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The properties and behaviour of mantle minerals: a computer-simulation approach

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The direct study of the majority of the physical properties of mantle-forming phases is currently beyond the limits of technology, because of the high pressures and temperatures (greater than 25 GPa and 1800 K) required to simulate lower-mantle conditions. As an alternative to direct study therefore, theoretical and computer-based techniques of lattice simulation and molecular dynamics have been employed to obtain an understanding of the behaviour of high-density silicates. The properties of perfect high-density silicate crystals, including their elastic and spectroscopic characteristics, have been investigated, but to date computer simulations of perfect lattice properties are insufficiently accurate to be used to solve geophysical problems. In contrast, the simulation of phase relations and defects properties are very successful. Small, negative Clapeyron slopes for perovskite-forming transformations are predicted, suggesting that the 670 km discontinuity may not be a rigid barrier to mantle convection. In addition, the activation energies for diffusion in forsterite and perovskite have been calculated, and the suggested high-temperature superionic conductivity of magnesium silicate perovskite has been confirmed.

INTRODUCTION

The aim of much recent research within the Earth sciences has been to determine the fundamental processes and mechanisms involved in mantle dynamics, lithospheric motion and plate tectonics. Many of the models, however, which have been advanced in an attempt to describe these vital processes rest upon unconfirmed assumptions concerning the response of rock-forming minerals to changes in their physical and chemical environment. This has led to the development of conflicting models for the behaviour of the Earth, epitomized by the two distinct and largely incompatible forms of model that currently exist to describe mantle convection; namely whole-mantle convection models and layered-convection models. The latter assume that a mineralogical phase transformation or chemical stratification occurring at depths close to 670 km below the crust, defines a boundary between the upper part of the mantle and a static or independently convecting lower mantle, whereas the former assume that no barrier to mantle convection exists. Strong arguments can be made in favour of both types of model, but it is neither possible to assess which best describes mantle convection, nor determine the effect of mineralogical or chemical changes on mantle behaviour, without knowing the properties of mantle-forming materials, such as magnesium silicate spinels, perovskites, garnets and ilmenites.

As a result of recent experimental research programmes, significant advances in our understanding of mantle-forming phases have been made, and although the nature of the

670 km discontinuity still remains unclear, the elastic constants (under ambient conditions) of mantle phases are now sufficiently well known that it is possible to conclude (figure 1) that the laterally averaged velocity and density structure of the lower part of the upper mantle and the transition zone (200–670 km) is at least consistent with, but does not demand, a chemically uniform, pyrolite mantle (see, for example, Weidner & Ito 1987; Irifune & Ringwood 1987). However, it is also widely recognized that the upper mantle, transition zone and lower mantle are significantly heterogeneous, with seismic velocity varying laterally by a few percent. The interpretation of these more subtle tomographic seismic observations provides a new challenge, as our current knowledge of the equations of state of mantle-forming phases is inadequate to establish unambiguously to what extent this heterogeneity is caused by thermal, chemical or crystal anisotropy effects. Similarly, our lack of understanding of the defect and rheological behaviour of these phases prevents us from developing a full description of mantle convection, the mantle viscosity profile, mantle conductivity (both thermal and electrical), the mantle geotherm, and the origins of the topography of the core–mantle boundary.

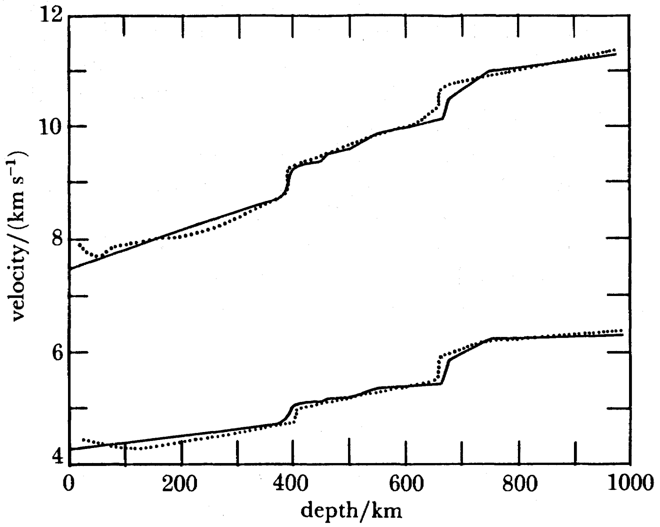

Figure 1. Calculated (solid lines) and observed (dotted lines) P- and S-wave velocities as a function of depth in the Earth's mantle, after the work of Weidner & Ito (1987).

Future progress in resolving these important geophysical problems depends upon being able to obtain highly accurate values for the seismic and defect properties of minerals, under pressure and temperature conditions appropriate to the mantle. To reproduce this environment experimentally represents a considerable challenge in itself, but one that has been met in recent years by the use of apparatus such as the diamond anvil cell (DAC) and the uniaxial split-sphere large-volume cell. However, to make *in situ* physical property measurements under these conditions, with the accuracy needed to be able to resolve existing geophysical problems, represents a challenge that is still to be overcome. Thus, the pressure and temperature derivatives of the elastic constants of mantle phases, their thermal-expansion coefficients, and their conductivity are as yet poorly constrained, and will be extremely difficult to measure with the accuracy that we require. It is the fact that there is little prospect of these experimental constraints being readily overcome that has led to the recent development of theoretical and computer-based, atomistic models of the behaviour and properties of high-density mantle-forming silicates (for recent reviews see Burnham 1985; Catti 1986; Catlow 1988). The aim of these computer-based studies is to provide an alternative way of establishing the properties of silicates at extremes of pressure and temperature, and to elucidate the microscopic or atomistic characteristics of mantle materials that determine their bulk, macroscopic or thermodynamic behaviour. In this paper, we will outline some of the approaches to the computer simulation of mantle-forming phases that have been adopted in recent years. We will attempt to highlight both the strengths and limitations of current techniques, and will discuss the course of possible future developments in the subject.

Approaches to silicate simulation

In principle, the bonding and related physical properties of any silicate can be established by the direct solution of the Schrödinger equation, which describes the interactions of electrons and nuclei within a given system. However, because of the complexity of most silicates, such quantum mechanical studies are usually limited to modelling simple structures or structural fragments. In contrast, the atomistic approach to modelling the behaviour of crystals is somewhat more simple and approximate, as it attempts only to describe the interactions between individual atoms or ions in the structure, rather than explicitly describing the interactions between each and every electron in the solid. This simplicity, however, allows the atomistic approach to be used to predict a wide range of physical and defect properties of crystals, while still providing useful insights into the nature of bonding within solids. In the atomistic approach, sets of interatomic potentials are developed, either *ab initio* or empirically, to describe the energy surface within a structure. The parametrization of the model potential is often designed to describe relatively simple, but effective concepts of chemical bonding, such as ionic interactions, short-range repulsion effects and van der Waals bonding.

The work of Cohen *et al.* (1988) exemplifies the current state of *ab initio*, total-energy calculations on crystalline silicates. These workers have used an approach based on the local-density approximation, derived from density functional theory, to perform total-energy calculations on cubic magnesium silicate perovskite. In their simulations they employ the linear augmented plane wave (LAPW) method to describe the charge density and potential surface within the unit cell. Although this approach is extremely accurate, it has the disadvantage that it is computationally very intensive, with the calculation of the energy of the cubic perovskite cell (containing only five atoms) taking between 10 and 20 central processing unit (CPU) hours on a Cray-XMP. Although useful in estimating the compressibility of the hypothetical cubic magnesium silicate perovskite, and revealing the predominantly ionic nature of the bonding in such highly coordinated silicates, this computationally intensive approach is not currently practical for the general study of geophysically important phases.

In contrast to performing total-energy calculations on silicate structures, Gibbs and co-workers (see Gibbs 1982; Lasaga & Gibbs 1987) have performed quantum mechanical simulations on 'silicate molecules', that can be envisaged as fragments of silicate minerals. Their calculations involve Hartree–Fock, *ab initio* solutions to the Schrödinger equation, which provide a potential energy surface that describes the interatomic interactions within the fragment. These calculations successfully model the known behaviour of true silicate molecules (such as disilic acid, $H_6Si_2O_7$), and the resulting potential energy surfaces have been parametrized and used to model simple silicates and silica polymorphs (Lasaga & Gibbs 1987).

A third approach, involving the potential induced breathing (PIB) model (Cohen *et al.* 1987;

Cohen 1987; Cohen *et al.* 1988), has also been successfully employed to model silicates. The PIB model avoids the need to solve the Schrödinger equation for the whole crystal, by employing the modified electron gas (MEG) model of Gordon & Kim (1972) to obtain interatomic potentials that can be used to simulate the overall potential energy surface within the crystal. In the MEG model, an approximate description of the crystal charge density is obtained by overlapping rigid ion charge densities, and the overall interatomic potential between two ions is obtained from their electrostatic interactions, their self-energy and the overlap energy between their charge densities. A problem exists, however, when modelling oxides with this approach, because of the fact that the O^{2-} ion is not stable in isolation. In MEG calculations, the O^{2-} ion must be stabilized by being contained within a charged sphere (the so-called Watson sphere), which simulates the stabilizing effect of the Madelung potential experienced by the oxygen ion when in the crystal lattice. In the PIB model, the oxygen interatomic potentials are parameterized in terms of the Madelung site potential; a change in the site potential induces a corresponding change in radius, or a 'breathing' of the Watson sphere. The PIB model potentials include not only pair-wise additive interactions but also many-body effects, and as a result, it successfully simulates trends in the Cauchy violations in alkaline earth oxides, that cannot be modelled by simple two-body potentials (Mehl *et al.* 1986).

Finally, the method that has been used most widely, and with considerable success, to describe the properties and behaviour of a large number of complex inorganic solids, including silicates, involves the use of empirical potential models (see Catlow 1987; Stoneham & Harding 1986). These potentials are empirical in the sense that they are described by an analytical form that is fitted to experimental data. The relative merits of empirical and *a priori* potentials depend on the proposed application. What is required in our geophysical studies is a quantitative prediction of physical properties, and as is pointed out by Stoneham & Harding (1986) 'at present the best empirical potentials have a far greater demonstrated accuracy than explicit solutions to the Schrödinger equation'. Indeed this point is echoed by Lasaga & Gibbs (1987), who point out the close agreement between their quantum mechanically derived Si–O potential and the empirical potential of Parker (1982), and conclude that the 'agreement supports the use of quantum mechanical calculations as a framework within which to shape interatomic potentials'.

In the empirical approach, sets of interatomic potentials are developed to describe the net forces acting upon atoms within a structure. The model potentials used can be polynomial fits to experimentally inferred potential energy surface, or can be based on functions designed to describe relatively simple concepts of chemical bonding. The ions in the structure can either be considered to be point charges, or can be viewed as having a more diffuse charge density. In either case, it appears that the electrostatic or Coulombic energy terms, which result from the ionic charges of the atomic species, are the most important component of the cohesive energy for ionic or semi-ionic solids such as silicates.

True ions are obviously not point charges, as is often assumed when calculating the Coulombic energy, but instead are composed of a nucleus and an associated electron cloud of finite size. In point-charge models, therefore, it is necessary to include a term in the potential that models the energetic effect of the overlap of the electron clouds, which results in a short-range repulsion effect that is most strongly felt by nearest-neighbour ions. Such short-range components of the two-body potential are well represented by the so-called Buckingham potential.

For fully ionic, rigid-ion models, the Coulombic and short-range terms are generally the only components of the potential to be considered. However, it is well established that bonding in a silicate, such as olivine, is not expected to be fully ionic, and in particular a degree of directional, covalent bonding between silicon and its coordinating oxygens is to be expected. In recent studies of silicates two approaches have been used in an attempt to model this more complex type of bonding. Price & Parker (1984) used non-integral or partial ionic charges, and used a Morse potential function to model the covalent Si–O bond. In contrast, Sanders *et al.* (1984) kept to full ionic charges, but modelled the directionality of the Si–O bond by introducing a bond-bending term into the potential. The use of a bond-bending term in the interatomic potential is a significant development, as it represents the consideration of effective three-body interactions within structure. Previous empirical models only considered purely two-body or pairwise additive effects, despite the fact that it has long been recognized that many-body interactions in crystal structures should be significant (Weidner & Price 1988). It is the success of potentials such as these that make possible the prospect of a detailed study of the equations of state of mantle phases.

It is often found that it is necessary to develop a so-called shell model (Dick & Overhauser 1958) as an alternative to the rigid-ion models described so far, to model correctly the dielectric properties of a crystal. A shell model provides a simple mechanical description of ionic polarizability, and it is therefore essential if the defect and high-frequency dielectric behaviour of a material are to be studied. In this model, the atom or ion (frequently it is assumed that oxygen is the only polarizable atom in the structure) is described as having a core containing all the mass, surrounded by a massless, charged shell, representing the outer valance electron cloud. The core and shell are coupled by a harmonic spring.

Computer modelling codes have been available for several years for the simulation of structural, elastic and dielectric properties of the perfect lattice and for calculations of defect energies, for a given set of interatomic potentials. Moreover, recent developments allow defect entropies and volumes to be calculated. The methods employ the 'effective potentials' discussed above, and provided that these are of adequate quality it is possible to perform reliable calculations of a wide range of perfect and defect lattice properties. In applying these methods to silicates, the main problem has been, and remains, obtaining reliable sets of potentials. The current status of the simulation of silicates will be reviewed briefly after we have summarized the principal types of methodology.

Simulation techniques

Full discussion of the techniques and the detailed theory behind them can be found in a number of standard papers (see, for example, Catlow & Mackrodt 1982; Catlow 1987), and so only a brief summary of the methods will be presented here.

Perfect-lattice simulations

In perfect-lattice simulations efficient summation techniques are used to evaluate the interatomic potentials, and to obtain the lattice energies of a compound and its first and second derivatives with respect to atomic coordinates. By coupling lattice-energy calculations with minimization routines, equilibrium crystal structures can be predicted. Moreover, these calculations can be performed to simulate the response of the structure to any required hydrostatic pressure. By using the first and second derivatives referred to above, it is possible to compute the predicted elastic, dielectric and piezoelectric constants of a structure, as well as all of its lattice vibrational properties (Catlow & Mackrodt 1982). From the lattice dynamical simulations, vibrational entropies and basic thermodynamic properties may be calculated by using standard relations (Born & Huang 1954), which when combined with the internal energy term, yield free energies. Successful applications of this technique have recently been reported by Price *et al.* (1987*a*, *b*) to the prediction of the thermodynamic properties and phase relations of magnesium silicate polymorphs.

Defect calculations

Defect energies may be calculated by using Mott–Littleton methods, the basis of which is the division of the crystal surrounding the defect into two regions: an inner region (containing typically 200–800 atoms) in which all atoms are relaxed to zero force; and an outer region whose response to the defect is treated by pseudo-continuum methods. There is now ample evidence available from work on halide and oxide crystals, that when suitable interatomic potentials are available these methods yield defect energies that agree very well with experimental values (see Catlow 1987; Catlow & Mackrodt 1982).

Defect formation leads to entropy changes due both to configurational and vibrational terms. The former is readily evaluated as $k \ln W$, where W is the orientational or site degeneracy associated with the defect. The latter is more difficult to determine; vibrational frequencies must be evaluated for both the perfect and defect lattice. However, recent developments allow this to be done by using both supercell and embedded crystallite methods. The calculations reported to date show the important role that entropy terms play in the total defect free energy.

Defect volumes are of vital importance in predicting the pressure-dependent defect-determined properties. The defect volume is defined by the thermodynamic relation

$$V = kV_0(\mathrm{d}G/\mathrm{d}V),$$

where k is the isothermal compressibility, V is the unit-cell volume and $(\mathrm{d}G/\mathrm{d}V)$ may be evaluated by performing calculations of the defect energies and entropies (and hence free energies) as a function of lattice parameter.

Atomic transport in solids is generally effected by defect migration processes. The rate of defect transport is governed by an Arrhenius expression of the type

$$A = A_0 \exp(-G^*/RT)$$

where G^* is the free energy of activation of the defect. Calculations of G^* are possible once the saddle-point for the migration process has been identified. In complex crystals this may involve an extensive search of the potential surface, a process that may require large amounts of computer time.

Simulating the effect of temperature

As discussed above, the simulation of temperature can be achieved by calculating the full lattice dynamical behaviour of a crystal. From this, standard statistical mechanics relations can be used to calculate heat capacity, entropy, thermal expansion coefficients, and other major thermodynamic properties of the material. The technique is limited, however, within the bounds of the quasiharmonic approximation, which leads to underestimates of high-temperature properties, because of the neglect of anharmonic effects. Such anharmonicity can only be studied via self-consistent phonon calculations or by molecular dynamics. Considerable progress has been made in developing a self-consistent lattice dynamics code (PARAPOCS), but further developments are required.

An alternative approach to the study of the effect of temperature is to use molecular dynamics simulation (MDS) techniques (see Dove 1988 for an extensive review). The approach was originally developed in the 1950s to study fluids, but it can also be used to model solids and has proved to be a useful technique for the study of superionic conductors and phase transformations. The advantage of using an MDS rather than a static stimulation is that it includes simulation of anharmonic temperature effects. Simulations of this type are, however, extremely costly in computer time.

The calculation is initiated with an array of atoms in a simulation box of fixed volume that must consist of a whole number of unit cells, but that may have any geometry. The forces on each ion are calculated according to the interatomic potential functions described above, and then Newton's equations of motion are solved to find their trajectory at all subsequent times by a series of iterations over a small time increment at a specified temperature.

Usually, because of the constraints on computer time it is only possible, to consider explicitly the trajectories of a few hundred particles. It is, therefore, necessary to eliminate surface effects. This is achieved by employing periodic boundary conditions in which the MDS box is embedded in an array of identical images extending to infinity. If a particle leaves the box through one face, its image enters with the same velocity through the opposite face. This does, however, impose an artificial periodicity on the system, and means that it is not possible for Schottky defects to form spontaneously during a simulation. Hence such defects must be introduced explicitly in setting up the simulation. Limitations on the amount of computing time available also normally dictate that simulations can only be run for 10–100 ps and, therefore, can only be used to study events that occur over this timescale. In addition, it is currently not feasible to include complex potentials, such as those that model polarizability.

APPLICATION AND RESULTS

Equations of state

The early simulations of silicates concentrated on being able to reproduce the structures and elastic properties of known minerals. This requires being able correctly to describe both the first and second derivatives of the potential energy surface within the crystal. It was generally found, however, that either the structure could be reproduced at the expense of predicting elastic constants that were too stiff to be realistic, or that reasonable elastic constants could be obtained at the expense of predicting a structure with an unrealistically low density. However, with the realization of the importance of accounting for three-body or many-body interactions, it has become possible to be able to obtain models that predict zero-pressure, zero-temperature densities to within 2%, and elastic constants to within 5–10% of those determined experimentally. The fact that computer models can now be used accurately to predict the physical properties of mantle-forming phases was recently illustrated by the PIB model calculation of the elastic properties of magnesium silicate perovskite (Cohen 1987). These were published before experimental data were available (table 1), and have been subsequently shown to be in very close agreement with the values that were eventually determined, after considerable experimental problems had been overcome (Yeganeh-Haeri *et al.* 1988).

Table 1. Observed and predicted structural and elastic properties of forsterite and magnesium silicate perovskite

(Cell parameters in ångströms (1 Å = 10^{-10} m = 10^{-1} nm), elastic constants in gigapascals. Observed data from Suzuki *et al.* (1983) and Yeganeh-Haeri *et al.* (1988). Calculated data at 300 K.)

	forsterite			perovskite			
	obs	THB1	THB2	obs	PIB	THB1	THB2
a	4.754	4.784	4.749	4.775	—	4.824	4.884
b	10.194	10.261	10.229	4.929	—	4.847	4.945
c	5.981	5.991	5.967	6.897	—	6.844	6.967
c11	328.6	357.1	320.0	520.0	531.0	660.9	600.8
c22	199.8	206.4	179.4	510.0	531.0	632.8	599.4
c33	235.5	280.3	248.9	437.0	425.0	551.2	485.5
c44	66.8	43.8	35.9	181.0	237.0	261.3	224.2
c55	80.9	74.0	73.2	202.0	249.0	251.1	220.6
c66	80.6	83.5	75.6	176.0	136.0	152.1	151.4
c12	66.7	92.1	66.4	114.0	44.0	147.4	100.2
c13	68.3	93.4	69.3	118.0	143.0	246.3	186.1
c23	72.6	87.8	62.7	139.0	166.0	245.3	176.1
K	128.9	154.5	128.1	245.0	249.0	347.0	290.0
G	81.4	78.2	73.3	184.0	192.0	213.0	200.7

Table 2. Potential form and parameters used in THB1 and THB2

(Units: A_{ij}, eV; B_{ij}, Å; C_{ij}, eV Å^6, $k_{\text{O-shell}}$, eV Å^{-2}, $k_{\text{O-Si-O}}$, eV rad^{-2}. Short-range cut off = 7.5 Å.)

$$U=\tfrac{1}{2}\Sigma[e^2 q_i q_j r_{ij}^{-1}+A_{ij}\exp(-r_{ij}/B_{ij})-C_{ij}r_{ij}^{-6}-D_{ijk}(1+3\cos\theta_{ijk}\cos\theta_{jki}\cos\theta_{kji})(r_{ijk}r_{jki}r_{kji})^{-3}+k_{ijk}(\theta_{ijk}-\theta_0)^2+k_i r_i^2]$$

	THB1	THB2		THB1	THB2
q_{Mg}	+2.0	+2.0	$q_{\text{O-shell}}$	−2.8480	−2.8480
q_{Si}	+4.0	+4.0	$q_{\text{O-core}}$	+0.8480	+0.8480
$A_{\text{Mg-O}}$	1428.5	875.0	$B_{\text{Mg-O}}$	0.2945	0.3225
$A_{\text{Si-O}}$	1283.9	1283.9	$B_{\text{Si-O}}$	0.3205	0.3205
$A_{\text{O-O}}$	22764.3	22764.3	$B_{\text{O-O}}$	0.1490	0.1490
$C_{\text{Si-O}}$	10.7	10.7	$C_{\text{O-O}}$	27.88	27.88
$D_{\text{O-Mg-O}}$	0.0	120.0	$D_{\text{O-O-O}}$	0.0	0.0
$k_{\text{O-shell}}$	74.9	74.9	$k_{\text{O-Si-O}}$	2.09	2.09

To illustrate the degree of accuracy that can now be expected from simulations, we also present in table 1 data for the structural and elastic properties of magnesium silicate perovskite and forsterite predicted by typical empirical or partially empirical potential models. Potentials THB1 and THB2 (table 2) are fully ionic models with short-range repulsive parameters empirically fitted to the structural and elastic properties of periclase (MgO) and quartz, and that are transferred to model the more complex silicate minerals considered here (see also Price *et al.* 1987*a*, *b*). Both potentials have polarizable oxygen ions. THB1 contains an O–Si–O three-body potential, whereas THB2 additionally contains an O–Mg–O three-body term. The importance of the O–Mg–O three-body term can be seen by its effect on the predicted elastic properties of forsterite. In the fully ionic description, its inclusion is necessary not only to obtain a reasonable prediction of the bulk modulus, but also to produce the correct prediction of the relative magnitudes of the shear and off-diagonal elastic constants (see also Weidner & Price 1988). Both potentials, however, are more successful in predicting the properties of forsterite than those of perovskite. This is probably because the coordination of Si and Mg are the same in forsterite as they are in the phases from which the potential parameters were derived, whereas in perovskite the coordination number of both ions is increased, with Si in octahedral coordination and Mg in 8–12-fold coordination. This problem illustrates one of the limitations of so-called transfer potentials, and is discussed more fully by Stoneham & Harding (1986). Other more accurate empirical, non-transferable potential models for magnesium silicate perovskite are, however, available (see Matsui *et al.* 1987; Wall 1988).

If potential models of silicates are to be geophysically useful, however, it is not sufficient for them to be able to reproduce the ambient properties of mantle minerals, they must also correctly predict their responses to changes in pressure and temperature. Cohen (1987) has shown that the PIB model prediction of the isothermal equation of state for magnesium silicate perovskite is in excellent agreement with experiment up to pressures in excess of 125 GPa (figure 2). PIB model predictions of the pressure derivative of the ambient temperature isentropic bulk modulus (K') and shear modulus (G') of 4.1 and 1.7, compare with the THB1 predicted values of 3.2 and 1.3, and the experimentally determined value of K' of 3.9 ± 0.4 (Knittle & Jeanloz 1987*a*). Similarly, the pressure derivatives of the bulk and shear moduli of forsterite predicted by THB2 are in accord with those determined experimentally, with predicted K' and G' values of 3.7 and 1.7 respectively, compared with accepted experimental values of 4.7 and 1.6 (Weidner 1986).

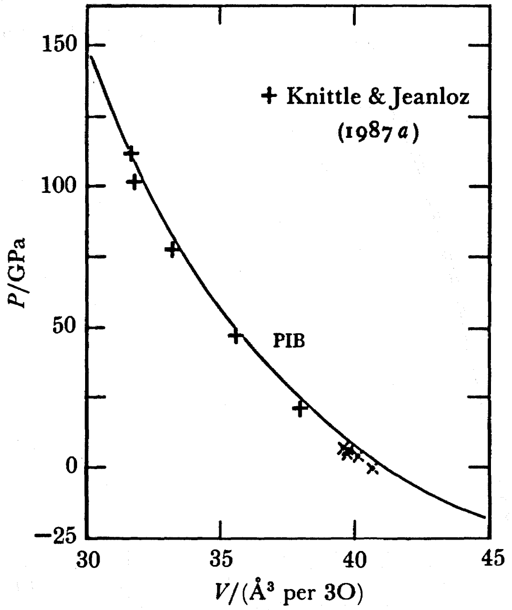

FIGURE 2. PIB model predicted and experimental equation of state for orthorhombic magnesium silicate perovskite at room temperature, after the work of Cohen (1987).

The predicted effect of temperature on the properties of silicates has recently been investigated by using quasiharmonic lattice dynamics (see, for example, Cohen 1987; Price *et al.* 1987*b*). From the calculation of the vibrational frequencies of the lattice, it is possible to obtain the heat capacity at constant volume (C_V) for the structure by using standard thermodynamic relations. The variation of the vibrational frequencies with pressure enables the mode Gruneisen parameters to be calculated which, in combination with predicted bulk modulus and heat capacity, enables the thermal expansion coefficient to be obtained. Price *et al.* (1987*a*, *b*) have shown that potential THB1 provides an excellent prediction of the lattice dynamical properties of forsterite, predicting infrared and Raman vibrational frequencies to within 30 wavenumbers and predicting phonon dispersion behaviour that is consistent with the limited experimental data that exists. The resulting predicted C_v curve (figure 3) is in outstanding agreement with experimental data; however, it should be noted that to obtain convergence the vibrational frequencies of at least eight points in the irreducible sector of the Brillouin zone must be used in the calculation. When the predicted thermal expansion coefficient (figure 4) is compared with measured values, however, it appears to be systematically underestimated by about 20%. This may reflect a shortcoming in the potential model used, or may reflect the fact that quasiharmonic calculations neglect anharmonic effects, which are known to be significant at high temperatures (see Ball 1986). This shortcoming could be overcome by developing a self-consistent phonons code or by using molecular dynamics to simulate these high temperatures.

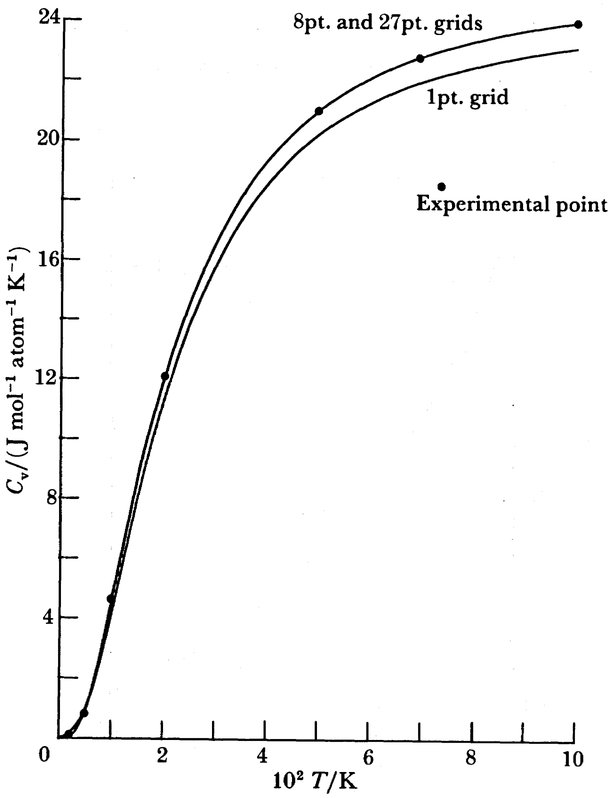

FIGURE 3. The THB1-predicted C_v curve for forsterite calculated with frequencies from 1, 8 and 27 point grids, from Price *et al.* (1987*b*).

Unfortunately, Cohen's PIB model potential for magnesium silicate perovskite is dynamically unstable, and imaginary frequencies are predicted. In addition, models such as PIB and the related MEG model used by Wolf & Bukowinski (1987) do not allow for anion polarizibility. As a result, it is impossible correctly to model LO–TO splitting in the infrared spectra of these silicates, and the predicted high-frequency lattice vibrations are seriously in error. As a result, the thermodynamic predictions of these models must be viewed with some caution.

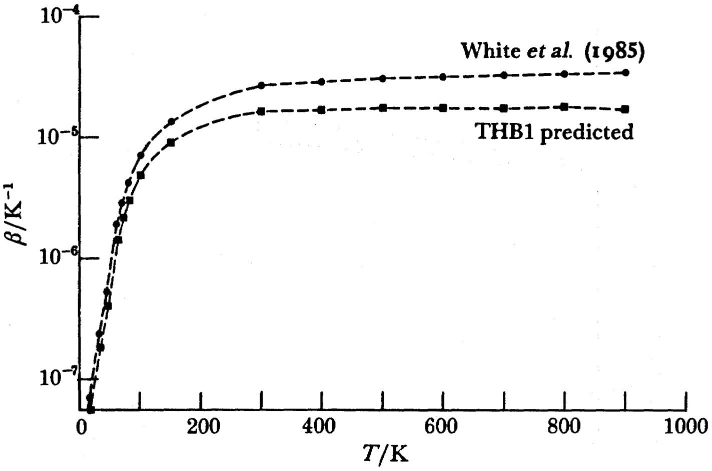

FIGURE 4. The observed and calculated thermal expansion coefficient of forsterite, from Price *et al.* (1987*b*).

Nevertheless, Cohen's model predicts a high-temperature (2000 K) coefficient of thermal expansion of 1.5×10^{-5} K^{-1}, and values of dK/dT and dG/dT of -0.014 and -0.007 GPa K^{-1} respectively, that are similar to those predicted by the dynamically stable THB1 and THB2 potentials. For magnesium silicate perovskite, these potentials predict a coefficient of thermal expansion of 1.6×10^{-5} K^{-1}, and dK/dT values of -0.027 and -0.009 GPa K^{-1} respectively. No experimental estimates of the temperature derivative of the elastic constants of perovskite exist; however, Knittle *et al.* (1986) have provided an estimate of the coefficient of thermal expansion of 4×10^{-5} K^{-1}. Recently, Matsui (1988) has published the results of a constant-pressure molecular dynamics simulation of perovskite, and predicted values of thermal expansion similar to those measured by Knittle *et al.* (1986). Because his study will have included all anharmonic effects, it is probable that Matsui's simulation provides a better model of the high-temperature behaviour of silicate perovskite than do those that are based on quasiharmonic simulations.

As discussed by Jackson (1983), Jeanloz & Thompson (1983), Weidner & Ito (1987) and others, if the chemical composition of the mantle is to be precisely defined, very accurate constraints must be placed upon the thermal expansion coefficients and elastic constants of mantle-forming phases. Weidner & Ito (1987) point out that a 10% uncertainty in K' for magnesium silicate perovskite, or an uncertainty of $\pm 2.0 \times 10^{-5}$ in its thermal expansion coefficient, has an equivalent effect on calculated seismic behaviour as changing the chemical composition of the lower mantle from pyrolite to chondritic. Thus, despite being able to predict seismic velocities with unprecedented accuracy (figure 5), we find ourselves in the frustrating position of still not being able to use these calculated equations of state to discriminate between various compositional models of the mantle.

Phase stability

In contrast to the limitations discussed above, computer simulations appear to be able to make an immediate contribution in the areas of the prediction of phases relations and of defect properties, where experimental results are poorly constrained. Thus, the experimental determination of the phase diagrams of the $(Mg,Fe)SiO_3$ and $(Mg,Fe)_2SiO_4$ systems are still

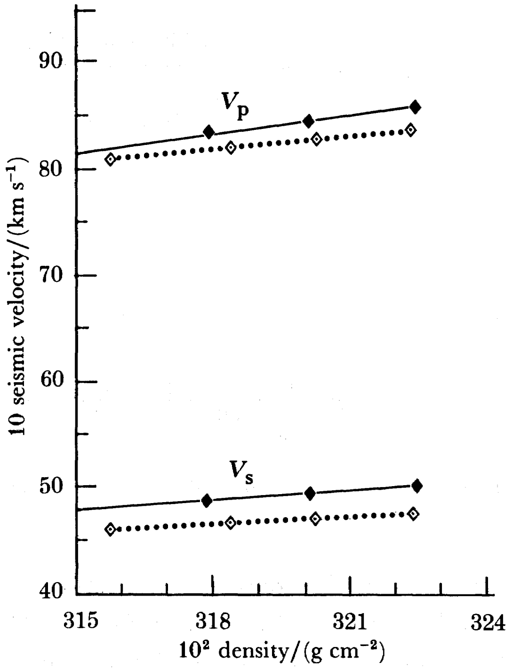

FIGURE 5. THB2-predicted and observed P- and S-wave velocities of forsterite as a function of density. Open symbols, calculated; filled symbols, from Suzuki *et al.* (1983).

subject to considerable uncertainty because of the difficulty in producing consistent pressure and temperature calibrations. The success that potentials such as THB1 have in reproducing the heat capacities of minerals, means that related thermodynamic properties, such as entropy, are also accurately predicted (Price *et al.* 1987*b*). By accurately simulating cell volumes and as well as free energies, these potentials can be used not only to predict the Clausius–Clapeyron slopes of phase boundaries (dS/dV), but also the whole phase diagram. Figure 6 (Marshall *et al.* 1988) shows the phase diagram for the Mg_2SiO_4 system as predicted by potential THB1 (coupled with an Si–O–Si bond bending term to simulate the Si_2O_7 group in the β-phase). The equations of the phase boundaries are very similar to those inferred experimentally (table 3), and confirm the shallow negative slope of the spinel/perovskite + MgO phase boundary. Comparable calculations on the $MgSiO_3$ system, predict the ilmenite/perovskite boundary to have a slope of -1.25 MPa K^{-1} in close agreement with experimentally derived values of between -1.2 and -2.5 MPa K^{-1}.

Following the fluid dynamical analysis of Christensen & Yuen (1984), such small negative Clapeyron slopes would be insufficient to cause these phase transformations to be a complete barrier to convection, unless the phase boundary also coincided with a chemical boundary that exhibited a chemical density contrast of greater than about 5%. Such a large chemical density contrast may be considered unlikely, but a slightly smaller chemical density contrast of *ca.* 2.5% would be compatible with current mineral physics data. In which case, the predicted Clapeyron slopes would suggest that significant penetration of a down going slab could be expected. Limited mixing between the upper and lower mantle could result therefore, but whole-mantle convection as such would not occur. Such a convective régime may indeed come closest to satisfying current mineral physics, seismological and geochemical constraints (Silver *et al.* 1987).

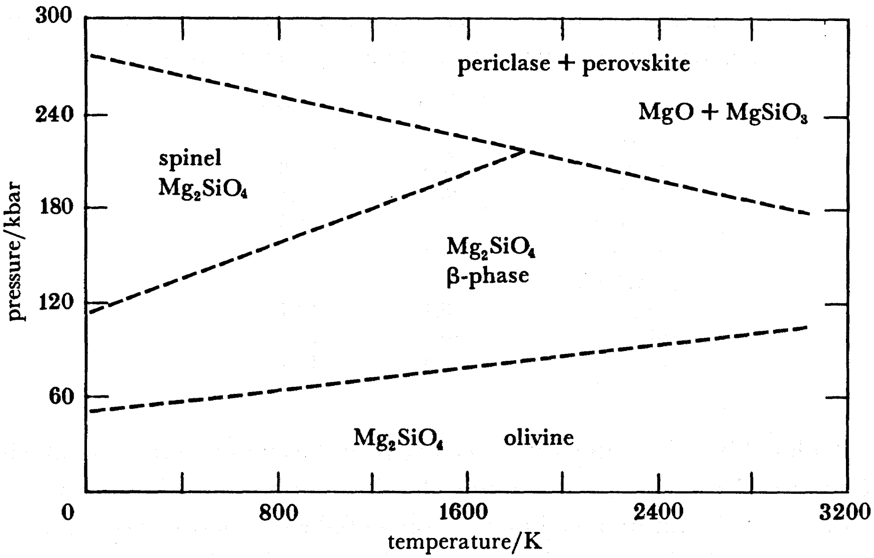

FIGURE 6. The calculated phase diagram for the magnesium orthosilicate system, from Marshall *et al.* (1988). (1 kbar = 10^8 Pa.)

TABLE 3. OBSERVED AND PREDICTED EQUATIONS FOR THE PHASE BOUNDARIES IN THE Mg_2SiO_4 SYSTEM, IN THE FORM $P = P_0 + aT$

(Units: P_0 in gigapascals, a in gigapascals per kelvin. Observed data from Ashida *et al.* (1987) and Ito & Yamada (1982).)

	observed	predicted
olivine – β-phase		
P_0	11.68	5.07
a	0.0025	0.0018
β-phase – spinel		
P_0	11.08	11.29
a	0.0048	0.0056
spinel – perovskite + MgO		
P_0	27.30	27.89
a	−0.002	−0.0033

Defect calculation

Because the viscosity and rheological behaviour of the mantle is likely to be determined by diffusion, controlled by intrinsic disorder within mantle-forming minerals, the calculation of the formation and migration energies of these intrinsic defects are of considerable importance. We have used potential THB1, in conjunction with the Mott–Littleton methodology discussed above, to model the defect behaviour of both forsterite and magnesium silicate perovskite (Wall & Price 1988). The predicted energies of Mg^{2+}, O^{2-} and Si^{4+} Frenkel defects pairs and a variety of Schottky defects are presented in table 4. In addition, we have examined the activation energies for magnesium vacancy and interstitial migration in forsterite, and for oxygen and magnesium vacancy migration in perovskite.

Calculations on forsterite indicate that Mg^{2+} Frenkel pairs are energetically most favourable, although a significant proportion of MgO Schottky defects would also be expected. The diffusion pathway for Mg^{2+} vacancies and interstitials was established by mapping out the potential energy surface within interstitial sites within the crystal. The jump energy for

TABLE 4. PREDICTED FRENKEL AND SCHOTTKY DEFECT ENERGIES (IN ELECTRONVOLTS) FOR FORSTERITE AND MAGNESIUM SILICATE PEROVSKITE

	forsterite	perovskite
Schottky		
MgO	7.8	7.6
SiO_2	25.4	15.1
$MgSiO_3$		21.3
Mg_2SiO_4	42.4	
Frenkel pair		
Mg	6.1	13.1
Si	30.8	24.0
O	8.4	11.1

diffusion was calculated by taking the difference between the energy of the crystal with a defect in the ground state and the energy maximum along the optimum diffusion pathway. Mg^{2+} interstitialcy motion was found to have jump energy of 0.8 eV, whereas Mg^{2+} vacancy motion has a jump energy of 1.1 eV. In the intrinsic régime therefore (i.e. at temperatures appropriate to mantle conditions), the predicted Arrhenius energy for Mg^{2+} diffusion is equal to the sum of half the Mg^{2+} Frenkel pair formation energy and the jump energy of the dominant diffusion process (in this case interstitialcy diffusion), and corresponds to a value of 3.85 eV. This value is in excellent agreement with experimental studies of Mg diffusion in olivine, which yield activation energies ranging between 3.7 and 4.5 eV (Anderson 1988). The success that we have in predicting the energetics of defects in forsterite leads us to believe that these potentials will also yield reasonable predictions of defect behaviour in perovskites.

In contrast to forsterite, Frenkel defects in the high-density perovskite structure are found to be energetically unfavourable, and the most common defect is predicted to be an MgO Schottky defect (table 4). With such a defect structure, it is probable that Mg and O diffusion in perovskite will occur by a vacancy migration mechanism. Assuming that O migration occurs by vacancy hopping, there are two possible pathways for O migration through the perovskite lattice: along the orthorhombic $\langle 100 \rangle_0$ direction (i.e. around the edges of the SiO_6 octahedra) or along the $\langle 110 \rangle_0$ direction (i.e. through the Mg_2O_4 octahedra). The jump energy for these two routes are predicted to be 0.8 eV and 3.2 eV respectively, and hence O migration along $\langle 100 \rangle_0$ is expected to be dominant. The Arrhenius energy of O diffusion in perovskite is expected, therefore, to be 4.6 eV in the intrinsic régime, but only 0.8 eV in the extrinsic régime. These calculations have been repeated at a simulated pressure of 100 GPa, and the activation volume for O diffusion has been calculated to be 1.6 $cm^3\ mol^{-1}$. The activation energy for Mg diffusion has also been calculated, for which it was assumed that the migrating Mg atom moved along a straight path through the centre of the Mg_2O_4 octahedron. The predicted jump energy for this process is 4.6 eV, and the resulting intrinsic Arrhenius energy is predicted to be 8.4 eV.

Perhaps not surprisingly, few experimental data exist on the energetics of diffusion processes in magnesium silicate perovskites. However, Knittle & Jeanloz (1987*b*) have reported the activation energy for the back-transformation of perovskite to pyroxene to be 70 ± 20 kJ mol^{-1} (0.7 ± 0.2 eV). Knittle & Jeanloz chose to interpret this energy in terms of the jump energy of Mg in the perovskite crystal. It is not obvious that this activation energy can be interpreted in terms of any jump process, but if it is, then we would suggest that it corresponds to extrinsic oxygen mobility (0.8 eV) rather than magnesium diffusion (4.6 eV). Knittle & Jeanloz

(1987*b*) also point out the importance of the activation volume in determining the effect of pressure on mantle diffusive processes. Our predicted value for the activation volume for O diffusion (1.6 $cm^3\ mol^{-1}$) is sufficiently small to mean that oxygen is likely to be mobile even at the base of the lower mantle. Indeed, Yuen & Zhang (1987) recently calculated that to explain the inferred magnitude of the topography of the core–mantle boundary, it is necessary for the activation volume of the process that determines lower mantle viscosity to be lower than 2 $cm^3\ mol^{-1}$. Our results suggest that oxygen migration would satisfy this criterion.

The movement of oxygen in the magnesium silicate perovskite lattice has also recently been studied by molecular dynamic simulations (Wall & Price 1988; Kapusta & Guillope 1988). The object of these studies has been to investigate whether magnesium silicate perovskite is a superionic conductor at mantle pressures and temperatures. According to some experiments carried out at atmospheric pressure, perovskites may exhibit anionic conductivities comparable to molten salts, and that the onset of superionic conductivity is associated with a significant reduction in viscosity (see Poirier *et al.* 1983). Should magnesium silicate perovskite also exhibit this behaviour, it would, therefore, have significant effects both on the electrical conductivity of the lower mantle and on its rheology. Although differing in detail, the general conclusion of both of these MDS studies is that at typical lower mantle temperatures and pressures (more than 2750 K and 100 GPa), where intrinsic defects would have a significant concentration, magnesium silicate perovskite is indeed predicted to be a superionic conductor, with a completely mobile oxygen sublattice. Wall & Price (1988) find that MDS supports their conclusion, drawn from static simulations, that oxygen diffusion occurs along $\langle 100 \rangle_0$. They also find that when the calculated diffusion coefficient of $0.4 \times 10^{-5}\ cm^2\ s^{-1}$ is used in the Nernst–Einstein equation, it is predicted that the conductivity of magnesium silicate perovskite in the lower mantle will be approximately 100 $S\ m^{-1}$. This predicted conductivity is exactly that inferred for the lower mantle from the modelling of the temporal variations of the geomagnetic field (Ducruix *et al.* 1980), but is in apparent conflict with the experiments of Li & Jeanloz (1987), who failed to measure any electrical conductivity in a laser-heated, DAC-contained perovskite sample. Given the extreme experimental difficulty in making *in situ* electrical conductivity measurements, we must conclude that the electrical properties of magnesium silicate are still not fully resolved.

CONCLUSION

The progress that has been made in the development of computer simulations of silicates in the past five years has been remarkable. Nevertheless, it is not yet possible to use atomistic simulations to predict the thermoelastic properties of mantle-forming silicates with sufficient accuracy as to be able to use them to resolve the outstanding geophysical questions concerning the detailed composition of the mantle. To achieve this goal, it will be necessary to improve both the calculation and description of interatomic potential energy surfaces within minerals, and to improve upon the way in which anharmonic effects are treated in the calculation of high-temperature properties. Simulations of defects and kinetic processes are, however, already able to add to our understanding of mantle processes. In the future, it is to be hoped that it will be possible to investigate the role of Fe in determining behaviour of silicate perovskites, to investigate the onset of melting of mantle phases, to model silicate surfaces, and to extend the study of the effect of pressure on diffusion processes in silicates.

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