity (Chen et al., 2015). However, the large positive Clapeyron slope of the coesite-stishovite transition is inconsistent with the seismological observation showing that the X-discontinuity does not have a clear Clapeyron slope (Deuss and Woodhouse, 2004). Orthopyroxene is a major component of the upper mantle (Frost, 2008). Along a typical mantle geotherm, OEn would

transform into its high-pressure polymorph HP-CEn with space group C2/c at ~260 km depth (Akashi et al., 2009). The OEn-HP-CEn transition completes within 5 km intervals (Woodland, 1998) and has also been proposed to explain the X-discontinuity. However, the impedance contrasts of this transition under mantle conditions, which are crucial to interpreting its role in generating the X-discontinuity, remain unclear. Woodland and Angel (1997) estimated an impedance contrast of transversal waves of ~3% for the OEn-HP-CEn transition based on the Birch's law, which assumes a linear relationship between V_P and density for each phase. Using the small impedance contrast, some recent seismic studies argued the OEn-HP-CEn transition cannot account for the formation of the X-discontinuity (e.g. Kemp et al., 2019; Pugh et al., 2021). Instead, Kung et al. (2005) reported much larger impedance contrasts of ~7% for P waves and ~10.8% for S waves, respectively. However, that work estimated the seismic wave velocities of orthoenstatite by extrapolating room-temperature experimental data to mantle conditions, while, on the other hand, seismic velocities of high-pressure clinoenstatite was directly obtained from HP-HT experiments. Until now, there are no impedance contrasts calculated for the OEn-HP-CEn transition on the basis of internally-consistent HP-HT data of both OEn and HP-CEn phases (Song et al., 2023).

In this section, the *ab initio* seismic properties calculated for pure MgSiO_3 orthoenstatite (OEn) and high-pressure clinoenstatite (HP-CEn) will be used to infer the impedance contrasts caused by the OEn-HP-CEn phase transition at pressure and temperature conditions compatible with the occurrence of the X-discontinuity in the Earth's mantle. Computed results are compared with seismological observations and experimental results and some ideas on the origin of the X-discontinuity are briefly discussed.

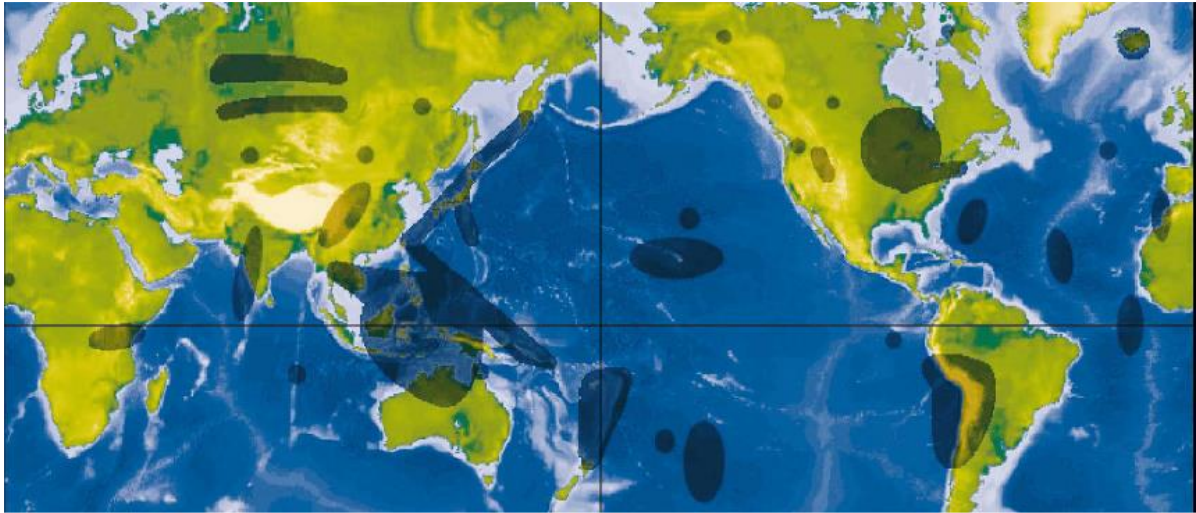


Figure 7.4.1. Worldwide distribution of the 300 km X-discontinuity (taken from Williams & Revenaugh, 2005).

7.4.1. Seismic properties of orthoenstatite and high-pressure clinoenstatite at high-pressure and high-temperature conditions

Static elastic constants of high-pressure clinoenstatite at high-pressure conditions and $T = 0$ K have been calculated ab initio at the following pressures: 5.0 GPa, 7.93 GPa and 12.5 GPa. The obtained results are reported in Table 7.4.1.1, along with the relative aggregate bulk and shear moduli and density values.

Table 7.4.1.1. Elastic constants (C_{ij}) and aggregate bulk (K_{voigt} , K_{reuss} , K_{VRH}) and shear (μ_{voigt} , μ_{reuss} , μ_{VRH}) moduli of MgSiO_3 high-pressure clinoenstatite (HP-CEn), computed at $T = 0$ K and high pressure conditions. Results of DFT-GGA calculations after Li et al. (2014) performed at $P = 5$ GPa are also added for comparison (L2014)

Elastic constants (Mbar)	This work (P=5.0GPa)	This work (P=7.93GPa)	This work (P=12.5GPa)	L2014 (P=5.0 GPa)
C_{11}	2.729	2.964	3.270	2.67
C_{22}	2.261	2.465	2.735	2.21
C_{33}	3.330	3.516	3.769	3.18
C_{44}	1.133	1.168	1.207	1.09
C_{55}	0.802	0.885	0.973	0.85
C_{66}	0.829	0.910	1.002	0.84
C_{12}	0.825	0.976	1.182	0.81
C_{13}	0.714	0.867	1.071	0.78
C_{15}	0.414	0.364	0.314	0.35
C_{23}	1.051	1.179	1.354	1.03
C_{25}	0.257	0.223	0.189	0.23
C_{35}	0.264	0.213	0.165	0.18
C_{46}	0.230	0.214	0.204	0.17
K_{voigt} (GPa)	150.03	166.60	188.81	
K_{reuss} (GPa)	134.58	155.56	181.03	
K_{VRH} (GPa)	142.31	161.08	184.92	
μ_{Voigt} (GPa)	93.53	98.80	104.77	
μ_{Reuss} (GPa)	85.97	92.95	100.10	
μ_{VRH} (GPa)	89.75	95.88	102.43	
ρ (g/cm ³)	3.329	3.398	3.492	

Aggregate bulk and shear moduli are also plotted on Figures 7.4.1.1a, b as compared with ultrasonic measurements by Kung et al. (2004).

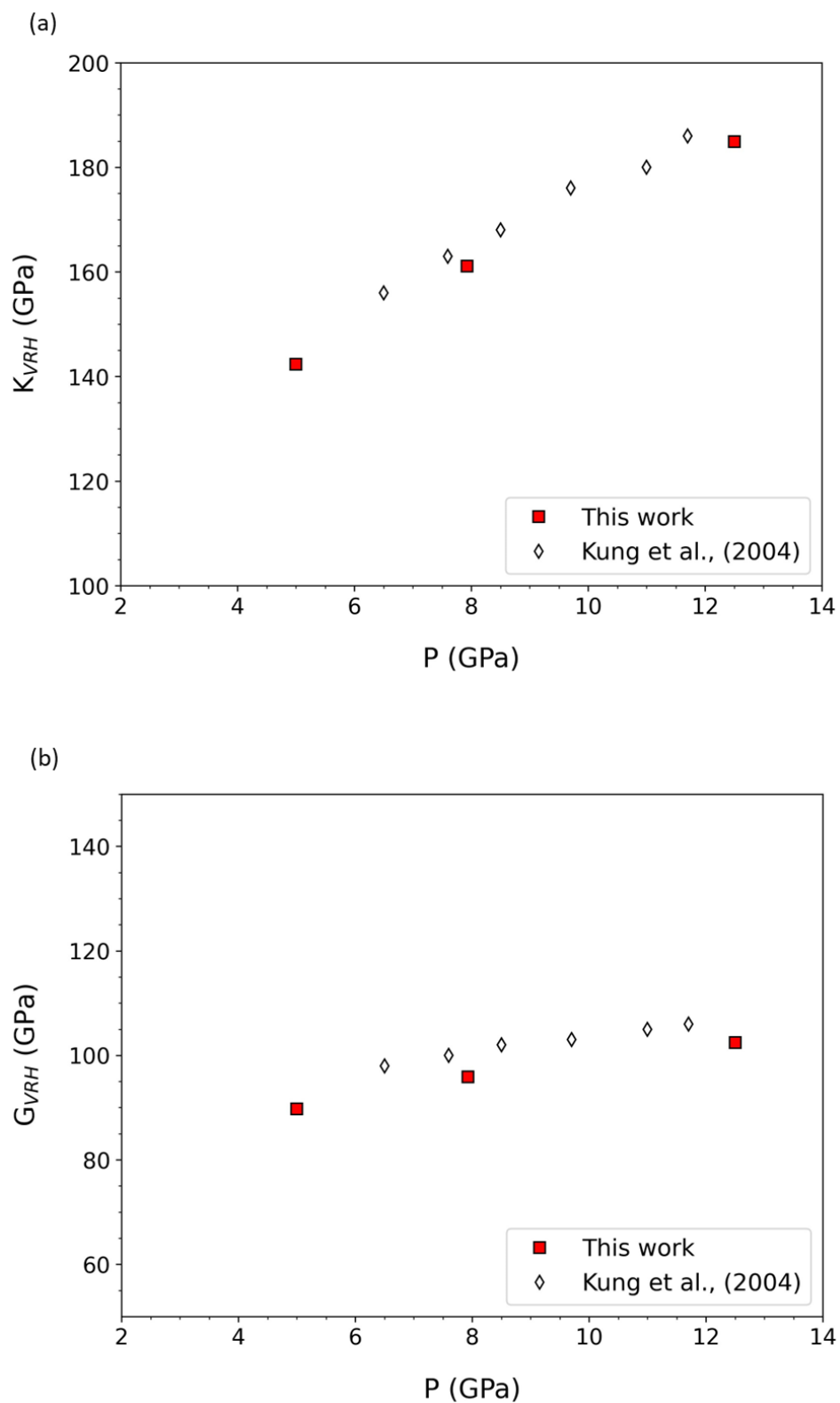
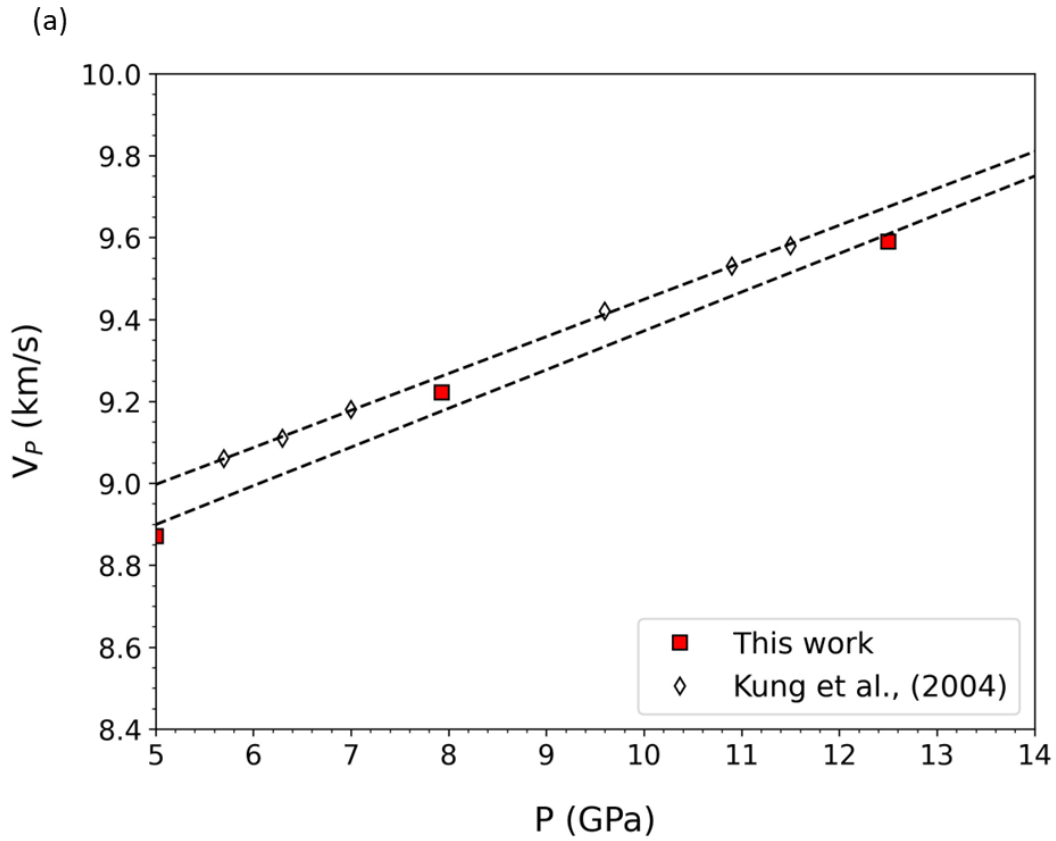


Figure 7.4.1.1. Ab initio B3LYP aggregate bulk (a) and shear (b) moduli of high-pressure clinoenstatite computed at $T = 0$ K and high pressure conditions in this work, as compared to ultrasonic measurements by Kung et al. (2004).

Ab initio longitudinal- and shear-wave seismic velocities are reported in Table 7.4.1.2 and plotted in Figure 7.4.1.2a, b.

Table 7.4.1.2. Ab initio B3LYP longitudinal- and shear-wave seismic velocities ($V_{P,VRH}$ and $V_{S,VRH}$, respectively) computed in this work at $T = 0$ K and high-pressure conditions for high-pressure clinoenstatite (HP-CEn).

	P=5.0GPa	P=7.93GPa	P=12.5GPa
$V_{P,VRH}$ (km/s)	8.87	9.22	9.59
$V_{S,VRH}$ (km/s)	5.19	5.31	5.42



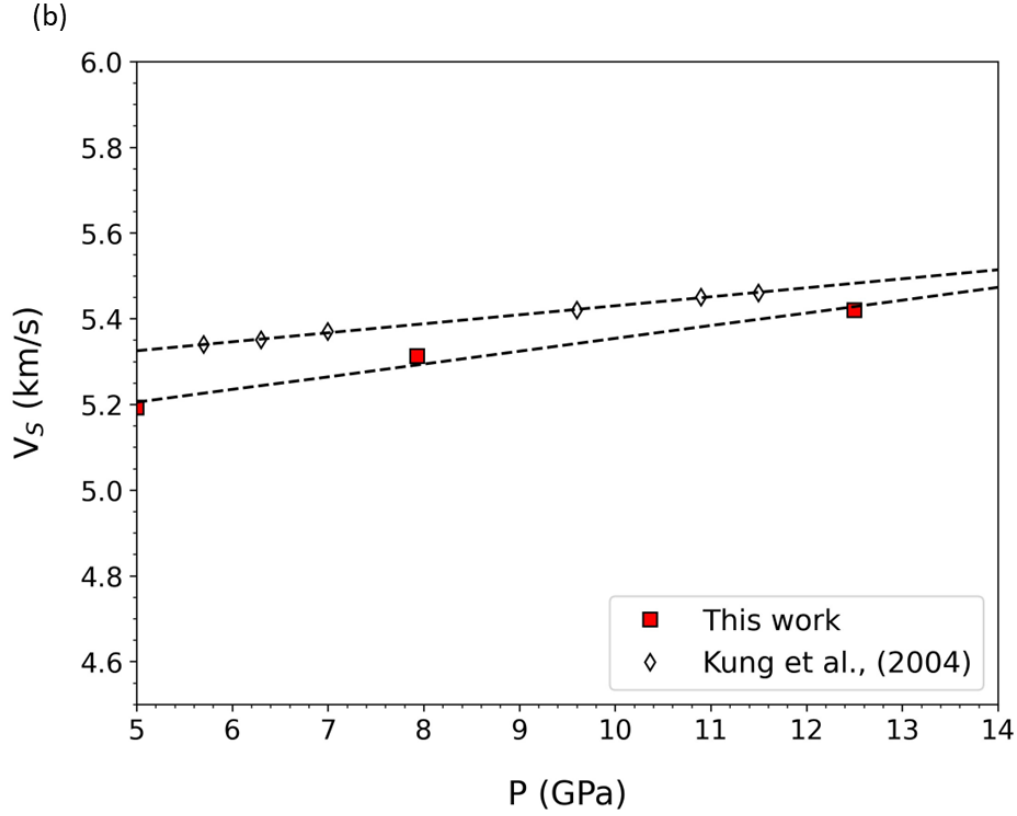


Figure 7.4.1.2. Longitudinal- (a) and shear-wave (b) seismic velocities (V_P and V_S , respectively) of high-pressure clinoenstatite (HP-CEn), calculated by ab initio B3LYP at $T = 0$ K and high pressure conditions, as compared to ultrasonic measurements by Kung et al. (2004). Dashed lines are linear interpolations of computational and experimental data.

Ab initio seismic velocities computed at high pressure conditions compare favourably with the results of ultrasonic measurements if the well-known volume overestimation by B3LYP is taken into account (which means ab initio density values are underestimated). Linear regression of ab initio velocity values yields $(\partial V_P / \partial P)_{T=0K} = 0.0946$ km/(s $\times$ GPa) and $(\partial V_S / \partial P)_{T=0K} = 0.0298$ km/(s $\times$ GPa), which are in very good agreement with the results obtained by fitting ultrasonic data of Kung et al. (2004) data, i.e. $(\partial V_P / \partial P)_{T=298.15K} = 0.0904$ km/(s $\times$ GPa) and $(\partial V_S / \partial P)_{T=298.15K} = 0.0209$ km/(s $\times$ GPa).

The combined effect of both pressure and temperature on seismic velocities of orthoenstatite and high-pressure clinoenstatite was taken into account by adopting

the pressure and temperature derivatives of the aggregate bulk and shear moduli, as well as the thermal EOS of OEn and HP-CEn to extrapolate the results of our calculations at HP-HT conditions. The pressure effect on the aggregate bulk moduli, shear moduli and density (and hence on seismic velocities) of orthoenstatite and high-pressure clinoenstatite was determined via the ab initio equation of state parameters. Concerning the effect of temperature, the T-dependence of the aggregate bulk moduli was considered via the theoretical $\partial K_T/\partial T$ obtained from the HT-equation of state, whereas the T-dependence of the shear moduli was taken from the experimental data of Kung et al. (2005) (i.e.: $\partial G/\partial T = -0.015$ for both minerals) due to the impossibility to perform calculations on the elastic constant tensor at high temperatures, which are hindered by the high computational costs. V_P and V_S were calculated along the OEn-HP-CEn phase transition along two reference mantle geotherms: a normal mantle geotherm according to Brown & Shankland (1981) (which gives $T = 1588$ K at $P = 9$ GPa and $T = 1626$ K at $P = 10$ GPa) and a colder slab geotherm according to Chen et al. (2015) (which gives $T = 1478$ K at $P = 9$ GPa and $T = 1566$ K at $P = 10$ GPa). These conditions correspond to depths of 270 and 300 km, respectively, which mark the boundaries where the X-discontinuity is usually observed in the mantle (Deuss and Woodhouse, 2002; Bagley and Revenaugh, 2008).

Elastic moduli and seismic properties simulated at selected P-T conditions along the two geotherms are reported in Tables 7.4.1.3 and 7.4.1.4.

Table 7.4.1.3. HP-HT seismic and elastic properties simulated for orthoenstatite (OEn) and high-pressure clinoenstatite (HP-CEn) along a normal mantle geotherm (Brown & Shankland, 1981).

	OEn		HP-CEn	
	T = 1588 K P = 9 GPa	T = 1626 K P = 10 GPa	T = 1588 K P = 9 GPa	T = 1626 K P = 10 GPa
K_{VRH} (GPa)	165.9	178.8	136.0	147.6
G_{VRH} (GPa)	61.2	62.3	46.9	48.0
ρ (g/cm ³)	3.249	3.270	3.327	3.353

V_P (km/s)	8.73	8.95	7.73	7.94
V_S (km/s)	4.34	4.37	3.76	3.78

Table 7.4.1.4. HP-HT seismic and elastic properties simulated for orthoenstatite (OEn) and high-pressure clinoenstatite (HP-CEn) along a cold slab geotherm (Chen et al., 2015; cf. green curve in Figure 6b of this paper).

	OEn		HP-CEn	
	T = 1478 K P = 9 GPa	T = 1566 K P = 10 GPa	T = 1478K P = 9 GPa	T = 1566 K P = 10 GPa
K_{VRH} (GPa)	168.37	180.17	139.40	149.40
G_{VRH} (GPa)	62.87	63.25	48.58	48.93
ρ (g/cm ³)	3.150	3.151	3.257	3.263
V_P (km/s)	8.95	9.16	7.92	8.11
V_S (km/s)	4.47	4.48	3.86	3.87

7.4.2. Implications for the origin of the X-discontinuity

Figure 7.4.2.1 shows the P-T location of the ab initio OEn – HP-CEn transition as determined in this work (solid black curve), compared with the depth range at which the X-discontinuity is usually observed (shaded area). The two geotherms used in the calculations are also reported (cf. dashed red and blue lines in Figure 7.4.2.1), as well as the OEn/HP-CEn phase boundary according to different Authors (Yamamoto & Akimoto, 1977; Pacalo & Gasparik, 1990; Ulmer & Stalder, 2001; cf. dashed and dotted black curves in the same Figure).

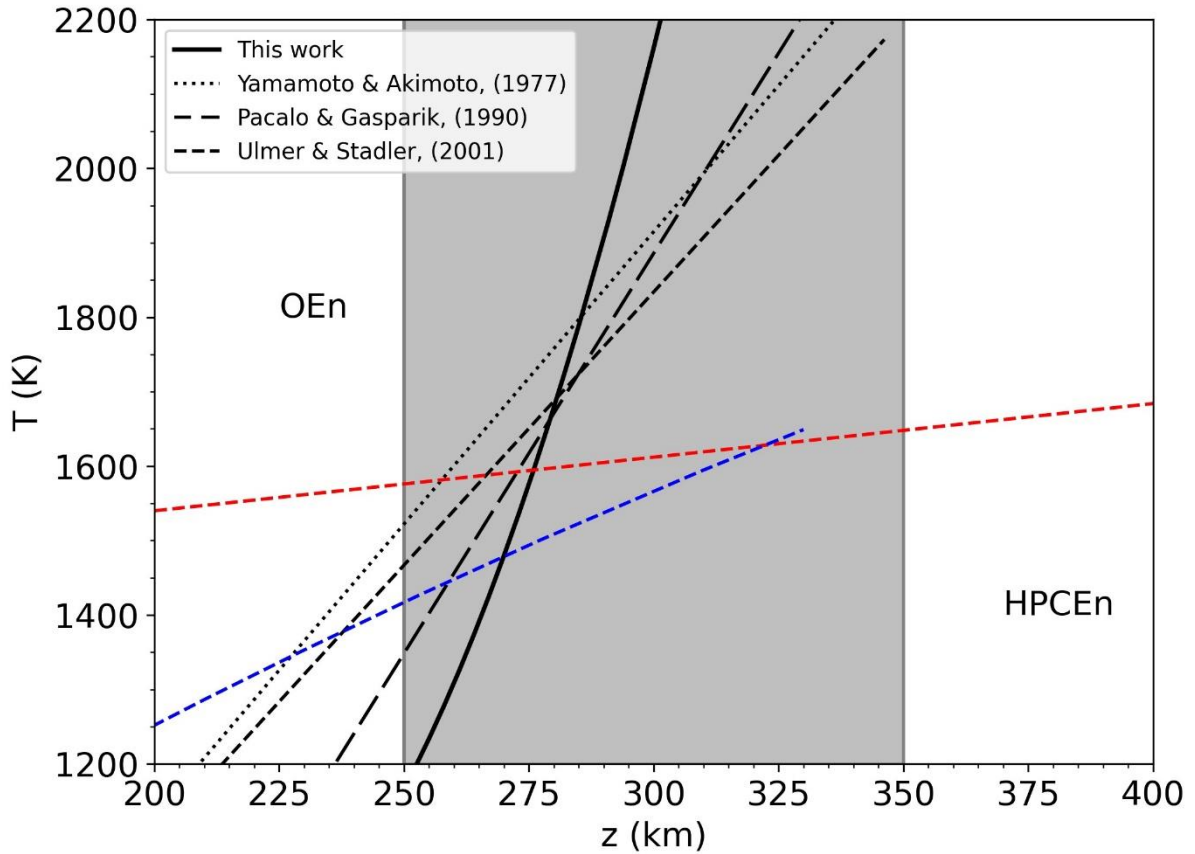


Figure 7.4.2.1. Ab initio and experimental phase boundaries of the orthoenstatite (OEn) – high-pressure clinoenstatite (HP-CEn) transition. Shaded area represents the depth range at which the X-discontinuity is commonly observed. Red and blue lines are the geotherms used as reference in the calculation, taken from Brown & Shankland (1981) and Chen et al. (2015), respectively and corresponding to a normal geotherm (red dashed line) and a cold slab geotherm (blue dashed line) (see also Tables 7.4.1.3 and 7.4.1.4).

The OEn to HP-CEn transition involves a significant density increase of $\sim 3\%$, which has been suggested to be the cause of the seismic reflectors at depths between 200 and 300 km (Woodland, 1998). The density jump across the OEn/HP-CEn phase transformation as simulated in this work is 3.2–3.4% in a pressure range corresponding to 270–300 km depths in the upper mantle along both geotherms. This value is directly comparable with the one inferred from experimental data by Kung et al. (2005) (i.e. 2.6–2.9%). The corresponding velocity jump is $\sim 13\%$ for P waves and

~15% for S waves, with no significant variation when considering a normal or a cold slab geotherm, with velocity jumps showing just a marginal increase when a colder gradient is taken into account (see Tables 7.4.2.1). Our results are markedly higher in the case of both P-waves and S-waves when compared to Kung et al. (2004) (i.e. 3-4% and 5-6%, respectively). A more recent DFT – LDA study (Song et al., 2023) found density and V_P jumps in agreement with Kung et al. (2004), except for an even lower V_S jump of 4.2%. Our results are also significantly higher than seismic jumps inferred from seismological observations (cf. Deuss & Woodhouse, 2004).

Table 7.4.2.1. Seismic velocity jumps simulated for the orthoenstatite (OEn) – high-pressure clinoenstatite (HP-CEn) phase transition along a reference mantle geotherm^a (Brown & Shankland, 1981) or a reference slab geotherm^b (Chen et al., 2015), in a depth range $z = 270$ - 300 km, as compared with seismological observations on a mineralogical aggregate (Deuss & Woodhouse, 2004; DW2004), ultrasonic experiments (Kung et al., 2004; K2004) and other DFT-LDA calculations (Song et al., 2023; S2023).

	P = 9 GPa T = 1588 K ^a /1478 K ^b	P = 10 GPa T = 1626 K ^a /1566 K ^b	DW2004	K2004	S2023
$\Delta\rho\%$	3.39 ^a /3.29 ^b	3.49 ^a /3.43 ^b		2.6-2.9	
$\Delta V_P\%$	12.97 ^a /13.01 ^b	12.67 ^a /12.97 ^b		3-4	2.65-3.05
$\Delta V_S\%$	15.57 ^a /15.68 ^b	15.37 ^a /15.70 ^b	2	5-6	4-4.13

As to seismic impedance contrasts (ΔZ), they can be calculated according to the following equation:

$$\Delta Z = \left(\frac{Z_{OEn} - Z_{HPCEn}}{Z_{HPCEn}} \right) \times 100 \quad (7.4.2.1)$$

where seismic impedance (Z) is the product between density and seismic velocity. The obtained results are reported in Tables 7.4.2.2.

Table 7.4.2.2. Seismic impedance contrast simulated for the orthoenstatite (OEn) – high-pressure clinoenstatite (HP-CEn) phase transition along a reference mantle geotherm^a (Brown & Shankland, 1981) or a reference slab geotherm^b (Chen et al., 2015), in a depth range $z = 270\text{--}300$ km, as compared with seismological observations on a mineralogical aggregate (Bagley & Revenaugh, 2008; BR2008), ultrasonic experiments (Kung et al., 2005; K2005) and other DFT-LDA calculations (Song et al., 2023; S2023).

	P = 9 GPa T = 1588 K ^a /1478 K ^b	P = 10 GPa T = 1626 K ^a /1566 K ^b	BR2008	K2005	S2023
$\Delta Z(V_P)\%$	10.33 ^a /9.29 ^b	9.88 ^a /9.09 ^b		7	5.2-5.8
$\Delta Z(V_S)\%$	12.87 ^a /11.87 ^b	12.51 ^a /11.72 ^b	3-8	10.8	6-8

The comparison between theoretical and reference impedance contrasts shows an identical trend to what observed for velocity jumps, with our data being significantly greater than seismological, experimental, and other theoretical data. Impedance contrasts calculated along a slab geotherm show an opposite trend with respect to velocity jump, in fact a slight decrease in ΔZ is observed. On the basis of these results, the orthoenstatite – high-pressure clinoenstatite transition cannot be advocated as the only responsible for the origin of the X-discontinuity. This conclusion is supported also by Akashi et al. (2009). In fact, those Authors argue that only the shallower part (240–280 km depths) of the X-discontinuity can be accounted for by the OEn transformation to HP-CEn, but the deeper part (>280 km depth) needs an alternative explanation. In conclusion, none of the above cited mineralogical reactions seems to be able to account for the origin of the X-discontinuity in the Earth’s mantle if taken alone. A possible limitation of our simulation is on the HP-HT seismic properties of orthoenstatite and high-pressure clinoenstatite, since this study does not properly take into account the effects of temperature on seismic properties in a fully consistent way, introducing a certain degree of uncertainty due to the coupling of theoretical and experimental data, that might affect the final result. Moreover, neither the effect of seismic properties in a real mantle aggregate, nor the effect of composition (e.g. Fe and

H₂O) on the elastic and seismic properties of OEn and HP-CEn are taken into account. Further work is thus needed on the origin of X-discontinuity.

Summary and future perspectives

This final chapter outlines the major results of this study in relation to the main goals of this research project and summarizes the most relevant contributions while also reviewing the limitations and open questions that arose during the work stages, finally proposing opportunities for future research perspectives or collaborations.

Thermodynamic properties of all MgSiO_3 pyroxenes allowed to obtain original insights on the thermodynamic behaviour of such phases at conditions compatible with their stability in the Earth mantle. Our calculations compare favourably with the experiments when available, proving the quality of the calculations performed in this work. The definition at simultaneous HT-HP conditions of ringwoodite volume thermal expansivity allows to better constrain the extrapolation of experimental results to HT and HP conditions, and could allow to interpret deep mantle processes, such as thermal convection, under a mineral physics and thermodynamic perspective.

Thermodynamic properties of most of the investigated phases have been determined for the very first time in a fully physically- and internally-consistent way. The entire thermodynamic dataset of high-temperature clinoenstatite was not fully established and the only data came from thermodynamic assessments. Some of the thermoelastic properties of protoenstatite have never been determined via experiments, like in the case of its volume thermal expansivity and its bulk modulus temperature derivative. This work enabled to obtain thermodynamic data avoiding experimental issues like the need of pure, good quality sample, synthesis issues or the unquenchable nature of some of these phases (like in the case of protoenstatite and high-pressure clinoenstatite).

All the main phase transitions occurring in the MgSiO_3 system have been investigated and calculated by employing the dataset obtained via first principles calculations. In particular, the following univariant equilibria have been determined: MgSiO_3 (low-pressure clinoenstatite) = MgSiO_3 (orthoenstatite), MgSiO_3 (orthoenstatite) = MgSiO_3

(protoenstatite), MgSiO_3 (protoenstatite) = MgSiO_3 (high-temperature clinoenstatite), MgSiO_3 (orthoensatite) = MgSiO_3 (high-pressure clinoenstatite), MgSiO_3 (low-pressure clinoenstatite) = MgSiO_3 (high-pressure clinoenstatite). The investigation of these phase equilibria allowed to obtain new information on the stability of pyroxenes at mantle conditions, and showed how some of these equilibria are extremely sensible and difficult to reproduce even employing a methodology fully predictive and capable of giving physically and internally consistent results. In particular, some uncertainties remain in the high temperature, low pressure side of the diagram, both on the 1 bar position of the low-pressure clinoenstatite - orthoenstatite transition and on the triple point protoenstatite – orthoenstatite – liquid. The quasi-harmonic analysis of vibrational modes of orthoenstatite had to be approximated by assuming an average Grüneisen parameter to avoid the high computational cost that arises from performing vibrational frequencies calculations at non-equilibrium volume conditions on supercells. Nevertheless, this approximation revealed too rough and thermodynamic properties predicted in this way for orthoenstatite may be not accurate enough to account for such subtle variations in Gibbs free energy that occur when this phase is involved in equilibria with other MgSiO_3 pyroxenes. Another possible explanation is that quasi-harmonic effects come in play in determining the stability of orthoenstatite, such effects cannot be taken into account in our modelling. In this sense, the QHA may not be an appropriate framework to rely on when investigating orthoenstatite thermodynamics.

The thermoelastic properties of MgSiO_3 pyroxenes, together with the Clapeyron slopes of the phase boundaries investigated in this study, provide useful and consistent data that can improve numerical modelling of mantle processes that are influenced by phase transformations, like for example the dynamics of subducting slabs.

Our calculations enabled to clarify the stability of pyroxenes that were previously studied relying on inconsistent thermodynamic data. In particular, high-temperature

clinoenstatite (HT-CEn) turns out to be unstable according to our investigation. This result puts in strong discussion the role of this mineral as the *liquidus* phase of the MgSiO_3 at low pressures, as is predicted by the modern version of the MgSiO_3 phase diagram. Instead, protoenstatite is stable at *liquidus* phase at low pressure, but further investigations are necessary to accurately locate its transition into orthoenstatite at high pressures. The instability of HT-CEn at *liquidus conditions* as predicted by this study not only is in contrast with the results of the assessments after Shi et al. (1996) and Gasparik (2003) (which are nonetheless lacking any experimental evidence to support their results), but confirms on a thermodynamic basis the suggestions of some experimental investigations that found HT-CEn as a metastable phase at temperature conditions far from the *liquidus*.

The melting curve of the MgSiO_3 system correctly reproduces the experimental results in the pressure range 0-11 GPa and has been determined by employing thermodynamic properties for the liquid phase that are thermodynamically consistent with those of the solid phases. Pyroxenes show a complex behaviour at melting conditions, with the melting behaviour of protoenstatite changing from incongruent to congruent between 2.5 and 3 GPa. It should be kept in mind that this result is affected by uncertainties on the onset of the protoenstatite – orthoenstatite transition discussed in Chapter 4.

The MgO-SiO_2 , despite being simplistic, can be considered a good chemical system to adopt to investigate phase stability relations at Earth mantle conditions. A further step in this computational study can be the introduction of a further chemical component (for example CaO or Al_2O_3 , hence moving to a CMS or MAS system respectively) to adopt a system that can be even more representative of the chemical and mineralogical composition of phases stable in the deep mantle. Some computational study that tried to assess solid-solid and solid-liquid phase relations in more complex system already exist (Belmonte et al., 2017a & b), but mainly rely on assessed thermodynamic properties for some of the solid phases that nucleate in those reference system, hence

lacking a completely theoretical definition of their thermodynamics. Concerning the effects of FeO, Woodland (1998) showed that the divariant loop in the instance of the orthoenstatite – high-pressure clinoenstatite transition, at a composition relevant for the Earth interior (i.e.: $X_{\text{FeO}} = 0.1$), has a width of only 0.15 GPa at 1473.15 K, meaning that at constant temperature, the phase transition will be completed over a depth interval of about 5-6 km in the mantle, so any effects attributed to the presence of iron could be disregarded. Moreover, Woodland, (1998) also showed that the univariant curve for the orthoenstatite – high-pressure clinoenstatite equilibrium having $X_{\text{FeO}} = 0.1$ is very close to that of the pure Mg- endmember, so our model, which is only considering pure phases, can be used as good proxy for a mantle relevant composition.

Elastic and seismic properties of orthoenstatite and HP-clinoenstatite were calculated by first principles at $P = 0$ GPa and $T = 0$ K and extrapolated at high pressure and temperature conditions by combining our theoretical results with experimental data to constrain the effects of temperature on aggregate bulk and shear moduli, as well as on longitudinal and transversal velocities. Seismic properties obtained in such way were tested by comparing computed velocity jumps and impedance contrasts with seismological observations in correspondence of the occurrence of the X-discontinuity (i.e.: 270 – 300 km). Our results are markedly higher [i.e.: $\Delta V_s \sim 15\%$; $\Delta Z(V_s) \sim 12\%$] with respect to both seismological and experimental data and allowed to exclude the orthoenstatite – HP clinoenstatite transition as the only possible candidate to address the origin of the X-discontinuity.

An originally planned part of this project involved to couple theoretical and experimental data to try to constrain the effect of more complex compositions (in particular compositions that involve FeO) on the elastic properties of deep mantle constituents mineral phases. The idea to perform experiments on $(\text{Mg,Fe})\text{SiO}_3$ pyroxenes was cast aside due to the impossibility to recover good quality samples. Instead, we chose an almandinic garnet as representative proxy to investigate the effect of iron on the elastic properties of majorite-garnet, which is another abundant

phase that constitutes the deepest parts of the Earth mantle, that is nonetheless very difficult to synthesize. The experimental measurements were carried out during a total of three months spent at the Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC) and consisted of X-ray Powder Diffraction (XR-PD) combined with acoustic picosecond measurements aimed at constraining the compressibility and elastic properties of almandine at ambient temperature and within a pressure range of 0-10 GPa. No conclusive data have been collected yet, but the collaboration with the experimental team is currently ongoing. Calculations on the elastic properties of almandine garnet at the athermal limit have already been carried out, and will be used to guide the extrapolation at HT-HP conditions of elastic properties of the more complex majorite-garnet solution, by including the effect of iron as determined by the experimental results.

In conclusion, pyroxene polymorphism still remains a masterpiece of complexity, either the experimental or the theoretical approach end up showing some limitations. Nevertheless, the results obtained in this Thesis allowed to shed new light on the thermodynamic behaviour and phase stability of major constituents of the Earth deep mantle, by defining via first principles the thermoelastic and thermodynamic properties of mineralogical phases poorly characterized from an experimental point of view and accurately predicting their phase relations from *subsolidus* up to melting conditions.

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I want to acknowledge both my cat and my neighbour's cat, the only beings that consistently provided me the affection I needed without asking anything in return.

Stay determined!



Supplementary materials

In this first section of this supplementary the most relevant thermoelastic and thermodynamic data calculated for minerals in the MgSiO_3 system are listed in the range $T = 298.15\text{K} - 2000\text{K}$. The tabulated data refer to the following minerals: MgSiO_3 (low-pressure clinoenstatite), MgSiO_3 (orthoenstatite), MgSiO_3 (protoenstatite), MgSiO_3 (high-temperature clinoenstatite), MgSiO_3 (high-pressure clinoenstatite). All the tabulated values have been calculated at $P=0$ by ab initio B3LYP theory.

S.1. MgSiO_3 LP-clinoenstatite

Table S.1. Ab initio B3LYP values of isochoric heat capacity (C_V), isobaric heat capacity (C_P), molar volume (V), enthalpy (H), entropy (S), Gibbs free energy (G), isothermal bulk modulus (K_T), volume thermal expansion coefficient (α_V), thermodynamic Grüneisen parameter ($\gamma_{\text{thermal}} = \alpha_V K_T V_T / C_V$) calculated for MgSiO_3 low-pressure clinoenstatite by phonon dispersion calculations at $P = 0$ GPa.

T(K)	C_V [J/(mol×K)]	C_P [J/(mol×K)]	V (cm ³ /mol)	H (kJ/mol)	S [J/(mol×K)]	G (kJ/mol)	K_T (GPa)	$\alpha_V \times 10^5$ (K ⁻¹)	γ_{thermal}
298.15	79.684	80.352	32.482	-1546.814	65.764	-1566.422	74.10	3.156	0.95
300	80.003	80.678	32.484	-1546.666	66.259	-1566.544	74.05	3.165	0.95
400	93.672	94.753	32.59	-1537.723	91.876	-1574.473	71.52	3.555	0.88
500	102.310	103.875	32.708	-1527.639	114.344	-1584.811	68.99	3.852	0.85
600	107.938	110.069	32.836	-1516.913	133.886	-1597.244	66.66	4.095	0.83
700	111.737	114.516	32.975	-1505.749	151.088	-1611.510	64.07	4.335	0.82
800	114.393	117.903	33.125	-1494.245	166.444	-1627.401	61.78	4.549	0.81
900	116.310	120.630	33.285	-1482.456	180.327	-1644.750	59.34	4.776	0.81
1000	117.732	122.936	33.457	-1470.413	193.013	-1663.426	56.83	5.017	0.81
1100	118.813	124.967	33.639	-1458.138	204.711	-1683.320	54.46	5.259	0.81
1200	119.653	126.816	33.833	-1445.645	215.58	-1704.341	52.00	5.528	0.81
1300	120.317	128.535	34.039	-1432.944	225.745	-1726.412	49.58	5.814	0.82
1400	120.850	130.157	34.256	-1420.045	235.303	-1749.469	47.14	6.128	0.82
1500	121.285	131.699	34.485	-1406.953	244.335	-1773.455	44.78	6.462	0.82
1600	121.644	133.167	34.726	-1393.677	252.902	-1798.321	42.26	6.858	0.83
1700	121.943	134.555	34.979	-1380.221	261.059	-1824.022	39.88	7.277	0.83
1800	122.195	135.854	35.245	-1366.593	268.849	-1850.521	37.38	7.771	0.84
1900	122.410	137.049	35.524	-1352.798	276.307	-1877.781	34.94	8.321	0.84
2000	122.594	138.117	35.816	-1338.843	283.465	-1905.772	32.33	9.000	0.85

S.2. MgSiO₃ orthoenstatite

Table S.2. Ab initio B3LYP values of isochoric heat capacity (C_V), isobaric heat capacity (C_P), molar volume (V), enthalpy (H), entropy (S), Gibbs free energy (G), isothermal bulk modulus (K_T), volume thermal expansion coefficient (α_V), thermodynamic Grüneisen parameter ($\gamma_{\text{thermal}} = \alpha_V K_T V_T / C_V$) calculated for MgSiO₃ orthoenstatite by phonon dispersion calculations $P = 0$ GPa.

T(K)	C_V [J/(mol×K)]	C_P [J/(mol×K)]	V (cm ³ /mol)	H (kJ/mol)	S [J/(mol×K)]	G (kJ/mol)	K_T (GPa)	$\alpha_V \times 10^5$ (K ⁻¹)	γ_{thermal}
298.15	79.890	80.540	32.619	-1546.485	66.371	-1566.274	71.21	3.096	0.90
300	80.208	80.863	32.621	-1546.338	66.861	-1566.396	71.18	3.103	0.90
400	93.857	94.920	32.728	-1537.376	92.524	-1574.385	68.59	3.487	0.83
500	102.491	104.034	32.847	-1527.186	115.226	-1584.799	66.27	3.769	0.80
600	108.119	110.134	32.976	-1516.344	134.980	-1597.332	64.13	3.998	0.78
700	111.919	114.412	33.112	-1505.086	152.327	-1611.715	61.56	4.235	0.77
800	114.577	117.582	33.255	-1493.525	167.761	-1627.734	59.67	4.419	0.77
900	116.495	120.067	33.405	-1481.721	181.662	-1645.216	57.44	4.628	0.76
1000	117.919	122.128	33.562	-1469.706	194.318	-1664.025	54.84	4.876	0.76
1100	119.001	123.927	33.729	-1457.500	205.950	-1684.046	52.98	5.070	0.76
1200	119.842	125.571	33.904	-1445.114	216.727	-1705.186	50.36	5.352	0.76
1300	120.506	127.124	34.09	-1432.553	226.780	-1727.367	48.52	5.570	0.76
1400	121.040	128.633	34.288	-1419.822	236.214	-1750.522	46.29	5.851	0.77
1500	121.476	130.122	34.497	-1406.920	245.114	-1774.592	44.08	6.155	0.77
1600	121.835	131.604	34.719	-1393.850	253.550	-1799.529	41.83	6.496	0.77
1700	122.135	133.084	34.954	-1380.609	261.576	-1825.289	39.71	6.851	0.78
1800	122.387	134.555	35.203	-1367.196	269.242	-1851.832	37.37	7.287	0.78
1900	122.602	136.005	35.467	-1353.610	276.588	-1879.126	35.14	7.756	0.79
2000	122.786	137.415	35.747	-1339.848	283.646	-1907.140	33.24	8.206	0.79

S.3. MgSiO₃ protoenstatite

Table S.3. Ab initio B3LYP values of isochoric heat capacity (C_V), isobaric heat capacity (C_P), molar volume (V), enthalpy (H), entropy (S), Gibbs free energy (G), isothermal bulk modulus (K_T), volume thermal expansion coefficient (α_V), thermodynamic Grüneisen parameter ($\gamma_{\text{thermal}} = \alpha_V K_T V_T / C_V$) calculated for MgSiO₃ protoenstatite by phonon dispersion calculations $P = 0$ GPa.

T(K)	C_V [J/(mol×K)]	C_P [J/(mol×K)]	V (cm ³ /mol)	H (kJ/mol)	S [J/(mol×K)]	G (kJ/mol)	K_T (GPa)	$\alpha_V \times 10^5$ (K ⁻¹)	γ_{thermal}
298.15	80.049	80.510	33.420	-1546.039	67.692	-1566.221	94.45	2.220	0.88
300	80.361	80.825	33.421	-1545.891	68.186	-1566.347	94.40	2.227	0.87
400	93.766	94.547	33.500	-1536.921	93.881	-1574.473	92.24	2.544	0.84
500	102.298	103.459	33.590	-1526.839	116.345	-1585.012	89.41	2.785	0.82
600	107.888	109.431	33.688	-1516.169	135.786	-1597.641	86.68	2.982	0.81
700	111.677	113.611	33.791	-1505.100	152.844	-1612.090	84.27	3.156	0.80
800	114.334	116.683	33.901	-1493.716	168.040	-1628.148	81.12	3.319	0.80
900	116.255	119.057	34.015	-1482.065	181.760	-1645.649	78.34	3.478	0.80
1000	117.683	120.986	34.135	-1470.175	194.285	-1664.460	76.30	3.637	0.80
1100	118.770	122.629	34.262	-1458.068	205.823	-1684.473	72.78	3.801	0.80
1200	119.614	124.088	34.395	-1445.759	216.532	-1705.597	70.81	3.972	0.81
1300	120.282	125.429	34.536	-1433.265	226.531	-1727.756	67.22	4.153	0.80
1400	120.819	126.697	34.684	-1420.601	235.916	-1750.883	64.44	4.346	0.80
1500	121.257	127.922	34.840	-1407.780	244.760	-1774.921	62.16	4.554	0.81
1600	121.619	129.119	35.005	-1394.820	253.124	-1799.819	58.88	4.779	0.81
1700	121.921	130.299	35.178	-1381.737	261.055	-1825.531	56.15	5.025	0.81
1800	122.175	131.462	35.361	-1368.548	268.594	-1852.017	53.32	5.294	0.82
1900	122.392	132.608	35.554	-1355.271	275.772	-1879.238	50.54	5.593	0.82
2000	122.577	133.726	35.756	-1341.926	282.617	-1907.160	46.49	5.925	0.80

S.4. MgSiO₃ HT-clinoenstatite

Table S.4. Ab initio B3LYP values of isochoric heat capacity (C_V), isobaric heat capacity (C_P), molar volume (V), enthalpy (H), entropy (S), Gibbs free energy (G), isothermal bulk modulus (K_T), volume thermal expansion coefficient (α_V), thermodynamic Grüneisen parameter ($\gamma_{\text{thermal}} = \alpha_V K_T V_T / C_V$) calculated for MgSiO₃ high-temperature clinoenstatite by phonon dispersion calculations $P = 0$ GPa.

	C_V	C_P	V	H	S	G	K_T	$\alpha_V \times 10^5$	
T(K)	[J/(mol×K)]	[J/(mol×K)]	(cm ³ /mol)	(kJ/mol)	[J/(mol×K)]	(kJ/mol)	(GPa)	(K ⁻¹)	γ_{thermal}
298.15	79.639	80.125	33.46	-1545.456	66.951	-1565.418	94.11	2.267	0.90
300	79.950	80.440	33.462	-1545.309	67.344	-1565.512	94.08	2.273	0.90
400	93.340	94.154	33.542	-1536.358	92.983	-1573.551	92.20	2.577	0.85
500	101.860	103.074	33.633	-1526.326	115.338	-1583.995	90.30	2.795	0.83
600	107.438	109.047	33.731	-1515.731	134.643	-1596.517	88.36	2.965	0.82
700	111.218	113.213	33.834	-1504.738	151.581	-1610.845	86.50	3.104	0.82
800	113.867	116.251	33.942	-1493.420	166.69	-1626.772	84.52	3.230	0.81
900	115.783	118.573	34.052	-1481.816	180.355	-1644.135	82.60	3.345	0.81
1000	117.206	120.429	34.167	-1469.954	192.85	-1662.804	80.70	3.454	0.81
1100	118.289	121.980	34.286	-1457.860	204.376	-1682.673	78.76	3.562	0.81
1200	119.130	123.329	34.408	-1445.556	215.08	-1703.652	76.85	3.669	0.81
1300	119.796	124.547	34.535	-1433.069	225.074	-1725.665	74.92	3.779	0.82
1400	120.331	125.682	34.667	-1420.424	234.444	-1748.646	73.00	3.891	0.82
1500	120.768	126.768	34.804	-1407.650	243.257	-1772.536	71.10	4.006	0.82
1600	121.128	127.826	34.946	-1394.777	251.565	-1797.281	69.16	4.127	0.82
1700	121.429	128.876	35.094	-1381.837	259.409	-1822.833	67.22	4.254	0.83
1800	121.682	129.928	35.248	-1368.864	266.824	-1849.148	65.32	4.384	0.83
1900	121.898	130.991	35.408	-1355.895	273.836	-1876.185	63.40	4.522	0.83
2000	122.083	132.069	35.574	-1342.969	280.467	-1903.903	61.43	4.673	0.84

S.5. MgSiO₃ HP-clinoenstatite

Table S.5. Ab initio B3LYP values of isochoric heat capacity (C_V), isobaric heat capacity (C_P), molar volume (V), enthalpy (H), entropy (S), Gibbs free energy (G), isothermal bulk modulus (K_T), volume thermal expansion coefficient (α_V), thermodynamic Grüneisen parameter ($\gamma_{\text{thermal}} = \alpha_V K_T V_T / C_V$) calculated for MgSiO₃ high-temperature clinoenstatite by phonon dispersion calculations $P = 0$ GPa.

T(K)	C_V [J/(mol×K)]	C_P [J/(mol×K)]	V (cm ³ /mol)	H (kJ/mol)	S [J/(mol×K)]	G (kJ/mol)	K_T (GPa)	$\alpha_V \times 10^5$ (K ⁻¹)	γ_{thermal}
298,15	79.277	80.128	31.808	-1544.593	64.094	-1563.703	101.55	2.974	1.21
300	79.599	80.458	31.809	-1544.445	64.590	-1563.822	101.64	2.976	1.21
400	93.383	94.699	31.908	-1535.635	89.834	-1571.569	100.51	3.203	1.10
500	102.052	103.855	32.013	-1525.657	112.061	-1581.688	98.27	3.385	1.04
600	107.676	109.966	32.124	-1514.931	131.600	-1593.891	96.84	3.502	1.01
700	111.462	114.246	32.238	-1503.705	148.896	-1607.933	95.56	3.593	0.99
800	114.103	117.401	32.355	-1492.123	164.358	-1623.609	94.08	3.680	0.98
900	116.006	119.847	32.476	-1480.270	178.316	-1640.754	92.28	3.774	0.97
1000	117.416	121.837	32.600	-1468.201	191.031	-1659.231	90.18	3.878	0.97
1100	118.487	123.532	32.729	-1455.948	202.707	-1678.926	87.84	3.994	0.97
1200	119.318	125.034	32.862	-1443.536	213.506	-1699.743	85.34	4.121	0.97
1300	119.975	126.413	33.000	-1430.976	223.559	-1721.602	82.74	4.259	0.97
1400	120.503	127.718	33.143	-1418.279	232.967	-1744.434	80.10	4.406	0.97
1500	120.933	128.983	33.292	-1405.450	241.818	-1768.177	77.46	4.562	0.97
1600	121.288	130.232	33.447	-1392.491	250.181	-1792.781	74.86	4.725	0.98
1700	121.583	131.485	33.608	-1379.403	258.115	-1818.199	72.32	4.895	0.98
1800	121.833	132.756	33.776	-1366.186	265.670	-1844.391	69.86	5.071	0.98
1900	122.045	134.057	33.951	-1352.837	272.887	-1871.322	67.49	5.253	0.99
2000	122.227	135.396	34.133	-1339.354	279.802	-1898.959	65.21	5.439	0.99

S.6. Thermodynamic data for the OEn-Pen transition

Table S.6.1a. Thermodynamic dataset used to calculate the upper, dashed blue phase boundary in Figure 4.7.1 in Chapter 4

	MgSiO ₃ protoenstatite	MgSiO ₃ orthoенstatite
H ⁰ _f (kJ/mol)	-1543.660	-1545.552
S ⁰ [J/(mol × K)]	67.692	66.17
a	106.90	106.90
b × 10 ³	16.761	16.761
c × 10 ⁻⁵	-2.812	-2.812
d	-135.10	-135.10
e × 10 ⁻⁸	-5.69790	-5.69790
f × 10 ⁶	3.8461	3.8461
g × 10 ⁹	-2.3662	-2.3662
V ⁰ (cm ³ /mol)	33.337	32.504
K ₀ (GPa)	101.88	105.798
K' ₀	6.59	8.5
dK _T /dT (bar/K)	-278	-206
α ₀ × 10 ⁷	0.31574	0.1
α ₁ × 10 ⁷	-203.221	278
α ₂ × 10 ³	36.79	0
α ₃	-13.5445	0
α ₄	1646.0216	0

Table S.6.1b. Thermodynamic dataset used to calculate the lower, dashed blue phase boundary in Figure 4.7.1. in Chapter 4

	MgSiO ₃ protoenstatite	MgSiO ₃ orthoенstatite
H ⁰ _f (kJ/mol)	-1543.959	-1545.552
S ⁰ [J/(mol × K)]	67.692	66.17
a	106.90	106.90
b × 10 ³	16.761	16.761
c × 10 ⁻⁵	-2.812	-2.812
d	-135.10	-135.10
e × 10 ⁻⁸	-5.69790	-5.69790
f × 10 ⁶	3.8461	3.8461
g × 10 ⁹	-2.3662	-2.3662
V ⁰ (cm ³ /mol)	33.337	32.504
K ₀ (GPa)	101.88	105.798
K' ₀	6.59	8.5
dK _T /dT (bar/K)	-278	-206
α ₀ × 10 ⁷	0.31574	0.1
α ₁ × 10 ⁷	-203.221	278
α ₂ × 10 ³	36.79	0
α ₃	-13.5445	0
α ₄	1646.0216	0

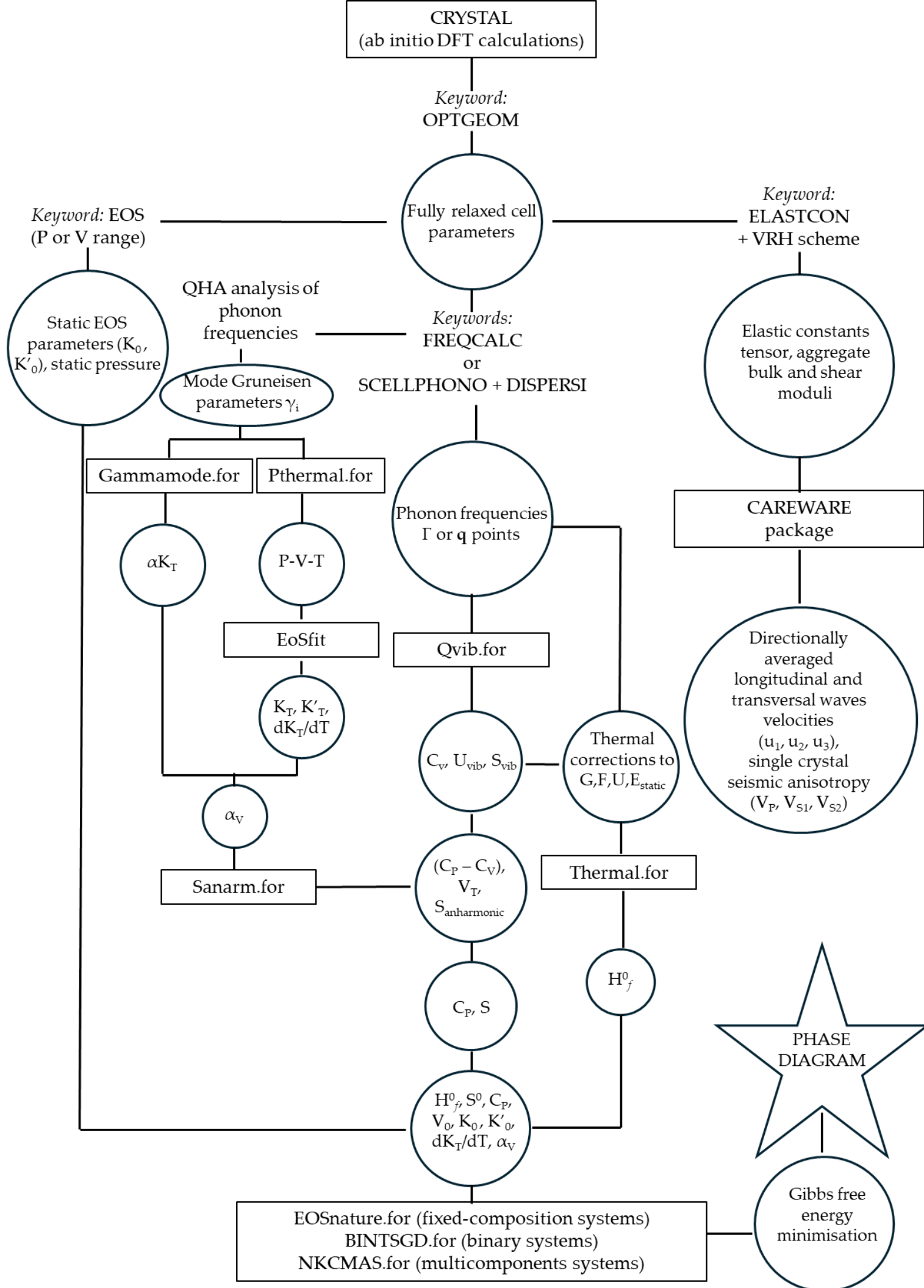
S.7. Compressibility of MgSiO₃ orthoenstatite

Table S.7. Compressibility of orthoenstatite as investigated by ab initio calculations adopting different functionals. Results of static energy vs volume and static energy vs strain are here compared and turn out to be consistent (first and third rows).

	LDA	PBE	PBESOL	PBE0	HSE06	PW91	B3LYP
K ₀ (3 rd order BM) (GPa)	130.45	92.99	114.12	99.35	99.22	94.33	76.29
K' (3 rd order BM)	6.16	10.69	7.1	11.13	11.13	10.42	13.77
K _{VRH} (GPa)	130.54	93.63	114.49	100.26	99.90	95.00	76.05

S.8. Synthetic workflow

The figure in the following page illustrates a synthetic workflow that summarizes the approach and the steps adopted in this Thesis to obtain the thermodynamic properties of pyroxenes, and ultimately simulating their phase stability, by ab initio DFT-QHA calculations. Names in boxes indicate either software or codes used in the calculations, whereas names in circles are input/output data.



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