Ab initio studies of structural instabilities in magnesium silicate perovskite

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Density-functional simulations are used to calculate structural properties and high-symmetry phonons of the hypothetical cubic phase, the stable orthorhombic phase and an intermediate tetragonal phase of magnesium silicate perovskite. We show that the structure of the stable phase is well described by freezing in a small number of unstable phonons into the cubic phase. We use the frequencies of these unstable modes to estimate transition temperatures for cubic → tetragonal and tetragonal → orthorhombic phase transitions. These are investigated further to find that the coupling with the strain suggests that phonons give a better representation than rigid unit modes. The phonons of an intermediate tetragonal phase were found to be stable except for two rotational modes. The eigenvectors of the most unstable mode of each of the cubic and tetragonal phases account for all the positional parameters of the orthorhombic phase. The phase boundary for the orthorhombic–tetragonal transition intersects possible mantle geotherms, suggesting that the tetragonal phase may be present in the lower mantle.

I. INTRODUCTION

Magnesium silicate makes up most of the material in the Earth’s lower mantle, and its properties and phase transitions determine much of the density distribution, thermal properties and discontinuities of the mantle (Catlow and Price 1990, Navrotsky and Weidner 1989). Such discontinuities, which may be chemical (involving substitution of iron for magnesium) or physical transitions, have been observed in the lower mantle at several depths (Stixrude and Cohen 1993, Kawakatsu and Niu, 1994). Convection in the upper and lower mantles, caused by temperature gradients, is also a topic under debate (Bukowinski and Wolf 1988, Jeanloz and Morris 1986), and the possibility of temperature-induced phase transitions in MgSiO$_3$ may help to ascertain the actual behaviour of the mantle.

The phase of MgSiO$_3$ believed to exist in the mantle has the perovskite structure displayed by many other compounds. This structure exhibits a wide variety of behaviour, with a multitude of possible phase transitions (Lines and Glass 1977). Despite much study (reviewed by Navrotsky and Weidner (1989) and Hemley and Cohen (1992)), the properties of MgSiO$_3$ are still not fully understood: attempts to produce samples for X-ray diffraction under mantle pressures have met with difficulty (Hemley et al. 1987, Mao et al. 1991, Ross and Hazen 1990). However, there has been evidence for an orthorhombic–tetragonal–cubic series of transitions from observations of twinning in the orthorhombic phase after quenching from high temperatures (Wang et al. 1992).

This work considers the observed orthorhombic (Pbnm) phase, the hypothetical high-temperature cubic phase (Pm3m) and an intermediate tetragonal phase (I4/mcm); symmetry increases with increasing temperature. The vibrational dynamics of these modes is very important since transitions between these phases are likely to proceed via soft-mode mechanisms (Hemley and Cohen 1992). We calculate the frequencies and eigenvectors of some high-symmetry phonons of all three phases using density-functional simulations, and also investigate which phonons would be involved in transitions between the three phases.

The triply degenerate zone-centre phonons of several other perovskites have already been found from first principles (Cohen and Krakauer 1990, Postnikov et al. 1994 and King-Smith and Vanderbilt 1994). The eigenvectors calculated by King-Smith and Vanderbilt (1994) correctly predict the symmetry of distorted phases with one formula unit in the unit cell (i.e. those in which only zone-centre phonons can freeze in). However, the orthorhombic phase of MgSiO$_3$ contains twenty atoms, as opposed to the five atoms in the cubic unit cells, so at least some of the phonons involved in any transition between cubic and orthorhombic phases must lie away from the zone centre of the cubic phase. A simulation of more than one unit cell of the cubic crystal is thus required to calculate these zone-boundary phonons.

The transition temperatures required for the cubic and tetragonal phases were estimated by using the phonon frequencies to parameterise a simple model. The variation of these temperatures under pressure is deduced from a combination of first-principles Gruneisen parameters and bulk modulus, and experimental thermal expansivities; compensation for the effect of the Local Density Approximation (LDA) is discussed in Section VI A.

The structure of this paper is as follows: Section II gives the phases studied; in Section III we describe our ab initio methods; Sections IV, V and VI give results for cubic, tetragonal and orthorhombic phases respectively; Section VII analyses the important phonons of the cubic phase and considers the role of the tetragonal phase. Section VIII discusses calculations of transition temperatures. Sections IX and X discuss the conclusions which have been reached.

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II. STRUCTURE

All phases of MgSiO$_3$ perovskite essentially consist of octahedral ‘cages’ of oxygen atoms, linked at the corners, each containing a silicon ion in the centre. In the spaces between the octahedra there are 12-fold coordinated magnesium ions. However, in the orthorhombic structure, the octahedra are rotated around the silicon (B) ions, and the magnesium (A) ions are displaced, as shown in Figure B, giving space group $Pbnm$. This is the form of MgSiO$_3$ observed under ambient conditions (Yagi et al. 1978) and assumed to be the dominant phase in the lower mantle. The tetrahedral structure is an intermediate, having octahedral rotations about only one axis, with $I4/mcm$ symmetry; the reasons for its consideration are given in Section VII B.

The oxygen octahedra are nearly perfectly rigid. The ‘rigid unit’ model of such structures (Giddy et al. 1993) assumes that they are incompressible and cannot be distorted. If they rotate, continuing to share oxygen atoms at the corners, the unit cell vectors perpendicular to the rotation axis must therefore decrease in length. Such rotational modes are known as ‘rigid unit modes’. At the other extreme, true phonon modes must preserve the size and shape of the unit cell, so the octahedra must enlarge and distort slightly if they are to rotate. The applicability of these models to MgSiO$_3$ is investigated and discussed in more detail in Section VII C.

III. AB INITIO LATTICE DYNAMICS

Density functional simulations have already been used to investigate lattice dynamics in many materials, e.g. Srivastava and Kunc (1988). The most popular ‘direct’ approach involves finding the change in energy and/or forces when one atom is displaced from its equilibrium position by a small amount, to give some of the harmonic force constants $\Phi$ of the crystal. A crystal is divided into $L$ primitive cells, labelled by $l$, each containing $r$ atoms, labelled by $\kappa$. If the displacement from equilibrium of the atoms is given by $u^{(l)}(\kappa)$ and the forces on the atoms by $F^{(l)}(\kappa)$, the force constants are defined by

$$ F_{\alpha}^{(l)}(\kappa) = \sum_{l'} \sum_{\kappa'} \sum_{\beta} \Phi_{\alpha\beta}(\kappa \kappa') u_{\beta}^{(l')} $$

The periodicity of the crystal, and hence of any phonon, can be used to reduce the problem of solving $3Lr$ equations of motion to $3r$ (Maradudin et al. 1971). The frequencies $\omega$ and eigenvectors $\epsilon$ of the phonons at a wavevector $q$ are now found by solving the eigenproblem:

$$ -\omega^2 \epsilon = D(q) \epsilon $$

The Fourier-transformed dynamical matrix $D(q)$ is given in mass-reduced coordinates by

$$ D_{\alpha\beta}(\kappa \kappa'|q) = \frac{1}{\sqrt{m_{\kappa}m_{\kappa'}}} \sum_{l} \Phi_{\alpha\beta}(\kappa \kappa') \exp(iq \cdot x^{(\kappa)} - \frac{x^{(\kappa)}}{m_{\kappa}m_{\kappa'}}) $$

Hence knowledge of all the force constants $\Phi$ of the structure enables all the phonons to be found. As it stands, the phonons at any wavevector can be found, but all the force constants of the infinite crystal must be known. A simulation of a ‘supercell’ consisting of a small number of unit cells can give only specific combinations of force constants. However, periodic boundary conditions restrict the phonons which may exist in such a supercell to those which have the periodicity of the supercell. For these modes, the combinations of force constants can be treated as the true force constants if the sum over $l$ in (3) now runs over only the unit cells in the supercell. In general, this restriction applies when the range of the forces is greater than the size of the supercell. Investigations in this case show this to be so, probably due to the large degree of ionicity in the structure. This method of calculating phonons does have limitations, but is simple to apply to existing density-functional schemes; in our case we are only concerned with phonons at high-symmetry points of the Brillouin Zone, which can be obtained in this way.

We used a self-consistent density-functional scheme within the LDA, employing norm-conserving, nonlocal, Kleinman-Bylander pseudopotentials (Kleinman and Bylander 1982, Kerker 1980). A plane-wave basis set was used for the electronic wavefunctions, with energies up to a cutoff of $E_{\text{cutoff}} = 500$ eV, corresponding to approximately 4000 plane waves at each $k$-point for a twenty atom cell. A Monkhorst-Pack $k$-point scheme (Monkhorst and Pack 1976) was used to give 4 $k$-points in the Brillouin Zone.

In this work, an adaptation of the castep code was used (Payne et al. 1992) which gives the Hellmann-Feynman forces on each atom, from which the force constants can be calculated. Each simulation of the crystal with one atom displaced from equilibrium gives one row of $\Phi$. In a structure with high symmetry, only a few such simulations are
needed to construct the entire dynamical matrix, by employing symmetry elements of the space group of the crystal. If an element \( \{ S | v (S) \} \) maps atom \( j \) to \( J \) and atom \( \kappa \) to \( K \) then it can be shown (Maradudin et al. 1971, pages 10–14) that a pair of force constants are related by

\[
\Phi(JK) = S \Phi(jk) S^T
\]  

(4)

Hence if all the symmetry elements of the structure are known, all the force constants can be deduced from a minimum number of simulations.

IV. CUBIC PHASE

The high-symmetry cubic phase has a unit cell of only one formula unit (5 atoms) and is thus the fastest to simulate. It shares many features with the tetragonal and orthorhombic phases, so much of this discussion applies to all three phases.

A. Equilibrium structure

The equilibrium lattice parameter was found by a first-principles quenched molecular dynamics simulation of a cubic unit cell of 5 atoms, allowing the volume \( \Omega \) of the simulation supercell to change under the stress, which was also calculated from first principles. A modification of the fictitious Parrinello-Rahman Lagrangian was used, which gives the supercell a ‘boxmass’ \( W \) (Parrinello and Rahman 1980, Wentzcovitch 1991). A matrix \( h \) is formed from the supercell vectors \( \{ a, b, c \} \), giving a metric tensor \( g = h^T h \). The fractional coordinates of the \( N \) atoms are denoted by \( s_i \) with masses \( m_i \), so \( r_i = hs_i \). Another tensor is created from the initial cell faces: \( f_0 = (\sigma_0^T \sigma_0) \) (Wentzcovitch 1991) which helps to eliminate spurious rotation of the cell. The Lagrangian is now

\[
\mathcal{L} = \sum_{i=1}^{N} \frac{m_i}{2} s_i^T g s_i - U(r_i) - P \Omega + \frac{W}{2} \text{Tr}(h f_0 h^T)
\]  

(5)

However, if the cell changes then the plane wave basis set also changes, and since it is computationally convenient to keep the number of plane waves fixed, this means that the energy of the most energetic plane wave will change. However, it is physically more sensible to keep the cutoff energy constant (Dacosta et al. 1986), and so a Pulay correction was added to the stress (Francis and Payne 1990) to compensate:

\[
\Pi_{P} = \frac{2}{3\Omega} \frac{\partial E}{\partial (\ln E_{\text{cutoff}})}
\]

The total energy and stresses were thus those which would be obtained if the cutoff energy were kept constant at 500eV. The structure stabilised at a lattice parameter of \( a_0 = 3.44 \) Å; this is consistent with other calculations to within the effect of the LDA. Further comment will be made on this effect below. The ionic positions are fixed by the cubic symmetry, which was enforced throughout the simulation. Approximately twenty PR steps were required to obtain the equilibrium cell.

This method was checked by performing simulations at different cell sizes, to find the bulk modulus. This confirmed a minimum energy at \( a_0 = 3.44 \) Å. The bulk modulus \( K \) is sensitive to the fitting procedure: a quartic polynomial fit (R=0.99992) gave \( K = 255 \) GPa, \( K' = \partial K / \partial P = 4 \pm 1 \), in agreement with Wentzcovitch et al. (1993) and a Murnaghan fit gave \( K = 241 \pm 3 \) GPa, \( K' = 3.6 \pm 0.1 \). These high results are comparable with the experimental values for the orthorhombic phase: \( K = 266 \pm 6 \) GPa and \( K' = 3.9 \pm 0.4 \); these are higher than most other oxide perovskites (Navrotsky and Weidner 1989).

The bonding was largely ionic, as shown by the plot of charge density in Figure 2. This is in agreement with the findings reported in Navrotsky and Weidner (1989), and confirms that long-range forces are important.

B. Phonons

1. Zone centre

A simulation of only one primitive cell (5 atoms) can only give reliable information about the fifteen zone centre phonons, due to the use of periodic boundary conditions over a distance smaller than the range of the forces. Four
displacements were needed to construct the zone-centre dynamical matrix: one each for the Si and Mg, and two for O (parallel and perpendicular to cell face). A separate simulation was performed for each distortion, using the appropriate reduced symmetry. The entire dynamical matrix was constructed for one unit cell, with the help of the full symmetry of the cubic structure. This matrix was diagonalised to find five sets of triply degenerate Γ phonons; because the phonons have wave vector strictly equal to zero, these are TO and TA modes (Cohen and Krakauer 1990).

The eigenvectors of the Γ-point modes are shown in Table I, in mass-reduced coordinates $\epsilon_i = \sqrt{m_i} u_i$. It is noteworthy that the unstable mode consists of motion of the magnesium (A) ions against the rest of the crystal, in contrast to most perovskites, in which it is the B atoms which ‘rattle’ inside the oxygen cage (King-Smith and Vanderbilt 1994, Lines and Glass 1977). We find no evidence of strong covalent Si–O bonds in MgSiO$_3$, so this motion is probably due to the relative sizes of the oxygen, silicon and magnesium ions (Hemley et al. 1987).

Three acoustic translation modes are expected with zero frequency; this requires each row of $\Phi$ (corresponding to the forces from the displacement of one coordinate) to sum to zero (Maradudin et al. 1971). This was achieved by adjusting the diagonal (self-interaction) elements of the dynamical matrix by less than 1%, giving an indication of the accuracy of the calculations. Anharmonicity was investigated by doing a similar set of runs with twice the displacement, giving force constants which differed from the originals by less than 0.1%, so anharmonicity was considered negligible. The effect of $k$-point sampling on phonons of other perovskites was found to be significant in (King-Smith and Vanderbilt 1994). However, we increased the $k$-point set from 4 points in the Brillouin Zone to 32 and found that the changes in frequency were approximately 0.2–0.4 THz, and that the changes in eigenvectors 10% at most. The effect of $k$-point sampling is even less in simulation of larger cells.

2. Zone boundary

A larger simulation is needed to investigate phonons away from the zone centre. A supercell of four primitive unit cells ($a' = b' = \sqrt{2}a_0; c' = 2a_0; 20$ atoms) was chosen, since this reflects the geometry of the orthorhombic phase. The lattice parameter $a_0$ obtained above was used, and the force constants obtained in a similar manner to the 5 atom cell.

Because the supercell was not cubic, displacements in the $z$ direction as well as the $x$ direction were needed. The Fourier-transformed dynamical matrix $D(q)$ was then constructed at the zone centre and boundaries. The frequencies obtained are shown in Figure 3. The shape of the supercell also had the effect of breaking the cubic symmetry so that phonons are not perfectly degenerate, e.g. at the $R$ point of the Brillouin Zone.

Unstable modes can be described by a simple model consisting of quartic local potentials interacting harmonically (described more fully in Section VIII). These give complete unstable bands if the local potential is a double well type, giving order-disorder type transitions (Bruce 1980), but if the local potentials have a single central minimum (displacive type) part of the band will be stable (Samuelsen et al. 1971, Zhong et al. 1994). In this case, it was found that there are unstable phonon modes at all points investigated, suggesting that any phase transition involving this band would have some order-disorder character.

The eigenvectors of all these modes were also obtained. The most unstable modes were found at $R$ and $M$, consisting of rotations of near-rigid octahedra about the silicon atoms. This is consistent with the unstable modes found by Stixrude and Cohen (1993), Bukowski and Wolf (1988) and Hemley et al. (1987), but those workers found no other unstable phonons, whereas we find several involving magnesium displacement. At $M$, the mode involves rotation about $z$, and is denoted $M_2$; rotations at $R$ around all three axes are denoted $R_{25}$. These modes have been previously predicted to be the only zone-boundary rigid unit modes in cubic perovskite (Giddy et al. 1993). The stable modes mostly involve squashing and distorting the octahedra and displacement of magnesium ions.

3. Effect of pressure on frequency

The CPU time required to simulate a fixed configuration of $N$ atoms varies as $N^4$, so the five-atom cell required much less time than the twenty-atom cell: the Hellmann-Feynman forces from one distortion could be found in under half an hour on an Alpha AXP supercomputer. It was hence practicable to investigate the variation of Γ mode frequencies with cell size and obtain estimates of the Grüneisen parameters $\gamma_i = -\partial(\ln \omega_i)/\partial \ln V$. These are important for predicting the thermal properties of materials. The results are shown in Figure 4. We found that larger cells were more unstable with respect to the magnesium unstable mode, and that the frequencies of all other Γ phonons decreased as the cell was enlarged, i.e. have positive $\gamma$, with similar magnitudes to those obtained experimentally in the orthorhombic phase (Navrotsky and Weidner 1989).
The effect of pressure on the \( M_2 \) unstable mode was also investigated, by rotating the octahedra at several different cell volumes. It was found that in this case the magnitude of the imaginary frequency increased with pressure, i.e. under compression the structure becomes more unstable with respect to this distortion, in contrast to the behaviour of the unstable mode at \( \Gamma \). This agrees with the trends found by Hemley et al. (1987) and implies that pressure does not favour the cubic phase.

V. PHONONS OF INTERMEDIATE STRUCTURES

There are two important intermediate tetragonal structures, with either the \( R_{25} \) or \( M_2 \) mode frozen into the cubic phase, to their local equilibrium. However, these structures may still contain some unstable phonons corresponding to those previously unstable modes which are not frozen in. In both cases, we calculated the normal modes using a similar procedure to that for the cubic phase.

A. Freezing in \( M_2 \) mode

We investigated the configuration with a \( M_2 \)-rotation of the oxygen octahedra frozen into the cubic phase, giving a unit cell of 10 atoms with space group \( I4/mmmm \). Only modes containing distortions in the \( xy \) plane were considered, since these \( z \) distortions form a separate space, and are likely to be very similar to those in the undistorted cubic phase.

Phonons with the same symmetry as the frozen mode, i.e. involving only \( O_{ii} \) distortion, remained normal modes, although their frequencies were changed. Other normal modes are combinations of the original cubic \( \Gamma \) and \( M \) phonons.

The \( M_2 \) rotation mode, which had a frequency of \( 11.1i \) THz in the cubic structure, is now stable with a frequency of \( 13.5 \) THz. In a quartic double-well model (see Section \( VII B \)), the stable frequency would be \( \sqrt{2} \omega_0 \) where \( i\omega_0 \) is the unstable frequency. The stable frequency found here is a little smaller than this, showing a small departure from a pure quartic potential; this is evident in the fit to a quartic in Figure 3. This phonon stiffened further in the full orthorhombic structure, to \( 14.1 \) THz.

The mode with the highest frequency in the cubic structure was still the highest, but the frequency was reduced from \( 29.6 \) THz to \( 24.3 \) THz. Two degenerate unstable modes were found, predominantly consisting of displacements of the magnesium ions, with the degree of instability (3.66 \( i \) THz) slightly decreased from that in the cubic structure (4.76 \( i \) THz).

B. Freezing in \( R_{25} \) mode

The cubic \( R_{25} \) mode can be frozen into the cubic supercell, to form a twenty atom body-centred tetragonal cell (space group \( I4/mcm \)). The cubic \( R_{25} \) mode is degenerate; we chose rotation about the \( x \) axis of the twenty-atom cell, since this is the rotation observed in the orthorhombic phase. At large amplitudes of \( R_{25} \), the cubic eigenvectors are no longer valid: non-negligible forces are now also exerted on the magnesiums. The general \( R_{25} \) mode can therefore be thought of as including some magnesium motion. To obtain the equilibrium amplitude, the structure was relaxed with the appropriate symmetry; the magnesium moved along \( x \) with approximately 25\% of the \( O_{ii} \) displacement. Sixty phonons (at tetragonal \( \Gamma \) and \( X \)) of this phase were found. The eigenvectors were compared to those of the cubic cell phonons, and each tetragonal phonon assigned to its closest match in the cubic structure; in what follows we shall denote the phonons by their equivalent cubic symmetry label. The tetragonal and orthorhombic phonons are plotted against this part of the cubic Brillouin Zone in Figure 3 to enable comparisons to be made. There are only two unstable modes in this structure: the \( R \) and \( M \) modes corresponding to rotation about the \( z \) axis, with the latter slightly more unstable (5.64 \( i \) THz). The eigenvector of the \( M \) mode consists of \( M_2 \)-type octahedral rotation together with some motion of Mg and O\( i \). We conclude that this is related to the original cubic \( M_2 \) mode. This mode is much less unstable than its cubic counterpart. All other modes, including the magnesium displacement modes, which were unstable in the cubic structure, are now stable. Since there is no longer a complete band of unstable phonons, a soft-mode transition from this tetragonal phase to the orthorhombic would have displacive character, in contrast to a cubic–tetragonal transition.

The \( R_{25} \) mode is the most unstable in the cubic phase, and this tetragonal structure has lower energy than the \( I4/mmmm \) phase discussed above, so we chose this structure as our intermediate tetragonal phase between cubic and
orthorhombic; on cooling from the cubic phase, it will freeze in first. The structure is shown in Figure 1 and in the remainder of this paper we consider the possibility that it forms a distinct thermodynamic phase.

VI. ORTHORHOMBIC PHASE

A. Structure

The orthorhombic phase has much less symmetry than the cubic phase, and hence requires more structural relaxation to find the equilibrium structure. As in the cubic phase, the three cell edges were allowed to move under the internal and Pulay stresses, but the ions were also relaxed under the Hellmann-Feynman forces, until the equilibrium structure was obtained. This simulation was started from values given by Wentzcovitch et al. (1993) and the symmetry was enforced throughout the run. There are ten structural parameters, and so this relaxation took a long time: several hundred hours of CPU time on a Alpha AXP. The ionic motion was controlled by a conjugate-gradient routine, and relaxed slowly compared to the cell. The conjugate-gradient scheme is not guaranteed to work for non-linear problems, such as ionic positions coupled to each other and to the cell parameters. Near equilibrium, the movement of the cell had to be terminated so that the structural parameters could be found accurately.

The structural parameters obtained are given in Table 2. The unit cell is smaller than most previous work, but the structural parameters follow the reported trend of an increase in distortion under compression, (Hemley et al. 1987, Wentzcovitch et al. 1993, Matsui 1988). Following Bukowski and Wolf (1988) we compare the rotation angles \( \theta = \cos^{-1}(a/b) \) of \( M_2 \) and \( \phi = \cos^{-1}(\sqrt{2}a/c) \) of the \( R_{25} \) rotations in Table 2, effectively assuming that the rotations are rigid unit modes. This confirms that our structure is the most distorted. However, the Si–O bondlength is only 1% smaller than that observed experimentally, which is typical for calculations using the LDA (Payne et al. 1992). These results suggest that the effect of LDA can be approximated by an external pressure, since both volume and structure are affected. The effect of the LDA has also been compared to a pressure by Zhong et al. (1994) and Akbarzadeh et al. (1993), and generalised-gradient corrections have been similarly treated by Kresse et al. (1994).

We can use this approach in comparing our work to previous density-functional calculations of MgSiO\(_3\): the cell parameters of Wentzcovitch et al. (1993), when compared to the results of Ross and Hazen (1990), suggest they are equivalent to a pressure of 8–10 GPa. The effect of pressure on cell parameters calculated by Wentzcovitch et al. (1993) suggests that the cell parameters of our work correspond to an additional 10–12 GPa. The experimental bulk modulus and equilibrium volume give a pressure of 20 GPa for the volume found in this work, which is consistent with these estimates. Hence we assume in what follows that our orthorhombic structure is under an effective pressure of 20 GPa.

The effect of the LDA on structural parameters is harder to match to a consistent pressure, since the experimental data in Ross and Hazen (1990) does not show the simple monotonic trends of Wentzcovitch et al. (1993) and does not extend to 20 GPa. However, the experimental data does show increasing octahedral rotation under pressure, and most of our structural parameters continue the trends calculated by Wentzcovitch et al. (1993), so we conclude that the structural parameters are also consistent with the LDA pressure approximation.

The remaining small differences between our calculations and Wentzcovitch et al. (1993) are probably due to differences in pseudopotential, which also cause the differing LDA pressures assumed.

To examine the coupling between distortion and strain, we have also relaxed the ionic positions within the equilibrium cell of twenty atoms of the cubic structure, i.e. using \( a = b = \sqrt{2}a_0 \), \( c = 2a_0 \). In this simulation, the distortion from the cubic structure is about 5% less than that of the full orthorhombic cell found above. This is discussed in more detail in VII C.

B. Orthorhombic phonons

The symmetry of the orthorhombic phase means that displacements are required along \( x \), \( y \) and \( z \). The ionic positions were relaxed to give forces below 0.001 eV/Å, so the remaining forces on the ‘equilibrium’ structure were subtracted from the forces on distorted structures, assuming that the harmonic approximation applies to sufficient accuracy. To minimise anharmonic effects, the force constants were averaged over pairs which must be symmetric; this process changed the phonon frequencies by a maximum of 2% for the optic phonons.

The highest frequency phonon was at 25.9 THz, which is much lower than that of the highest cubic phonon. As expected, there were no unstable modes. Only the \( \Gamma \) phonons of the orthorhombic Brillouin Zone can be found, since only one unit cell is simulated. These correspond to the \( \Gamma \), \( X \), \( M \) and \( R \) phonons of the cubic phase, due to the quadrupling of the unit cell, and are again plotted in Figure 3 against the appropriate part of the cubic BZ.
The phonon with the highest frequency at each point of the BZ is the same in cubic, tetragonal and orthorhombic phases, although at lower frequencies the orthorhombic eigenvectors are often linear combinations of several cubic phonons. The phonons which were unstable in the cubic phase are now all stable, and mostly have low frequency. The eigenvectors are used to determine the symmetry of the phonons: the 24 symmetric modes were found, which are the Raman modes, and within this group seven \( A_g \) modes can be identified. These are likely to include the strongest Raman reflections, and are compared with experimental values in Table 4.

We further investigated the degree of anharmonicity by recalculating some force constants using half the original displacement. This only had a small effect on the calculated phonons and eigenvectors: the maximum change in frequency was 0.5 THz when force constants from Mg and O\( \text{i}\)z displacements were recalculated in this way.

### VII. INVESTIGATIONS OF INDIVIDUAL PHONONS

#### A. Cubic phonon modes contributing to orthorhombic structure

We describe the structure of the stable orthorhombic phase by freezing in phonons from the cubic phase. Since these apply to displacements at constant volume, we use only the fractional positions of the orthorhombic cell, as if it had the same cell parameters as the cubic cell, and allow coupling to the strain once these positions are fixed. We define coefficients \( c_j \) by

\[
d = \sum_j c_j p^j
\]

where \( p \) are the mass-reduced eigenvectors of the cubic crystal, and \( d \) is the mass-reduced displacement from cubic found in the stable orthorhombic structure. It is straightforward to find the coefficients \( c_j \) since the eigenvectors \( p \) are orthonormal, and for the equilibrium orthorhombic cell we denote them \( c_0 \).

This is not an ideal description of the structure, since the harmonic eigenvectors do not always describe the mode at large displacement. However, the \( \Gamma, X, M \) and \( R \) cubic eigenvectors do span the complete set of all possible strain-conserving distortions in a twenty atom cell. The orthorhombic cell consists of the equivalent of four cubic unit cells, so we know that all distortions not involving strain can be expressed by using cubic phonons as a basis set.

The results are shown in Table 5. Only two of the 42 stable phonons have significant non-zero coefficients, and only four of the fifteen unstable cubic modes are required to form the orthorhombic structure. Phonons consisting mainly of magnesium displacement are present much more weakly than those involving octahedral rotations, and are very strongly coupled to the positions of the oxygens (discussed in Section V B). Hence we concentrate on the octahedral rotation phonons. We have also calculated these coefficients for the distorted structure in the cubic cell, where we find all coefficients to be smaller.

#### B. Energy surfaces of rotational modes

A single unstable mode which becomes stable after a certain displacement can be considered as motion in a potential of a double well form. We will take as a first approximation to the energy

\[
E(c) = -\alpha c^2 + \beta c^4
\]

where \( \alpha \) and \( \beta \) are positive constants and \( c \) is the amplitude of one phonon mode. \( E(c) \) has a central maximum and a minimum on either side, as shown in Figure 5. In the case of the unstable modes in cubic perovskite, the cubic phase corresponds to the maximum at \( c = 0 \), but there are minima at \( c' = \sqrt{\alpha/2\beta} \) which correspond to a stable distorted phase. In the absence of phonon-phonon or phonon-strain coupling, the \( c_0 \) given in Table 5 would correspond to these minima, and we have estimated the depths of the associated wells \( E_0 \) on this assumption.

However, if two or more such phonons are present in a system, with amplitudes \( c_1 \) and \( c_2 \), there will in general be a coupling between them. This could be represented by, for example:

\[
E(c_1, c_2) = -\alpha_1 c_1^2 + \beta_1 c_1^4 - \alpha_2 c_2^2 + \beta_2 c_2^4 + hc_1^2 c_2^2
\]

The minima of this system are not at \((c'_1, c'_2)\) as defined above, but depend on the coupling \( h \). For example, negative \( h \) results in minima which are deeper and further from the origin than those of the one-phonon well. The frequencies of the normal modes of the one-dimensional model at the origin are unchanged by coupling, but at the saddle points
corresponding to the equilibrium amplitude \( c' \) of one mode, the instability of the other mode is increased by negative coupling or decreased by positive coupling.

The coefficients obtained from the orthorhombic structure, using Equation (5), are those of the overall minimum of all phonon modes, not of isolated wells. The orthorhombic structure contains only distortions with \( \Gamma, X, M \) and \( R \) cubic symmetry, as described in Section VII A.

To investigate this coupling in MgSiO\(_3\), we can ‘freeze in’ one cubic phonon at a time into the cubic phase, and use the energies and forces to parameterise the model described in (5). We can then compare the amplitude \( \alpha_0 \) of each cubic phonon required to describe the orthorhombic structure with the equilibrium amplitude \( c' \) from such a simulation of the isolated cubic phonon.

The eigenvectors of the \( M_2 \) octahedral rotation remain unchanged as the amplitude \( c \) increases. However, there can be coupling to other modes when the phonon amplitude is beyond the harmonic limit: for example, large \( R_{25} \) displacement causes forces on the Mg atoms in the \( x \) direction, so this coordinate was also relaxed to equilibrium. This demonstrates the coupling between rotational and magnesium modes suggested above, which was accounted for in freezing in \( R_{25} \) to form the tetragonal phase.

Table 6 shows the results of this process for the \( M_2 \) and \( R_{25} \) phonons. The \( M_2 \) rotation was also combined with a change of the size and shape of the unit cell, such that the size of the octahedra remained constant, to simulate a rigid unit mode rather than a phonon. The results are shown in Figure 6, and discussed further in Section VII C.

We find that for the \( M_2 \) rotation, the orthorhombic structure has a smaller rotation angle than that of the isolated phonon in equilibrium. The equilibrium amplitude of the isolated \( R_{25} \) rotation, including coupling with Mg displacement modes, is smaller in the orthorhombic structure than in the isolated phonon. Thus the coupling \( \beta \) between these modes, defined in (5), is positive. In both cases, this effect is even stronger when the unit cell is not relaxed, so this is a true phonon-phonon interaction rather than due to interaction via the strain. This is in agreement with similar investigations using modified electron gas theory (Wolf and Bukowski 1988) but differs from the negative \( h \) value found by Stixrude and Cohen (1993), where it is not clear whether coupling with Mg distortion modes was considered. It is also consistent with the reduction in the instability of the \( M_2 \) mode when the \( R_{25} \) mode is frozen in.

We used the values of \( \omega_R/\omega_M, c'(M), c_0(R) \), and \( \alpha_0(M) \) to parameterise the model in Equation (5), to give \( \beta_1 = 0.01683, \beta_2 = 1.13, \beta_2 = 0.01150 \) and \( h = 0.0085 \) when \( \alpha_1 \) is normalised to unity. The amount of coupling can be considered as \( h^2/4\beta_1\beta_2 \approx 0.09 \); the differences between the equilibrium amplitudes of isolated and coupled phonons are small. When the \( \alpha_0 \) values from relaxation in a cubic cell were used, the coupling increased to \( h^2/4\beta_1\beta_2 \approx 0.15 \), since the normal mode coefficients were even more reduced from their isolated values.

C. Coupling of rotational modes to strain

The orthorhombic unit cell has a volume only 93\% of that of the cubic phase, but the oxygen octahedra are larger by about 9\% in volume. The angle between Si–O\(_i\) and Si–O\(_{i+1}\) bonds is \( 2^\circ \) from perpendicular, so there is also a small degree of distortion. The orthorhombic relaxation of ions within the cubic cell described in Section VII A (i.e. allowing only pure phonon modes to freeze in) gave octahedra 18\% larger than in the cubic phase, with approximately 1\(^\circ\) distortion.

This was further investigated as described above, by changing the unit cell to be such that the size of the octahedra was constant while an \( M_2 \) rotation was frozen in, to create a rigid unit mode. The resulting potential well had a minimum at approximately the same rotation angle, but was not quite as deep, implying that this combination is not as good a description as a phonon rotation with fixed unit cell, in which the octahedra expand. These results are shown in Figure 6.

The stress on the unit cell was also calculated (with Pulay corrections) for the two cases: the phonon rotation with constant unit cell had positive stress but the rigid unit mode with constant octahedra always had negative stress. This implies that the absolute minimum of rotation and strain lies somewhere between these two extreme pictures. This is consistent with the equilibrium orthorhombic structure, in which the unit cell and octahedral size are intermediate between phonons and rigid unit modes. In the case of relaxed ions in the cubic cell, the enlargement of the octahedra is much greater, since there can only be pure phonon modes.

VIII. TRANSITION TEMPERATURES

The transition temperature between the orthorhombic and cubic phases has been naively estimated by Stixrude and Cohen (1993) as \( \Delta E/k_B \), where \( \Delta E \) is the energy difference between the two phases for one cubic unit cell. Applying this to our results gives \( T_e \approx 20,000 \) K for the cubic–tetragonal transition, and approximately 5,500 K for
the tetragonal–orthorhombic transition. These are slightly different from the results found by Stixrude and Cohen (1993) which considered only octahedral rotations, and are both considerably higher than the ambient temperature in the mantle. These estimates suggest that it is very unlikely that the orthorhombic–cubic phase transition occurs in the mantle.

However, it is more reliable to calculate the transition temperature from the energy stored in the interaction between unit cells, rather than the total energy stored (Samuelsen et al. 1971). The transition is modelled as a one-dimensional quartic well (e.g. local amplitude of phonon eigenvector as coordinate) at each site, with harmonic interactions between cells. The lowest energy configuration consists of these coordinates ordered with the wavevector $\mathbf{q}_i$ of an unstable phonon, dependent on the form of the interaction. The interaction energy as a fraction of the total energy can be obtained from the dispersion between $\Gamma$ and $\mathbf{q}_i$ of the appropriate phonon band, as described in Appendix $X$. In this case we have two modes contributing so we consider two such transitions.

We assume that a transition would proceed via the tetragonal intermediate. We can then consider the cubic→tetragonal and tetragonal→orthorhombic steps separately. For each step, the strength of the interaction and local potentials were found from the dispersion from $\Gamma$ to the appropriate part of the Brillouin Zone (Appendix $X$). The fraction of the total energy due to the interaction for the $R_{25}$ phonon, $(E_J/E_0)$, was found to be 71%, and 87% for the $M_2$ phonon in the tetragonal phase, the remainder being stored locally. Using $k_B T_c = 2E_J/3$ from Samuelsen et al. (1971), we find that the transition temperature for the tetragonal–cubic step is approximately 10,000 K, which is still much higher than typical mantle temperatures. However, the orthorhombic to tetragonal phase transition occurs at $T'_c = (E_{\text{tet}} - E_{\text{orth}})/k_B E_J/E_0 \approx 2,600$ K, which is quite possible in the mantle. For the calculation of $E_0 = E_{\text{tet}} - E_{\text{orth}}$, the unit cell of the tetragonal phase was relaxed to equilibrium, as well as the structural parameters, giving an orthorhombic structure with space group $I\text{mma}$; this decreased the energy difference between this and the orthorhombic phase. For simplicity this intermediate phase is still referred to as ‘tetragonal’.

Since the $M_2$ cubic phonon becomes more unstable with compression, pressure will have a large effect on these transitions. The temperatures given above are for the ambient pressure in our simulations, which is nominally zero pressure, and do not take account of thermal expansion. However, as discussed above, a unit cell which is 7% too small and the observed structural parameters are consistent with an external pressure of 20 GPa. The effective pressure used in calculations of the phase boundary is thus mantle pressure less this LDA pressure.

We thus calculated the phase boundary using $k_B T'_c = \frac{2}{3}(E_0 + P\Delta V)(E_J/E_0)$: $(E_J/E_0)$ is the fraction found above, varying with pressure and temperature via Gruneisen parameters estimated from the cubic phase and experimental thermal expansivity; $P$ is the effective pressure; $\Delta V$ is the difference in volume between the two phases at pressure $P$; $E_0$ is the energy difference between equilibrium orthorhombic and tetragonal phases at zero temperature and LDA pressure. This phase boundary is shown in Figure $X$ with a range of estimates of lower mantle geotherms (Jeanloz and Morris 1986, Poirier 1991).

**IX. DISCUSSION**

We have found that only a small subset of the cubic phonons are required to freeze in to create the orthorhombic phase. Many unstable phonons involve rotations of nearly-rigid oxygen octahedra, and it is mainly these that are involved in forming the tetragonal and orthorhombic phases from the cubic. Some stable phonons are involved, due to coupling between the unstable and stable modes away from the harmonic limit. This work finds that several modes predominantly involving displacement of magnesium ions are also unstable in the cubic phase, in contrast to previous studies (Bukowski and Wolf 1988, Hemley et al. 1987). We find that the magnesium displacement observed in the orthorhombic phase is due to coupling of magnesium modes into the octahedral rotation modes at large amplitude, rather than a separate freezing-in of magnesium modes. Hence we have concentrated on the octahedral rotation. The cubic structure becomes more unstable under compression, suggesting that the cubic structure is not favoured by high pressure.

The coupling to the strain was found to be small: there was little difference between phonons at constant volume and rigid unit modes, and the fractional positions of relaxed ions in a cubic unit cell were very similar to those with a relaxed unit cell. Rigid unit models are known not to be a perfect description of perovskite rotational modes (Giddy et al. 1993) and this work suggests that phonons are in fact a better description of these modes since they give lower total energy. The true picture lies somewhere between these two extremes, with octahedra which are not perfectly rigid, as observed in the equilibrium orthorhombic structure. Pure rigid unit mode transitions also exhibit displacive behaviour (Sollich et al. 1994), whereas the distribution of unstable modes throughout the Brillouin Zone suggests that a transition from the cubic phase would have some order-disorder character.

There is positive coupling between the two rotational unstable cubic phonons frozen into the orthorhombic phase ($M_2$ and $R_{25}$), such that the overall minimum is less distorted than individual distortions would suggest. This coupling
is also manifested by the decrease in the instability of the $M_2$ phonon after a $R_{25}$ phonon (the most unstable in the cubic phase) is frozen in. Because freezing in the $R_{25}$ mode only partially stabilises the $M_2$ rotation, this forms an intermediate tetragonal phase and the $M_2$ rotation is required to freeze in to form the orthorhombic phase. This tetragonal structure may, however, exist as a distinct thermodynamic phase (Hemley and Cohen 1992) above some transition temperature $T_c'$, which will be lower than the temperature $T_c$ required to obtain the cubic phase.

The tetragonal structure has displacements from the cubic which account for three of the seven positional parameters of the orthorhombic phase. The $M_2$-like phonon is the most unstable tetragonal mode, and contains the remaining four displacements necessary to reach the orthorhombic phase, so we conclude that the cubic phase can be considered to be formed from the orthorhombic in two soft-mode steps, via this phase. The relative magnitudes and directions of the displacements in the tetragonal phase and of the tetragonal $M_2$ phonon are in approximate agreement with those observed in the orthorhombic phase; the difference can be ascribed to coupling between the modes, and volume differences between the tetragonal and orthorhombic phases. The tetragonal–orthorhombic transition would probably have displacive character, since the relevant phonon band in the tetragonal phase is not unstable at every point in the Brillouin Zone.

The calculation of the transition temperature assumes that the transition would proceed via this intermediate phase ($I4/mcm$ or $Imma$, both referred to as tetragonal). It is clear that a complete orthorhombic–cubic phase transition is out of the range of mantle temperatures. However, we find that the phase boundary for the orthorhombic–tetragonal transition intersects some models of lower mantle geotherms near the boundary with the upper mantle; this transition might thus account for some of the discontinuities observed in the lower mantle. These results are also supportive of experimental observations of twinning in MgSiO$_3$ perovskite (Wang et al. 1992), which suggested a transition temperature of 1900±200 K at 26 GPa for an orthorhombic–cubic or orthorhombic–tetragonal phase transition. Typical mantle temperatures are considered to be in the range 2,000–3,200 K with the upper bound given by the experimentally-determined melting temperature. These bounds encompass two models of the mantle, giving ‘hot’ and ‘cold’ geotherms depending on whether the upper and lower parts of the mantle convect together or separately (Jeanloz and Morris 1986). Hence the possibility of a tetragonal phase suggested by this work has important consequences for the behaviour of the mantle.

X. CONCLUSION

We have found the structure and an important set of phonons of cubic, tetragonal and orthorhombic phases of MgSiO$_3$. The unstable phonons of the cubic structure are distributed throughout the Brillouin Zone, but all become stable after the transition to the orthorhombic structure. The structure and phonons of a tetragonal intermediate consisting of one frozen-in rotation accounts for the distortions in the orthorhombic phase. Rotations of octahedra play the largest part in the transition, and are the most unstable. The coupling between these rotation phonons and the strain implies that phonons are a better description of these modes than the rigid-unit model. It seems unlikely that the full orthorhombic–cubic transition could occur in the mantle, since the energy required is much larger than that available at usual mantle temperatures. However, a tetragonal intermediate may well be accessible to mantle temperatures, and merits further study to see whether it might explain some of the observed discontinuities and hence have consequences for the properties of the whole mantle. We believe that the sources of error in our calculation are now smaller than the variation between different mantle models.

Calculation of $T_c$

A simple model for structural phase transitions uses one coordinate $x_i$ at each site at position $r_i$. There is a quartic double well at each site and harmonic inter-site coupling (the $\phi^4$ model described by Sollich et al. 1994), shown schematically in Figure 7. The total static energy is written as

$$U = \sum_i (\alpha x_i^2 + \beta x_i^4) + \sum_{ij} J_{ij} x_i x_j$$

The phonon frequencies of the undistorted phase at wavevector $q$ are then given by

$$\omega^2(q) = 2\alpha + J(q)$$

where $J(q) = 2 \sum_j J_{0j} \exp i q \cdot r_j$.

If we assume nearest neighbour coupling (here between five-atom cells), we have $J(q) = -J(0) = J$, so we can find $\alpha$ and $J$ from the calculated frequencies for the appropriate band. The total energy stored per site when all $x$ are totally ordered (at $x_0^2 = (\alpha + J/2)/2\beta$) with wavevector $q$ is given by
\[ E_0 = \frac{(\alpha + J/2)^2}{4\beta} = \frac{x_0^2(\alpha + J/2)}{2} \]

and the total energy stored in the interaction per site is \( Jx_0^2/2 \), so the fraction of the total energy which is stored in the interaction is

\[ \frac{E_I}{E_0} = \frac{J}{\alpha + J/2} \]

Since we know \( E_0 \) from \textit{ab initio} total energy calculations, we can hence find \( E_I \), which is used to find the transition temperature.

**APPENDIX: ACKNOWLEDGMENTS**

The authors thank M.C. Payne for the original code and J.S. Lin for pseudopotentials. M.C.W. thanks the E.P.S.R.C. for support and S.J. Clark, J. Crain, G.S. Pawley and V. Heine for useful discussions; G.J.A. thanks B.P. and The Royal Society of Edinburgh for a fellowship, and the E.P.S.R.C. for assistance in providing computing facilities.

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| $\Gamma_{15}$ | $\Gamma_{15}$ | $\Gamma_{15}$ | $\Gamma_{15}$ |
|-------------|-------------|-------------|-------------|
| $\omega$(THz) | Mg | OI | OII | OIII | Si |
| 26.33 | 0.02 | -0.89 | 0.22 | 0.22 | 0.32 |
| 13.37 | -0.253 | 0.070 | -0.398 | -0.398 | 0.783 |
| 0.00 | 0.492 | 0.400 | 0.400 | 0.400 | 0.529 |
| 6.01$^i$ | -0.833 | 0.189 | 0.363 | 0.363 | 0.084 |
| 5.189 | 0 | 0 | -1 | 1 | 0 |

An imaginary frequency represents an unstable mode.
TABLE 2. Structural parameters of equilibrium structure of orthorhombic perovskite, with assumed pressure allowing for the effects of the LDA. [1] Wentzcovitch et al. 1993; [2] Ross and Hazen 1990

|        | this work | previous [1] | experiment [2] |
|--------|-----------|--------------|----------------|
|        | 20 GPa    | 10 GPa       | 0 GPa          | 10.6 GPa       |
| a(Å)   | 4.635     | 4.711        | 4.777          | 4.710          |
| b(Å)   | 4.833     | 4.880        | 4.927          | 4.873          |
| c(Å)   | 6.771     | 6.851        | 6.898          | 6.790          |
| Mg_x   | 0.5157    | 0.5174       | 0.5131         | 0.511          |
| Mg_y   | 0.5603    | 0.5614       | 0.5563         | 0.557          |
| O_x    | 0.1155    | 0.1128       | 0.1031         | 0.099          |
| O_y    | 0.4572    | 0.4608       | 0.4654         | 0.464          |
| O_z    | 0.1914    | 0.1928       | 0.1953         | 0.196          |
| O_2    | 0.1968    | 0.1995       | 0.2010         | 0.201          |
| O_3    | 0.5594    | 0.5582       | 0.5510         | 0.561          |

TABLE 3. Octahedral rotation angles inferred from cell shape, and mean Si–O bondlength. This work gives the most distorted structure, but also has the smallest cell, supporting the approximation of the effect of the LDA as an external pressure. [1] Wentzcovitch et al. 1993; [2] Bukowski and Wolf 1988; [3] Hemley et al. 1987; [4] Ross and Hazen 1990.

|        | θ(M2) (°) | φ(R25) (°) | Si–O (Å) |
|--------|-----------|------------|----------|
| this work | 16.5     | 14.5       | 1.77     |
| other ab initio [1] | 15.1     | 13.5       | 1.79     |
| MEG [2]    | 10.41    | 7.03       | 1.904    |
| SSMEG [3]  | 10.8     | 9.8        | 1.776    |
| expt, 0 GPa [4] | 14.3     | 11.6       | 1.792    |
| expt, 10.6 GPa [4] | 14.9     | 11.9       | 1.777    |

TABLE 4. Calculated and measured frequencies of A_g modes of orthorhombic phase, which are expected to give strong Raman signals. [1] Navrotsky and Weidner 1989.

|        | experimental |
|--------|--------------|
| this work | Raman modes [1] |
| A_g modes |              |
| 25.5    | 20.7         |
| 20.0    |              |
| 18.8    | 11.4         |
| 15.2    | 15.0         |
| 11.4    | 11.4         |
| 10.0    | 8.6          |
| 8.6     | 8.49         |

3-13
TABLE 5. Calculation of the coefficients of phonons frozen into the orthorhombic distorted phase. The phonons are identified by the point of the BZ at which they occur, with degeneracies given in brackets. The depth $E_0$ of the minima of the well has been calculated for unstable phonons, using $c_0$ and the frequency, assuming no coupling. Stable phonons correspond to a well with only one minimum, at the origin, so $E_0$ is zero.

| frequency | $c_0$ | $E_0$ | description                        |
|-----------|-------|-------|------------------------------------|
|           | (THz) | (√a.m.u. Å) | (eV) |                                   |
| $R$ (2)   | 11.8$i$ | 4.58 | 2.99 | rotation of octahedra about $xy$ |
| $M$ (1)   | 11.1$i$ | 4.35 | 2.38 | rotation of octahedra about $z$  |
| $X$ (2)   | 4.73$i$ | 2.29 | 0.120 | mostly Mg displacement            |
| $R$ (2)   | 3.48$i$ | 0.505 | 0.0021 | mostly Mg displacement            |
| $X$ (2)   | 10.5   | 0.551 | stable | Mg and Oi displacement           |
| $M$ (1)   | 19.6   | 0.210 | stable | octahedral squash                |

TABLE 6. Normal mode coordinates of cubic rotational phonons in the fully relaxed orthorhombic phase, $c_0$(orth), ionic relaxation in a cubic cell, $c_0$(cubic), and of the equilibrium structure when the phonon is frozen in alone, $c'$. In both orthorhombic cases, the structure is not as distorted as the minima of the isolated phonons. Only the magnitudes of the coordinates are given.

| phonon   | $c'$  | $c_0$(orth) | $c_0$(cubic) |
|----------|-------|-------------|--------------|
| $M_2$    | 5.45 ± 0.02 | 4.35        | 4.14         |
| $M_2 +$ strain | 5.10 ± 0.3 | 4.35        | 4.14         |
| $R_{25}$ | 4.7 ± 0.3  | 4.58        | 4.37         |
FIG. 1. Cubic, tetragonal and orthorhombic structures of MgSiO$_3$ perovskite. Twenty atoms of each structure are drawn, corresponding to four unit cells of the cubic phase and one of the orthorhombic. Silicon ions are enclosed in an octahedral cage of oxygen atoms, with magnesium ions in interstices. The cell drawn has axes $x,y$ and $z$ as referred to in the text. The tetragonal phase is formed from the cubic by rotating the octahedra around the $y$ axis and displacing the magnesiums along $x$. In the orthorhombic phase, the oxygen octahedra are rotated from their cubic positions around $y$ and $z$, and the magnesium atoms are displaced along $x$ and $y$.

FIG. 2. Charge density through a plane containing Si ion in centre and two oxygen atoms at edge, showing the large degree of ionicity.

FIG. 3. Cubic, tetragonal and orthorhombic phonons at each part of the BZ of the corresponding cubic phonon. There are unstable phonons at all parts of the Brillouin Zone in the cubic phase, but all the phonons in the orthorhombic phase are stable. The tetragonal structure results from freezing in the $R$ rotation phonon to equilibrium, and has only two unstable modes. The horizontal axes follow the progression from cubic to orthorhombic; the arrows link phonons with similar eigenvectors as the structure becomes more distorted. Loss of degeneracy is due to the choice of supercell.

FIG. 4. Variation of frequency of cubic zone-centre phonons with cell size, to give Grüneisen parameters.

FIG. 5. Double well model of energy as a function of phonon displacement as described by $E(c) = -\alpha c^2 + \beta c^4$. The cubic phase corresponds to the central maximum and the stable orthorhombic phase corresponds to one of the minima. The saddle points correspond to the tetragonal phases: that of the $R_{25}$ rotation has the lowest energy and is therefore considered as our intermediate phase.

FIG. 6. (a) Energies, (b) forces and (c) stresses for $M_2$ rotation of the octahedra through different amounts (labelled with change in fractional coordinate of oxygen). The energies are fitted to a quartic well, and the forces to a cubic. The results with constant cell size ($M_2$ only) are very similar to those with constant octahedral size ($M_2 + $ strain), except for the stresses. These results suggest that the optimum combination lies somewhere between the two.
FIG. 7. One-dimensional example of double well local potentials coupled by harmonic interactions (the ‘φ⁴’ model), which is used to model the structural phase transitions of MgSiO₃. A high-symmetry ordered phase corresponds to all \( x_i = 0 \), and ferro- or antiferromagnetic distorted phases, with all \( x_i \) near the bottom of local wells, minimise the energy, depending on the sign of the \( J_{ij} \). The harmonic phonon frequencies for oscillation around the central maxima are used to fit the parameters of this model.

FIG. 8. Comparison of the calculated phase boundary for the orthorhombic–tetragonal phase transition and models of lower mantle geotherms. The phase boundary intersects some geotherm models near the top of the lower mantle, suggesting that the tetragonal phase may be present in the mantle. The melting temperature is also shown: this limits the temperatures possible in the lower mantle, but itself has considerable error.
(a) energy
(b) force
(c) stress

M only
M + strain
