Elastic properties of MgSiO₃-perovskite under lower mantle conditions and the composition of the deep Earth

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A R T I C L E   I N F O

Article history:
Received 22 March 2013
Received in revised form 24 July 2013
Accepted 26 July 2013
Available online 24 August 2013

Editor: P. Shearer

Keywords:
lower mantle
perovskite
elastic properties
first principles
anharmonicity
pyrolite

M A R K

Elastic properties of MgSiO₃-perovskite are of fundamental importance for our understanding of the thermal and chemical state of the lower mantle. However, the elastic moduli and especially their derivatives with respect to temperature and pressure at lower mantle conditions are still uncertain. In this study, we have carried out extensive first principles molecular dynamics simulations to determine the equation of state, elastic constants, moduli and velocities of MgSiO₃-perovskite over a wide temperature and pressure regime (from static conditions to 3500 K and from 36 GPa to 140 GPa). Systematic errors arising from approximations to the exchange–correlation functional in density functional theory have been essentially eliminated with a generalized re-scaling method. Molecular dynamics trajectories were carefully converged with respect to duration and system size and analyzed to distinguish the effects of anharmonicity. Based on the new elastic properties derived in this study, the pyrolite mineralogical model is found to predict wave velocities in close agreement with those of seismic observations in most of lower mantle regime.

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1. Introduction

The lower mantle, spanning 660 km to 2890 km in depth, is the largest single layer in the interior of Earth and plays a major role in its evolution. Despite its importance, the lower mantle is still poorly understood due to its inaccessibility to direct observation and the extreme values of pressure and temperature that characterize it (24–136 GPa; ∼ 1900–4000 K) (Bovolo, 2005). One of the central outstanding questions is the bulk composition of this layer: is it similar to that of the well-sampled upper mantle (pyrolite), or does it differ substantially? A difference in chemical composition between upper and lower mantle implies some degree of dynamical layering with important implications for our understanding of Earth’s thermal evolution. Discussions of the origins of lateral heterogeneity of apparently non-thermal origin in the lower mantle are also frustrated by our lack of understanding of lower mantle composition (Karato and Karki, 2001).

In order to understand the major element composition of the lower mantle, many previous studies have compared the seismically observed properties of this region to the elastic properties of candidate mineral assemblages (Marton and Cohen, 2002; Mattern et al., 2005; Oganov et al., 2001b; Stixrude et al., 1992; Wentzcovitch et al., 2004). The conclusions of such studies rely on the quality of the estimates of the elastic properties of the constituent minerals: uncertainty in lower mantle composition is largely a function of uncertainty in these properties. Despite remarkable progress in experimental methods, the elastic properties of relevant phases have rarely been measured experimentally at lower mantle pressure–temperature conditions because of the experimental challenges (Murakami et al., 2009).

The key to understanding lower mantle composition is the elastic properties of its most abundant phase Mg-rich silicate perovskite. First suggested by Ringwood almost a century ago (Ringwood, 1962), the properties of MgSiO₃-perovskite (MgSiO₃-pv) have attracted enormous attention from different approaches. For decades, there have accumulated several hundred experimental data on the thermodynamic and elastic properties of MgSiO₃-pv. However, most of these data have been collected at room temperature (e.g., Murakami et al., 2007), and measurements at combined lower mantle pressure and temperature have been essentially limited to the density (e.g., Fiquet et al., 2000; Tange et al., 2012). Very recently the shear wave velocity of MgSiO₃-pv was measured at lower mantle pressure–temperature conditions for the first time (Chantel et al., 2012; Murakami et al., 2012).

Here we take a different approach, using first principles molecular dynamics simulations to predict the elastic properties of MgSiO₃-perovskite over the entire range of lower mantle pressure–temperature conditions. First principles theory has been used before to predict the elasticity of MgSiO₃-perovskite (Oganov et
2. Theory

2.1. Computational methods

All simulations were carried out with VASP (Kresse and Furthmuller, 1996) with the projector-augmented-wave (PAW) method (Kresse and Joubert, 1999) and two kinds of exchange–correlation functionals: the Local Density Approximation (LDA) and the PBE form of Generalized Gradient Approximation (GGA) (Perdew et al., 1996) at each temperature and volume. In order to further explore the influence of the exchange–correlation function, we also present a limited number of results using the recent implementation of the TPSS self-consistent meta-generalized gradient approximation (metaGGA) in VASP (Sun et al., 2011a). The core radii are 1.06 Å for Mg (valence configuration with p semi-core valence state, 2p63s2), 0.85/0.79/1.01 Å (LDA/GGA/metaGGA) for Si (3s23p2), 0.80 Å for O (2s22p2).

We calculated both static and high temperature elastic constants at each pressure. In each static simulation, we used a unit cell with 20 atoms and 4 × 4 × 4 k-point mesh, and the basis set size was set by the energy cutoff (Ecut) of 800 ev, the ground state was self-consistently iterated to within Ediff = 10^-6 ev. In the much more expensive high temperature molecular dynamics simulations, we used supercells of 80 atoms (2a × 2b × 1c), sampled the Brillouin zone at the Γ-point only, and used a slightly loosened but still sufficiently energy cutoff (Ecut = 500 ev) and energetic convergence criterion (Ediff = 10^-4 ev). Molecular dynamics trajectories were propagated in the NVT ensemble with the Nosé thermostat (Nosé, 1984) for 6–12 ps (12 ps for undeformed state, 6 ps for strained states). To check for possible finite size effects, we also carried out simulations with larger systems (from 160 atoms (2a × 2b × 2c) to 1280 atoms (4a × 4b × 4c)) and found the final results were unchanged within the uncertainties (Table A.1 of the online appendix). For high temperature molecular dynamics simulations the full kinetic contribution was carefully included in the calculation of stress tensor (Allen and Tildesley, 1989; Hess and Evans, 2001). We have not applied the quantum corrections since the finite temperatures involved in this study are higher than the Debye temperature (less than 1000 K for MgSiO3-pv) and quantum effects should be negligibly small (Matsui, 1989).

The method of calculating isothermal elastic constants essentially follows previous work (Karki et al., 2001; Oganov et al., 2001b; Wallace, 1972). In all cases stresses are computed via the method of Nielsen and Martin (1985). For each volume, the hydrostatic state is found by fully relaxing the structure (including atomic positions and lattice vectors) at static conditions or carefully adjusting the lattice vectors at finite temperatures, as shown in Fig. A.1(a) of the on-line appendix as an example. We applied four strain magnitudes (±0.02, ±0.01) of four different types (one triclinic and three axial strains) to each hydrostatic state. In static calculations, the atomic positions were relaxed to incorporate the possible couplings between strains and vibrational modes. The isothermal elastic constants were then calculated from the stress–strain relations, which were found to be very well represented with a second order polynomial (Fig. A.1(b) of the online appendix). Since we are interested in the infinitesimal strain limit, the final elastic constant is the first order coefficient. We have confirmed that our results are insensitive to the choice of strain measure (Cauchy vs. Lagrangian) (Karki et al., 2001).

Adiabatic elastic constants were calculated from the isothermal elastic constants using standard thermodynamically self-consistent formulae (Davies, 1974), and thermodynamic parameters determined via linear-least-square fitting of pressure and internal energy along isochoros. Finally, we calculated Voigt–Reuss–Hill bulk and shear moduli (Watt et al., 1976), Gruneisen parameters, thermal expansions, longitudinal and shear wave velocities from these results.

Uncertainties in directly simulated quantities are determined using appropriate non-Gaussian statistics via the blocking method (Flyvbjerg and Petersen, 1989). These errors are propagated to quantities such as elastic constants and the isochoric heat capacity via weighted least squares fitting, and finally to derived quantities such as the Gruneisen parameter, thermal expansion coefficient, and velocities.

2.2. Anharmonicity

Vibrational modes in crystal lattices are only approximately harmonic and this approximation becomes increasingly poor with increasing temperature. Lattice dynamics ignores anharmonicity and it is difficult to judge a-priori how serious a limitation this may be. Various ansätze have been developed to estimate the temperature below which quasi-harmonicity remains valid, for example, based on the inflection point of the thermal expansion versus temperature (Wentzcovitch et al., 2004). These are often intuitively reasonable but may need more rigorous evaluation by comparing with another theoretical method that includes anharmonicity completely.

Molecular dynamics simulations, which we use, account fully for anharmonicity. Much of the discussion of the nature of anharmonicity in the physics literature is specific to simple systems with only one atom in the unit cell and no internal or lattice degrees of freedom. In earth materials the situation is more complex, and one must distinguish between at least three consequences of anharmonicity:

1. Intrinsic anharmonicity. Higher-order terms become increasingly important with greater vibrational amplitude at high temperature. One consequence is that vibrational frequencies depend on temperature at constant volume, violating the quasi-harmonic approximation in which frequencies depend only on volume. Intrinsic anharmonicity has been measured experimentally in several systems (Gillet et al., 1997, 1996).
(2) Temperature-dependence of the internal degrees of freedom. As temperature increases the equilibrium positions of the atoms change if the crystal has internal degrees of freedom. For example, in many perovskites, including MgSiO$_3$, it is known that octahedral rotation tends to diminish with increasing temperature (Liu and Liebermann, 1993; Ross and Hazen, 1989).

(3) Temperature-dependence of the lattice. As temperature increases the lattice vectors change if permitted by symmetry. For example, many perovskites, including MgSiO$_3$, approach the pseudo-cubic aristotype on heating.

Based on our molecular dynamics results, we are able to evaluate each of these anharmonic contributions separately and to estimate the likely impact of anharmonicity on predictions of the elastic constants at lower mantle conditions. To measure intrinsic anharmonicity, we use the temperature dependence of the isotropic temperature factor (Debye–Waller or $B$ factor), which is directly related to the atomic mean square displacement $\langle u^2 \rangle$:

$$B = \frac{8 \pi^2}{3} \langle u^2 \rangle = \frac{8 \pi^2}{3} \langle (r - r_0)^2 \rangle$$

where $\langle \rangle$ denotes the time average and $r_0 = (x_0, y_0, z_0)^T = (r)$ is the time-averaged position of each atom. For a (quasi-)harmonic system, $B$ varies linearly with temperature on isochoric heating (Reisland, 1973). $B$ is measured directly in our molecular dynamics simulations by tracking particle trajectories. The second and third contributions to anharmonicity as listed above are readily measured simply by tracking the change in the (time-average) crystal structure on heating. This analysis is discussed further in the results section below.

2.3. Systematic errors and corrections

Density functional theory is exact, however the exact form of the exchange–correlation functional is unknown. Thus all density functional theory calculations, including ours, rely on an approximation to this term. The two most widely used approximations: LDA and GGA, yield slightly different predictions for quantities such as the equation of state. Experience in a wide variety of systems shows that LDA typically over-binds structures, while GGA is that LDA and GGA yield essentially identical lattice cell shapes, atomic positions, and vibrational frequencies when compared at the same volume. They proposed that the correction to the energy take the simplest possible volume-dependent form, i.e. be linear in volume. This form of the correction, which is equivalent to a constant shift in the pressure, has been widely used (Boettger and Trickey, 1984; Oganov et al., 2001a, 2001b; Stixrude and Karik, 2005; Wentzcovitch et al., 2004).

A variety of recent results show however, that a constant shift in pressure is not sufficient to bring LDA and GGA predictions into agreement over a wide range of pressure (Kunc and Syassen, 2010; Sun et al., 2011b). Kunc and Syassen (2010) have proposed an alternative form for the correction, which involves a simple re-scaling of the volume and pressure. They solely investigated the performance of their re-scaling method at static conditions and only applied it to the equation of state. Otero-de-la-Roza and Luanha (2011) have proposed an extension to high temperatures, but did not consider anisotropic properties such as the shear modulus.

Here we further develop the Kunc and Syassen re-scaling method by applying it to high temperatures, and to a much greater range of thermodynamic quantities, including anisotropic quantities such as the shear modulus.

Here we derive a generalized re-scaling method from the appropriate thermodynamic fundamental relation in order to demonstrate thermodynamic self-consistency. We propose the following expression for the re-scaled Helmholtz free energy

$$F(V, T) = F(V_0^{exp}, T) + \frac{V_0^{exp}}{V_0^{DFT}} K_0^{exp} \frac{V_0^{DFT}}{V_0^{exp}} F_0^{DFT}(V_0^{DFT}) \times \left[ F_0^{DFT}\left(V, V_0^{exp}\right) - F_0^{DFT}(V_0^{exp}) \right] + \Delta F_0^{DFT}(V, T)$$

(2)

where subscript 0 refers to properties at zero pressure and static conditions, quantities lacking temperature dependence are thermal (static), $K$ is the isothermal bulk modulus, and the Delta notation denotes the change in the quantity from static conditions to the temperature of interest, e.g. $\Delta F_0^{DFT}(V, T) = F_0^{DFT}(V, T) - F_0^{DFT}(V)$. Note that the experimental static properties are not just the room temperature measurements, but have to be corrected to 0 K and have the effect of zero-point motion removed. We begin with the re-scaled Helmholtz free energy because this is a fundamental thermodynamic relation from which all other re-scaled equilibrium thermodynamic properties may be derived (Callen, 1960). Expressions for other re-scaled quantities are derived via volume and temperature derivatives of Eq. (2), guaranteeing thermodynamic self-consistency among all quantities. We note that the analysis of Otero-de-la-Roza and Luanha (2011) is equivalent to our expression (Eq. (2)) aside from the choice of value for the integration constant, which does not influence any of the results presented here since we are interested only in quantities that are given by volume and temperature derivatives of the free energy.

The fundamental relation (Eq. (2)) follows the usual procedure of separating the Helmholtz free energy into cold (static) and thermal parts (last term in Eq. (2)). The expression for the cold part is derived by integrating the re-scaled equation of state as introduced by Kunc and Syassen (2010). The thermal part is left in its original form because of the observation that temperature derivatives of the free energy tend to be: (1) predicted with high accuracy by DFT in either LDA or GGA form; (2) very similar regardless of the form of the exchange–correlation functional (LDA or GGA) (Narasimhan and de_Gironcoli, 2002; Sun et al., 2011b).

From the thermodynamic identity $P = -(dF/dV)_T$ we find from Eq. (2)

$$P(V, T) = \frac{K_0^{exp}}{K_0^{DFT}} P_0^{DFT}\left(V, V_0^{DFT}\right) + \Delta P_0^{DFT}(V, T)$$

(3)

which recovers the form of the re-scaled equation of state of Kunc and Syassen (2010) for the static part. From the definition of the isothermal bulk modulus and Eq. (3) we find

$$K(V, T) = \frac{K_0^{exp}}{K_0^{DFT}} K_0^{DFT}\left(V, V_0^{DFT}\right) + \Delta K_0^{DFT}(V, T)$$

(4)

also identical to the expression found by Kunc and Syassen (2010) for the static part.

In our study, we wish to go beyond previous analyses (Kunc and Syassen, 2010; Otero-de-la-Roza and Luanha, 2011), who focused on the pressure and the bulk modulus, to all other equilibrium thermodynamic properties, including the full elastic constant tensor.
The elastic constant tensor is related to the Helmholtz free energy (Stixrude and Lithgow-Bertelloni, 2005)

\[
c_{ijkl}(V, T) = \frac{1}{V} \left( \frac{\partial^2 F(V, T)}{\partial S_{ij} \partial S_{kl}} \right)_{\delta_k} + P(V, T)\delta_{ij} \delta_{kl}
\]  

(5)

where \( S_{ij} \) is the strain tensor and \( \delta_{ij} \delta_{kl} = \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \) is the Kronecker delta. Substituting Eqs. (2), (3)

\[
c_{ijkl}(V, T) = \frac{K_{exp}^{(x)}}{K_{DFT}^{(x)}} \left[ \frac{1}{x} \left( \frac{\partial^2 F_{DFT}(x)}{\partial S_{ij} \partial S_{kl}} \right)_{\delta_k} + P_{DFT}(x)\delta_{ij} \delta_{kl} \right]
\]  

\[+ \Delta c_{ijkl}^{DFT}(V, T) \]

(6)

where we have introduced \( x = V V_{exp}^{DFT}/V_0^{exp} \) and the quantity in brackets is just the elastic constant computed via DFT at \( x \), so that the final expression reads

\[
c_{ijkl}(V, T) = \frac{K_{exp}^{(x)}}{K_{DFT}^{(x)}} c_{ijkl}^{DFT}(x) + \Delta c_{ijkl}^{DFT}(V, T). \]

(7)

All the elastic constants, and combinations of the elastic constants thus scale with the bulk modulus, e.g.

\[ G(V, T) = \frac{K_{exp}^{(x)}}{K_{DFT}^{(x)}} G_{DFT}(x) + \Delta G_{DFT}(V, T) \]

(8)

where \( G \) is the Voigt–Reuss–Hill average shear modulus as reported below.

Similarly, we may evaluate the re-scaled values of other thermodynamic quantities. Those involving temperature derivatives are unchanged by re-scaling since the only part of the fundamental relation (Eq. (2)) that depends on temperature is not re-scaled

\[ B(V, T) = \alpha K_T(V, T) = \left( \frac{\partial P(V, T)}{\partial T} \right)_{V} = B_{DFT}(V, T) \]

(9)

\[ C_V(V, T) = -T \left( \frac{\partial^2 F(V, T)}{\partial T^2} \right) = C_{DFT}^V(V, T) \]

(10)

\[ \gamma(V, T) = \frac{B(V, T)}{C_V(V, T)} = \gamma_{DFT}(V, T) \]

(11)

where \( B, \alpha, C_V, \) and \( \gamma \) are respectively the thermal pressure coefficient, thermal expansivity, isochoric heat capacity, and Grüneisen parameter.

We adopt the following for the experimental values at zero pressure and static conditions computed from the thermodynamic model of Stixrude and Lithgow-Bertelloni (2011): \( V_0^{exp} = 24.12(2) \text{ cm}^3/\text{mol} \) (as above), \( K_0^{exp} = 262.0(3.0) \text{ GPa} \). These are respectively smaller and larger than experimental values at ambient conditions, reflecting the influence of lattice vibrations.

We also evaluate the constant pressure–shift form of the correction in order to compare its performance with the re-scaling method and to make contact with the large number of previous studies that have used the constant pressure shift correction. The form of the constant pressure–shift correction reads

\[ P(V, T) = P_{DFT}^{(x)}(V, T) + P_{XC} \]

(12)

where \( P \) is the corrected pressure, \( P_{DFT}^{(x)} \) is the pressure from the density functional theory, and \( P_{XC} \) is the empirical correction for systematic bias in the approximation to the exchange–correlation potential (LDA or GGA), which is assumed to be independent of volume and temperature. We compute the correction as in de Koker et al. (2008)

\[ P_{XC} = -P_{DFT}^{(x)}(V_0^{exp}, \text{static}) \]

(13)

where \( P_{DFT}^{(x)} \) is the pressure computed by VASP for the fully relaxed static structure of crystalline MgSiO$_3$-perovskite (20 atom primitive unit cell, space group Pbnm, and \( V_0^{exp} = 24.12(2) \text{ cm}^3/\text{mol} \) is the experimental zero-pressure volume of crystalline MgSiO$_3$-perovskite at static conditions, computed via the thermodynamic model of Stixrude and Lithgow-Bertelloni (2011) and uncertainty computed via formal error propagation. The values obtained for LDA: \( P_{XC} = 1.9(2) \text{ GPa} \), and GGA: \( P_{XC} = -10.6(2) \text{ GPa} \) are consistent with the well-known over-binding tendency of LDA, and the somewhat greater under-binding tendency of GGA and are similar in magnitude to previous estimates for MgSiO$_3$ composition (Oganov et al., 2001b; Stixrude and Karki, 2005).

3. Results

3.1. Simulated elastic properties of MgSiO$_3$-pv

Elastic properties of MgSiO$_3$-pv simulated in this study are listed in Tables A.2 and A.3 of the online appendix. As shown in Fig. 1, results are in reasonably good agreement with experimental measurements of equation of state and elastic moduli, although systematic deviations are apparent: LDA tends to over-bind (underestimate the pressure and moduli) and GGA tends to under-bind (overestimate the pressure and moduli). Systematic discrepancies exist between LDA and GGA results in pressure (up to 20 GPa), bulk modulus (up to 35 GPa) and shear modulus (2–8 GPa). Our results are in generally good agreement with previous theoretical studies including results of Oganov et al. (2001a, 2001b) and Stackhouse et al. (2005b), which used ultrasoft pseudopotentials and a slightly different form of GGA. The results of Karki et al. (1997) are in better agreement with those simulated in this study with GGA. In the limit of quasi-harmonic validity, the isothermal bulk moduli from Karki et al. (2000) and shear moduli from Wentzcovitch et al. (2004) are in overall accordance with those simulated in this study with GGA and LDA respectively but both show stiffer volumetric dependences.

The temperature variations of the bulk and shear moduli simulated in several studies are shown in Fig. 2 and Fig. 3. From our simulation results we find that the elastic moduli vary linearly with temperature and that the high temperature linear trend goes through the static values within the statistical uncertainty, as expected of the trend defined by classical high temperature dynamical simulations. Temperature derivatives of the elastic moduli turn out to be insensitive to the exchange–correlation functional, as shown by the very similar values of \( |dG/dT| \) and \( |d\kappa_S/dT| \) determined with LDA and GGA. The quasi-harmonic results of Wentzcovitch et al. (2004) show a larger value of \( |dG/dT| \), especially at the lowest pressure. The molecular dynamics simulations of Oganov et al. (2001b) also show a substantially larger value of \( |dG/dT| \) than in our results, although excluding their highest temperature point at 38 GPa (which may have been affected by incipient melting as pointed out by the authors) yields a value of the derivative in much better agreement with our results. The molecular dynamics results of Stackhouse et al. (2005b) yield a value of \( |dG/dT| \) that is in good agreement with our calculations.

3.2. Correcting systematic DFT errors and comparison with experiment

We report our results corrected by the re-scaling method from static conditions to lower mantle conditions in Table 1. The re-scaling method yields essentially perfect agreement between LDA and GGA, within the numerical uncertainty of our molecular dynamic simulations, for the pressure and bulk modulus. In contrast, we found that the constant pressure-shifting method is inadequate: the corrected pressures of LDA and GGA differ by more than
Table 1

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<th>Temperature in K</th>
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Elastic properties of MgSiO3-perovskite from static conditions to lower mantle conditions, rescaled and averaged from the simulation results of LDA and GGA (listed in Tables A.2, A.3). Parameters for the rescaling formulae have been corrected to static conditions (see text).
Fig. 2. Adiabatic bulk modulus and shear modulus along four groups of similar isobaric conditions (labeled as P1–P4). Note that the data points located at 0 K are the simulated moduli at static conditions (without zero point contributions). Lines are weighted linear least-square fits to our simulations with absolute values of the slopes in MPa/K indicated. All the results are presented here without correcting for systematic errors from density functional theory.

9 GPa at compressed conditions; results for the bulk modulus differ by even larger amounts. Differences between the re-scaled LDA and GGA results for the shear modulus are somewhat larger than for the bulk-modulus, but only slightly more than numerical uncertainties.

As shown in Fig. 1, the re-scaled results agree very well with existing experimental data on equation of state and moduli. To facilitate precise comparisons between our static calculations and room temperature experiments, we correct experimental measurements to static conditions using the thermodynamic model of Stixrude and Lithgow-Bertelloni (2011). Removing the zero-point-motion and thermal contributions from the 300 K experimental data isochorically decreases the pressure by 3–4 GPa, decreases the isothermal bulk modulus by 2–5 GPa and increases the shear modulus by 5–6 GPa. For the equation of state, re-scaled theory and all experiments are in excellent mutual agreement at pressure less than 40 GPa. At much higher pressure, our re-scaled bulk moduli are in good accordance with all experimental measurements, and our re-scaled shear moduli agree closely with those measured by Murakami et al. (2007).

Recently Murakami et al. (2012) measured the volume and shear wave velocity under simultaneous high-pressure and high-temperature conditions corresponding to those in the lower mantle for the first time. Their measured volumes and shear moduli are substantially larger than our results (Fig. 1 and Figs. A.2(a–c) of the online appendix). We note that their measured volumes are also significantly larger than those of previous experimental measurements, with which our simulations agree well (Fig. 1(a) and Figs. A.2(a–c) of the online appendix). These discrepancies between theory and experiment and between different experiments call for further measurements at the challenging conditions of the lower mantle to evaluate the accuracy of experiments by Murakami et al. (2012) and our calculations.
Intrinsic anharmonicity is also illustrated by atomic trajectories (Fig. 4(b)). At high temperature, some atoms were found occasionally to wander significantly away from their mean spatial positions (in the case of Mg occasionally by more than 1.0 Å away from the time-averaged position). This behavior distorts the atomic spatial probability density distributions away from the trivariate Gaussian probability ellipsoids expected in the (quasi-) harmonic limit (Reilly et al., 2011).

We investigate the temperature-induced variation of internal degrees of freedom with a careful analysis of the time-averaged structures over all the pressure–temperature conditions involved in this study. Since the perovskite structure is closely related with the bending of octahedral framework, we define a tilt angle as the complement of $\angle$Si–O(2)–Si and choose it as the primary structural parameter to show the effects of temperature and pressure. Other tilt angles (such as $180^\circ - \angle$Si–O–Si, or tilt angles about the axes suggested by Zhao et al. (1993)) show similar trends. In agreement with experiments (e.g. Ross and Hazen (1989); Sasaki et al. (1983)), we find the degree of octahedral tilt tends to increase with pressure and decrease with temperature. As shown in Fig. 5(a), the tilt angle varies up to 6.8° over the conditions involved in this study. With compensating effects of temperature and pressure, the tilt angle along the two isochores still changes up to 1.6° at 22.23 cm$^3$/mol and 0.8° at 19.95 cm$^3$/mol.

In Figs. 5(b, c) we analyze the variations of the other structural parameters. Following Sasaki et al. (1983), we calculated the mean Mg–O distance of the MgO$_{12}$ polyhedron ($\bar{r}_{\text{Mg–O}}$) and the mean Si–O distance of the SiO$_6$ octahedron ($\bar{r}_{\text{Si–O}}$) and their relative ratio ($\bar{r}_{\text{Mg–O}}/\sqrt{2}\bar{r}_{\text{Si–O}}$, known as Sasaki tolerance factor). Similar to previous analyses, we find that temperature and pressure have opposite effects on these three parameters. Along each isochore, $\bar{r}_{\text{Mg–O}}$ and $\bar{r}_{\text{Si–O}}$ decrease slightly: by 0.012 Å at 22.23 cm$^3$/mol and 0.008 Å at 19.95 cm$^3$/mol. The increase of $t_S$ with increasing temperature at 22.23 cm$^3$/mol indicates the structure tends to approach the cubic aristotype (which has $t_S = 1.00$) upon heating at lower pressures, however this tendency is diminished with compression and $t_S$ is less sensitive to temperature at 19.95 cm$^3$/mol. The bond-length distortion ($\Delta = \frac{1}{2} \sum (t(i) - f(i))^2 / r^{100}$) shown in Fig. 5(c) further demonstrates temperature effects: while the MgO$_{12}$ polyhedron tends to be more regular upon heating and compression, the SiO$_6$ octahedron is found to be slightly more distorted on isochoric heating.

The tilt of the octahedral framework can also be closely correlated with the cell shape of the hydrostatic perovskite structure (Fig. 6). Temperature decreases the tilt angle and the cell approaches the cubic aristotype as the ratios $b/a$ and $c/\sqrt{2}b$ both gradually approach unity. LDA and GGA results agree essentially perfectly in the trends. The sign of these trends are consistent with those found in experiments at lower pressure and temperature (Hemley and Cohen, 1992) and in quasi-harmonic lattice dynamics calculations that have been corrected for deviatoric stress (Carrier et al., 2007).

### 3.4. Comparison with seismology

We compare our results to the thermodynamic model of Stixrude and Lithgow-Bertelloni (2011) (SLB11) over lower mantle conditions (Fig. 7). In SLB11, values of the thermodynamic parameters are determined by fitting to a combination of experimental data and previous first principles calculations. We find that our shear wave velocity is higher than that in SLB11 (Fig. 7(b)). As shown in the inset plot of Fig. 7(b), our simulations are in better agreement than the SLB11 model with the most recent measurements by Chantel et al. (2012) and Murakami et al. (2012), although systematic discrepancies still exist with the latter. As
Fig. 5. Variations of the time-averaged structure from our simulations (LDA) with pressure and temperature. (a) The tilt angle (180°-Si–O(2)–Si) of SiO\textsubscript{6} octahedrons over the T-P conditions explored in this study. Note that the data points located at 0 K are the simulated values at static conditions (without zero point contributions). Dashed line in light magenta is the quasi-harmonic limit reported by Wentzcovitch et al. (2004). (b) and (c): Relationships between the tilt angle and the other structural parameters of MgO\textsubscript{12} polyhedron and SiO\textsubscript{6} octahedron (inter-atomic distance and Sasaki observed tolerance factor in (b) and bond-length distortion in (c)). The dashed/dash-dotted lines are linear fits to the data points along each isobaric/isochoric condition (labeled as P\textsubscript{1}–P\textsubscript{4} and V\textsubscript{1}, V\textsubscript{2}, as indicated in (a)). The arrows show the direction of increasing temperature.

Fig. 6. Hydrostatic unit cell shape variations from 1000 K to 4000 K on isochoric heating at 19.95 cm\textsuperscript{3}/mol and 22.23 cm\textsuperscript{3}/mol. Experimental determinations by Tange et al. (2012) (blue) and Fiquet et al. (2000) (purple) at similar volumes are included for comparisons. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mentioned in Section 3.2, the experimental results need independent evaluation by further experiments under similar conditions.

We have re-determined the best fitting parameters of MgSiO\textsubscript{3}-perovskite within the framework of the thermodynamic model of SLB11 but based now on our new re-scaled first principles molecular dynamics results. We have retained the same values of \( V_0, K_0, G_0, \) and the Debye temperature \( \theta_0 \) as in SLB11, and re-determined best fitting values to the present results for the pressure derivatives of the moduli \( K_0' \) and \( G_0' \), and the parameters that control the temperature derivatives of the moduli: the Grüneisen parameter \( \gamma_0 \), its logarithmic volume derivative \( q_0 \), and the parameter \( \eta_{SD0} \), which controls \( dG/dT \). The values of these re-determined parameters are reported in the caption of Table 1. Although the SLB11 thermodynamic model is based on quasi-harmonic physics, we have found that it is possible to represent our simulation results with this quasi-harmonic theory within statistical uncertainty over the lower mantle pressure–temperature regime. The values of the parameters resulting from this fit are thus effective (renormalized) values that include the effect of anharmonicity.

Using the re-determined parameters for MgSiO\textsubscript{3}-perovskite, and retaining all other mineral properties from SLB11, including those of the FeSiO\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} end-members of Mg-rich silicate perovskite, as well as those of other phases including CaSiO\textsubscript{3} perovskite, and (Mg, Fe)O (with parameters as listed in Table A1 of SLB11), we have computed the densities and seismic wave velocities of pyrolite at lower mantle conditions. We adopt the same phase proportions and isentropic temperature profile (with a potential temperature of 1500 K, which agrees well with the temperature profile of Brown and Shankland (1981) over the whole lower mantle regime) computed with SLB11. We find that the density and longitudinal wave velocity are only marginally changed with the new parameters refined in this study as compared with SLB11 (not shown here for brevity). As shown in Fig. 8, the agreement in shear wave velocity is essentially perfect within uncertainties from seismology (as measured by the difference between two radial models: PREM (Dziewonski and Anderson, 1981) and AK135 (Kennett et al., 1995)) and from our calculations (as measured by the difference between Voigt and Reuss bounds on the elastic properties of the assemblage). The difference in Voigt and Reuss bounds (\( \sim 0.4\% \) in \( V_S \)) is similar in magnitude to the uncertainty in the shear wave velocity due to statistical uncertainties in our
Fig. 7. Comparisons of the longitudinal and shear wave velocities over lower mantle conditions from this study (listed in Table 1) and those predicted from Stixrude and Lithgow-Bertelloni (2011). The point at 1200 K from recent measurement by Chantel et al. (2012) is included for comparison. The inset compares our results with those of Murakami et al. (2012).

We estimate uncertainties due to the influence of Fe and Al incorporation on MgSiO₃-perovskite elasticity via the following analysis. Several previous studies have found that the elastic wave velocities of Mg-rich silicate perovskite depend approximately linearly on composition according to

\[ V_M(x) = V_M(0)(1 - bMx) \]  

where \( x \) is the mole fraction of the impurity, \( V_M \) is the elastic wave velocity, \( M \) refers to the type of wave (\( M = S, P \)), \( V_M(0) \) is the velocity of the Mg end-member, and \( b_M \) is a constant, assumed to be independent of pressure and temperature. We recomputed the shear wave velocity of the pyrolite model using Eq. (14) to estimate the change in \( V_S \) of Mg-rich silicate perovskite due to incorporation of FeSiO₃ and Al₂O₃ components. We use the velocity of MgSiO₃-perovskite from our results in this study for the value of \( V_S(0) \) and a range of values for \( b_S = 0.18-0.24 \) for FeSiO₃ and \( b_S = 0.06-0.08 \) for Al₂O₃ as determined in previous theoretical studies (Kiefer et al., 2002; Stackhouse et al. 2005a, 2007; Tsuchiya and Tsuchiya, 2006). The parameters for all other species, including CaSiO₃ perovskite, and (Mg, Fe)O ferropericlase are identical to those in SLB11. This alternative calculation shows that uncertainties due to Fe and Al incorporation are comparable in magnitude to the difference between the Voigt and Reuss bounds on the pyrolite model velocity, as illustrated in Fig. 8.

### 4. Discussion and conclusions

A limitation of previous first principles studies has been the systematic error due to the approximation to the exchange–correlation functional. While various schemes have been proposed for overcoming these biases, their robustness has not been carefully examined in the context of major earth materials.

Our generalized re-scaling method based on Kunc and Syassen (2010) appears to overcome these limitations, at least in the case of MgSiO₃ perovskite. Re-scaled LDA and GGA are in very good accord, essentially eliminating the dependence of first principles results on the choice of exchange–correlation functional. As shown in Fig. A3 in the online appendix, additional simulations with metaGGA verify the perfect convergence of the re-scaled results. These results also agree very well with existing experimental data up to the highest pressure and temperature and overlap substantially within the pressure–temperature range of the lower mantle. In contrast, the constant pressure shift that has been widely used in the past yields much poorer consistency among different functionals, as demonstrated in Fig. 1 and Fig. A3.

The coincidence of the re-scaled results with various forms of exchange–correlation functional has also been illustrated by previous studies (e.g. Kunc and Syassen (2010) and Otero-de-la-Roza and Luaña (2011) and references therein). The re-scaling method is founded on the arguments of van de Walle and Ceder (1999) that the exchange–correlation error should be a function of volume alone, and the observation that vibrational frequencies and temperature derivatives tend to be insensitive to the form of
the exchange–correlation functional (Narasimhan and de Gironcoli, 2002; Sun et al., 2011b).

Our analyses of the molecular dynamics trajectories provide a comprehensive way from the microscopic point of view to investigate anharmonic effects. Anharmonicity is manifested in the variations of the Debye–Waller factor, time-averaged internal atomic coordinates and the cell shape with temperature at constant volume. The presence of anharmonicity in our simulations accounts to some extent for the differences at high temperatures and low pressures between our results and those of quasi-harmonic lattice dynamics which ignore anharmonicity (Karki et al., 2000; Wentzcovitch et al., 2004). In particular, we find that the shear modulus depends more weakly on temperature than in previous quasi-harmonic studies at lower pressures. Previous analyses indicate that anharmonicity should become less important at high pressures (Hardy, 1980; Oganov and Dorogokupets, 2004; Wentzcovitch et al., 2004), and our results agree with this trend. While the method proposed by Carrier et al. (2008) can partially correct the deviatoric thermal stresses from the anisotropic strain gradients in the framework of quasi-harmonic theory, this approach still does not account for intrinsic anharmonicity and changes to the internal degrees of freedom with increasing temperature. We find that atomic positions vary significantly on isochoric heating; the approximation adopted by Carrier et al. (2007; 2008) that the structure is “statically constrained”, i.e. purely volume-dependent, does not agree with our simulation results. Molecular dynamics simulation, therefore, is a more universally valid method to accurately predict the elastic properties of minerals over the possible temperature–pressure regime in the lower mantle.

The results in this study provide important constraints on the thermochemical interpretation of seismic observations of the lower mantle. By using the re-scaled simulation results in this study, the wave velocity profiles of a pyrolitic adiabatic model match seismic models of the lower mantle. As shown in Fig. 8, the shear wave velocity agrees almost perfectly with the preliminary reference earth model (PREM, by Dziewonski and Anderson, 1981) within the Voigt–Reuss bound from 800 km to 2500 km. The good agreement indicates that a pyrolitic composition for the lower mantle cannot be ruled out on the basis of comparisons with global one-dimensional seismological models. We note that a lower mantle consisting of a mechanical mixture of basalt and harzburgite has virtually the same seismic wave velocity as homogeneous pyrolite in the lower mantle (Xu et al., 2008): a mechanical mixture of overall pyrolic bulk composition would fit the lower mantle as well as homogeneous pyrolite.

Our results require re-evaluation of the many previous analyses of lower mantle bulk composition based on comparisons of seismic structure with the elastic properties of candidate mineral assemblages. All of these previous studies have suffered from uncertainty in the elastic properties of perovskite. It is this uncertainty that accounts for the divergent results of previous studies, with some arguing for a pyrolic mantle, and other arguing for silica and/or iron enrichment. Uncertainties in previous studies have included: neglect of the shear modulus due to lack of experimental or first principles information on its pressure or temperature dependence (Stixrude et al., 1992); estimate of shear properties based on systematic relations (Mattern et al., 2005); extrapolation of data at lower temperatures and/or pressures to the conditions of the lower mantle (Cammarano et al., 2005; Cobden et al., 2009); and unknown errors due to the neglect of anharmonicity (Wentzcovitch et al., 2004). In contrast, the results of the present study are based on first principles determinations of shear and bulk elasticity at the pressure and temperature conditions of the lower mantle that are consistent with available experimental data (with the exception of those of Murakami et al. (2012), as discussed above) and with density functional theory.

Our analysis of lower mantle composition disagrees with the very recent arguments made by Murakami et al. (2012). Those authors argued on the basis of their new measurements that the lower mantle is more perovskite-rich than pyrolite. This conclusion is inconsistent with our analysis because their MgSiO$_3$-pv is faster than ours, implying the need for an even higher proportion of slow phases (e.g. ferropericlase) to recover the good agreement with pyrolite that we find.

The excellent agreement that we find between pyrolite and lower mantle seismological models is significant because it limits the kinds of chemical heterogeneity that can be expected in the mantle. For example, without resorting to a much higher temperature profile, a lower mantle of chondritic composition, implying very limited mass flux between lower mantle and upper mantle over geologic time, is most probably ruled out as the greater silica fraction in the chondritic composition as compared with pyrolite would produce velocities faster than those seen in seismological models. Very basalt rich compositions are similarly ruled out for the lower mantle, as also pointed out by Tsuchiya (2011), although some degree of basalt enrichment with increasing depth as seen in geodynamical models is permitted by our comparison (Nakagawa et al., 2010).

Important uncertainties remain in our comparison of pyrolite to lower mantle seismic properties. These include: (1) the elastic constants of the other species in the lower mantle, all of which are at least as uncertain at lower mantle pressure–temperature conditions as MgSiO$_3$-perovskite; (2) The influence of Fe and Al on the elasticity of Mg-rich silicate perovskite, which we have estimated above; (3) physical effects not considered in this study or in the thermodynamic model of Stixrude and Lithgow-Bertelloni (2011), such as the high-spin low-spin transition in Fe or the possibility of auto-oxidation of Fe in the lower mantle. Nevertheless, our results show that the available experimental and theoretical data on lower mantle minerals is consistent with a pyrolitic mantle, and that there is currently no reason to suspect a strong chemical layering in the lower mantle.

Acknowledgements

We thank Dr. Zhu Mao for providing the high pressure PVT data measured in their recent study. We are grateful to three anonymous reviewers for their helpful comments to improve the manuscript and P. Shearer for his handling as an editor. Z.Z. would like to acknowledge the funds from the general program (#40973048) and the key programs (#90914010 and #41020134003) granted by National Natural Science Foundation of China and supporting from the China Scholarship Council for visiting research in UCL. L.S. and J.B. acknowledge support from the National Environmental Research Council. All the simulations were carried out on HECTOR (the UK national high-performance computing service) and the computational facilities in the Computer Simulation Lab of IGGCAS.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2013.07.034.

References
