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LETTERS

An ab initio study of the compressional behavior of forsterite

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Abstract

Ab initio calculations using the local density approximation and pseudopotentials were made on forsterite from 0 to 700 kbar. Our calculations are generally consistent with almost all the experimental cell-parameter and bond-length data. In contrast to some experimental data, however, we find no evidence for abrupt changes in compressional mechanism at any pressure.

Introduction

The compressional mechanisms of forsterite, the major phase in the upper mantle, are of considerable interest to geophysicists. In particular, the elastic properties are fundamental to the interpretation of seismic data. There have been several experimental studies on the elastic moduli of forsterite up to 700 kbar, resulting in a value for the bulk modulus (K) between 1230 and 1360 kbar and a pressure derivative (dK/dP) between 3.5 and 4.5 [see Knittle (1995) for a review]. Although the elastic moduli of different experimental studies are apparently in agreement, it has been argued that the compression of forsterite is not a smooth function of pressure but in fact exhibits abrupt discontinuities in cell parameters and bond lengths. Kudoh and Takéuchi (1985) found that the *a* and *b* cell parameters (in this paper we use the space group *Pnma*) suddenly become significantly less compressible near 80 kbar, which is also reflected in V/V_0. They also found that the M1-O bond distance becomes incompressible at the same pressure. More recently, the experiments of Andrault et al. (1995) also appeared to show a sharp decrease in the compressibility of olivine, but in this case breaks occurred in all three cell dimensions and at the much higher pressure of about 400 kbar. This is seen in olivines with Fe/Mg ranging from 0 to 1. In contrast to these two studies, the experiments of Will et al. (1986) showed no discontinuous breaks in the compressional behavior of forsterite from 0 to 300 kbar, and the data are fitted very adequately with a single set of elastic constants.

Further evidence for discontinuities in the compressibility of forsterite is given by Raman spectroscopy, which shows a distinct decrease in the pressure gradient of several bands at 91 kbar (Chopelas 1990). This was interpreted as a second-order phase transformation. Because it occurred at a pressure similar to the 80 kbar "locking up" of the M1-O bond seen by Kudoh and Takéuchi (1985), it is tempting to associate the change in the Raman bands with that mechanism. This interpretation is inconsistent with the compressional data, however, because abrupt changes in higher frequency bands assigned to internal SiO_4 modes are also observed in the Raman data; and the compressional data exhibit a smooth decrease in length of the Si-O bond (Kudoh and Takéuchi 1985).

To test whether there are sudden changes in the compressional mechanisms of forsterite with pressure, we performed ab initio density-functional calculations (DFT) on forsterite from 0 to 700 kbar. In summary we find no evidence for discontinuous changes in any of the cell parameters or bond lengths, and the compressional behavior of forsterite is very well described by a single Birch-Murnaghan finite-strain equation of state over the entire pressure range.

Calculations

Calculations were performed using the parallel density-functional (DFT) code CETEP (Payne et al. 1992). This code utilizes the local density approximation (LDA) (Perdew and Zunger 1981) for the exchange-correlation potential and ab initio norm-conserving, nonlocal, Kleinman-Bylander-type pseudopotentials for the valence-core electron interactions (Kleinman and Bylander 1982; Lin et al. 1993). The use of pseudopotentials means that only the valence electrons are considered explicitly, which results in significant savings in computational requirement. Periodic boundary conditions were employed, and the valence orbitals were represented by a plane-wave expansion. There are no adjustable parameters at this level of theory, and no experimental data are used except for the mass and charge of the electron and Planck's constant. There are no significant approximations in these calculations except that of the exchange-correlation function. A substantial advantage of the plane-wave basis set is that forces and stresses may be easily evaluated using the

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TABLE 1. Summary of calculated cell parameters

P (kbar)	a (Å)	b (Å)	c (Å)	V (Å^3)
0.0	9.988	6.074	4.643	281.67
50.0	9.828	6.009	4.603	271.84
100.0	9.695	5.953	4.568	263.64
150.0	9.571	5.906	4.537	256.46
200.0	9.460	5.864	4.510	250.18
300.0	9.253	5.798	4.463	239.44
400.0	9.059	5.750	4.423	230.39
500.0	8.883	5.714	4.388	222.72
600.0	8.713	5.689	4.356	215.92
700.0	8.542	5.677	4.325	209.73

Hellman-Feynman theorem (Payne et al. 1992) and used to relax both the atomic coordinates and the unit-cell parameters to minimize the total energy (Wentzcovitch et al. 1993).

The cell parameters were optimized until the pressure was within 0.5 kbar of the desired value, and all 28 atoms in the unit cell were allowed to relax fully until the net force on any atom was <0.002 eV/Å. Owing to the size of the system and the number of degrees of freedom that were optimized (the positions of 28 atoms and the three cell parameters), only the Γ point (0,0,0) was used to sample the Brillouin zone. Convergence as a function of k-point sampling was investigated by comparing sample calculations at the Γ point with a four-point set chosen using the Monkhorst-Pack (Monkhorst and Pack 1976) scheme. The total energies are within 0.04 eV/atom. Energy differences are much better converged: The energy changes between 0 and 200 kbar are within 1.0×10^{-5} eV/atom of each other. Cell parameters are also well converged, with results from the two k-point schemes agreeing to within 1% at both pressures. Most important though is the fact that the compressional behavior was unchanged. M1-O, M2-O, and Si-O bond lengths calculated with one k point are within 0.3% of those calculated with four k points. The insensitivity of the bond lengths, in particular, to k-point sampling confers a high level of confidence about the robustness of our results. Plane waves up to an energy of 600 eV were accepted, allowing a basis set of 9693 plane waves. This resulted in almost completely converged total energies and energy differences that were completely converged.

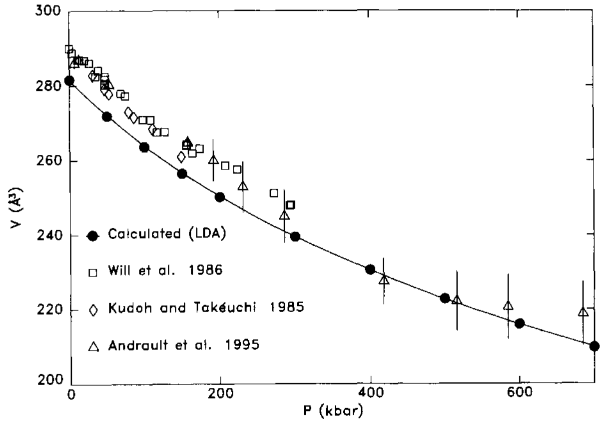

FIGURE 1. Comparison of the calculated volumes and the experimental data. The cell volumes are slightly underestimated, which is usual in LDA calculations.

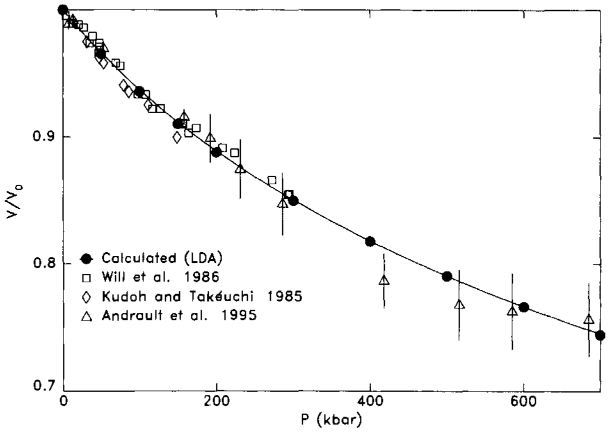

FIGURE 2. The experimental compression data for forsterite are reproduced very well over the entire pressure range by the calculations. Note that there is no evidence for any changes in compressional mechanism at any pressure and that the calculated volumes are well fit by a Birch-Murnaghan equation of state (solid line through the calculated points).

When using pseudopotentials for compression calculations, a possible source of error arises if the core regions of neighboring atoms overlap. A change in overlap as bond length decreases can alter the compressive strength of the bond. In our case, however, the only overlap occurs in the Si-O bond, which compresses from 1.6 to 1.55 Å. Other calculations on Si-O bond compression in $CaSiO_3$ perovskite show the maximum consequent errors in the total energy and bond lengths are 0.04 eV/bond and 0.004 Å, respectively (Refson, in preparation).

RESULTS

Table 1 summarizes the cell parameters and volumes for pressures ranging from 0 to 700 kbar, and Figure 1 compares the calculated V as a function of pressure with the experimental data. As is generally the case with LDA-type calculations, the cell parameters are slightly too small. In contrast, Figure 2 compares V/V_0 with the experimental data and shows that, if all the data are taken together, the observed compressibility is reproduced very accurately over the entire pressure range. A Birch-Murnaghan fit of the calculated data yields a value for K of 1344 ± 7 kbar and dK/dP of 3.88 ± 0.04. This is in very good agreement with other estimates (see Introduction).

The individual cell parameters are also accurately reproduced by the LDA calculations. Figure 3 compares the calculated values of a/a_0, b/b_0, and c/c_0 with experimental data. At lower pressures (<300 kbar) the agreement between the calculated values and the experimental

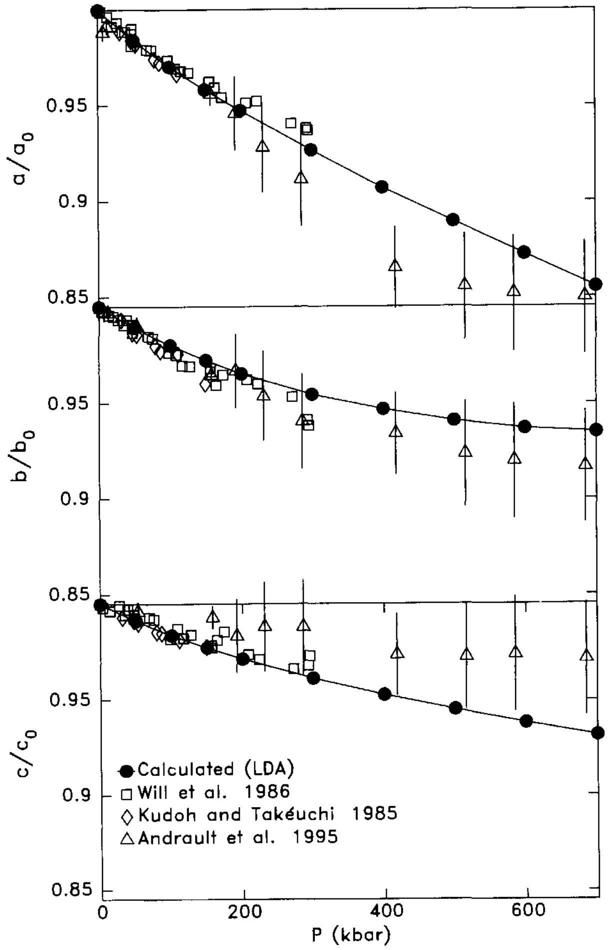

FIGURE 3. The experimental compression data for the individual cell parameters are well reproduced by the LDA calculations. At higher pressures the calculated values of a/a_0 and c/c_0 are somewhat higher and lower, respectively, than the data of Andrault et al. (1995) (see text). There is no evidence for a change in compressional behavior for any of the calculated cell parameters.

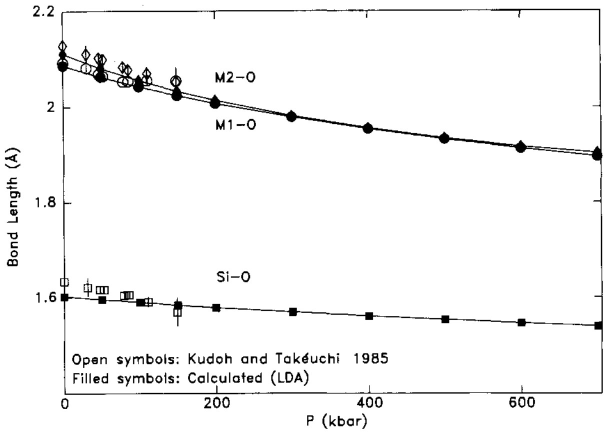

FIGURE 4. The calculated M1-O bond length does not show the sudden decrease in compressibility at 80 kbar that is seen in the experimental data. M1-O, M2-O, and Si-O show smooth continuous compression from 0 to 700 kbar.

data is exceptionally good. However, at higher pressures the agreement with the experimental data appears to be not so good, with calculated values of a/a_0 just outside the error bars of Andrault et al. (1995). In fact, their lower pressure data agree with the other data only at the extremes of the error bars; this is particularly clear for c/c_0. The data of Andrault et al. (1995) were collected as part of a study concerned with pressure-induced amorphization, so nonhydrostatic conditions were purposely created by not using a pressure medium. This best explains the observed differences, and we believe, therefore, that our calculated values for the compressibility of the cell parameters are accurate over the entire pressure range examined here.

Figure 4 shows average M1-O, M2-O, and Si-O bond lengths obtained from the experiments of Kudoh and Takéuchi (1985) and from the LDA calculations. The experimental data show that the M1-O bond becomes essentially incompressible at 80 kbar. This is not seen in the calculated bond lengths, which maintain smooth compressional behavior over the entire pressure range. The calculated Si-O bonds also maintain a smooth and practically linear decrease in length over the entire pressure range. This is consistent with the experimental data.

DISCUSSION

The calculations performed here provide no evidence for any change in the compressional behavior of forsterite at any pressure from 0 to 700 kbar. All three cell parameters compress smoothly, and there are no discontinuous changes in the compressibilities of the M1-O, M2-O, and Si-O bonds. Given the fact that there is excellent overall agreement between our calculations and the experimental cell parameters and bond lengths (both at low and high pressures), we believe that there is sufficient reason to have a high level of confidence in these results.

The large nonhydrostatic stresses in the experiments of Andrault et al. (1995) make any comparison with our results difficult. The changes in compressional behavior that they observed were probably caused by the large nonhydrostatic stresses and perhaps were associated with the onset of amorphization.

Kudoh and Takéuchi (1985) argued for a sudden decrease in the compressibilities of the *a* and *c* axes at 80 kbar. A critical examination of their Figure 1 shows, however, that this interpretation depends heavily on experiments between 130 and 150 kbar, which have quite significant uncertainties. We believe that their data could be fitted well with one Birch-Murnaghan equation of state and that an analysis would show that fitting with two equations of state is not statistically valid. (We did not do this because they tabulated only about one-third of the data shown in their figure.) Their analysis of the bond lengths also depends heavily on one experimental point. With the exception of their 111 kbar experiment our calculated M1-O bonds agree with theirs within experimental error.

Lastly we consider the spectroscopic data of Chopelas (1990), which show abrupt breaks in the slopes of six Raman bands at 91 kbar. These breaks occur not only in low-frequency modes, which can be associated with Mg-O bonds, but also at higher frequencies, which are associated with internal SiO_4 modes. Although the low-frequency bands could be consistent with the compressional changes in the M1-O bond seen by Kudoh and Takéuchi (1985), the break in the higher frequency bands is inconsistent because the compressional data show smooth compressibility of the Si-O bond from 0 to 150 kbar. Although we cannot determine what the breaks in the Raman bands represent, we do not believe they are caused by a simple change in compressional mechanism owing to a sudden incompressibility of the M1-O bond.

In conclusion, our calculations on the compressibility of forsterite are inconsistent with the claimed sudden changes in compressional mechanisms in forsterite at any pressure between 0 and 700 kbar.

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REFERENCES CITED

Andrault, D., Bouhifd, M.A., Itié, J.P., and Richet, P. (1995) Compression and amorphization of $(Mg,Fe)_2SiO_4$ olivines: An X-ray diffraction study up to 70 GPa. Physics and Chemistry of Minerals, 22, 99–107.

Chopelas, A. (1990) Thermal properties of forsterite at mantle pressures derived from vibrational spectroscopy. Physics and Chemistry of Minerals, 17, 149–156.

Kleinman, L., and Bylander, D.M. (1982) Efficacious form for model pseudopotentials. Physical Review Letters, 48, 1425–1428.

Knittle, E. (1995) Static compression measurements of equations of state. In T.J. Ahrens, Ed., Mineral physics and crystallograpy: A handbook of physical constants, p. 98–142. American Geophysical Union, Washington, DC.

Kudoh, Y., and Takeúchi, Y. (1985) The crystal structure of forsterite Mg_2SiO_4 under higher pressure up to 149 kb. Zeitschrift für Kristallographie, 171, 291–302.

Lin, J.S., Qteish, A., Payne, M.C., and Heine, V. (1993) Optimized and transferable non-local separable ab initio pseudopotentials. Physical Review B, 47, 4174–4180.

Monkhorst, H.J., and Pack, J.D. (1976) Special points for brillouin-zone integrations. Physical Review B, 13, 5188–5192.

Payne, M.C., Teter, M.P., Allan, D.C., Arias, T., and Joannopoulos, J.D. (1992) Iterative minimization techniques for ab-initio total energy calculations: Molecular dynamics and conjugate gradients. Reviews of Modern Physics, 64, 1045–1097.

Perdew, J.P., and Zunger, A. (1981) Self-interaction correction of density-functional approximations for many-electron systems. Physical Review B, 23, 5048–5079.

Wentzcovitch, R.M., Martins, J.M., and Price, G.D. (1993) Ab-Initio molecular dynamics with variable cell shape: Application to $MgSiO_3$. Physical Review Letters, 70, 3947–3050.

Will, G., Hoffbauer, W., Hinze, E., and Lauterjung, J. (1986) The compressibility of forsterite up to 300 kbar measured with synchrotron radiation. Physica, 139 and 140B, 193–197.

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