Crystal chemistry of forsterite: A first-principles study

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ABSTRACT

We present a first-principles study (local density approximation) of the structural properties of forsterite under pressure. This highly anisotropic magnesium orthosilicate is the most abundant phase of the Earth’s upper mantle, and its elastic properties determine the rheology of this region. We perform full structural optimizations and investigate its compressive behavior up to 25 GPa. We obtain a pressure dependence of lattice parameters that agrees well with experiments to 17.2 GPa. We predict that the coordination polyhedra compress essentially isotropically, and we explain the anisotropy of forsterite in terms of the nonuniform distribution of coordination polyhedra having different but nearly uniform compressibilities. In agreement with Brodholt et al. (1996), we do not find theoretical evidence for sudden changes in compression mechanisms in this mineral as had been suggested from experiments. Our results support the hypothesis that such compressive anomalies are caused by solidification of the pressure medium.

INTRODUCTION

The magnesium orthosilicate polymorphs are the dominant mineral phases of the top-most 660 km of Earth’s mantle. The low-pressure phase olivine is the major phase of the upper mantle, which represents nearly 20% of the planet’s volume. The composition of olivine in the upper mantle consists of ~90% forsterite, the Mg end-member. The properties and behavior of forsterite have been intensively studied because they determine the elasticity and rheology of the asthenospheric mantle and, in turn, plate-tectonic processes. An important observational constraint on the nature of flow in the sub-lithospheric mantle comes from seismological observations of anisotropy, which originate in the intrinsic elastic anisotropy of olivine. Moreover, the pressure-induced transformation of forsterite to wadsleyite under equilibrium conditions is largely responsible for the seismic discontinuity observed at depths of 400 km within the Earth. Lower temperatures suppress this transformation, however, and forsterite may persist metastably to much higher pressures and may be present in subducted lithospheric slabs to depths as great as 660 km (24 GPa) (Sung and Burns 1976; Rubie and Ross 1994).

The need to understand the structure and behavior of the upper mantle and of subducted lithospheric slabs has prompted numerous experimental investigations of the properties of forsterite at high pressure. Experimental X-ray diffraction and vibrational spectroscopy studies have both found evidence for a sudden change in the compressional behavior of forsterite near 9 GPa (Kudoh and Takeuchi 1985; Chopelas 1990). However, the compressional anomalies seen in single-crystal X-ray diffraction experiments have not been reproduced by more recent experiments that used a more hydrostatic pressure medium (Downs et al. 1996). An understanding of these results is essential because rapid changes in compression mechanism have important consequences for the elastic constants, and therefore for the seismic wave velocities of this geophysically important mineral.

In this paper we present a first-principles study of forsterite’s behavior under compression at zero temperature. The aim is to elucidate the origin of the anisotropic behavior under pressure and to investigate the nature of the compressional anomaly, if any, at the atomic scale.

COMPUTATIONAL METHOD

We use the plane-wave pseudopotential method (e.g., Cohen and Chelikowsky 1988) to solve the equations of density functional theory (Kohn and Sham 1965) in the local density approximation (LDA). An important issue in computations of complex structures, such as that of forsterite, is the efficient determination of the ground state (equilibrium) arrangement of the atoms. To find the equilibrium structure of forsterite at each pressure, we have used a first-principles implementation (Wentzcovitch et al. 1995) of a variable cell-shape molecular dynamics (VCSDM) algorithm (Wentzcovitch 1991). This method has been successfully used to determine the compressive and elastic behavior of other minerals under compression (Wentzcovitch et al. 1995a, 1995b). It is a quite conventional implementation of first principles molecular dynamics (MD) in which forces and stresses are calculated self-consistently (Wentzcovitch and Martins 1991) at every time step by resorting of iterative diagonalization
The equilibrium structure at arbitrary pressures can be found by performing this dynamics in damped mode and searching efficiently for the atomic configuration with zero stresses and forces (Wentzcovitch et al. 1993). For a structure with 14 degrees of freedom like forsterite, typically it takes 20–30 time steps to determine these parameters with three decimal digits. Care must be taken initially to choose a convenient fictitious cell mass that produces strain oscillations with periods similar to those of the atomic oscillations. The atomic masses can also be freely chosen. Whenever possible it is convenient to set all of them equal so we have a smaller range of frequencies for phonon modes. In the present case this was not the best approach. The Mg-O bonds are substantially more compressible than the Si-O bonds (smaller force constants), therefore Mg ions should be assigned smaller masses. The final choice was $M_{\text{Si}} = M_{\text{O}} = 15 \, m_{\text{p}}$, and $M_{\text{Mg}} = 10 \, m_{\text{p}}$ (proton masses), and the fictitious cell mass $W = 0.001 \, m_{\text{p}} a_{0}^{2}$ ($a_{0}$ is the Bohr radius). The MD time step is another free parameter in this algorithm, and it is chosen to minimize the number of total steps during the minimization. It is related to the average frequency of normal modes such that it takes 4–10 steps per average period. Ideally it would be desirable to have all normal modes with the same period and about two time steps per period; however, it is difficult to “guess” suitable free parameters to produce this situation, and practical experience usually dictates the choice. Note that the final structure does not depend on masses or time steps.

In this particular formulation of VCSMD the initial space group symmetry of the structure ($Pbnm$) is conserved if there are no thermal fluctuations, as it happens in the damped dynamics minimization (Wentzcovitch 1991). This property can be exploited in first-principles calculations by reducing $k$-point sampling to the irreducible wedge of the Brillouin zone (IBZ) and symmetrizing the resulting charge densities, forces, and stresses. Our results were obtained with one $k$ point ($\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$) in the IBZ, corresponding to a Monkhorst-Pack grid of $2 \times 2 \times 2$. The plane-wave expansion energy cut off ($E_{\text{pw}}$) have been chosen as 70 and 280 Ry for the wave functions and charge density-potentials, respectively (Calc. I). We have used the same Troullier-Martins (1991) pseudopotentials for Si, Mg, and O from previous studies of other silicates of magnesium polymorphs (Wentzcovitch and Price 1996). The convergence of the present results have been tested by performing completely similar calculations at the same $k$ point and $E_{\text{pw}}$ equal to 64 Ry for wave functions, charge densities, and potential (Calc. II). This second set of calculations provided a comparison of compressibilities and structural parameters. A third series of calculations (Calc. III) using eight $k$ points and the same $E_{\text{pw}}$ as Calculation I at the lowest pressure provided a better estimate of the accuracy of the zero-pressure parameters.

**RESULTS**

The crystal structure of forsterite is shown in Figure 1 as viewed along the three main crystallographic axes. There are two crystallographically distinct octahedral sites occupied by Mg ions (M1 and M2) represented by spheres of different shades, one tetrahedral site occupied by S, and three distinct O positions (O1, O2, and O3) at
tetrahedral corners. The O substructure forms a significantly distorted hexagonal close-packed arrangement because of the presence of non-uniform occupation of interstitial sites by Mg and S. This non-uniform occupation also gives rise to highly anisotropic behavior under compression, which has been the subject of several previous investigations (Hazen 1976; Kudoh and Takéuchi 1985) including one previous first-principles calculation (Brod-
larger than the experimental value of 127 GPa (Zha et al. 1996).

The pressure dependence of the lattice parameters obtained theoretically also agrees well with experiment: We find that the \( a \) axis compresses the least, while the \( b \) axis is most compressible, as observed experimentally (Fig. 3, Table 1). We compare our results with X-ray diffraction experiments and with recent determinations of the elastic constants of forsterite to 16 GPa (Zha et al. 1996). We obtain the pressure dependence of the lattice parameters implied by the elastic constant measurements by integrating

\[
\frac{\alpha(P)}{\alpha_0} = \exp \left[ - \int_0^P K_\alpha(P') dP' \right]
\]

where \( \alpha = a, b, \) and \( c, \) the lattice parameters at pressure \( P \) are \( \alpha(P) \), and \( \alpha_0 \) are the lattice parameters at zero pressure. The linear bulk moduli are defined by \( K_\alpha = (\partial P/\partial \ln \alpha)_T \) and are given in terms of the measured elastic constants, \( C_{ij} \), by (Nye 1985)

\[
K_a = \frac{D}{(C_{33} - C_{13})(C_{22} - C_{12}) - (C_{23} - C_{13})(C_{33} - C_{23})}
\]
\[
K_b = \frac{D}{(C_{33} - C_{13})(C_{11} - C_{21}) - (C_{13} - C_{12})(C_{33} - C_{23})}
\]
\[
K_c = \frac{D}{(C_{22} - C_{23})(C_{11} - C_{12}) - (C_{12} - C_{13})(C_{22} - C_{23})}
\]
\[
D = C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2
\]
\[
- C_{13}C_{23}^2.
\]

Our theoretical values of \( \alpha/\alpha_0 \) agree within 0.3% with those experimentally inferred from elastic constant measurements and with the results of most previous X-ray diffraction measurements (Fig. 3). The agreement between theory and the X-ray diffraction results of Will et al. (1986) and Andrault et al. (1995) is significantly worse, possibly due to non-hydrostaticity in these experiments.

Our theoretical results confirm the anisotropic compression of olivine seen experimentally and show that this anisotropy persists throughout its stability field. To show this, we determined the linear bulk moduli from our theoretical calculations by fitting our determinations of the lattice parameters as a function of pressure to linear finite-strain expansions (Davies 1974; Weaver 1976; Meade and Jeanloz 1990)

\[
F_a = K_a + m_f_a
\]

where \( f_a \) is the Eulerian finite strain

\[
f_a = \frac{1}{2} \left[ \frac{\alpha}{\alpha_0} \right]^2 - 1
\]

\[
F_a = \frac{P}{f_a(1 + 2f_a)(1 + 2f_a)}
\]

\( f_v \) is the volume Eulerian finite strain.
An examination of pressure-induced changes in internal structural parameters allows us to test this picture. The SiO₄ tetrahedron in forsterite has three unique bond lengths. Theoretically predicted Si-O bond lengths are within 0.3% of experimental values at zero pressure (Fig. 5). In agreement with the experimental zero-pressure structure, we find that Si-O₂ is the longest, Si-O₁ is the shortest, and that these differ by 2.5%. Predicted bond lengths in the M₁ and M₂ octahedra are somewhat smaller than experimentally observed (by 2.5%). This discrepancy, also found by Brodholt et al. (1996) and in LDA calculations of enstatite (Wentzcovitch et al. 1995b), accounts for the smaller zero-pressure volume and larger bulk modulus of our theoretical results compared with experiment. Its origin is most likely related to the use of the LDA. As a result, our calculations find the correct ordering and dispersion of Mg-O bond lengths: In the M₁ octahedron, M₁-O₃ (longest) and M₁-O₂ ≈ M₁-O₁ (shortest) differ by 3%; whereas in the M₂ octahedron, M₂-O₃ (longest) and M₂-O₂ (shortest) differ by 7%. This is important because the relative lengths of bonds are expected to control compressional anisotropy and compression mechanisms.

We find that SiO₄ and MgO₆ polyhedra compress nearly isotropically (Fig. 5). The ordering of Si-O bond lengths remains unchanged up to 25 GPa, while the difference between longest and shortest increases only slightly with compression. Except for an increase in the difference between M₁-O₁ and M₁-O₂ bond lengths, the ordering of Mg-O bond lengths is also unchanged by compression. The nearly isotropic compression of the coordination polyhedra can also be characterized by the quadratic elongation (Robinson et al. 1971). We find that the Mg octahedron become slightly more ideal (smaller quadratic elongation) with increasing pressure, whereas the tetrahedron becomes slightly more distorted (larger quadratic elongation) with increasing pressure. The pressure-induced changes in quadratic elongations are small: Elongations of the Si, M₁, and M₂ polyhedra change by 0.3, 0.6, and 0.6%, respectively, between 0 and 25 GPa. Although these are significant differences in terms of the precision of our calculations, they are small compared with the decrease in bond lengths experienced by these polyhedra over the same pressure range.

Our calculations show that the SiO₄ polyhedra compress much less than the Mg polyhedra, as expected on the basis of the greater strength of the Si-O bond and experimental studies of other silicates (Hazen and Finger 1982). The total change in volume of the Si, M₁, and M₂ polyhedra between 0 and 25 GPa is 6, 13, and 16%, respectively. The zero-pressure polyhedral bulk moduli (Hazen and Finger 1979) span the bulk modulus of the crystal (Table 2).

The theoretical calculations show important similarities to the high-pressure crystal structure refinements of Kudoh and Takéuchi (1985). Though the scatter in the data is substantial, the tendency of the polyhedra to compress approximately isotropically is evident in some cases (Fig.
5). As in our calculations, M1-O1 remains the shortest bond in the M1 octahedron, and M1-O3 the longest over the experimental pressure range (Fig. 5). In the M2 octahedron, except for the highest experimental refinement, where uncertainties are substantial, the M2-O3 bond remains the longest, and M2-O2 the shortest. In the Si tetrahedron, Si-O3 remains longer than Si-O1, but Si-O2 compresses much more in the experiments than in our calculations.

There are also significant differences between experiment and theory. The experimental data show that the SiO₄ tetrahedron is as compressible as the Mg octahedra, in disagreement with our results and with the behavior of essentially all other high-pressure silicate crystal structure refinements (Fig. 6). In comparison with our results, the

<p>| Table 2. Crystal and polyhedral bulk moduli |</p>
<table>
<thead>
<tr>
<th>Calc. I</th>
<th>Calc. II</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsterite</td>
<td>$K_0$</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>$K'$</td>
<td>4.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>$K_0$</td>
<td>407</td>
</tr>
<tr>
<td>M1O₆</td>
<td>$K_0$</td>
<td>158</td>
</tr>
<tr>
<td>M2O₆</td>
<td>$K_0$</td>
<td>118</td>
</tr>
</tbody>
</table>

Note: Polyhedral bulk moduli obtained from second-order Eulerian finite-strain fits ($K_0' = 4.0$); third-order fits were not significantly better.
† Olinger (1977).
‡ Hazen (1976).
**FIGURE 7.** Pressure dependence of the ratios of real cell volume, $V$, to ideal calculated cell volume, $V_{hcp}$, for three arbitrary definitions of $V_{hcp}$ in terms of lattice parameters $a$, $b$, and $c$. See text.

Experimental data exhibit much more anisotropic and irregular compression of the polyhedra as shown by the measured polyhedral elongations as a function of pressure. Kudoh and Takéuchi found that M1-O3, M1-O2, M2-O1, and M2-O3 increase with pressure in disagreement with our results and with experimental data for other minerals. This pressure-induced increase in Mg-O bond lengths is reflected in a sudden change in the compressibility of the M1 octahedron near 9 GPa. This result is inconsistent with our theoretical calculations. We find no evidence in the pressure dependence of bond lengths and polyhedral volumes for a sudden change in compressibility of any structural element between 0 and 25 GPa. Our theoretical results support those of Brodholt et al. (1996) who analyzed variations in internal structural parameters only in terms of average bond lengths.

Another issue raised by Kudoh and Takéuchi’s analysis of their data concerns the distortion of the O substructure.

**DISCUSSION**

We find no anomalies in the compression of forsterite to a pressure of 25 GPa. The volume and lattice parameters show no sudden changes in their compressibilities. Moreover, bond lengths and polyhedral volumes also decrease smoothly with pressure. We therefore find that no obvious changes occur in compression mechanism over the pressure range studied. These results are inconsistent with the existence of sudden changes in the compressibility of lattice parameters or bond lengths (Kudoh and Takéuchi 1985) or with sudden changes in mode Grünisen parameters (Chopelas 1990) and support the results of Brodholt et al. (1996). The theoretical calculations lend support to the conclusions of Downs et al. (1996) that previous evidence for compressional anomalies in forsterite are due to the sudden onset of non-hydrostaticity.
The compression of forsterite is found to be significantly anisotropic up to at least 25 GPa. The b axis is nearly twice as compressible as the a axis over the entire pressure range. The compressional anisotropy of olivine is only weakly dependent on pressure. This result is of seismological as well as crystal-chemical interest. The anisotropy of olivine plays a central role in the interpretation of seismological measurements of the radial and transverse anisotropy of the upper mantle (Tanimoto and Anderson 1984). We note however, that our theoretical results provide only a partial description of P- and S-wave anisotropies in this mineral, constraining only the three combinations of elastic constants (Eq. 2–5). A complete theoretical description of the anisotropy of forsterite and its pressure dependence awaits a theoretical determination of the full elastic constant tensor.

Despite the strongly anisotropic compression of the forsterite structure, we find that the coordination polyhedra compress nearly isotropically. This seeming contradiction is resolved by recognizing that the forsterite structure is inherently anisotropic, with rows of relatively compressible (Mg1 octahedra) and incompressible (Si tetrahedra) polyhedra alternating along [100] (Hazan 1987). To illustrate this, we show that the relative magnitudes of \( K_a, K_b, \) and \( K_c \) can be rationalized in terms of polyhedral compressibilities. We assume that the polyhedra compress perfectly isotropically and that they suffer no rotation under compression. A consideration of the elements of the forsterite structure then allows us to relate directly polyhedral and axial compressibilities. Parallel to [001] are chains of edge-sharing M1 octahedra. These chains of M1 octahedra alternate along the [010] axis with M2 octahedra. Along the [100] axis, the M1 octahedral chains alternate with rows of Si tetrahedra. Remembering that linear and volume compressibilities are related by a factor of three, and using the polyhedral moduli from our LDA results, the axial compressibilities can be approximated by:

\[
K_a \approx 6(1/K_{\text{Mg1}} + 1/K_{\text{Si}})^{-1} = 683 \text{ GPa}
\]

\[
K_b \approx 6(1/K_{\text{Mg1}} + 1/K_{\text{Mg2}})^{-1} = 405 \text{ GPa}
\]

\[
K_c \approx 3K_{\text{Mg1}} = 474 \text{ GPa}.
\]

The axial moduli predicted by this simple structural model are all significantly overestimated in comparison with the results of our quantum mechanical calculations (Fig. 4). The reason for this is that the structural model is oversimplified. If we take into account polyhedral distortions and the rotation of octahedra, for instance rotations of the M1 octahedra about their shared edges, the predicted moduli are smaller and in better agreement with our LDA results. However, the relative magnitudes of the axial moduli are correct (\( K_b > K_a > K_c \)) and the ratios of the moduli (\( K_b/K_a = 1.46, K_c/K_a = 1.68 \)) are similar to those derived from the LDA results. This shows that the anisotropic compression of the forsterite structure can be explained essentially in terms of isotropic polyhedral compressibilities. Hazen (1987) came to a similar conclusion. However, he assumed that \( K_{\text{Mg1}} \approx K_{\text{Mg2}} \) and restricted his analysis to the ratio \( K_b/K_a \). He further assumed, as we have done, that the polyhedra compress approximately isotropically. Our LDA calculations, which show that pressure-induced changes in quadratic elongation are small, lend substantial theoretical support to this assumption. This prediction must be tested against new high-resolution crystal-structure refinements at high pressure.

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in the experiments, which is known to occur at approximately the same pressure at which the compressional anomalies were seen (9 GPa).


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