# First Principles Quasiharmonic Thermoelasticity of Mantle Minerals

Renata M. Wentzcovitch

Department of Chemical Engineering and Materials Sciences and Minnesota Supercomputer Institute University of Minnesota Minneapolis, Minnesota, 55455, U.S.A.

wentzcov@cems.umn.edu

# **Zhongqing Wu**

Department of Physics & Astronomy University of Southern California Los Angeles, California, 90089-0484, U.S.A.

# **Pierre Carrier**

Department of Computer Science University of Minnesota Minneapolis, Minnesota, 55455, U.S.A.

## INTRODUCTION

Thermodynamic (Anderson 2005) and elastic properties (Musgrave 1970) of minerals provide the fundamental information needed to analyze seismic observations and to model Earth's dynamic state. The connection between pressure, temperature, chemical composition, and mineralogy that produce seismic velocity gradients, heterogeneities, and discontinuities, can be established with knowledge of thermoelastic and thermodynamic equilibrium properties of single phases and their aggregates.

There is a broad-based need in solid Earth geophysics for these thermoelastic properties to model the Earth. However, the materials and conditions of the Earth's interior present several challenges. The chemical composition of the Earth's mantle is complex with at least five major oxide components and tens of solid phases. Today, this type of challenge is more effectively addressed by a combination of experimental and computational methods. Experiments offer accurate information at lower pressures and temperatures, while computations offer more complete and detailed information at higher pressures and temperatures, where experimental uncertainties are large and conditions difficult to control in the laboratory.

The overwhelming success of density functional theory (Hohenberg and Kohn 1964; Kohn and Sham 1965) combined with the quasiharmonic approximation (QHA) (Born and Huang 1956; Wallace 1972) for computations of thermodynamic properties of major mantle minerals has been reviewed in this book (Wentzcovitch et al. 2010). Although these properties were cited and compared with experiments only at ambient conditions, in general, quasiharmonic calculations perform even better at higher pressures (see references in Wentzcovitch et al. 2010). In this paper we review the extension of these calculations to high pressure and high temperature elasticity. There are important exceptions, such as CaSiO<sub>3</sub>-perovskite, whose high temperature structure is stabilized by anharmonic fluctuations (Stixrude et al. 1996). Such cases cannot be addressed using the QHA and one must resort of molecular dynamics (MD) in some form. Great progress has been made in the last decade in this area of first principles computations of elastic constants, whether by MD (Oganov et al. 2001; Li et al. 2005, 2006b,c, 2009; Stackhouse et al. 2005) or QHA calculations (Karki et al. 1999; Wentzcovitch et al. 2004, 2006). This progress resulted from the maturing of theoretical and computational methods (Car and Parrinello 1985; Giannozzi et al. 1991; Wentzcovitch and Martins 1991; Payne et al. 1992; Baroni et al. 2001) and from the availability of stable and well-tested public domain software (Payne et al. 1992; Kresse and Furthmüller 1996; Gonze et al. 2002; Giannozzi et al. 2009) for materials computations.

The purpose of our effort has been to provide the most significant and accurate information needed to understand the fine- and large-scale structure of the mantle. A wide variety of geophysical issues of fundamental importance remain to be resolved, e.g., the geodynamic implications of upper mantle anisotropy, the causes and significance of an upper mantle low velocity zone, the significance of seismic discontinuities and high velocity gradients in the transition zone for possible mantle stratification, and whether heterogeneity in the lower mantle is primarily of chemical/mineralogical versus thermal in origin. Experimental elasticity and thermodynamic data for upper mantle and transition zone minerals are more numerous. The pressures and temperatures in the upper mantle (including the transition zone) can be more closely approached experimentally and with relatively high accuracy. While it is possible to produce extremely high pressures and temperatures in the laser heated diamond anvil cell (DAC), elasticity of relevant phases at these conditions are less well established experimentally for various reasons, including uncertainties in pressure scales, thermal gradients across laserheated samples, and other technical difficulties in characterizing the most extreme pressures and temperatures. Therefore, the emphasis of our effort has been on lower mantle phases at extreme conditions. This is the pressures and temperatures regime where theory can make the greatest impact in augmenting experimental data and producing essential information.

# THEORETICAL BACKGROUND

Several fundamental formal papers on elasticity theory have been written throughout the years (Barron and Klein 1965; Thomsen 1972; Davies 1974). There are also excellent textbooks on more fundamental aspects and one usually starts research on elasticity by studying them (Musgrave 1970; Nye 1985). Here we present a distilled version of the basic formalism for calculations of thermoelastic properties of materials. Because our calculations are performed numerically and *access directly the free energy* computed by first principles, the need for analytical treatment and approximations is minimal. The tricks are in the numerical implementation, not in the analytical development. The simplicity of the basic formalism contrasts with elaborate formal developments addressing analytically the consequences of the free energy expansion (Thomsen 1972; Davies 1974), by necessity truncated, in a power series of strains. Formal developments originated in the practical *impossibility of measurements to access directly the free energy*, but only its derivative with respect to volume, i.e., pressure, or the elastic constants via velocity measurements. Reviews of static (Karki et al. 2001a) and semi-empirical (Stixrude and Lithgow-Bertelloni 2005) approaches to elasticity of minerals discuss several useful details of elasticity calculations.

Here we focus on details of high-pressure and high-temperature QHA calculations that have not been explicitly presented yet. We treat a crystal as a homogeneous, anisotropic medium and assume that stress and strain are anisotropic. The propagation of acoustic waves in an aeolotropic medium is described by Cristoffel's equation (Musgrave 1970):

$$[C_{ijkl}n_jn_l - \rho v^2 \delta_{ik}]p_k = 0 \tag{1}$$

 $C_{ijkl}$  are the components of the (4<sup>th</sup> rank) elastic constant tensor in Cartesian coordinates, with *i*, *j*, *k*, and *l* as one of the Cartesian indexes *x*, *y*, or *z*,  $n_j$ 's are the direction cosines of the propagation direction, and  $p_k$ 's are the components of the polarization vector. This equation is true at any temperature or pressure and the eigen-solutions are three waves, one quasi-longitudinal and two quasi-transversal. Purely longitudinal and transversal polarizations occur only in isotropic materials. We will return to this point at the end of this section.

These calculations of  $C_{ijkl}$  require the definition of a finite strain induced by a large compression and of an additional superposed infinitesimal strain. The large finite strain of choice is the frame invariant Eulerian strain  $E_{ij}$ :

$$E_{ij} = \frac{1}{2} \left( f_{ij} + f_{ji} - f_{ik} f_{jk} \right)$$
(2)

with

$$X_i - a_i = f_{ij} X_j \tag{3}$$

where  $\vec{a}$  is the position vector of a point in a material in the unstrained state and  $\vec{X}$  is the position vector of the same point after the material is compressed.  $E_{ij}$  is invariably assumed to be isotropic in finite strain expansions of the free energy used to derive equations of state. This is assumed here as well.

$$E_{ij} = -f\delta_{ij} \tag{4a}$$

$$f = \frac{1}{2} \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]$$
(4b)

where  $V_0$  is a reference volume and f > 0 (< 0) corresponds to compression (extension). The Helmholtz free energy of a compressed state is then expanded in a Taylor series in these strains.

$$F(f) = a + bf + cf^{2} + df^{3} + \dots$$
(5)

This expansion includes a linear term, meaning, the reference state with  $V = V_0$  is not the zero pressure state. The temperature dependence of this free energy is temporarily omitted. The second infinitesimal strain,  $u_{ij}$ , is a Lagrangian strain associated with the deformation of the pre-compressed state:

$$x_i - X_i = u_{ij}X_j \tag{6}$$

The choice of Lagrangian versus Eulerian strain is indifferent. Lagrangian strains seem more natural in practical calculations. Its frame invariant form is:

$$e_{ij} = \frac{1}{2} \left( u_{ij} + u_{ji} - u_{ik} u_{jk} \right)$$
(7a)

or simply

$$e_{ij} = \frac{1}{2} \left( u_{ij} + u_{ji} \right)$$
(7b)

Superposition of a deformation on pre-compressed states changes Equation (5) into:

$$F(f, e_{ij}) = a(e_{ij}) + b(e_{ij})f + c(e_{ij})f^{2} + d(e_{ij})f^{3} + \dots$$
(8)

It is implicit in this formula that volume is expressed also in terms of two independent strains, f and  $e_{ij}$ . Therefore,  $V_0$  in Equation (4b) is  $V_0(0,e_{ij})$ .

The isothermal stress-strain coefficient tensor at a certain pressure and temperature  $C_{iikl}^{T}(P,T)$  is:

$$C_{ijkl}^{T}(P,T) = \frac{1}{V} \left( \frac{\partial^2 G}{\partial e_{ij} \partial e_{kl}} \right)_{P,T}$$
(9a)

with (in contracted notation)

$$P(V,T)\Big|_{T} = -\frac{\partial F(V,T)}{\partial f} \frac{\partial f}{\partial V}\Big|_{e_{ij},T} - \frac{\partial F(V,T)}{\partial e_{ij}} \frac{\partial e_{ij}}{\partial V}\Big|_{f,T}$$
(9b)

For volume conserving combinations of  $e_{ij}$ , the second term on the right-hand side of Equation (9b) essentially vanishes. The first term is essentially independent of  $e_{ij}$  for any infinitesimal strain. Then, Equation (9a) becomes:

$$C_{ijkl}^{T}(P,T) = \frac{1}{V} \left( \frac{\partial^{2} F}{\partial e_{ij} \partial e_{kl}} \right)_{f,T} + P \delta_{kl}^{ij}$$
(10a)

with

$$\delta_{kl}^{ij} = \frac{1}{V} \left( \frac{\partial^2 V}{\partial e_{ij} \partial e_{kl}} \right)_{f,T} = \frac{1}{2} \left( 2\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} \right)$$
(10b)

For these strains, one can also write changes in the free energy in the following convenient form (Wallace 1972):

$$\left. \frac{\delta F}{\mathbf{V}} \right|_{f,T} = \sigma_{ij} e_{ij} + \frac{1}{2} C^T_{ijkl} e_{ij} e_{kl}$$
(11a)

or, because of Equations (9a,b):

$$\left. \frac{\delta G}{\mathrm{V}} \right|_{P,T} = \frac{1}{2} C_{ijkl}^{T} e_{ij} e_{kl} \tag{11b}$$

Although the natural variables of the Gibbs free energy are temperature, T, and stresses,  $\sigma_{ij}$  (see Stixrude and Lithgow-Bertelloni 2005), the use of strains,  $e_{ij}$ , is possible as long as one can calculate this free energy. This is possible because pressure, i.e., the first term in the right-hand side of Equation (9b) is basically independent of  $e_{ij}$ .

Our implementation of quasiharmonic elasticity calculations proceeds as follows: a) equilibrate the crystal structure at several pressures (several f's) (Wentzcovitch et al. 1993); b) apply a series of combinations of strains,  $e_{ij}$ , positive and negative, as many as necessary, for each equilibrium structure and relax the atomic coordinates with fixed cell shape; c) compute the vibrational density of states for equilibrium and strained configurations (Baroni et al. 2001); d) the quasiharmonic free energy is then computed for all configurations generated:

$$F(f, e_{i,j}, T) = E(f, e_{i,j}) + \frac{1}{2} \sum_{q} \hbar \omega_{q}(f, e_{i,j}) + k_{B} T \sum_{q} \ln \left( 1 - \exp\left(-\frac{\hbar \omega_{q}(f, e_{i,j})}{k_{B} T}\right) \right)$$
(12)

where  $E(f,e_{ij})$  is the static total energy from first principles calculations; e) fit Equation 8 for each strain  $e_{ij}$  and temperature *T*. The temperature grid is as dense as desired. The pressure grid (read compressive Eulerian strain grid) is sparse. For example, to cover the entire pressure range of the mantle, up to ~135 GPa, the calculation in MgSiO<sub>3</sub>- perovskite required 10-15 pressures -20 GPa < P < 200 GPa. This enlarged pressure interval warrants smoothness of free energy derivatives at the end of the desired pressure interval and provides information on expanded volumes necessary to describe the state of the system at low pressures and high temperatures. Once these free energies are available one can proceed with the finite difference calculation of the second derivatives in Equation (9a) or Equation (10). Thermodynamic properties are obtained simultaneously from F(V(f), T). This procedure for calculating high-*P*, *T* elasticity is analogous to that of static elasticity calculations (Wentzcovich et al. 1995; Karki et al. 1997, 2001a), although in static calculations one obtains the first principles stress tensor (Nielsen and Martin 1985) directly.

High temperature isothermal stresses can also be calculated (Davies 1974):

$$\sigma_{ij}^{T}(P,T) = \frac{1}{V} \frac{\partial F}{\partial e_{ij}}\Big|_{f,T}$$
(13)

The isothermal constants given by Equation (9a) are relevant for comparisons with measurements in static compression experiments only. The time scale of deformation in seismic events, or in laboratory measurements of acoustic wave velocities using Brillouin scattering or resonant ultra-sonic spectroscopy, is much shorter than that of thermal diffusion for relevant length scales. Therefore, one needs to compute instead the adiabatic elastic constants. Standard algebraic manipulations involving changes of variables give:

$$C_{ijkl}^{S}(P,T) = C_{ijkl}^{T}(P,T) + \frac{VT\lambda_{ij}\lambda_{kl}}{C_{V}}$$
(14a)

with

$$\lambda_{ij}(P,T) = \left[\frac{\partial S(P,T)}{\partial e_{ij}}\right]_{f,T}$$
(14b)

where S(P,T) is the entropy. Similarly, adiabatic stresses become:

$$\sigma_{ij}^{s}(f,T) = \frac{1}{V} \frac{\partial U}{\partial \varepsilon_{ij}} \bigg|_{s,f} = \sigma_{ij}^{T}(f,T) + \frac{ST\lambda_{ij}}{C_{V}}$$
(15)

In Cartesian notation, there are 81 independent elastic constants, but this number is reduced to 21 by the requirement that  $C_{ijkl}$  are symmetric with respect to interchanges (i,j), (k,l), and (ij,kl). This allows the replacement of a pair of Cartesian indices ij by a single index  $\alpha$ , the Voigt index, according to:  $11 \rightarrow 1$ ,  $22 \rightarrow 2$ ,  $33 \rightarrow 3$ , 23 or  $32 \rightarrow 4$ , 13 or  $31 \rightarrow 5$ , 12 or  $21 \rightarrow 6$ . Simultaneously, one should also replace Cartesian strains by Voigt strains,  $\varepsilon_{\alpha}$ , such that:  $e_{ii} = \varepsilon_{\alpha}$ ,  $e_{ij} = e_{ji} = \varepsilon_{\alpha}/2$ , and  $\sigma_{ij} = \sigma_{ji} = \sigma_{\alpha}$ , with the relationship between  $ij \rightarrow \alpha$  shown above. With this replacement, one can re-write Equations (11a,b) using also Voigt indices varying from 1 to 6:

$$\left.\frac{\delta F}{V}\right|_{f,T} = \sigma_{\alpha}\varepsilon_{\alpha} + \frac{1}{2}C_{\alpha\beta}^{T}\varepsilon_{\alpha}\varepsilon_{\beta}$$
(16a)

and

$$\left. \frac{\delta G}{\mathrm{V}} \right|_{P,T} = \frac{1}{2} C_{\alpha\beta}^{T} \varepsilon_{\alpha} \varepsilon_{\beta} \tag{16b}$$

We are interested also in computing elastic properties of polycrystalline aggregates. This is an extensive subject thoroughly discussed in textbooks dedicated to elasticity (Musgrave 1970). Besides, we follow a treatment of this topic that is standard and extensively used in mineral physics. Therefore, we simply mention it here.

A purely isotropic material is viewed as a polycrystalline aggregate without preferred orientation of grains. The average elastic constants of this material are defined by the relationship between macroscopic stresses and strains. There are basically two ways to think about and calculate this relationship: i) assuming the stress is uniform across grains and strain is not or ii) assuming strain is uniform and stress is not. The uniform stress case corresponds to a state with internal relaxation at grain boundaries and gives lower bounds for the elastic constants (Musgrave 1970). This is the so-called Reuss average. The second case is the Voigt average and gives upper bounds. The average of the two averages is the Hill or Voigt-Reuss-Hill (VRH) average (Watt et al. 1976). The Voigt and the Reuss averages consist in computing the orientational averages of the elastic constant tensor, C, and compliance tensor,  $S = C^{-1}$ , respectively. The average elastic constant tensor so computed, contains only two independent elastic constants with their respective bounds:  $K_{VRH} \pm \delta K_{VRH}$  and  $G_{VRH} \pm \delta G_{VRH}$ , with  $\delta M_{VRH} = \frac{1}{2}(M_V - M_R)$ . Elastic constant tensors with preferred lattice orientations can also be calculated this way. For a detailed presentation of this topic, see Musgrave (1970). Isotropic elastic constants with tighter bounds can be obtained using the Hashin-Shtrickman variational principle (Hashin and Strikman 1962). Results for several crystalline systems have been summarized by Watt (1980).

Finally, in a isotropic medium there are two distinct wave velocities obtained from Crystoffel's equation: the longitudinal or primary velocity,  $V_p$ , and the twofold degenerate shear velocity,  $V_s$ :

$$V_{P} = \sqrt{\frac{K + \frac{4}{3}G}{\rho}}$$
 and  $V_{S} = \sqrt{\frac{G}{\rho}}$  (17)

from which the bulk sound velocity can be defined:

$$V_{\varphi} = \sqrt{\frac{K}{\rho}} = \sqrt{V_{\rho}^{2} - \frac{4}{3}V_{s}^{2}}$$
(18)

These are the basic ingredients of our calculations. We now summarize results on the high temperature elastic properties of the major lower mantle phases, MgO, MgSiO<sub>3</sub>-perovskite, and MgSiO<sub>3</sub>-perovskite, and some geophysical consequences derived from these results. Although there is by now a considerable number of papers on high temperature elasticity of mantle phases computed using MD (Oganov et al. 2001; Li et al. 2005, 2006b,c, 2009; Stackhouse et al. 2005), here we restrict ourselves to review quasiharmonic calculations only. These calculations offer elastic properties in a continuum of pressure and temperature, which is important when computing gradients of these properties. This is quite common in geophysics, particularly when trying to distinguish thermal versus compositional effects, as will be pointed out below.

#### **ELASTICITY OF LOWER MANTLE PHASES**

Earth's internal structure, temperature, and mantle phases have been summarized in the previous paper (see Figs. 1, 2, and 3 in Wentzcovitch et al. 2010). We have been primarily concerned with the elastic properties of lower mantle phases: (Mg,Fe,Al)(Si,Al)O<sub>3</sub>-perovskite, (Mg,Fe,Al)(Si,Al)O<sub>3</sub>-perovskite, (Mg,Fe)O, and CaSiO<sub>3</sub>-perovskite. Here we review the high temperature quasiharmonic elasticity of MgSiO<sub>3</sub>-perovskite, MgSiO<sub>3</sub>-post-perovskite, and MgO. Some properties of the (Mg,Fe) phases have been reviewed by Hsu et al. (2010) in this volume. Static elastic properties of the perovskite and post-perovskite containing aluminum and iron have been reported by Caracas and Cohen (2007). High temperature properties of CaSiO<sub>3</sub>-perovskite cannot be investigated using the QHA. It is a very anharmonic phase and its high temperature structure is stabilized by anharmonic fluctuations (Stixrude et al. 1996; Caracas et

al. 2005). Its elastic properties have been investigated by molecular dynamics (Li et al. 2005) and by using a free energy expansion in terms of its structural parameters (Stixrude et al. 2007). In first approximation Earth is spherical and homogeneous but there are important deviations of both. Seismic tomography (Woodhouse and Dziewonski 1984; Grand 1994; van der Hilst et al. 1997; Masters et al. 2000) reveals the 3D velocity structure of the mantle, local and global. The starting point for understanding these observations is knowledge of individual phases' elastic properties at *in situ* conditions.

These calculations have used the local density approximation (LDA) (Ceperley and Alder 1980; Perdew and Zunger 1981) combined with quasiharmonic theory (Born and Huang 1956; Wallace 1972) and density functional perturbation theory (DFPT) (Baroni et al. 2001) for phonon calculations. Variable cell shape MD is used for structural equilibration at desired pressures (Wentzcovitch 1991). The same pseudopotentials of Troullier and Martins (1991), Vanderbilt (1990) and Von Barth and Car (unpublished), cited in the appendix of Wentzcovitch et al. (2010), were used here. Computations were performed using codes of the Quantum ESPRESSO distribution (Giannozzi et al. 2009).

## MgO

Periclase (MgO) was the first system to have its high temperature elastic properties investigated by this fully first principles approach (Karki et al. 1999). The original results, including some small discrepancies from experiments, have been reproduced since then. MgO is the most anisotropic phase of the lower mantle (Wentzcovitch et al. 2006) and its anisotropy is strongly pressure dependent. Its thermodynamic properties (Karki et al. 2000b), including anharmonic effects (Wu et al. 2008; Wu and Wentzcovitch 2009) were summarized in Wentzcovitch et al. (2010). Although temperature effects on its elasticity at ambient conditions are known to be substantial and to counteract the effect of pressure (Isaak et al. 1989; Chen et al. 1998), elasticity at deep lower mantle conditions have not been measured so far. *A posteriori* inspection of the quasiharmonic thermal expansivity (see Wentzcovitch et al. 2010) indicates that this is a good approximation for MgO at 0 GPa up to ~1,100 K and even better at geophysically relevant conditions (Wu and Wentzcovitch 2009).

The elastic constants of this materials with rocksalt structure (see Wentzcovitch et al. 2010), C<sub>11</sub>, C<sub>12</sub>, and C<sub>44</sub>, were obtained up to 150 GPa and 3,000 K (Karki et al. 1999) by calculating the free energies for strained lattices. For cubic systems, volume conserving strains (tetragonal and trigonal) allow the determination of  $C_{44}$  and of  $C_s = (C_{11} - C_{12})/2$ , for which isothermal and adiabatic values are identical. Isothermal or adiabatic values of the bulk modulus,  $K = (C_{11} + 2 C_{12})/3$ , are then used together to obtain the corresponding values of  $C_{11}$  and  $C_{12}$ . The predicted ambient values and their initial pressure and temperature gradients agree quite well with measurements (Isaak et al. 1989; Sinogeikin and Bass 1999) (see Table 1, Figs. 1 and 2). As seen in Table 1, except for  $C_{11}$ , the predicted  $C_{ii}$  at ambient conditions are smaller than the experimental values. This is typical of DFT calculations that overestimate the equilibrium volume (see Table 1), in this case  $\sim 0.5\%$ . So far, LDA has proved to be the best functional for calculations of structural and elastic properties of minerals at finite temperatures (Wentzcovitch et al. 2010) but the small volume overestimation causes the elastic constants to be underestimated.  $C_{44}$  in particular is the most underestimated. The reason is unclear but this result is reproduced still today. However, the temperature dependence of  $C_{44}$  is best reproduced (see Fig. 1). The temperature gradients of  $C_{ij}$  at 0 GPa are well predicted for all  $C_{ij}$ , but above ~1,250 K the QHA gradients, especially of  $C_{11}$  and  $C_{12}$  start deviating from experimental values. As discussed in Wentzcovitch et al. (2010) this is caused by unharmonic effects. The predicted cross P-T derivatives of  $C_{ii}$  are smaller (with opposite sign) than those obtained by experiments on MgO to 8 GPa and 1600 K (Chen et al. 1998). However, QHA results are consistent with earlier data to 0.8 GPa and 800 K (Spetzler 1970) (Table 1) and potential-induced breathing (PIB) model calculations (Isaak et al. 1990).

	<i>c</i> <sub>11</sub>	<i>c</i> <sub>12</sub>	C <sub>44</sub>	<i>c</i> <sub>110</sub>	K <sub>S</sub>	G
LDA+QHA ( $V_0 = 18$	.81Å <sup>3</sup> /cell)					
M (GPa)	298	94	147	344	162	128
$\partial M/\partial P$	9.56	1.45	1.03	6.39	4.15	2.44
$\partial M/\partial T$ (GPa/K)	-0.0598	0.0089	-0.0088	-0.0343	-0.0140	-0.0216
$\partial M^2/\partial P \partial T (10^{-3}/\mathrm{K})$	0.56	-0.06	0.20	0.45	0.14	0.44
Experiments ( $V_{exp} =$	18.69Å <sup>3</sup> /cell	I)				
<i>M</i> (GPa) *	297.9(15)	95.8(10)	154.4(20)	351.3(22)	163.2(10)	130.2(10)
$\partial M / \partial P *$	9.05(20)	1.34(15)	0.84(20)	6.04(37)	4.0(1)	2.4(1)
$\partial M/\partial T$ (GPa/K) +	-0.0585	0.0075	-0.0126	-0.0381	-0.0145	-0.024
$\partial M^2/\partial P \partial T^{\#}(10^{-3}/\mathrm{K})^{\$}$	-1.3(4)	5.1(24)	-0.2(3)	1.7(7)	3.0(15)	-1.8(10)
	0.1(4)	0.1(3)	0.1(1)	0.0(1)	0.1(3)	0.l(2)

**Table 1.** Adiabatic elastic moduli (*M*) of MgO and their pressure and temperature derivatives at ambient conditions. The modulus  $c_{110}$  corresponds to elastic modulus for the longitudinal wave along [110] direction. Numbers in parentheses are experimental uncertainties. From Karki et al. (1999).

\* Sinogeikin et al. (1998), + Isaak et al. (1989), # Chen et al. (1998), \$ Spetzler (1970)

The pressure-induced change of sign in the single-crystal anisotropy, as expressed by the anisotropy factor:

$$A = \frac{(2C_{44} - C_{11} + C_{12})}{C_{11}}$$
(19)

is characteristic of MgO (Sinogeikin and Bass 1999; Duffy et al. 1995). This quantity expresses the breakdown of the Cauchy relation that holds for isotropic materials. Our results show that the strong pressure dependence of the anisotropy in MgO is preserved at high temperatures (Fig. 3). Temperature effects counteract pressure effects and are monotonically suppressed with increasing pressure. MgO is the most anisotropic phase of the lower mantle at core-mantle boundary (CMB) conditions, as will be seen below. Therefore, lattice-preferred orientation (LPO) in MgO is a possible cause of anisotropy observed in this region.

The isotropic longitudinal  $(V_P)$  and shear  $(V_S)$  wave velocities of MgO along several isotherms are shown in Figure 4. The pressure dependence of  $V_S$  agrees very well with 300 K experiments up to ~100 GPa (Murakami et al. 2009). In the lower mantle, the properties of MgO are modified by the presence of iron (see Hsu et al. 2010). The wave velocities of ferropericlase, (Mg,Fe)O, are smaller and the longitudinal velocity is affected by the high spin to low spin crossover of iron at lower mantle pressures (Wentzcovitch et al. 2009; Hsu et al. 2010). In fact all thermodynamic properties are affected by this crossover (Wu et al. 2009).

The seismic parameters:

$$R_{S/P} = \frac{\partial(\ln V_S)}{\partial(\ln V_P)}\Big|_{P}, \quad R_{\phi/S} = \frac{\partial(\ln V_{\phi})}{\partial(\ln V_S)}\Big|_{P}, \quad \text{and} \quad R_{\rho/S} = \frac{\partial(\ln \rho)}{\partial(\ln V_S)}\Big|_{P}$$
(20)

express the relative magnitude of lateral (isobaric) variations in  $V_S$ ,  $V_P$ ,  $V_{\phi}$  (Eqn. 17 and 18), and density  $\rho$  in the mantle. Seismic tomography (Dziewonski and Woodhouse 1987; Grand 1994; Masters et al. 2000), as summarized by Karato and Karki (2001), indicates that  $R_{S/P}$  increases



**Figure 1.** Temperature dependence of the elastic moduli of MgO at 0 GPa. Experimental data (Isaak et al. 1989) are shown as open circles.

150



Bass 1999). The zero pressure data at 300, 1000, and 1800 K are indicated by diamonds (Isaak et al. 1989). From Karki et al. (uppermost curve) K isotherms. Dashed lines correspond to lowpressure (18.6 GPa) data at ambient temperature (Sinogeikin and of MgO along 300 (lowest curve), 1,000, 2,000, and 3,000 1999.



Figure 4. Pressure dependence of velocities of MgO along various isotherms. Experimental data are denoted by solid triangles (Li et al. 2006a), open circle (Sinogeikin and Bass 1999),

solid circles (Murakami et al. 2009), and dashed lines (Zha et al. 2000), respectively.

from more than ~2.0 to more than 3.0 from the top to the bottom of the lower mantle. Possible causes of lateral velocity variations include variations of temperature, composition, phase, etc. High temperature experiments at ambient pressure have yielded  $R_{S/P} \sim 1.5$  for thermally induced v (Isaak et al. 1989). These QHA velocities constrain "thermal"  $R_{S/P}$  in MgO to vary from ~1.4 at the top to ~1.9 at the bottom of the lower mantle. Earlier PIB calculations estimated  $R_{S/P} \sim 2.5$  in this region (Isaak et al. 1990). As will be seen below, lateral temperature change in the bottom of the mantle can induce the post-perovskite transition (Tsuchiya et al. 2004; Oganov and Ono 2004; Wentzcovitch et al. 2010). Lateral temperature *and* phase change can increase considerably this parameter (Wentzcovitch et al. 2006). For a more extensive discussion of lateral variations in the mantle see Stixrude and Lithgow-Bertelloni (2007).

#### MgSiO<sub>3</sub>-perovskite

Owing to its abundance in the Earth lower mantle (LM) (see Fig. 1 and 2 in Wentzcovitch et al. 2010) the elastic properties of MgSiO<sub>3</sub>-perovskite (perovskite henceforth), more precisely (Mg,Fe)SiO<sub>3</sub>, determine to a great extent the properties of this region. *In situ* conditions, with temperatures varying from ~1,900 K to 4,000 K, are still challenging for elasticity measurements, even though elasticity measurements in the entire pressure range of the mantle is now possible (Murakami et al. 2009). Therefore, these first principles calculations have been essential to advance understanding of the state of the lower mantle. Single crystal and aggregate elastic properties of perovskite and of other mantle phases have been used to predict acoustic velocities of hypothetical lower mantle aggregates. Comparison with the spherically averaged seismic velocity profiles of this region (Dziewonski and Anderson 1981) have then made to test the plausibility of homogeneous mineralogical models (Stixrude et al. 1992; da Silva et al. 2000; Karki et al. 2001b; Wentzcovitch et al. 2004; Xu et al. 2008). These comparisons aim to resolve, for instance, the problem of compositional stratification in the mantle, with implications for the style of thermochemical convection that has been operating in the Earth.

Perovskite has orthorhombic (*Pbnm*) symmetry and 9 independent elastic constants ( $C_{ij}$ henceforth), 3 diagonal ( $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ), 3 off-diagonal ( $C_{12}$ ,  $C_{13}$ ,  $C_{23}$ ), and 3 shear ( $C_{44}$ ,  $C_{55}$ ,  $C_{66}$ )  $C_{ij}$ . Its adiabatic  $C_{ij}$  at ambient conditions are summarized and compared to experimental data in Table 2. As can be seen, the LDA/QHA (Wentzcovitch et al. 2004) equilibrium volume at ambient conditions is  $\sim 1.2\%$  larger than the experimental volume (Karki et al. 2000b). This "expanded" volume causes substantial underestimation of  $C_{ij}$ . The thermodynamics properties of perovskite were summarized in Wentzcovitch et al. (2010) and the source of this discrepancy does not appear to be the QHA. The generalized gradient approximation (GGA) (Wang and Perdew 1991; Perdew et al. 1996) overestimates this volume even further (Carrier et al. 2007) (on these two issues, see discussion in Wentzcovitch et al. 2010). However, this discrepancy should decrease with pressure and these predictions should be more reliable, especially predictions of pressure and temperature gradients.  $C_{ii}$  at LM conditions are shown in Figure 5 compared with results of MD simulations using the GGA (Oganov et al. 2001). Both sets of results "shifted" pressure to bring ambient condition values into agreement with experimental values. The overall good agreement between these results is more than coincidence. Pressure shift to correct problems with DFT results is not a good practice (Wu et al. 2008) since the problem caused by DFT decreases with pressure (increasing density). A better perspective of the discrepancy between calculations and measurements of aggregated elasticity and velocities is shown in Figure 6, where no shift is applied to QHA/LDA results. In the overall scale of changes in  $C_{ij}$  caused by pressure and temperature, as well as experimental uncertainties, the discrepancy is relatively small, and the accuracy of these results is still useful.

Without losing perspective of these errors and uncertainties, it is still possible to extract sensible information about the state of the lower mantle. Figure 7 displays the adiabatic bulk and shear moduli,  $K_S$  and G, for isotropic and homogeneous mineralogical models along a standard adiabatic geotherm (Brown and Shankland 1981) that nearly coincides with the isentropes

results at ambient conditions (Wentzcovitch et al. 2004); equilibrium volume is listed in parentheses in first column; (2) range of values obtained in static ultrasonic measurements (<sup>+</sup>) (Sinelnikov et al. 1998), (\*) (Li and Zhang 2005), and (<sup>#</sup>) (Sinogeikin et al. 2004) the experimental equilibrium volume is listed at parentheses of first column; (4) at ambient conditions and (4') at 300 K and 100 GPa; (5) experimental values at ambient conditions obtained by ultrasonic Table 2. Adiabatic elastic constants, their pressure and temperature derivatives, and wave velocities of MgSiO<sub>3</sub>-perovskite predicted by LDA+QHA: (1) density functional theory calculations (Wentzcovitch et al. 1998; Kiefer et al. 2002); (3) experimental values obtained by Brillouin (Yeganeh-Haeri 1994), measurements (Li and Zhang 2005). From Wentzcovitch et al. (2004)

$V_{ m S}$	6.32	6.53	 6.51	6.57, 6.56+, 6.49*,6.53#	0.028	0.003		-0.0002	-0.0001		0.00001
$V_{ m P}$	10.58	10.94	 10.89	$11.04, 10.88^{\#}$ $10.86^{*}$	0.07	0.020		-0.0003	-0.0001		0.00002
G	162	179	 175	177, 173*, 175 <sup>+,#</sup>	2.1	1.0	2.0	-0.0231	-0.01	-0.028	0.0005
Ks	238	263	 257	264, 253*,#	5.07	3.11	4.4	-0.027	-0.006	-0.021	0.0006
C 23	142	156	 144	146	3.7	2.3		-0.001	0.004		0.00
c <sub>13</sub>	127	144	 135	147	3.4	2.3		-0.002	0.002		0.0001
c <sub>12</sub>	121	134	 128	144	4.5	3.2		-0.018	-0.002		0.0004
C 66	138	153	 145	147	2.7	1.4		-0.030	-0.016		0.0004
C <sub>55</sub>	165	186	 173	186	2.0	0.7		-00.00	0.001		0.0002
C44	185	203	 198	204	2.5	1.3		-0.025	-0.014		0.0003
C33	428	474	 456	485	9.4	5.0		-0.073	-0.020		0.0015
C 22	496	560	 524	537	8.7	5.0		-0.072	-0.031		0.000
¢11	444	491	 477	482	7.6	3.1		-0.058	-0.015		0.0012
	(1) $M(164.1 \text{\AA}^3)$	(2) <i>M</i>		(3) $M$ (162.3Å <sup>3</sup> )	(4) <i>∂M/∂P</i>	(4') <i>∂M/∂P</i>	(5) <i>∂M/∂P</i>	(4) <i>∂M/∂T</i>	(4') <i>∂M/∂T</i>	(5) <i>∂M/∂T</i>	(4) <i>∂M<sup>2</sup>/∂P∂T</i>





111

Presure (GPa)

dynamic simulation results of Oganov et al. (2001) (empty symbols) and Marton and Cohen

(2002) (solid symbols).



**Figure 7.** Bulk ( $K_S$ ) and shear (G) moduli for (Mg<sub>(1-x)</sub>Fe<sub>x</sub>)SiO<sub>3</sub>-perovskite and pyrolite with 20% <  $V_{\rm fp}$  < 30% (ferropericlase = Mg<sub>(1-y)</sub> Fe<sub>y</sub>O) along the Brown and Shankland (1981) geotherm. 0.0 < x < 0.12 and 1 < y/x < 4. The effect of iron on the elastic moduli of perovskite and ferropericlase were extracted from Kiefer et al. (2002) and Jackson (1998), respectively. From Wentzcovitch et al. (2004).

of MgSiO<sub>3</sub> and MgO (Karki et al. 2000a,b). The mineralogical models consist of pure perovskite,  $(Mg_{(1-x)}Fe_x)SiO_3$ , with *x*~0.12 and pyrolite (Jackson 1998), which contains ~20 vol% of ferropericlase,  $(Mg_{(1-y)}Fe_y)O$ , with *y*~0.18. Iron partitioning (*y/x*) between these phases was allowed to vary in the range 1 < y/x < 4 for fixed Fe/Mg ratio. The effect of iron on the elasticity of perovskite was taken from static calculations (Kiefer et al. 2002) and was assumed to be temperature independent. The effect of iron on the elasticity of ferropericlase was taken from 300 K experiments (Jackson 1998) (see Fig. 7 caption). The effect of Al<sub>2</sub>O<sub>3</sub> in solid solution with perovskite (Tschermak substitution, with an Al-Al pair replacing a pair of Mg-Si in perovskite) on its elastic moduli, was assumed to be small in view of the large difference between the elastic moduli of perovskite and ferropericlase and was disregarded. The elastic moduli of CaSiO<sub>3</sub>-perovskite in the LM (~5 mol%) was also taken to be similar to that of perovskite in view of the same differences. Voigt-Reuss-Hill aggregate averages for *K<sub>S</sub>* and *G* result in the profiles shown in Figure 7.

The overall smaller  $K_S$  of pyrolite agrees reasonably well with  $K_{PREM}$ , the bulk modulus of the preliminary reference Earth model (PREM) (Dziewonski and Anderson 1981), in the upper part of the lower mantle (down to ~1,400 km depth or 55 GPa). Both mineralogical models describe  $G_{PREM}$  reasonably well in the upper lower mantle for reasonable ranges of x and y/x. However, regardless of the content of ferropericlase, x, or, y/x, with increasing depth  $K_{PREM}$ and  $G_{PREM}$  seem to depart consistently and in opposite directions from the values predicted along the geotherm. For depths greater than ~1,400 km,  $K_s$  and G develop pressure gradients that are slightly larger and somewhat smaller than PREM values. Modification of the geotherm would alter  $K_S$  and G simultaneously in the same direction. Inclusion of possible anelastic effects (Karato and Karki 2001) would make it even more difficult to reconcile  $G_{PREM}$  with values of G predicted for reasonable geotherms and compositions in this range. The elasticity CaSiO<sub>3</sub>-perovskite and of Al<sub>2</sub>O<sub>3</sub> in solid solution with perovskite, still need to be incorporated in the model. However, unless their elastic behaviors differ considerably from perovskite's, particularly their pressure and temperature gradients, these results suggested that the deep and the shallow lower mantle differ somehow. In particular,  $G_{PREM}$  appears to be larger than the predicted G. There are several possible geophysical reasons for this, besides the number of approximations involved in this calculation. Radial chemical and/or phase heterogeneity are some of the possibilities. Indeed, we know today that there is a new phase present in the deep mantle, i.e., MgSiO<sub>3</sub>-post-perovskite (to be discussed next). The shear modulus of this phase is larger than that of perovskite by ~20 GPa at D" conditions, which extends up to ~300 km above the CMB. PREM does not show the discontinuity most likely associated with this phase change. It has wide topography (~300 km wide) and the positive velocity jump in *G* associated with this phase change is smoothed by PREM. This topic is reviewed next.

## MgSiO<sub>3</sub>-post-perovskite

Post-perovskite is almost unanimously accepted to be the predominant phase of MgSiO<sub>3</sub> just above the core mantle boundary (CMB), the D" region. Its discovery (Murakami et al. 2004; Oganov and Ono 2004; Tsuchiya et al. 2004) has had multidisciplinary impact in geophysics. High temperature elasticity calculations of this phase produced revealing results that, when compared with seismic data, suggest its presence in the D" layer. Therefore, in this section will make reference to geophysical issues more than in any other. The importance of these calculations to geophysics will be abundantly demonstrated here.

Post-perovskite has orthorhombic structure (*Cmcm*) and 9 independent  $C_{ij}$ , like perovskite (Tsuchiya et al. 2004; Wentzcovitch et al. 2006). They are quite different from perovskite's (see Table 3). Post-perovskite has a layered structure (see Fig. 6b in Wentzcovitch et al. 2010), expands anisotropically, and has complex pressure- and temperature-dependent elastic behavior. However, its aggregate moduli do not differ so much from those of perovskite. Thermodynamic properties of both phases,  $K_s$ , are quite similar beyond ~80 GPa (Tsuchiya et al. 2005). The shear modulus of post-perovskite, G (Fig. 8a), is larger and has larger pressure and temperature gradients. This result and the fact that post-perovskite is  $\sim 1.5\%$  denser than perovskite at deep lower mantle conditions determine the velocity contrasts between these phases. The shear velocity,  $V_S$ , of post-perovskite and its gradients (Fig. 8b) are larger than those of perovskite (Fig. 6b). Because of G,  $V_S$  of post-perovskite is also larger and has larger gradients. In contrast, the bulk velocity,  $V_{\phi}$  (Eqn. 18), is smaller than that of perovskite because of their similar  $K_S$ and post-perovskite's larger density. Figure 8c shows the velocity jumps across the calculated phase boundary (see Fig. 21 in Wentzcovitch et al. 2010) (see Fig. 8c caption). These results are consistent with the increase in seismic velocities observed ~200-300 km above the core-mantle boundary in certain places (Lay and Helmberger 1983) but most easily detected beneath regions of past subduction, presumably colder places, such as beneath Central America (Lay and Helmberger 1983; Wyssession et al. 1998; Garnero 2004). There,  $V_{\rm S} > V_{\rm P}$  and  $\Delta V_{\rm S} \sim 2-3\%$  is observed, but this observation is clearly a regional property of a notably heterogeneous layer.

Another baffling property of D" revealed by global tomographic models (Woodhouse and Dziewonski 1984; Grand 1994; Masters et al. 2000) is the anti-correlation between lateral (isobaric) heterogeneities in  $V_{\phi}$  and  $V_{s}$ . The likely causes are usually addressed by comparing the seismic parameters,  $R_{S/P}$ ,  $R_{\phi/S}$ , and  $R_{\rho/S}$  (see Eqn. 20) to theoretical or experimental predictions of these ratios at relevant conditions (Karato and Karki 2001). It is known that in the shallow lower mantle  $R_{S/P} \sim 2.3$  and  $R_{\phi/S} \sim 0.0$ , whereas in D"  $R_{S/P} \sim 3.4$  and  $R_{\phi/S} \sim -0.2$  (Masters et al. 2000). Velocity anomaly ratios produced by isobaric temperature changes in pure post-perovskite and perovskite aggregates are displayed in Figure 9a,b along with the seismic parameters extracted from Karato and Karki (2001). In pure perovskite aggregates,  $R_{SP}$  increases with pressure and temperature but reaches at most ~2.3 at 135 GPa and 4,000 K, whereas  $R_{\phi/S}$  is approximately pressure independent and slightly decreases with temperature to reach ~0.16 at similar conditions (see Fig. 2a). In post-perovskite  $R_{S/P}$  decreases with pressure, but because of its larger  $(\partial G/\partial T)_P$ , it increases more rapidly with temperature to reach ~ 2.8 at the same conditions.  $R_{\phi/S}$  is smaller than that of perovskite, ~0.1, at these conditions (see Fig. 9a,b). It has been argued that anelasticity, anisotropy, and lateral variations in calcium content in the deepest mantle might be necessary to produce these large  $R_{S/P}$  and negative values for  $R_{\phi/S}$  (Karato and Karki 2001). Figure 9c compares the seismic parameters with the computed ratios of velocity anomalies

<b>Table 3.</b> Elastic profand $(3)$ 140 GPa and $1\%$ . $B_s$ and $G$ are Vo tions in individual $c_{ij}$	erties in GPa, km 4000 K. Diagona igt-Reuss-Hill av are averaged out	Ns, and K of Mg ll $c_{ijs}$ are typicall- eraged adiabatic (). $V_{\rm P}$ , $V_{\rm S}$ and $V_{\Phi}$	(SiO <sub>3</sub> (1) perovsly underestimated y underestimated is bulk and shear are are compression	ite and post-per lby ~2%, off dia moduli. Typicall al, shear, and bu	ovskite ((2), (4), gonal ones by ~1 y they are undere ilk velocities. [Fr	(5), (6)) at 125 G .5%, and shear or stimated by 2% om Wentzcovitch	iPa and 2500 K nes by less than (random devia- n et al. 2006.]
	$c_{11}$	$c_{22}$	$c_{33}$	C <sub>12</sub>	$c_{13}$	C 23	$c_{44}$
(1) M	874	1095	1077	539	436	469	311
(2) M	1146	888	1139	454	418	507	311
(3) M	1119	006	1131	498	486	536	343
(4) <i>∂M/∂P</i>	6.4	4.5	6.3	2.9	2.3	2.5	3.1
(5) <i>∂M/∂T</i>	-0.083	-0.037	-0.069	0.0011	0.022	-0.0054	-0.011
(6) $\partial^2 M / \partial P \partial T$	0.00061	0.00017	0.00026	-0.000063	0.000089	-0.00013	0.00076
	C <sub>55</sub>	$c_{66}$	$B_{\rm S}$	G	$V_{ m P}$	$V_{ m S}$	$V_{\Phi}$
(1) <i>M</i>	255	296	655	276	13.9	7.2	11.1
(2) M	238	352	656	294	14.0	7.4	11.1
(3) M	231	326	685	284	14.0	7.3	11.3
(4) <i>∂M/∂P</i>	2.2	2.7	3.6	2.2	0.032	0.022	0.022
(5) <i>∂M/∂T</i>	-0.028	-0.045	-0.017	-0.030	-0.00029	-0.0003	-0.000073
(6) $\partial^2 M / \partial P \partial T$	0.00030	0.00014	0.000063	0.00032	0.0000035	0.0000053	0.0000012



**Figure 8.** Pressure dependence of (A) aggregate adiabatic bulk (BS) and shear (G) moduli and density ( $\rho$ ) of post-perovskite along the 300 K (uppermost), 1000 K (second from top), 2000 K (thrid from top), 3000 K (fourth from top) and 4000 K (fifth from top) isotherms; (B) isotropic longitudinal ( $V_P = [(B_S + 4G/3)/\rho]^{1/2}$ ), shear ( $V_S = (G/\rho)^{1/2}$ ) and bulk ( $V_S = (B/\rho)^{1/2}$ ) wave velocities. Filled circles in (A,B) are PREM values (Dziewonski and Anderson 1981) for comparison; (C) velocity jumps across the previously obtained phase boundary (Tsuchiya et al. 2004). Thick black lines represent the jumps at the center of our phase boundary with a DFT related uncertainty of 10 GPa. Shaded areas are possible values throughout the boundary uncertainty domain (Tsuchiya et al. 2004)). Open triangles and squares are respectively results from MD simulations at 135 GPa and 4,000K and 136 GPa and 3,000 K (Stackhouse et al. 2005). The vertical dashed line indicates approximately the topmost location of the D" discontinuity. From Wentzcovitch et al. (2006).



**Figure 9.** Seismic parameters  $R_{S/P} = (\partial \ln V_{S}/\partial \ln V_P)_P$ ,  $R_{\phi/S} = (\partial \ln V_{\phi}/\partial \ln V_P)_P$ , and  $R_{\rho/S} = (\partial \ln p/\partial \ln V_S)_P$  at several temperatures for post-perovskite (A) and perovskite (B) (sequence same as in Fig. 8 but now starting from 1000 K). These values are presented for comparison. Filled circles with error bar ( $\pm 20\%$ ) are from MD simulations (Stackhouse et al. 2005). (C) Contribution of phase transition to these parameters with uncertainties (shaded blue areas) related to phase boundary computation (same as in Fig. 8C). Seismic values extracted from (Master et al. 2000) and uncertainties (gray shaded areas) were summarized in (Karato and Karki 2001). From Wentzcovitch et al. 2006.

caused by the post-perovskite transition along our phase boundary (Fig. 21 in Wentzcovitch et al. 2010). Very large values for  $R_{S/P}$  (~6) and negative values for  $R_{\phi/S}$  (-0.5) result from this phase change. Therefore, lateral variation in phase abundances enhances the seismic parameters in the correct directions. The presence of secondary phases, such as ferropericlase and CaSiO<sub>3</sub>, should decrease these ratios. Besides, the real multicomponent system should produce a *PT* domain for co-existence between these phases, decreasing these anomalies. Nevertheless, lateral variation in the abundances of these phases produces robust results in the right direction.

As pointed out from the outset, the topography of D'' is consistent with a solid-solid phase transition with positive Clapeyron slope (4-10 MPa/K) induced by lateral temperature variations

(Sidorin et al. 1999). Interestingly, the correlation between geographic location and nature of  $V_{\phi}$  and  $V_{S}$  anomalies is also consistent with this assumption if post-perovskite is present in D". Beneath the Central Pacific  $V_{\phi}$  is faster and  $V_{S}$  is slower than their spherical mantle averages, whereas beneath the Circum-Pacific the opposite holds (see Masters et al. 2000 and references therein). These regions are generally considered to be respectively hotter and colder than average. The positive Clapeyron slope of this transition implies that hotter regions should contain less post-perovskite and therefore have faster  $V_{\phi}$  and slower  $V_{S}$ , whereas colder regions should be enriched in the latter and have slower  $V_{\phi}$  and faster  $V_{S}$ , as observed. Lateral variations in phase abundances alone do not account for the complex structure and properties of D". However, this perspective should be useful as a reference model from which interpretations of deviations might be sought.

These results indicate that  $R_{\rho/S}$ , the third parameter in Equation (20), caused by the postperovskite transition, should be positive and perhaps increase with depth in the lowermost mantle (see bottom row in Fig. 9), unless anelasticity or chemical heterogeneities occur simultaneously. Some 3D density models do not support this prediction (Ishii and Tromp 1999), whereas others do (Romanowicz 2001). Estimates of this parameter obtained by joint inversions of seismic and geodynamic data also tend to offer a positive ratio (Forte et al. 1994). It appears that until a consensus on the 3D structure of  $\rho$  is reached, this issue will remain open. It has been pointed out that an average excess density of 0.4% in the lowermost mantle is possible (Masters and Gubbins 2003), in agreement with our expectations.

Another pressing issue is the anisotropy of D", a case of boundary layer anisotropy. Flow in these regions have a significant horizontal component and can align grains with preferred orientation if some of the phases present are in the dislocation creep regime. Despite multiple anisotropy styles observed (Wysession et al. 1998) and the numerous possible sources of anisotropy (Kendall and Silver 1998), evidences suggest that anisotropy in certain places of D" could result from lattice preferred orientation in largely strained aggregates produced be mantle circulation. Beneath regions of past and present subduction, such as the Caribbean, where colder than average and largely deformed paleo-plates are expected to reside and horizontal flow is expected, transverse anisotropy with  $V_{\text{SH}} > V_{\text{SV}}$  is generally observed ( $V_{\text{SH(SV)}}$ is the velocity of horizontally (vertically) polarized shear waves propagating horizontally). It is plausible that in post-perovskite the primary slip system involves (010) (silica "layers" reside in this plane). Lateral material displacement could then align mainly the silica layers parallel to the horizontal plane. However, this simple picture did not provide a satisfactory explanation for the anisotropy in D" (Tsuchiya et al. 2004).

Figure 10 shows "shear wave splittings" at conditions of the thermodynamic postperovskite phase boundary (see Figure 21 in Wentzcovitch et al. 2010) for some preferred alignments of the crystalline axes of MgO, perovskite, and post-perovskite in the vertical direction of transversely anisotropic aggregates. Such aggregates have a particular crystalline axis oriented vertically and random orientation of axes in the horizontal plane (see Fig. 10 caption). It is seen that at relevant conditions (i) the vertical alignment of [001] in postperovskite produces the largest positive  $(V_{SH} - V_{SV})$  splitting; (ii) the shear wave splittings in perovskite and post-perovskite have similar magnitudes regardless of orientation; (iii) vertical alignment of perovskite's [100] produces positive  $(V_{SH} - V_{SV})$ ; and (iv) horizontal alignment of MgO's {100}, its primary slip plane at high Ps (Yamazaki and Karato 2002), produces considerably larger ( $V_{\rm SH} - V_{\rm SV}$ ). Despite lack of direct information on the slip systems of these phases at D" conditions, it appears that unlikely that post-perovskite can be a more significant source of anisotropy in D" than perovskite. Despite being less abundant (20 vol%) periclase is the most anisotropic phase. It is also weaker than the other phases. It is therefore likely to undergo more extensive deformation (Yamazaki and Karato 2002) and be a more important source of anisotropy in D''.



Figure 10. Shear wave splittings,  $(V_{\rm SH} - V_{\rm SV})$ , in MgSiO<sub>3</sub> post-perovskite and perovskite at the post-perovskite phase boundary conditions with respective uncertainty.  $V_{SH(SV)}$  is the velocity of a horizontally (vertically) polarized shear wave propagating horizontally in aggregates with transverse anisotropy. Such aggregates have one crystalline axis aligned vertically and randomly oriented of axes in the horizontal plane. For [001] aligned vertically,  $V_{\rm SH} = (N/\rho)^{1/2}$  and  $V_{\rm SV} = (L/\rho)$  where, N = (1/8) $(C_{11} + C_{22}) - (1/4)C_{12} + (1/2)$  $C_{66}$  and  $L = (1/2)(C_{44} + C_{55})$ (Wentzcovitch et al. 1998). Velocities for aggregates with [100] and [010] aligned vertically can be obtained by cyclic permutation of indices. From Wentzcovitch et al. (2006).

## SELF-CONSISTENT QHA

The QHA, as discussed here and in the previous article (Wentzcovitch et al. 2010), is a simple and powerful method for evaluating free energies using phonon frequencies obtained by first principles (Baroni et al. 2010 in this volume). There is still another useful consequence of this approximation not often appreciated: it can predict also complex crystal structures at high pressures and temperatures using only results obtained for equilibrium ( $e_{ij} = 0$ ) configurations (Carrier et al. 2007). For clarity sake we repeat here the expression of the QHA free energy:

$$F(V,T) = E(V) + \frac{1}{2} \sum_{q} \hbar \omega_{q}(V) + k_{B}T \sum_{q} \ln \left( 1 - \exp\left(-\frac{\hbar \omega_{q}(V)}{k_{B}T}\right) \right)$$
(21)

U(V) is the DFT static energy versus volume obtained after full structural relaxation under isotropic pressure and  $\omega_q(V)$  is the phonon spectrum for these fully relaxed structures. Crystal structure parameters and phonon frequencies are uniquely related to volume since their values under pressure have been determined by static calculations and are given at  $P_{stat}(V)$  only. At T=T', the pressure P'(V,T'), contains the following contributions:

$$P' = P_{stat} + P_{ZP} + P_{th} \tag{22}$$

where,  $P_{stat}$ ,  $P_{ZP}$ , and  $P_{th}$  are the negative volume derivatives of the three terms in the righthand side of Equation (21), respectively. No further structural relaxation is performed at T'. The function V(P',T') is obtained by inverting P'(V,T'). Therefore, if  $V(P',T') = V(P_{stat})$ , structural parameters at P', T' are equal to those at  $P_{stat}$ . This is the *statically constrained QHA* (sc-QHA). The validity of this approximation can be tested by comparing its predictions with some available high *P*,*T* experimental data. If the result is favorable, it asserts the validity of the sc-QHA in that *P*,*T* range. In general, this is expected if the temperature is in the domain of validity of the QHA. This can be assessed by *a posteriori* inspection of the predicted QHA thermal expansivity (see Fig. 8 in Wentzcovitch et al. 2010).

MgSiO<sub>3</sub>-perovskite is one of the materials most studied at high pressures and temperature. There is a wealth of crystallographic data (Fiquet et al. 1998; Funamori et al. 1996; Ross and Hazen 1989, 1990; Utsumi et al. 1995) available up to 60 GPa and ~2,670 K. Its orthorhombic structure has 20 atoms per primitive cell and 10 degrees of freedom: 3 lattice parameters and 7 internal parameters. Figure 11 (see caption) displays experimental lattice parameters (data points) obtained at various conditions plotted against volume, irrespective of pressure and temperature, and compares them with parameters determined by static LDA calculations (full line) (Carrier et al. 2007). Clearly *all* experimental lattice parameters obtained at various



**Figure 11.** Comparison between lattice parameters predicted by the QHA and experimental data as a function of volume. The LDA and LDA + zero-point-motion-energy equilibrium volumes are also compared to the experimental equilibrium volume at 0 GPa. Experimental data are from Figuet et al. (1998), Funamori et al. (1996), Ross and Hazen (1989, 1990), Utsumi et al. (1995), Wang et al. (1994). Temperatures vary from 295 to 1024 K for Wang et al. (1994) from 293 to 2668 K for Fiquet et al. (1998), from 298 to 1173 K for Utsumi et al. (1995), from 293 to 2000 K for Funamori et al. (1996) and from 77 to 400 K for Ross and Hazen (1989, 1990). Solid lines are from static calculations. From Carrier et al. (2007).

*P*,*T*'s lie on or very close to the theoretical lines. Although  $V_{LDA} < V_{exp}$  at 0 GPa, measured and computed structural parameters *at the same volume* agree very well. The effect of zero point motion energy on the calculated zero pressure volume is indicated as well. It increases volume significantly and should be taken into account in the performance analysis of exchange-correlation energy functionals. Closer examination of Figure 11 at small volumes indicates a small but systematic deviation of experimental data from the theoretical lines. Some of these data points include very high temperature data. For instance, both data of Fiquet et al. (1998) and of Funamori et al. (1996) for the lattice parameter **a** are slightly larger (~0.3% or 0.01 Å) than the QHA prediction. The opposite is observed for **b** (~ -0.1% or -0.005 Å). No clear discrepancies are noticeable in the lattice parameter **c**. Since these points are the highest *T* data sets, one might suspect the validity of the QHA is questionable, but this is not the case.

The origin of these discrepancies can be traced to deviatoric thermal stresses.  $P_{stat}$  in Equation (22) is isotropic by construction, since structures were optimized under hydrostatic conditions (Wentzcovitch et al. 1993). However,  $P_{ZP}$  and  $P_{th}$  are not necessarily isotropic. Deviatoric thermal stresses (in Voigt notation) are:

$$\delta \sigma_i^T(T, P) = P + \frac{1}{V} \frac{\partial F}{\partial e_i} \Big|_{FT}$$
(23)

These stresses along [100], [010], and [001] are shown in Figure 12. Negative (positive) values indicate the structure should expand (contract) along the corresponding direction. One can see



Figure 12. Deviatoric stresses (Eqn. 23) along a, b, and c axes. From Carrier et al. (2007).

that there is a natural relation between the high *T* deviations seen in Figure 11 and the deviatoric stresses in Figure 12. These deviatoric stresses can be relaxed to first order if one knows the compliance tensor:

$$\kappa_{ii}(T,P) = C_{ii}^{-1}(T,P)$$
(24)

Since  $C_{ij}$  are available for perovskite (Fig. 5), deviatoric stresses in Equation (23) can be relaxed by application of the following strains:

$$\varepsilon_i(P,T) = \kappa_{ii}(P,T)\delta\sigma_i(P,T)$$
<sup>(25)</sup>

Figure 13 displays the resulting corrections on the lattice parameters as a function of volume at various temperatures, combined with the experimental data of Fiquet et al. (1998) and Funamori et al. (1996). The agreement between predicted and measured experimental data improves considerably despite fluctuations in the experimental data. The relaxed volume,  $V^{(I)}(P,T)$ , under "hydrostatic" conditions differs from  $V_{stat}(P)$ . Therefore, phonon frequencies  $\omega_a(V^{(I)})$ , might be recalculated and also become temperature dependent. This dependence is



**Figure 13.** Corrected lattice parameters  $[\mathbf{a}-\varepsilon_1\mathbf{a}], [\mathbf{b}-\varepsilon_2\mathbf{b}]$ , and  $[\mathbf{c}-\varepsilon_3\mathbf{c}]$  where  $\varepsilon_i$ 's are given by Equation (25), compared with the data of Funamori et al. (1996) data between 400 and 1500 K (dots) and Fiquet et al. (1998) data above 1500 K (triangles). Solid lines are from theory. As indicated by the Fiquet et al. (1989) data, experimental errors increase with temperature. From Carrier et al. (2007).

not caused by the usual phonon-phonon interaction but by the non-isotropic nature of the thermal pressure. This procedure should be repeated until deviatoric thermal stresses vanish, at which point all thermally induced forces should also vanish. This is the *self-consistent QHA* (sc-QHA).

Corrections of elastic constants to first order are also possible and have been carried out for perovskite and post-perovskite (Carrier et al. 2008) at D" conditions ( $P \sim 120$  GPa and  $T \sim 3,000$  K). For these *orthorhombic* materials, the diagonal and off diagonal components of  $c_{ij}$  expanded in a Taylor series of strains (in Voigt's notation) are:

$$C_{ij}(P,T,\varepsilon) = C_{ij}(P,T,0) + \sum_{k=1}^{6} \frac{\partial C_{ij}}{\partial \varepsilon_k} \bigg|_{P,T} \varepsilon_k + \dots$$
(26)

or

$$C_{ij}(P,T,\varepsilon) = C_{ij}(P,T,0) + \sum_{k=1}^{6} \sum_{m=1}^{6} \frac{\partial C_{ij}}{\partial P'} \bigg|_{P,T} \frac{\partial P'}{\partial \sigma_m} \bigg|_{P,T} \frac{\partial \sigma_m}{\partial \varepsilon_k} \bigg|_{P,T} \varepsilon_k \dots$$
(27)

where

$$P' = \frac{1}{3} \sum_{m=1}^{3} \sigma_m$$
 (28)

Therefore the first-order corrected elastic constants at the strains given by Equation (25) are:

$$C_{ij}(P,T,\varepsilon) = C_{ij}(P,T,0) + \frac{\partial C_{ij}}{\partial P'} \bigg|_{P,T} \frac{\delta \sigma_{\Sigma}}{3} + \dots$$
(29)

where  $\delta \sigma_{\Sigma}$  is the sum of deviatoric stresses:

$$\delta \sigma_{\Sigma} = \sum_{m=1}^{3} \delta \sigma_m \tag{30}$$

each given by:

$$\delta\sigma_m = \sum_{k=1}^6 C_{mk} \varepsilon_k \tag{31}$$

This correction requires knowledge of  $dC_{ij}/dP$  and of the deviatoric stresses, both of which are known from the sc-QHA calculation.

Changes in the isothermal bulk and shear moduli of perovskite and post-perovskite after one cycle of thermal stress relaxation are displayed in Figure 14. In perovskite, these changes are within 0.5 GPa up to 150 GPa and 4,000 K. This is within the margin of uncertainty of the calculations. In post-perovskite the changes are a little larger and negative. The changes are largest at the highest P,T but still relatively very small compared with values shown in Figs. 6a and 8a.

#### **SUMMARY**

We have presented the formalism used to compute thermoelastic properties of solids using the statically constrained QHA (sc-QHA). Combined with first principles LDA calculations it is a simple and accurate although computationally intensive method to compute thermoelastic properties of crystals from which elasticity of aggregates can be obtained within bounds. Results for MgO, MgSiO<sub>3</sub>-perovskite, and MgSiO<sub>3</sub>-post-perovskite and comparisons with high



**Figure 14**. Corrections to bulk and shear moduli of (a) pervskite (Wentzcovitch et al. 2004) and (b) postperovskite (Wentzcovitch et al. 2006). From Carrier et al. (2008).

pressure and high temperature experimental data have been reviewed to illustrate the accuracy possible to achieve.

An interesting byproduct of QHA calculations is the prediction of high temperature crystal structures. This is possible because, by construction, the QHA relates crystal structure parameters and (non-interacting) phonon frequencies uniquely with volume and such structure-volume relationship is well established by static calculations. In non-cubic solids, sc-QHA calculations develop deviatoric thermal stresses at high temperatures. *Thermal pressure is not isotropic*. Relaxation of these stresses leads to a series of corrections to the structure that may be taken to any desired order, up to self-consistency. This is the self-consistent QHA (sc-QHA). We have shown how to correct elastic constants for deviatoric stresses generated by the sc-QHA. We have illus-

trated the procedure by correcting to first order the elastic constants of perovskite and post-perovskite, the major silicate phases of the Earth's lower mantle. This correction is very satisfactory for obtaining the aggregate elastic constants and velocities of these minerals at *in situ* conditions of the lower mantle. This procedure can also be used to predict elastic constants in the presence of deviatoric stresses, or to correct elasticity measurements performed under non-hydrostatic conditions, as often happen in diamond-anvil cells, if deviatoric stresses are known.

Several insights of geophysical significance have been obtained from high temperature elasticity calculations: 1) MgO is the most anisotropic phase in the lower mantle. Since it is also the weakest, it is a potentially important source of anisotropy in aggregates with lattice preferred orientation produced by mantle flow; 2) aggregates with typical pyrolite Mg/Si ratio, i.e., ~20 vol% of MgO and ~80 vol% of perovskite, appear to reproduce the elastic properties of the lower mantle better than the pure perovskite aggregate, at least down to  $\sim$ 1,600 km depth. This suggests that shallow to mid lower mantle has the same chemistry of the upper mantle (as far as Mg/Si ratio is concerned); 3) in the deep lower mantle, post-perovskite free aggregates appear to slowly develop elastic properties that deviate from those of the Preliminary Reference Earth Model (PREM). The elastic properties of post-perovskite suggest that this deviation is caused by its presence in the D" layer, the deepest  $\sim$  300 km of the mantle; 4) the post-perovskite transition causes velocity jumps similar to those detected in some places in D" beneath subduction zones. This is consistent with expectations based on the post-perovskite phase boundary with positive Clapeyron slope; 5) velocity changes across the post-perovskite transition suggest that the anticorrelation between lateral bulk and shear velocity changes in D" could be caused by lateral changes in the perovskite/post-perovskite abundances.

For almost two decades the D" region has remained an enigma. It is a complex layer at the interface of two chemically distinct regions, mantle and core. Post-perovskite should co-exist with other solid phases, and probably also with melts, in this region. There are still several mysteries, in the details, to be resolved; but, the insights offered by these calculations have advanced considerably knowledge of the puzzling D" layer. These successes show that first principles calculations of thermoelastic properties of mantle minerals are poised to contribute much more to our understanding of the planet in the years ahead.

#### ACKNOWLEDGMENTS

This research was supported by NSF grants EAR 0810272, EAT 0635990, ATM 0428774 (VLab), and EAR 0757903.

#### REFERENCES

- Anderson GM (2005) Thermodynamics of Natural Systems. 2<sup>nd</sup> edition. Cambridge Univ. Press, Cambridge, UK
- Baroni S, Giannozzi P, Isaev E (2010) Density-functional perturbation theory for quasi-harmonic calculations. Rev Mineral Geochem 71:39-57
- Baroni S, Dal Corso A, Giannozzi P, de Gironcoli S (2001) Phonons and related crystal properties from densityfunctional perturbation theory. Rev Mod Phys 73:515-562
- Barron THK, Klein ML (1965) Second-order elastic constants of a solid under stress. Proc Phys Soc 85:523-532
- Born M, Huang K (1956) Dynamical Theory of Crystal Lattices. International Series of Monographs on Physics. Oxford at the Clarendon Press, Hong Kong
- Brown JM, Shankland TJ (1981) Thermodynamic parameters in the Earth as determined from seismic profiles. Geophys J R Astron Soc 66:579-596
- Car R, Parrinello M (1985) Unified approach for molecular dynamics and density functional theory. Phys Rev Lett 55:2471-2474

- Caracas R, Cohen R (2007) The effect of chemistry on the physical properties of perovskite and post-perovskite. *In:* Post-perovskite. The Last Mantle Phase Transition. Hirose K, Brodholt J, Lay T, Yuen D (eds) AGU Monograph Series 174:115-128
- Caracas R, Wentzcovitch RM, Price GD, Brodholt J (2005) CaSiO<sub>3</sub> perovskite at lower mantle pressures. Geohys Res Lett 144:L06306
- Carrier P, Justo JF, Wentzcovitch RM (2008) Quasiharmonic elastic constants corrected for deviatoric thermal stresses. Phys Rev B 78:144302
- Carrier P, Wentzcovitch RM, Tsuchiya J (2007) First principles prediction of crystal structures at high temperatures using the quasiharmonic approximation. Phys Rev B 76:064116
- Ceperley DM, Alder BJ (1980) Ground state of the electron gas by a stochastic method. Phys Rev Lett 45:566-569
- Chen G, Liebermann RC, Weidner DJ (1998) Elasticity of single crystal MgO to 8 gigapascals and 1600 Kelvin. Science 280:1913-1916
- da Silva CRS, Wentzcovitch RM, Patel A, Price GD, Karato S-I (2000) The composition and geotherm of the lower mantle: constraints from the calculated elasticity of silicate perovskite. Phys Earth Planet Inter 118:103-109
- Davies GF (1974) Effective elastic-moduli under hydrostatic stress. 1. Quasiharmonic theory. J Phys Chem Solids 35:1513-1520
- Duffy TS, Hemley RJ, Mao HK (1995) Equation of state and shear strength at multi-Mbar pressures: magnesiumoxide to 227 GPa. Phys Rev Lett 70:1371-1374
- Dziewonski AM, Anderson DL (1981) Preliminary reference Earth model. Phys Earth Planet Inter 25: 297-356

Dziewonski AM, Woodhouse JH (1987) Global images of the Earth interior. Science 236:37-48

- Fiquet G, Andrault D, Dewaele A, Charpin T, Kunz M, Haüsermann D (1998) P-V-T equation of state of MgSiO<sub>3</sub> perovskite. Phys Earth Planet Inter 105:21-31
- Forte AM, Woodward RL, Dziewonski AM (1994) Joint inversions of seismic and geodynamic data for models of 3 dimensional mantle heterogeneity. J Geophys Res 99:21857-21878
- Funamori N, Yagi T, Utsumi W, Kondo T, Uchida T, Funamori M (1996) Thermoelastic properties of MgSiO<sub>3</sub> perovskite determined by in situ x-ray observations up to 30 GPa and 2000 K. J Geophys Res 101:8257-8269
- Garnero E (2004) A new paradigm for Earth's core-mantle boundary. Science 304:834-836
- Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti GL, Cococcioni M, Dabo I, Dal Corso A, de Gironcoli S, Fabris S, Fratesi G, Gebauer R, Gerstmann U, Gougoussis C, Kokalj A, Lazzeri M, Martin-Samos L, Marzari N, Mauri F, Mazzarello R, Paolini S, Pasquarello A, Paulatto L, Sbraccia C, Scandolo S, Sclauzero G, Seitsonen AP, Smogunov A, Umari P, Wentzcovitch RM (2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J Phys Condens Matter 21:395502
- Giannozzi P, de Gironcoli S, Pavone P, Baroni S (1991) Ab initio phonon dispersions in elemental semiconductors Phys Rev Lett 43:7231-7234
- Gonze X, Beuken J-M, Caracas R, Detraux F, Fuchs M, Rignanese G-M, Sindic L, Verstraete M, Zerah G, Jollet F, Torrent M, Roy A, Mikami M, Ghosez Ph, Raty J-Y, Allan DC (2002) First-principles computation of material properties : the ABINIT software project. Comput Mater Sci 25:478-492
- Grand SP (1994) Mantle shear structure beneath the America and surrounding oceans. J Geophys Res 99:11591-11621
- Hashin Z, Strikman S (1962) A variational approach to the theory of the elastic behavior of polycrystals. J Mech Phys Solids 10:343-352
- Hohenberg P, Kohn W (1964) Inhomogeneous electron gas. Phys Rev 136:B864-B871
- Hsu H, Umemoto K, Wu A, Wentzcovitch RM (2010) Spin-state crossover of iron in lower-mantle minerals: results of DFT+U investigations. Rev Mineral Geochem 71:169-199
- Isaak DG, Andersen OL, Goto T (1989) Measured elastic moduli of single-crystal MgO up to 1800 K. Phys Chem Miner 16:704-713
- Isaak DG, Cohen RE, Mehl MJ (1990) Calculated elastic and thermal properties of MgO at high pressures and temperatures. J Geophys Res 95:7055-7067
- Ishii M, Tromp J (1999) Normal-mode and free-air gravity constraints on lateral variations in velocity and density of Earth's mantle. Science 285:1231-1236
- Jackson I (1998) Elasticity, composition and temperature of the Earth's lower mantle: a reappraisal. Geophys J Int 134:291-311
- Jackson JM, Zhang J, Shu J, Sinogeikin SV, Bass JD (2005) High-pressure sound velocities and elasticity of aluminous MgSiO<sub>3</sub> perovskite to 45 GPa: Implications for lateral heterogeneity in Earth's lower mantle. Geophys Rev Lett 32:L21305
- Karato S-I, Karki BB (2001) Origin of lateral variation of seismic wave velocities and density in the deep mantle. J Geophys Res 106:B21771-B21783

- Karki BB, Stixrude L, Clark SJ, Warren MC, Ackland GJ, Crain J (1997) Structure and elasticity of MgO at high pressure. Am Mineral 82:51-60
- Karki BB, Stixrude L, Wentzcovitch RM (2001a) High-pressure elastic properties of major materials of earth's mantle from first principles. Rev Geophys 39: 507-534
- Karki BB, Wentzcovitch RM, de Gironcoli S, Baroni S (1999) First-principles determination of elastic anisotropy and wave velocities of MgO at lower mantle conditions. Science 286:1705-1707
- Karki BB, Wentzcovitch RM, de Gironcoli S, Baroni S (2000a) Ab initio lattice dynamics of MgSiO<sub>3</sub>-perovskite. Phys Rev B 62:14750-14756
- Karki BB, Wentzcovitch RM, de Gironcoli S, Baroni S (2000b) High-pressure lattice dynamics and thermoelasticity of MgO. Phys Rev B 61:8793-8800
- Karki BB, Wentzcovitch RM, de Gironcoli S, Baroni S (2001b) First principles thermoelasticity of MgSiO<sub>3</sub>-perovskite: consequences for the inferred properties of the lower mantle. Geophys Res Lett 28:2699-2702
- Kendall J-M, Silver PG (1998) Investigating causes of D" anisotropy. In: Core-Mantle Boundary Region. Geodynamics Series. Volume 28. Gurnis M, Wysession ME, Knittle E, Buffet B (eds) Am Geophys Union, Washington, DC, p 97-118
- Kiefer B, Stixrude L, Wentzcovitch RM (2002) Elasticity of (Mg,Fe)SiO<sub>3</sub>-Perovskite at high pressures. Geophys Res Lett 29:14683
- Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. Phys Rev 140:1133-1138
- Kresse G, Furthmuller J (1996) Efficient iterative schemes for ab initio total-energy calculations using a planewave basis set. Phys Rev B 54:11169-11186
- Lay T, Helmberger DV (1983) A lower mantle S-wave triplication and the shear velocity structure of D". Geophys J R Astron Soc 75:799-838
- Li B, Zhang J (2005) Pressure and temperature dependence of elastic wave velocity of MgSiO<sub>3</sub> perovskite and the composition of lower mantle. Phys Earth Planet Inter 151:143-154
- Li BS, Woody K, Kung J (2006a) Elasticity of MgO to 11 GPa with an independent absolute pressure scale: Implication for pressure calibration. J Geophys Res 111:B11206
- Li L, Brodholt J, Stackhouse S, Weidner DJ, Alfredsson M, Price GD (2005) Elasticity of (Mg, Fe)(Si, Al)O<sub>3</sub>perovskite at high pressure. Earth Planet Sci Lett 240:529-536
- Li L, Weidner DJ, Brodholt J, Alfè D, Price GD (2006b) Elasticity of Mg<sub>2</sub>SiO<sub>4</sub> ringwoodite at mantle conditions. Phys Earth Planet Inter 157:181-187
- Li L, Weidner DJ, Brodholt J, Alfè D, Price GD (2009) Ab initio molecular dynamics study of elasticity of akimotoite MgSiO<sub>3</sub> at mantle conditions. Phys Earth Planet Inter 173:115-120
- Li L, Weidner DJ, Brodholt J, Alfè D, Price GD, Caracas R, Wentzcovitch R (2006c) Elasticity of CaSiO<sub>3</sub> perovskite at high pressure and high temperature. Phys Earth Planet Inter 155:249-259
- Marton FC, Cohen RE (2002) Constraints on lower mantle composition from molecular dynamics simulations of MgSiO<sub>3</sub> perovskite. Phys Earth Planet Inter 134:239-252
- Masters G, Gubbins D (2003) On the resolution of density within the Earth. Phys Earth Planet Inter 140:159-167
- Masters G, Laske G, Bolton H, Dziewonski A (2000) The relative behavior of shear velocity, bulk sound speed, and compressional velocity in the mantle: implications for chemical and thermal structure. *In:* Earth's Deep Interior: From Mineral Physics and Tomography from Atomic to the Global Scale. Karato S-I, Forte AM, Liebermann RC, Masters G, Stixrude L (eds) American Geophysical Union, Washington DC. Geophysical Monograph Series 117:63-87
- Murakami M, Hirose K, Kawamura K, Sata N, Ohishi Y (2004) Post-perovskite phase transition in MgSiO<sub>3</sub>. Science 304:855-858
- Murakami M, Ohishi Y, Hirao N, Hirose K (2009) Elasticity of MgO to 130 GPa: Implications for lower mantle mineralogy. Earth Planet Sci Lett 277:123-129
- Musgrave MJP (1970) Crystal Acoustics. Holden-Day, Boca Raton, FL
- Nielsen OH, Martin RM (1985) Quantum mechanical theory of stress and force. Phys Rev B 32:5780-3891
- Nye JF (1985) Physical Properties of Crystals: Their Representation by Tensors and Matrices, 2nd ed. Oxford University Press, Oxford
- Oganov AR, Brodholt JP, Price GD (2001) The elastic constant of MgSiO<sub>3</sub> perovskite at pressure and temperatures of the Earth's mantle. Nature 411:934-937
- Oganov AR, Ono S (2004) Theoretical and experimental evidence for a post-perovskite phase of MgSiO<sub>3</sub> in Earth's D" layer. Nature 430: 445-448
- Payne MC, Teter MP, Allan DC, Arias TA, Joannopoulos JD (1992) Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. Rev Mod Phys 64:1045-1097

- Perdew J, Zunger A (1981) Self-interaction correction to density-functional approximations for many electron systems. Phys Rev B 23: 5048–5079
- Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77:3865-3868
- Romanowicz B (2001) Can we resolve 3D density heterogeneity in the lower mantle? Geophys Res Lett 28:1107-1110
- Ross N, Hazen R (1989) Single crystal X-ray diffraction study of MgSiO<sub>3</sub> perovskite from 77 to 400 K. Phys Chem Miner 16:415-420
- Ross N, Hazen R (1990) High-pressure crystal chemistry of MgSiO<sub>3</sub> perovskite. Phys Chem Miner 17:228-237
- Sidorin I, Gurnis M, Helmberger D (1999) Evidence for a ubiquitous seismic discontinuity at the base of the mantle. Science 286:1326-1331
- Sinelnikov YD, Chen G, Neuville DR, Vaughan MT, Liebermann RC (1998) Ultrasonic shear wave velocities of MgSiO<sub>3</sub> perovskite at 8 GPa and 800 K and lower mantle composition. Science 281:677-679
- Sinogeikin SV, Bass JD (1999) Single-crystal elasticity of MgO at high pressure. Phys Rev B 59:R14141-R14144
- Sinogeikin SV, Bass JD, Katsura T (1998) Single crystal elasticity of MgO at high pressure. Phys Rev B 59: R14141-R14144
- Sinogeikin SV, Zhang J, Bass JD (2004) Elasticity of single crystal and polycrystalline MgSiO<sub>3</sub> perovskite by Brillouin spectroscopy. Geophys Rev Lett 31:L06620
- Spetzler HA (1970) Equation of state of polycrystalline and single-crystal MgO to 8 kbars and 800 K. J Geophys Res 75:2073-2087
- Stackhouse S, Brodholt JP, Wookey J, Kendall JM, Price GD (2005) The effect of temperature on acoustic anisotropy of the perovskite and post-perovskite polymorphs of MgSiO<sub>3</sub>. Earth Planet Sci Lett 230:1-10
- Stixrude L, Cohen RE, Yu RC, Krakauer H (1996) Prediction of phase transition in CaSiO<sub>3</sub> perovskite and implications for lower mantle structure. Am Mineral 81:1293-1296
- Stixrude L, Hemley RJ, Fei Y, Mao HK (1992) Thermoelasticity of silicate perovskite and magnesiowustite and stratification of the Earth mantle. Science 257:1099-1101
- Stixrude L, Lithgow-Bertelloni C (2005) Thermodynamics of mantle minerals. I. Physical properties. Geophys J Int 162:610-632
- Stixrude L, Lithgow-Bertelloni C (2007) Influence of phase transformations on lateral heterogeneity and dynamics in Earth's mantle. Earth Planet Sci Lett 263:45-55
- Stixrude L, Lithgow-Bertelloni C (2010) Thermodynamics of the Earth's mantle. Rev Mineral Geochem 71:465-484
- Stixrude L, Lithgow-Bertelloni C, Kiefer B, Fumagalli P (2007) Phase stability and shear softening in CaSiO<sub>3</sub> perovskite at high pressure, Phys Rev B 75:24108
- Thomsen L (1972) Fourth-order anharmonic theory-elasticity and stability. J Phys Chem Solids 33:363-378
- Troullier N, Martins JL (1991) Efficient pseudopotentials for plane-wave calculations. Phys Rev B 43:1993-2006
- Tsuchiya J, Tsuchiya T, Wentzcovitch RM (2005) Vibrational and thermodynamic properties of MgSiO<sub>3</sub> postperovskite. J Geophys Res 110:B02204, doi:10.1029/2004JB003409
- Tsuchiya T, Tsuchiya J, Umemoto K, Wentzcovitch RM (2004) Phase transition in MgSiO<sub>3</sub> perovskite in the earth's lower mantle. Earth Planet Sci Lett 224:241–248
- Utsumi W, Funamori N, Yagi T, Ito E, Kikegawa T, Shimomura O (1995) Thermal expansivity of MgSiO<sub>3</sub> perovskite under high pressures up to 20 GPa. Geophys Res Lett 22:1005-1008
- van der Hilst RD, Widiyantoro S, Engdahl ER (1997) Evidence for deep mantle circulation from global tomography. Nature 386:578-584
- Vanderbilt D (1990) Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys Rev B 41:7892-7895
- Wallace DC (1972) Thermodynamics of Crystals. 1st Edition. John Wiley and Sons, New York
- Wang Y, Perdew J (1991) Correlation hole of the spin-polarized electron-gas, with exact small-wave-vector and high-density scaling. Phys Rev B 24:13298-13307
- Wang Y, Weidner DJ, Liebermann RC, Zhao Y (1994) P-V-T equation of state of (Mg,Fe)SiO<sub>3</sub> perovskite: constraints on composition of the lower mantle. Phys Earth Planet Inter 83:13-40
- Watt JP (1980) Hashin-Shtrikman bounds on the effective elastic moduli of polycrystals with monoclinic symmetry. J Appl Phys 51:1520-1524
- Watt JP, Davies GF, Connell RJO (1976) Elastic properties of composite materials. Rev Geophys Space Phys 14:541-563
- Wentzcovitch RM (1991) Invariant molecular dynamics approach to structural phase transitions. Phys Rev B 44:2358-2361

- Wentzcovitch RM, Justo JF, Wu Z, da Silva CRS, Yuen D, Kohlstedt D (2009) Anomalous compressibility of ferropericlase throughout the iron spin crossover. Proc Nat Acad Sci USA 106:8447-8452
- Wentzcovitch RM, Karki BB, Cococcioni M, de Gironcoli S (2004) Thermoelastic properties of MgSiO<sub>3</sub>perovskite: insights on the nature of the Earth's lower mantle. Phys Rev Lett 92:018501
- Wentzcovitch RM, Karki BB, Karato SI, da Silva CRS (1998) High pressure elastic anisotropy of MgSiO<sub>3</sub>perovskite and geophysical implications. Earth Planet Sci Lett 164:371-378
- Wentzcovitch RM, Martins JL (1991) First principles molecular dynamics of Li: Test of a new algorithm. Solid State Commun 78:831-834
- Wentzcovitch RM, Martins JL, Price GD (1993) Ab initio molecular dynamics with variable cell shape: Application to MgSiO<sub>3</sub> perovskite. Phys Rev Lett 70:3947-3950
- Wentzcovitch RM, Ross N, Price GD (1995) Ab initio investigation of MgSiO<sub>3</sub> and CaSiO<sub>3</sub>-perovskites at lower mantle pressures. Phys Earth Planet Inter 90:101-112
- Wentzcovitch RM, Tsuchiya T, Tsuchiya J (2006) MgSiO<sub>3</sub> post perovskite at D" conditions. Proc Nat Acad Sci 103:543-546
- Wentzcovitch RM, Yu YG, Wu Z (2010) Thermodynamic properties and phase relations in mantle minerals investigated by first principles quasiharmonic theory. Rev Mineral Geochem 71:59-98
- Woodhouse JH, Dziewonski AM (1984) Mapping the upper mantle: three-dimensional modeling of earth structure by inversion of seismic waveforms, J Geophys Res 89:5953-5986
- Wu Z, Justo JF, da Silva CRS, de Gironcoli S, Wentzcovitch RM (2009) Anomalous thermodynamic properties in ferropericlase throughout its spin crossover transition. Phys Rev B 80:014409
- Wu Z, Wentzcovitch RM (2009) Effective semiempirical ansatz for computing anharmonic free energies. Phys Rev B 79:104304
- Wu Z, Wentzcovitch RM, Umemoto K, Li B, Hirose K (2008) P-V-T relations in MgO: an ultrahigh P-T scale for planetary sciences applications. J Geophys Res 113:B06204
- Wysession ME, Lay T, Revenaugh J, Williams Q, Garnero EJ, Jeanloz R, Kellogg LH (1998) The D" discontinuity and its implications. *In:* Core-Mantle Boundary Region. Geodynamics Series. Volume 28. Gurnis M, Wysession ME, Knittle E, Buffet B (eds) Am Geophys Union, Washington, DC, p 273-297
- Xu WB, Lithgow-Bertelloni C, Stixrude L, Ritsema J (2008) The effect of bulk composition and temperature on mantle seismic structure. Earth Planet Sci Lett 275:70-79
- Yamazaki D, Karato S (2002) Fabric development in (Mg,Fe)O during large strain, shear deformation: implications for seismic anisotropy in Earth's lower mantle. Earth Planet Sci Lett 131:251-267
- Yeganeh-Haeri A (1994) Synthesis and re-investigation of the elastic properties of single-crystal magnesium silicate perovskite. Phys Earth Planet Inter 87:111-121
- Zha CS, Mao HK, Hemley R (2000) Elasticity of MgO and a primary pressure scale to 55 GPa. Proc Nat Acad Sci USA 97:13494-13499