

## Elasticity of Mantle Phases at High Pressure and Temperature

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We review theoretical approaches and results in the study of the elasticity of mantle materials under extreme conditions. First principles methods for calculating the elastic constants of minerals with complex structures are described and are compared with alternative approaches. These include models at the ab initio, semi-empirical and continuum levels. Special attention is paid to the continuum description as embodied in the extension of finite strain theory to anisotropic strains, and to the description of the variation of the elastic constants with pressure and temperature. First principles results on a number of important mantle phases are reviewed. Comparison of theory and experiment is featured including an account of predictions of first principles calculations that have subsequently been confirmed by experiment. A discussion of the effect of pressure on elastic constants is focused around three issues: 1) acoustic anisotropy, which is shown to change qualitatively (in sign and magnitude) over the mantle pressure regime, 2) elastic instabilities, which occur in silica in the vicinity of the phase transition from stishovite to the  $\text{CaCl}_2$ -structure near 47 GPa, and 3) an evaluation of the anisotropic generalization of finite-strain theory, which is shown to converge rapidly for the elastic constants of  $\text{MgSiO}_3$  perovskite. The possible effect of high temperature on elastic properties is explored by extending the first principles calculations with a semi-empirical thermal correction based on finite strain theory. In the case of the elastic anisotropy of periclase, temperature is found to have an effect secondary to that of pressure over the mantle regime.

### 1. INTRODUCTION

Seismic observations are in principle a rich source of information on the thermal and rheological properties of the earth's interior, its composition and dynamics. At present, our ability to extract this information from the observations is primarily limited by our ignorance of the elasticity of major mantle materials at the relevant conditions.

Measurements of the elastic constants of mantle materials exist at ambient pressure and up to mantle temperatures for some materials. Experiments performed at mantle pressures are more rare, especially for transition zone and lower mantle phases. This is a serious limitation because one expects pressure to have a greater effect than temperature on the elastic properties of minerals over the range of mantle conditions.

There are three approaches that have been used to overcome these limitations: 1) Pioneering experiments at combined high temperatures and pressures are now being performed; in some cases approaching the conditions of the mantle. 2) First-principles theory has now

been used to examine the athermal elasticity of a number of mantle phases throughout the pressure regime of the earth's mantle. The first-principles approach can be extended to examine elasticity at high temperature although this has not yet been accomplished for mantle materials. 3) Empirical or semi-empirical extrapolation of existing experimental or theoretical results to mantle conditions.

In this review, we focus on theoretical methods and results, experimental work being reviewed Liebermann (in this volume). The first principles theoretical approach is briefly outlined, focusing on density functional theory and the planewave pseudopotential method. The concept of the static lattice is discussed as well as ways of going beyond this idealization in theoretical calculations. First principles results are reviewed and used to illustrate the effect of pressure on the elasticity of minerals in the mantle, focusing on the acoustic anisotropy, the origin of pressure-induced elastic instabilities, and a comparison with behavior expected from finite strain theory. We discuss the challenges that must be overcome before finite temperature calculations become routinely possible and examine some future prospects.

Because first principles theory has not yet been widely successful at examining elasticity at finite temperature, we also explore semi-empirical methods of extrapolation based on a continuum picture. The generalization of finite-strain theory to anisotropic strains and elevated temperature [Davies, 1974] is reviewed and illustrated. To explore the likely effect of temperature at mantle conditions, we use quasi-harmonic finite strain theory to extrapolate our first principles results to mantle conditions of pressure and temperature.

## 2. THEORY

### 2.1. First Principles Level

Density functional theory [Hohenberg and Kohn, 1964; Kohn and Sham, 1965] has become a powerful tool for examining the behavior of earth materials at high pressure. Central to the theory is the proof that ground state properties are a unique functional of the charge density; it is not necessary to solve for the complete  $10^{23}$  dimensional total wavefunction. This is appealing because the charge density, a scalar function of position, is readily observable experimentally, e.g. by x-ray diffraction.

The Schrödinger-like Kohn-Sham equations

$$[-\nabla^2 + V_{KS}] \psi_i = \epsilon_i \psi_i \quad (1)$$

where the Kohn-Sham potential

$$V_{KS}[\rho(\vec{r})] = \sum_{i=1}^N \frac{2Z_i}{|\vec{r} - \vec{R}_i|} + \int \frac{2\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}[\rho(\vec{r})] \quad (2)$$

where  $Z_i$  and  $R_i$  are the nuclear charges and positions, respectively, and  $V_{xc}$  is the exchange-correlation potential, are solved self-consistently with the charge density,  $\rho$ . The Kohn-Sham equations are exact in principle. However, the exact form of the many-body exchange-correlation functional is not known. In practice, approximations to this term are adopted, the simplest being the local density approximation (LDA) which sets the exchange-correlation functional at every point in the crystal to that of the free-electron gas of the same charge density at that point [Lundqvist and March, 1987]. The Generalized Gradient Approximation (GGA) also depends on local charge density gradients [Perdew *et al.*, 1996]. Comparison with experiment has demonstrated that the LDA is a good approximation for silicates and oxides, and most representatives of all other classes of materials. There is some evidence that the GGA may be more accurate in some cases for silicates [Hamann, 1996].

It is possible to solve the Kohn-Sham equations without any further essential approximation beyond that to the exchange-correlation functional. For example, the Linearized Augmented Plane Wave (LAPW) includes all electrons and contains no uncontrolled approximations to the shape of the charge density or potential [Anderson, 1975; Wei and Krakauer, 1985]. The LAPW method has been applied to systems containing as many as 20 atoms in the unit cell [Stixrude and Cohen, 1993]. However, the method is relatively slow and still prohibitive for many of the large and complex structures examined here.

An alternative method which is much more efficient, though at the cost of additional approximations, is the plane wave pseudopotential method. The development is based on the observation that over the range of conditions normally encountered only the valence electrons are altered by changes in state of stress or temperature; the core electrons are essentially static or frozen. The nucleus and core electrons are then replaced by a simpler object, the pseudopotential which has the same scattering properties [Pickett, 1989]. This is computationally advantageous because the pseudopotential is much softer (much more slowly varying in space) than the bare Coulomb potential of the nucleus. Moreover, one need solve self-consistently only for the valence electrons which also show much more gentle spatial variations. As a result, the charge density and potential may

be represented by a set of plane waves of manageable size, speeding the calculation by perhaps an order of magnitude compared with the LAPW method. Calculations show that, as long as the quality of the pseudopotential is carefully evaluated by comparison with limited all electron calculations, the pseudopotential approximation is generally not serious in the case of silicates and oxides.

*2.1.1. Static Lattice.* Given an arrangement of nuclei, density functional theory allows one to calculate the resulting electronic charge density and total energy. By examining the variations in the total energy with respect to displacements of the nuclei or strains applied to the structure, one makes contact with a number of experimentally observable quantities. For example, by differentiating the relationship between total energy and volume, one obtains the static equation of state. The full elastic constant tensor can be calculated by examining the variation of the total energy with respect to small applied strains.

The scope of density functional calculations has been substantially expanded with the development of first principles molecular dynamics [Car and Parrinello, 1985; Wentzcovitch *et al.*, 1993]. This development is based on the Hellman-Feynman theorem which says that it is possible to calculate directly the forces acting on the nuclei and the stresses acting on the lattice. This is important for at least two related reasons. It allows one to determine efficiently and accurately: 1) Equilibrium structures. The equilibrium structure at a given volume or pressure is found by systematically adjusting the positions of the nuclei and the lattice parameters until forces and deviatoric stresses vanish (e.g. by steepest descent). It is then possible to examine the compression of complex crystal structures, and to study structural compression mechanisms in detail. 2) Elastic constants. Once the equilibrium structure has been determined, the elastic constants are calculated in a way that mimics experimental methods. A small deviatoric strain is applied to the lattice and the resulting stresses calculated. The ratio of stress to strain components yields a subset of the elastic constants of the material. By applying a small set of strains of different symmetry it is possible to obtain the full elastic constant tensor. Because elastic constants generally couple to vibrational modes in complex structures such as those of silicates, it is important to redetermine the equilibrium arrangement of the nuclei in each strained configuration.

*2.1.2. Finite Temperature.* The calculations described so far apply to the static lattice. This is an athermal idealization that is not accessible experimentally: not

only is temperature absent, but so is zero point motion. For many materials at room temperature, including most silicates, the effect of zero point motion and temperature on material properties and crystal structures is small, often smaller than the effect of the LDA or GGA approximations. As a result, comparison of static calculations to room temperature experimental measurement can yield considerable insight. Thermal effects are however important at conditions typical of the earth's interior.

The generalization of the first principles methods described so far to the calculation of properties at finite temperature is straightforward but computationally extremely challenging. The reason that temperature plays a special role in this context is that it breaks the symmetry of the structure. Experimentally, one generally deals only with the average positions of atoms as they vibrate about their equilibrium positions. From the theoretical point of view, we must deal with instantaneous snapshots of the structure. In general, each snapshot will display only P1 symmetry with an infinitely large unit cell, regardless of the symmetry of the underlying average structure.

The high temperature properties of the materials of the earth's mantle have not yet been investigated by first principles techniques. Many simpler systems have been studied using first principles molecular dynamics [Galli *et al.*, 1989; *d. Wijs et al.*, 1998]. In molecular dynamics, one represents the high temperature crystal structure with a periodically repeated supercell of order 100 atoms. Computing the Hellman-Feynman forces allows one to solve Newton's equations of motion for the system and obtain thermodynamic properties averaged over the dynamical phase space trajectory.

## *2.2. Ab Initio Level*

Whereas first-principles methods seek to reduce approximations to a bare minimum, ab initio methods construct an approximate model of some aspects of the relevant physics, such as the charge density or the interactions between orbitals. The cost of additional approximation is often outweighed by the increase in computational simplicity and efficiency. For example, ab initio models have been used to explore transport properties which are very difficult (costly) to examine with fully first-principles approaches [Ita and Cohen, 1997]. Moreover, these models often yield insight that is sometimes difficult to extract from more complex and elaborate first principles calculations.

Examples of ab initio methods that have been applied to the calculation of elastic constants of earth ma-

materials include: 1) Methods based on the electron gas picture of Gordon and Kim [Gordon and Kim, 1972] in which the material is viewed as being composed of spherically symmetric closed-shell ions. Modern elaborations of this approach that account for the deformability of the ions, including the Potential Induced Breathing model (PIB) and the Variationally Induced Breathing (VIB) model have enjoyed wide success, especially as applied to simple oxides such as MgO [Cohen *et al.*, 1987; Wolf and Bukowinski, 1988]. 2) Parametric total energy tight binding methods [Slater, 1951]. Here the interactions between atomic-like orbitals are approximated by simple functional forms that are made to fit accurate first principles total energy and band structure results. One recent method of this type has successfully been used to examine the elasticity of monatomic transition metals, insulators, and semi-conductors [Cohen *et al.*, 1994; Cohen *et al.*, 1997].

### 2.3. Semi-Empirical Level

Semi-empirical methods differ from those discussed so far in that they require input from experiment. These methods often do not view the solid as being composed of nuclei and electrons, but of larger entities. Interatomic force models view the solid as being composed of atoms or ions that interact as a unit with their neighbors. Models of this type have been widely used to study the elasticity of minerals [Matsui *et al.*, 1987]. They are generally less predictive than first principles or *ab initio* calculations because they ignore much of the essential physics. For example, a pair-wise central interatomic force model exactly satisfies the Cauchy relation, which, for cubic materials, reads

$$c_{12} - c_{44} - 2P = 0 \quad (3)$$

in disagreement with observations on many minerals. The primary advantage of interatomic force models is that they are simple and rapid. They are useful to the extent that they faithfully interpolate or extrapolate existing experimental or theoretical results or provide additional insight not otherwise available.

**2.3.1. Quasi-Harmonic Finite-Strain Theory.** Another broad class of semi-empirical methods are based on a continuum picture in which one deals with material behavior at the macroscopic level of thermodynamics. An important example in geophysics is the Eulerian finite strain theory of Birch [Birch, 1952] which has been widely used in the extrapolation of the equation of state to high pressure. In the case of isotropic properties,

this theory has been demonstrated to converge rapidly in most cases.

Here we review the generalization of this approach to anisotropic strains, which has not been widely studied [Davies, 1974]. This generalization is required for the examination of the pressure- and temperature-dependence of the elastic constants. In geophysics, it serves as the basis of the parametrization of the PREM model [Dziewonski and Anderson, 1981]

The elastic moduli are related to strain derivatives of the Helmholtz free energy,  $F$ . Knowledge of the function

$$F = F(\epsilon, T) \quad (4)$$

where  $\epsilon$  is the strain tensor and  $T$  is the temperature would then constitute complete information of the thermoelastic properties of a non-magnetic material. In the context of geophysics, it is sensible to consider the dependence of  $F$  on the isotropic and deviatoric portions of the strain tensor separately. The reason is that the deviatoric portion of the strain tensor is small: it is limited by the elastic strength of typical earth materials. Moreover, the deviatoric strain induced by the passage of seismic waves, the primary application of interest here, is smaller still.

The isotropic portion of the strain is large (finite), corresponding to the large pressures of the earth's interior, and requires special consideration. Of the infinite number of (reference-frame dependent) possible choices for the finite isotropic strain tensor, we choose the Eulerian strain

$$f = \frac{1}{2} [(V/V_0)^{-2/3} - 1] \quad (5)$$

where  $V$  is the volume and subscript 0 indicates the reference state. The dependence of the Helmholtz free energy on finite strain may be described by a Taylor series

$$F = a_0 + a_1 f + \frac{1}{2} a_2 f^2 + \dots \quad (6)$$

where the coefficients  $a_n$  involve  $n$ th and lower strain derivatives of  $F$  evaluated at the reference state, e.g. the free energy, the pressure, the bulk modulus, and so on [Stizrude and Bukowinski, 1990]. The internal energy,  $E$  can be written as a similar expansion in the isotropic finite strain.

The finite strain expansion for the adiabatic elastic constants is found by evaluating the appropriate derivatives of the internal energy with respect to the deviatoric strains

$$c_{ijkl}(f, T) = (1 + 2f)^{7/2} (R_{ijkl}^{(0)} + R_{ijkl}^{(1)} f)$$

$$+ \frac{1}{2} R_{ijkl}^{(2)} f^2 + \dots) - P \Delta_{ijkl} \quad (7)$$

where

$$R_{ijkl}^{(0)} = c_{ijklo} + P_0 \Delta_{ijkl} \quad (8)$$

$$R_{ijkl}^{(1)} = 3K_0(c'_{ijklo} + \Delta_{ijkl}) - 7R_{ijkl}^{(0)} \quad (9)$$

$$R_{ijkl}^{(2)} = 9K_0^2 c''_{ijklo} + 3K_0'(R_{ijkl}^{(1)} + 7R_{ijkl}^{(0)}) - 16R_{ijkl}^{(1)} - 49R_{ijkl}^{(0)} \quad (10)$$

where  $K$  is the bulk modulus and primes indicate pressure derivatives,

$$\Delta_{ijkl} = -\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - \delta_{ij}\delta_{kl} \quad (11)$$

and  $\delta_{ij}$  is the Kroenecker delta tensor. Because we have defined  $f$  as positive on compression the coefficients in the Taylor series expansion are related to those of [Davies, 1974] by  $R_{ijkl}^{(n)} = (-1)^n \rho_0 r_{ijkl}^{(n)}$ , where  $\rho$  is the density. Because alternative definitions are possible, it is important to note explicitly that the elastic constants as defined here are the stress-strain coefficients. These are of primary interest in geophysics because they determine the velocity of propagation of elastic waves at arbitrary pressure [Wallace, 1972].

The expression for the elastic constants can be rearranged in a form that is useful for evaluating the convergence properties of the series

$$D_{ijkl}(f, T) = R_{ijkl}^{(0)} + R_{ijkl}^{(1)} f + \frac{1}{2} R_{ijkl}^{(2)} f^2 + \dots \quad (12)$$

where, by analogy with Birch's definition of the normalized pressure

$$D_{ijkl}(f, T) = \frac{c_{ijkl}(f, T) + P \Delta_{ijkl}}{(1 + 2f)^{7/2}} \quad (13)$$

are the normalized elastic constants. Notice that in the limit of zero strain and zero pressure,  $D_{ijkl} = c_{ijklo}$ .

The reference state, in which  $f = 0$  and  $T$  is the temperature of interest is indicated by subscript 0. Here, we will choose our reference state to be one of constant pressure,  $P_0 = 0$ . In this case, reference state quantities, including the coefficients of the expansion,  $R^{(n)}$  depend on temperature in general.

The effects of temperature are included within the quasi-harmonic approximation. The strain dependence of the vibrational frequencies,  $\omega_\nu$ , where the subscript absorbs the wavevector and branch index, may be described by an expansion in the strain

$$\omega_\nu^2 = \omega_{\nu 0}^2 \left( 1 - g_{ij}^\nu f_{ij} + \frac{1}{2} h_{ijkl}^\nu f_{ij} f_{kl} + \dots \right) \quad (14)$$

where  $g_{ij}^\nu$  and  $h_{ijkl}^\nu$  are constants that will in general be different for each mode and so will depend on wavevector and frequency. In what follows, we assume that these constants can be replaced by appropriate averages over all the modes,  $g_{ij}$  and  $h_{ijkl}$ .

In this approximation, the elastic moduli at high temperature are given by (7) with

$$R_{ijkl}^{(0)} = c_{ijklo} + \frac{1}{4} (2h_{ijkl} - g_{ij}g_{kl}) [E_{TH0}(T) - E_{TH0}(T_0)] / V_0 \quad (15)$$

and  $R^{(n)}$  for  $n > 0$  evaluated at the reference strain and reference temperature  $T = T_0$ . Subscript 00 indicates values at the reference strain and temperature  $T = T_0$ , and  $E_{TH}$  is the thermal energy, calculated here in the Debye approximation. By explicitly accounting for the temperature dependence of only the first expansion coefficient, we introduce errors of order  $\delta^2 f$  where  $\delta$  is the relative magnitude of the anharmonic contributions to the crystal Hamiltonian [Davies, 1974]. This error is small (few percent in the elastic moduli) for mantle conditions. It is worth pointing out that if one is interested in higher order quantities such as the temperature (or pressure) derivatives of the elastic constants, then the temperature dependence of  $R^{(1)}$  and perhaps higher order coefficients would have to be evaluated in general.

The parameters  $g$  and  $h$  are evaluated by relating them to thermodynamic quantities. For the special case of a cubic material

$$g_{ij} = -2\gamma_0 \delta_{ij} \quad (16)$$

where  $\gamma$  is the Grüneisen parameter,

$$\gamma = \frac{K_T \alpha V}{C_V} \quad (17)$$

and

$$h_{ijkl} = -2\gamma_0 \left[ \xi_0 \delta_{ij} \delta_{kl} + \delta_{ijklo}^T - \left( \frac{\partial c_{ijkl}^T}{\partial P} \right)_0 \right] + 4\gamma_0^2 \delta_{ij} \delta_{kl} - 2\gamma_0 \delta_{ik} \delta_{jl} - 2\gamma_0 \delta_{jk} \delta_{il} \quad (18)$$

where

$$\xi = 1 - \left( \frac{\partial \ln C_V}{\partial \ln V} \right)_T \quad (19)$$

$$\delta_{ijkl}^T = -\frac{1}{\alpha K_T} \left( \frac{\partial c_{ijkl}^T}{\partial T} \right)_P \quad (20)$$

where  $c_{ijkl}^T$  are the isothermal elastic moduli, and  $C_V$  is the heat capacity at constant volume.

Table 1. Experimentally Determined Thermoelastic Parameters of Periclase

Property	Isotropic	11	12	44	Ref.
$\delta_{ij}^T$		11.23	1.84	2.79	1
$\theta_{00}$ (K)	780				2
$\gamma_{00}$	1.50				2
$q$	1.84				1

Note: The volume dependence of the Debye temperature,  $\theta$  is given by the Grüneisen parameter,  $\gamma_0 = \gamma_{00}(V_0/V)^{\alpha}$  (see Ref. 2). The parameters  $\delta_{ij}^T$  are assumed independent of temperature and are calculated at  $T = 1300$  K from the tables of Ref. 1 by finite difference and performing the appropriate correction from adiabatic to isothermal elastic moduli. The parameter  $q$  is calculated from  $q \approx \delta^T - K'_0 + 1$  where  $\delta^T = (\delta_{11}^T + 2\delta_{12}^T)/3$ . References: 1, [Anderson and Isaak, 1995]; 2, [Ita and Stizude, 1992].

At high temperatures ( $T > \theta$ ), we have  $\xi \approx 1$ , and all other quantities appearing in (16-20) have been measured for a variety of geophysical materials. We focus on periclase below since its properties are well known (Table 1). Application of this approach to other lower mantle minerals requires a generalization to non-cubic systems. For example, the Grüneisen tensor will not be isotropic in general.

### 3. ELASTICITY AT HIGH PRESSURE

We examine the effects of pressure separately from those of temperature, which are discussed in the following section. There are two reasons for this separation. First, as discussed in the previous section, first principles methods have, to date, been applied to the calculation of the elastic constants of mantle minerals only under static conditions. Second, we wish to evaluate the relative importance of the effects of pressure and temperature on mineral elasticity over the range of mantle conditions.

The example of  $\text{MgSiO}_3$  perovskite illustrates many of the essential features (Fig. 1). First principles calculations of the elastic constants have been performed throughout the pressure regime of the earth's mantle [Karki *et al.*, 1997a]. These represent predictions which must be tested against future high pressure experimental data. Comparison to existing data at ambient conditions shows excellent agreement. In fact, the differences between experiment and theory are comparable to the differences between two different experiments (Table 2).

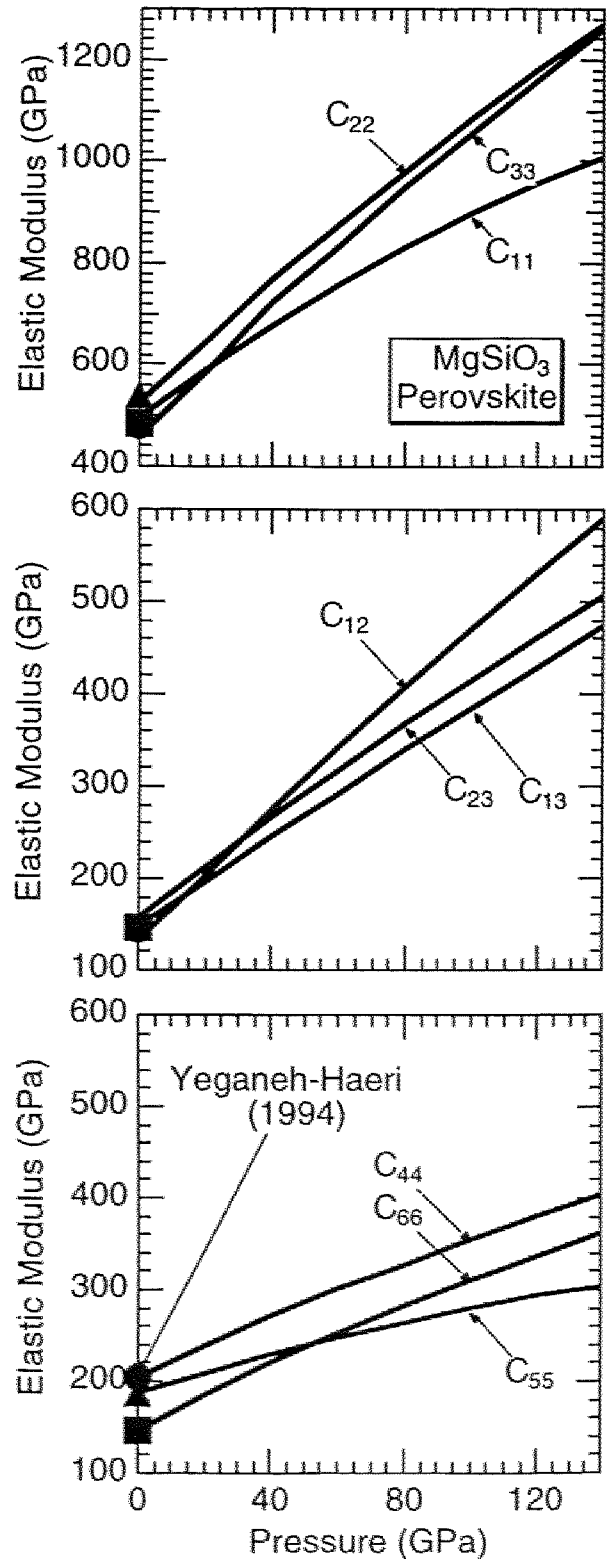


Figure 1. Elastic constants of  $\text{MgSiO}_3$  perovskite calculated from first principles (lines) [Karki *et al.*, 1997a] and compared with experimental measurements at ambient conditions (symbols).

Table 2. Elastic Constants of MgSiO<sub>3</sub> Perovskite

	$c_{11}$	$c_{22}$	$c_{33}$	$c_{12}$	$c_{13}$	$c_{23}$	$c_{44}$	$c_{55}$	$c_{66}$	$K$	$G$
<i>Semi-Empirical</i>											
Matsui et al. (1987)	460	506	378	139	184	177	162	159	112	260	140
<i>Ab Initio</i>											
Cohen (1987) (300 K)	531	531	425	44	143	166	237	249	136	249	192
<i>First Principles</i>											
Wentzcovitch et al. (1995)	496	560	504	132	136	156	151	198	171	267	179
Karki et al. (1997)	487	524	456	128	144	156	203	186	145	258	175
<i>Experiment</i>											
Yeganeh-Haeri et al. (1988)	520	510	437	114	118	139	181	202	176	245	184
Yeganeh-Haeri (1994)	482	537	485	144	147	146	204	186	147	264	177

Some of the differences between first principles theory and experiment are no doubt significant and arise from: 1) the fact that the theoretical calculations, while state-of-the-art, are approximate, in particular, the LDA and pseudopotential approximations and 2) the effect of zero point motion and room temperature, which is expected to be a few percent. The results of first principles theory agree much better with experiment than the results of semi-empirical pair potential calculations or ab initio models. This is expected, since essential aspects of the physics are neglected in the more approximate theoretical methods.

The effect of pressure on all the elastic constants is large. The longitudinal moduli vary by more than a factor of two over the mantle pressure regime; off-diagonal moduli vary by more than a factor of three; the effect of pressure is weakest for the shear elastic constants. For MgSiO<sub>3</sub>, the elastic moduli vary monotonically with pressure, but this is not true for all mantle minerals that have been studied. For example, in forsterite, two of the shear elastic constants are predicted to decrease with increasing pressure at very high pressures (outside of the mineral's stability field) [da Silva et al., 1997]. Also, a rapid decrease with increasing pressure is predicted for a combination of elastic constants near the stishovite to CaCl<sub>2</sub>-structure transition in silica (discussed below).

First principles calculations allow us to compare the expected effect of pressure on the elastic constants with the Eulerian finite strain expansion over a large range of strain (Fig. 2). The normalized elastic constants of

perovskite are found to depend nearly linearly on finite strain over a compression range of more than 10%. The finite strain expansion truncated at the linear term fits the theoretical elastic constants to within 1%. For the off-diagonal moduli ( $c_{12}, c_{13}, c_{23}$ ) the first principles results appear to resolve a small non-linear term.

These results indicate that, at least for MgSiO<sub>3</sub> perovskite, the finite strain expansion converges rapidly. Precise experimental measurements of the first pressure derivative of the elastic constants near ambient conditions may then be sufficient for reliable extrapolation to mantle pressure conditions, if the finite strain expansion is used for the extrapolation. It is worth pointing out explicitly that other expansions will not converge as rapidly. For example, a Taylor series expansion in the pressure is expected to converge very slowly: in the case of periclase, expansions linear and quadratic in the pressure, respectively, differ by 100% at relatively low pressures (60 GPa) [Karki et al., 1997b]. Other materials may require higher order terms in the finite strain expansion to accurately capture the pressure dependence of their elastic constants. For example, we found that a fourth order expansion was required to reproduce our predictions of the pressure dependence of  $c_{44}$  of periclase to within 1% (Fig. 3).

The theoretical results also show that single-crystal anisotropy may be qualitatively altered by increasing pressure. This is important because it means that measurements of elasticity at ambient pressure may not provide an accurate picture of the anisotropy of man-

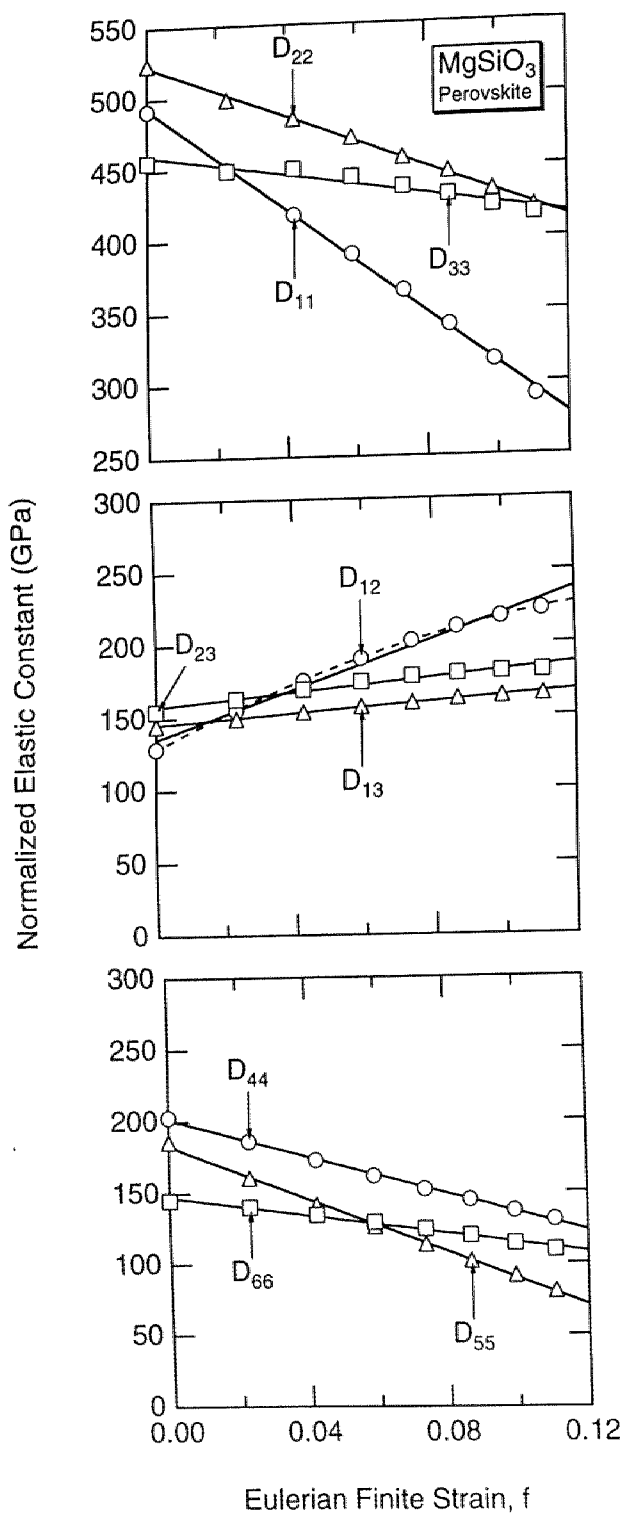


Figure 2. Analysis of the Eulerian finite strain expansion of the elastic constants. First principles results for  $\text{MgSiO}_3$  are plotted as normalized elastic constants versus the finite strain. Solid lines are linear fits to the results. Dashed line is a quadratic fit.

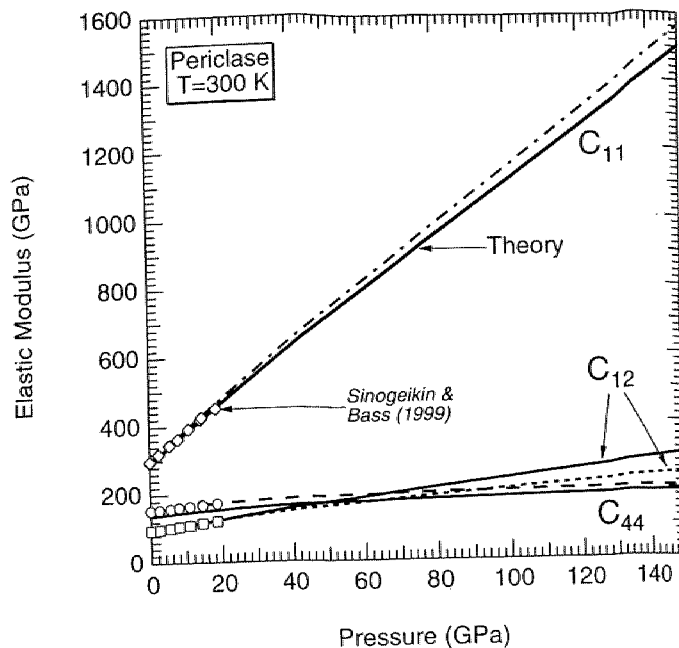


Figure 3. Elastic constants of periclase. Shown are: (solid lines) the results of athermal first-principles calculations [Karki *et al.*, 1997b], (dashed lines) finite-strain extrapolations of low pressure experimental measurements [Jackson and Niesler, 1982], and (symbols) recent experimental data.

tle phases at the relevant conditions. In the case of  $\text{MgSiO}_3$  perovskite, the change in anisotropy is most readily seen as a change in the relative magnitude of the longitudinal moduli: whereas  $c_{33}$  is the smallest of these at ambient pressure,  $c_{11}$  becomes smallest at pressures above 20 GPa. This change entails a change in the direction of slowest P-wave propagation from along the  $c$ -axis at ambient conditions, to along the  $a$ -axis at high pressure. Changes in the relative magnitude of shear and off-diagonal elastic constants are also apparent. These will be associated with changes in the directions of fastest and slowest shear wave propagation and polarization.

### 3.1. Anisotropy

Periclase shows the largest pressure-induced variation in anisotropy of the mantle materials studied to date [Karki *et al.*, 1997b]. Its anisotropy decreases with increasing pressure initially, vanishing at 15 GPa before increasing in magnitude upon further compression. At pressures corresponding to those of the core-mantle boundary, the shear wave anisotropy reaches a value of 59%, or more than three times the magnitude at ambient pressure. The non-monotonic dependence of



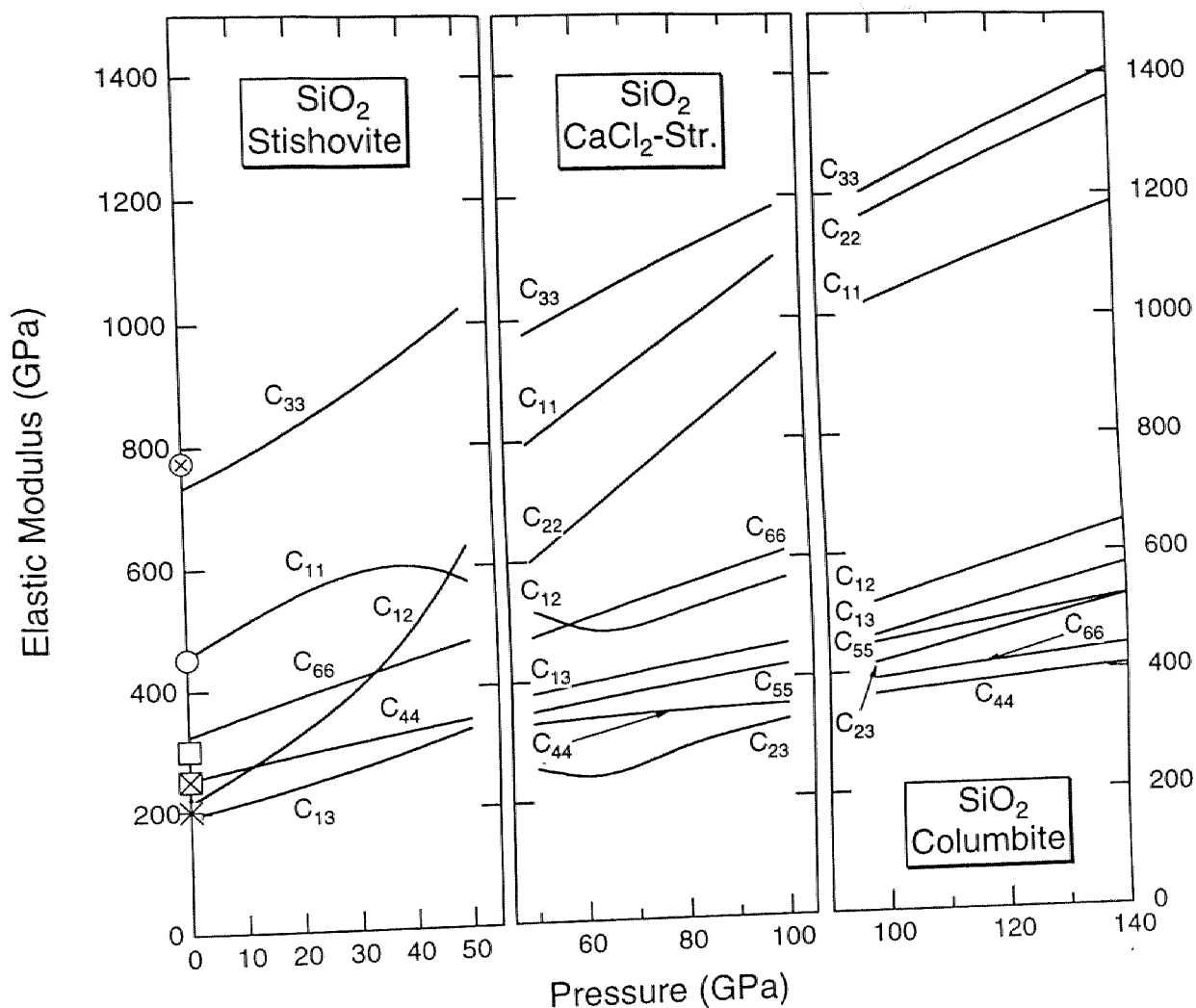


Figure 4. Elastic constants of silica from first principles (lines) for the three phases of silica that are predicted to exist throughout the mantle pressure regime. Results are compared with (symbols) experimental data on stishovite at ambient conditions [Weidner et al., 1982]. From [Karki et al., 1997c].

the anisotropy on pressure is associated with an interchange of fast and slow propagation directions: at high pressure, the sense of the anisotropy is the reverse of that at low pressure.

The pressure dependence of the anisotropy can be understood in terms of the anisotropy factor, which controls its sense and magnitude

$$A = \frac{c_{12} + 2c_{44}}{c_{11}} - 1 \quad (21)$$

For example, the velocity of pure longitudinal waves in a cubic crystal is

$$\frac{\rho V_P^2}{c_{11}} = 1 + 2A(n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2) \quad (22)$$

where  $n$  is the unit propagation vector. Because in MgO the pressure dependence of  $c_{11}$  is much greater than that of  $c_{12}$  or  $c_{44}$ , the anisotropy factor changes sign at a pressure of 15 GPa, leading to an interchange in the directions of fastest and slowest P- and S-wave propagation. For example, while P-waves travel fastest along  $\langle 111 \rangle$  at low pressure (corresponding to a positive value of  $A$ ),  $\langle 100 \rangle$  is the fast direction at pressures higher than 15 GPa (negative value of  $A$ ). Theoretically,

cal predictions of this behavior have recently been confirmed experimentally [Chen *et al.*, 1998; Sinogeikin and Bass, 1999].

Other minerals show qualitative changes in anisotropy as a function of pressure. The anisotropy of ringwoodite, though much smaller in magnitude, shows behavior similar to that of MgO: the anisotropy decreases with pressure initially and vanishes at a pressure of 18 GPa before increasing again at higher pressures [Kiefer *et al.*, 1997]. The pressure-induced changes in the anisotropy of MgSiO<sub>3</sub> perovskite are less marked but are also non-monotonic: the P-wave anisotropy decreases upon initial compression, reaches a minimum non-zero value near 20 GPa and then increases again at higher pressures; the S-wave velocity anisotropy shows similar behavior but with the anisotropy reaching a minimum at higher pressures [Karki *et al.*, 1997a]. The single-crystal anisotropy of silica actually diverges at a pressure near 47 GPa. This behavior is caused by an elastic instability and an associated phase transition.

### 3.2. Elastic Instability

The transformation from stishovite to the CaCl<sub>2</sub> structure was first predicted by Cohen [Cohen, 1992] and subsequently confirmed experimentally [Kingma *et al.*, 1995; Andraut *et al.*, 1998]. The two structures are related by a soft Raman mode that involves rotation of the SiO<sub>6</sub> octahedra about the *c*-axis. The coupling of this vibrational mode to a lattice strain in the *a*-*b* plane causes the combination of elastic constants ( $c_{11}-c_{12}$ ) to vanish at the transition [Karki *et al.*, 1997d] (Fig. 4).

This behavior leads to large elastic anomalies including the divergent anisotropy already noted. Computing the elastic properties of isotropic aggregates of silica in the neighborhood of the transition, one finds that the shear and longitudinal elastic wave velocities decrease substantially [Karki *et al.*, 1997c] (Fig. 5). The Hashin-Shtrikman averaged shear wave velocity decreases by nearly a factor of two, or 3 km s<sup>-1</sup>, before increasing sharply again as the transition is completed.

The anomaly is so large that it may be seismologically detectable, even if only small amounts of free silica are present in the earth's lower mantle [Karki *et al.*, 1997c]. Calculations show that as little as 3 % free silica would lead to a reflection coefficient of 1 %. The pressure at which the transition occurs under static conditions corresponds to a depth of 1180 km. The depth at which this transition would occur in the earth is uncertain because the effect of temperature on the phase transition is unknown. Reflectivity of unknown origin has been observed in a similar depth range in the lower man-

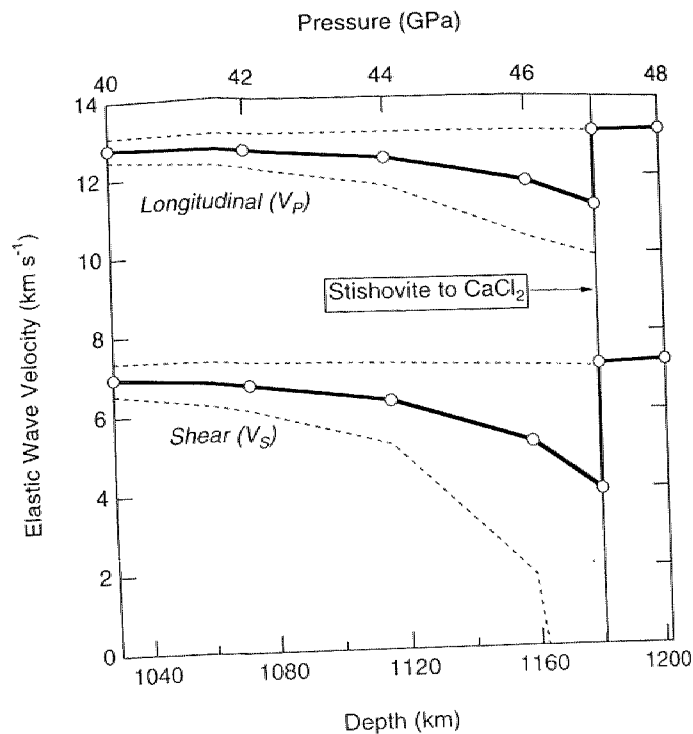


Figure 5. Isotropically averaged acoustic wave velocities in silica in the vicinity of the stishovite to CaCl<sub>2</sub>-structure transition. Solid and dashed lines are the Hashin-Shtrikman average values and bounds, respectively. From [Karki *et al.*, 1997c].

tle including at 920 km depth [Revenaugh and Jordan, 1991; Kawakatsu and Niu, 1995].

## 4. ELASTICITY AT HIGH TEMPERATURE AND PRESSURE

First principles calculations have not yet been successfully applied to the calculation of elasticity at high temperature, as discussed above. In order to investigate thermal effects, we extend our first principles results by adding to them a semi-empirical thermal correction based on quasi-harmonic finite strain theory. This represents an extrapolation to mantle temperature conditions that, in the absence of first principles or experimental results at mantle conditions is not certain. Because of this uncertainty, we focus on what qualitative effects temperature might have on elasticity.

We focus on the elastic anisotropy of periclase, in particular whether the very strong effect of pressure on the sense and magnitude of the anisotropy may be qualitatively altered by the effect of temperature. Thermal effects are calculated with Eqs. (7.15) using thermo-

elastic parameters that have been determined experimentally (Table 1).

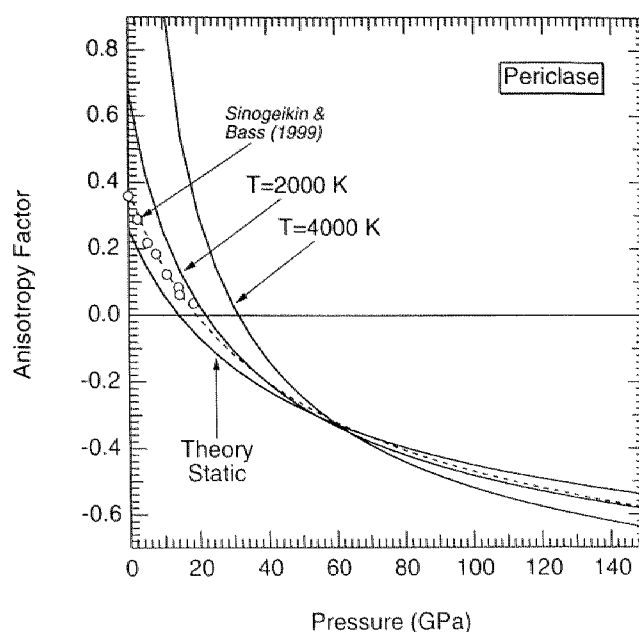
The effect of temperature at low pressures is to increase the anisotropy of periclase (Fig. 6). One result of this is that the pressure at which periclase becomes isotropic increases with increasing temperature: whereas periclase is predicted to become isotropic at 15 GPa under static conditions, at 2000 K it becomes isotropic at a pressure of 24 GPa. These results are in reasonable agreement with experimental observations [Chen *et al.*, 1998; Sinogeikin and Bass, 1999]. Experiments find a somewhat higher anisotropy than theory at low pressures; this difference is primarily due to the underestimate of  $c_{44}$  in the first principles calculations. At higher pressures, corresponding to those throughout most of the lower mantle, increasing temperature also increases the magnitude of the anisotropy, but the effect of temperature is less than at low pressure. At 140 GPa, the anisotropy changes by only 10 % between 0 and 4000 K.

These results indicate that, at least for the anisotropy of periclase, the effect of temperature is secondary to that of pressure in the lower mantle. Whether this pattern holds for other minerals and for other aspects of their elasticity awaits high temperature first principles calculations or experimental measurements at mantle conditions. However, it is worth pointing out that the result is not unexpected. To the extent that the elastic constants obey Birch's law, temperature should have a smaller effect because it affects density less than does pressure over the mantle regime [Karato, 1998].

## 5. CONCLUSIONS

It is now possible to predict from first principles the full elastic constant tensor, and the resultant elastic properties, for major materials of the earth's mantle. This approach is completely independent of experiment and therefore ideally complementary to it. First principles results are now capable not only of reproducing existing experimental results but of making predictions of the values of elastic constants, and of behavior such as elastic instability and anisotropy at high pressure, that have subsequently been confirmed by experiment.

We have found that the quasi-harmonic finite-strain theory of Davies [1974] provides an adequate description of the pressure- and temperature- dependence of the elastic moduli of periclase. Our extrapolations of first principles results to mantle temperatures confirm earlier first principles predictions that the elastic anisotropy of major mantle materials may change rad-



**Figure 6.** Elastic anisotropy of periclase. First principles results (static) and semi-empirical extrapolations to higher temperatures (lines) are compared with: (dashed lines) the finite strain extrapolation of low pressure experimental results [Jackson and Niesler, 1982] and (symbols) recent higher pressure results.

ically upon compression. This result is significant because it highlights the importance of the theoretical and experimental investigation of mantle minerals in situ at high pressure. In particular, the elastic anisotropy in the deep mantle is expected to be qualitatively different from that at ambient conditions, differing both in sense and magnitude.

One important direction of future work in the area of first principles studies of mantle materials will be the calculation of elastic properties at high temperature. The difficulties involved in such calculations were discussed in some detail above. With the development of first principles molecular dynamics, and existing computational power, such calculations may now be marginally feasible. Such an advance would be in step with parallel advances in experimental technique that now allow measurements at simultaneously high pressures and temperatures, and will be important for obtaining a better understanding of the origin of heterogeneity and anisotropy in the earth's mantle.

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