

Calculations of Pressure-Induced Phase Transitions in Mantle Minerals

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Abstract. The crystal structures and energies of SiO_2 stishovite, MgO periclase, Mg_2SiO_4 spinel, and MgSiO_3 perovskite were calculated as a function of pressure with the polarization-included electron gas (PEG) model. The calculated pressures of the spinel to perovskite phase transitions in the Mg_2SiO_4 and MgSiO_3 systems are 26.0 GPa and 27.0 GPa, respectively, compared to the experimental zero temperature extrapolations of 27.4 GPa and 27.7 GPa. The two oxide phases are found to be the most stable form in the pressure range 24.5 GPa to 31.5 GPa, compared to the experimental zero temperature extrapolation of 26.7 GPa to 28.0 GPa. The volume changes associated with the phase transitions are in good agreement with experiment. The transition pressures calculated with the PEG model, which allows the ions to distort from spherical symmetry, are in much better agreement with experiment than those calculated with the modified electron gas (MEG) model, which constrains the ions to be spherical.

Introduction

The seismic discontinuity occurring in the mantle at a depth of 670 km is attributed to the phase transition from the spinel phase to the perovskite phase, and it is this discontinuity that marks the separation between the upper and lower mantle. The present paper examines this phase transition in the MgSiO_3 and Mg_2SiO_4 systems, which approximately model the composition of the earth's mantle.

The most rigorous methods of calculating the energy of a crystal solve the Hartree-Fock or Kohn-Sham equations for the periodic system, and have recently been applied to minerals such as periclase (Bukowinski 1985; Mehl et al. 1988), stishovite (Cohen 1991, 1992; Keskar et al. 1991; Sherman 1993), Mg_2SiO_4 spinel (D'Arco et al. 1991; Silvi et al. 1993), and MgSiO_3 perovskite

(Wentzcovitch 1993; D'Arco et al. 1993). However the difficulty of the calculation increases very rapidly with the size of the unit cell, and for larger structures the calculation times prohibit the use of large basis sets and full structure optimizations. For example, a recent Hartree-Fock calculation on Mg_2SiO_4 olivine was carried out on the experimental structure only, without any structure optimization (Silvi et al. 1993).

The electron gas method is an approximate, but computationally efficient and non-empirical method for calculating the energy of a crystal. In this method Hartree-Fock calculations are carried out on the individual ions in the crystal and the interaction energy between the ions is calculated approximately with density functionals. The computational demand scales more slowly with the unit cell size for the electron gas method than for the more rigorous crystalline Hartree-Fock or Kohn-Sham methods. The original formulations of the electron gas method were based on spherical ions, and many such calculations have been carried out on minerals (Cohen and Gordon 1976; Post and Burnham 1986; Cohen 1987; Hemley et al. 1987; Isaak et al. 1990; Zhang and Bukowinski 1991). We have recently extended the method to include the non-spherical distortions of the ions due to both induction and covalent bonding effects (Lacks and Gordon 1993a).

These calculations correspond to zero temperature, and thus must be compared to extrapolations of experimental results to zero temperature. The experimental studies of phase transitions in magnesian silicates are performed at high temperatures (usually over 1000 K) because the experiments attempt to study the phase transitions under mantle conditions, and need high temperatures to overcome the energy barrier for the phase transition. Extrapolations of the experimental results are carried out with the data of Gasparik (1992).

Computational method

The present calculations use the Polarization-included Electron Gas (PEG) model (Lacks and Gordon 1993a),

which is an extension of the Modified Electron Gas (MEG) model (Gordon and LeSar 1990; Muhlhausen and Gordon 1981 a, 1981 b). Whereas in the MEG model the ions are restricted to have spherical shapes, the PEG model allows the ions to distort, or polarize, to a non-spherical shape and thus account for induction and covalent bonding effects. The theoretical bases of the two models are otherwise the same. The MEG model has given good results for a wide variety of crystals in which the anions occupy high symmetry positions, and the PEG model has successfully extended the scope of electron gas calculations to crystals in which the anions occupy low symmetry positions. A detailed description of the PEG model is given elsewhere (Lacks and Gordon 1993 a).

Electron gas methods are characterized by three assumptions (Gordon and Kim 1972):

1. The interaction energy ΔE is calculated with energy functionals of the electron density,

$$\Delta E = \int \{ \varepsilon[\rho(\mathbf{r})] - \sum_i \varepsilon[\rho_i(\mathbf{r} - \mathbf{r}_{0i})] \} d\mathbf{r} \quad (1)$$

where ε is the energy functional, ρ is the electron density of the total system, ρ_i is the electron density of the ion centered at \mathbf{r}_{0i} , and the sum is over the interacting ions in the system. The accuracy of density functionals for the calculation of interaction energies is investigated elsewhere (Lacks and Gordon 1993 b, d).

2. The total electron density $\rho(\mathbf{r})$ is the sum of the electron densities of the ions ρ_i in the system:

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r} - \mathbf{r}_{0i}). \quad (2)$$

3. The electron densities of the ions are obtained from an accurate quantum mechanical calculation, such as a Hartree-Fock calculation, on the isolated ion. The changes in the ionic densities due to the ion's environment can be incorporated by including a perturbative potential in the ionic calculation. Since the cation electron density remains relatively constant in all environments (such as in different crystals or in free space) (Muhlhausen and Gordon 1981 a), gas phase Hartree-Fock electronic densities are used for the cations in crystal calculations. In contrast, the anion electron density varies considerably with the environment, and therefore the anion densities are obtained by Hartree-Fock calculation on the anion with a stabilizing perturbation which simulates the effect of the rest of the crystal on the anion.

The total crystal energy is given as the energy of interaction of the ions in the crystal, determined from Eq.(1), plus the distortion energy of the anions, where the distortion energy is defined as the energy of the anion with the perturbed density (the energy does not include the perturbation energy) minus the energy of the gas phase, stable anion. For oxides, since O^{2-} is unstable in the gas phase, the reference ion used is O^- .

The MEG model includes a positively charged spherical shell as a perturbation in the Hartree-Fock calcula-

tion for the anion, to allow for spherically symmetric distortions (Gordon and LeSar 1990; Muhlhausen and Gordon 1981 a). The MEG model, however, gives poor results for crystals in which the anions occupy low symmetry positions (Jackson and Gordon 1988; Post and Burnham 1986). The poor results arise because the MEG model does not allow the non-spherical distortions that occur in anions in low symmetry positions due to induction and covalent effects.

The PEG model allows for this non-spherical distortion by including positive point charges as perturbations in the anion Hartree-Fock calculation, rather than a positively charged spherical shell. To facilitate polarization, two "floating" spherical gaussian functions per bond are included in the basis set, at the positions of the point charges. The magnitude of the point charges, the position of the point charges and floating gaussian basis functions, the exponents of the floating gaussian basis functions, and the exponent of the set of the most diffuse nucleus-based basis functions are varied to minimize the *total energy of the crystal*. The positions of the point charges and floating functions which lead to the minimum energy are generally in the bond directions, at approximately half the bond length; many energy minimizations from various starting positions led to the same equilibrium positions, suggesting the absence of multiple minima with respect to the point charge positions. The magnitudes of the point charges which lead to the minimum energy are approximately 0.5 el. By Mulliken population analysis, the population of electrons in the basis functions situated at the point charges is approximately 0.3–0.5 el. We discuss more fully the resulting electron distributions elsewhere (Lacks and Gordon 1993 a).

Calculations were carried out on the SiO_2 stishovite, MgO periclase, Mg_2SiO_4 spinel, and $MgSiO_3$ perovskite crystal structures, at pressures of 0, 250 and 500 kbar. The stishovite and perovskite calculations are described in detail elsewhere (Lacks and Gordon 1993 a). The present spinel calculation slightly different from that in our previous report (Lacks and Gordon 1993 a): In our previous calculation, we found that very little charge density (0.07 electrons, by Mulliken population analysis) went into the polarization functions directed towards the magnesium ions, and therefore in the present calculations the polarization functions towards the magnesium ions were omitted and an extra set of nucleus-based functions was used instead. Three additional point charges were also included, in positions such that they formed a tetrahedron along with the point charge directed towards the silicon ion. The periclase calculation, due to the high symmetry of the oxygen ion, is carried out without any polarization functions but with an extra set of nucleus-based functions instead. Six point charges, forming an octahedron, are included in the periclase calculation.

The MEG calculations presented in this paper use the absolute value of the anion charge as the sphere charge, and vary the sphere radius to minimize the total crystal energy. We note that many spherical ion electron gas model calculations have previously been presented for these systems (Cohen and Gordon 1976; Jackson 1986; Cohen 1987; Hemley et al. 1987; Isaak et al. 1990;

Table 1. MgO Periclase and Mg₂SiO₄ spinel at zero pressure

	Periclase			Spinel		
	Experiment ^a	PEG	MEG	Experiment ^b	PEG	MEG
Energy (kJ/mol)	-3040	-3037	-3051	-17620	-17580	-17040
Volume (Å ³)	18.7	18.2	18.9	65.5	64.3	63.9
a (Å)	4.213	4.176	4.231	8.065	8.014	8.000
u				0.369	0.371	0.365
Si-O (Å)				1.66	1.68	1.60
Mg-O (Å)	2.11	2.09	2.12	2.07	2.04	2.08

^a Quoted from Muhlhausen and Gordon (1981a)

^b Structural parameters from Sasaki and Prewitt (1982); Energy from Woods and Garrels (1987)

Zhang and Bukowinski 1991); however, to determine phase relations, the energies of the different structures must be calculated with the same spherical ion model, and therefore we carried out new MEG calculations with the specific model described above. This MEG model is very similar to the PEG model in that the same density functionals are used in both models, and in both models the anion charge distributions are determined by varying a coulombic perturbation to minimize the total crystal energy: A spherical perturbation is used for the MEG model, and a non-spherical perturbation is used for the PEG model.

Results

Crystal Structures

The results for the structures and cohesive energies of stishovite and perovskite were given previously (Lacks and Gordon 1993a). For stishovite the PEG model calculated the lattice parameters to within 2% of the experimental values. Although the PEG model did not lead to improvements over the MEG model in the structure, the PEG model did lead to significantly improved cohesive energies and electron densities (the latter property was compared to the results of accurate band structure calculations). For perovskite, the PEG results were similar to the MEG results, and the nonspherical distortions of the oxygen anions were found to be small (the PEG results for the structure are in slightly worse agreement with experiment than the MEG results, due to other sources of error in the electron gas method). The calculated lattice parameters in perovskite are underestimated by about 2%.

The results of the PEG model for the periclase and spinel structures are given in Table 1. For periclase, the results of the PEG model are similar to those of the MEG model, as is expected because the oxygen anion is in a high symmetry position. For spinel, the PEG model gives slightly better results for the structure, but significantly better results for the cohesive energy. The optimized electronic parameters for these structures are given in Table 2.

Table 2. Electronic parameters for periclase and spinel at zero pressure

	Periclase	Spinel
Nucleus-based orbital exponents:		
1 (fixed)	17.246	17.246
2 (fixed)	3.740	3.740
3 (fixed)	1.005	1.005
4 (varied)	0.247	0.259
Floating orbital exponents:		
1		0.856
2		0.264
Point charge magnitudes:		
1	0.228 ^a	0.565 ^b
2		0.087 ^c
Point charge position ^d		
	2.047	1.655

^a There are 6 point charges of this magnitude, at the vertices of an octahedron

^b Toward the silicon ion

^c Toward the magnesium ions. There are 3 point charges of this magnitude. These 3 point charges, along with the point charge directed toward the silicon ion, form a tetrahedron

^d Distance from oxygen nucleus to point charge in atomic units

The changes in volume with pressure for the stishovite, periclase, spinel and perovskite crystals are shown in Fig. 1. The agreement with experiment is reasonable, although for all of these structures the calculated compressibilities are somewhat smaller than the experimental values (i.e., the bulk moduli are too high), and are in general (but not always) less accurate than those obtained by the more rigorous band structure calculations (Mehl et al. 1988; Cohen 1991, 1992; Keskar et al. 1991; Sherman 1993; Silvi et al. 1993; Wentzcovitch 1993; D'Arco et al. 1993).

Phase Transitions

The phase transitions investigated are the spinel to perovskite transitions in the MgSiO₃ and Mg₂SiO₄ stoichiometries and the phase transitions to and from the two oxides,

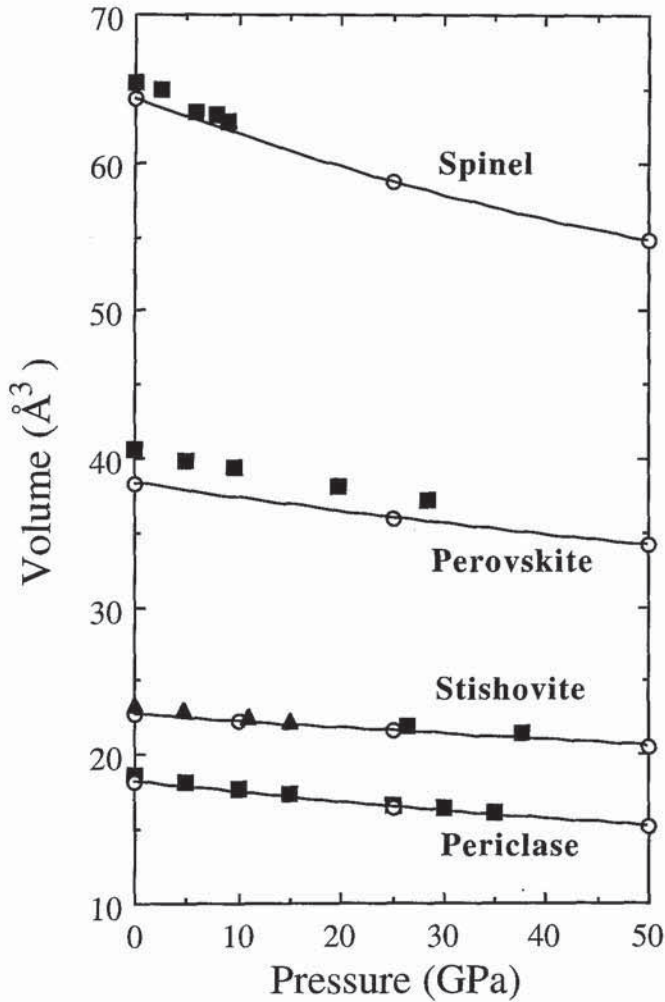


Fig. 1. Compression of crystals with pressure. *Open circles* are results of the PEG model. *Filled squares* are experimental results: periclase: Perez-Albuerné and Drikamer (1965); spinel: Mizukami et al. (1975); perovskite: Hemley et al. (1992); stishovite: Ross et al. (1990). *Filled triangles* are the experimental stishovite results of Tsuchida and Yagi (1989). For perovskite, Hemley et al. found that for $(\text{Fe}_x\text{Mg}_{1-x})\text{SiO}_3$ perovskite, the compression V/V_0 is identical within the limits of the experiments for iron fractions $x=0, 0.1, 0.2$ (Hemley et al. 1992). Therefore, we obtained some of the high pressure experimental volumes by $[(V/V_0)_{x=0}] \cdot [(V_0)_{x=0}]$

- (I) $\text{Mg}_2\text{SiO}_4(\text{sp}) \rightarrow \text{MgSiO}_3(\text{pv}) + \text{MgO}(\text{pc})$
- (II) $\frac{1}{2}\text{Mg}_2\text{SiO}_4(\text{sp}) + \frac{1}{2}\text{SiO}_2(\text{st}) \rightarrow \text{MgSiO}_3(\text{pv})$
- (III) $\text{Mg}_2\text{SiO}_4(\text{sp}) \rightarrow \text{SiO}_2(\text{st}) + 2\text{MgO}(\text{pc})$
- (IV) $\text{SiO}_2(\text{st}) + \text{MgO}(\text{pc}) \rightarrow \text{MgSiO}_3(\text{pv})$

where sp refers to spinel, pv to perovskite, pc to periclase, and st to stishovite.

The results of our PEG calculations are shown in Fig. 2a. At zero pressure, spinel is the most stable phase. At 24.5 GPa, phase transition III occurs and the two-oxide assemblage become stable. The two oxides remain stable to 31.5 GPa, at which point phase transition IV occurs and the perovskite phase becomes stable. The spinel to perovskite phase transition occurs at 26.0 GPa for the Mg_2SiO_4 stoichiometry (phase transition I), and at 27.0 GPa for the MgSiO_3 stoichiometry (phase transition II).

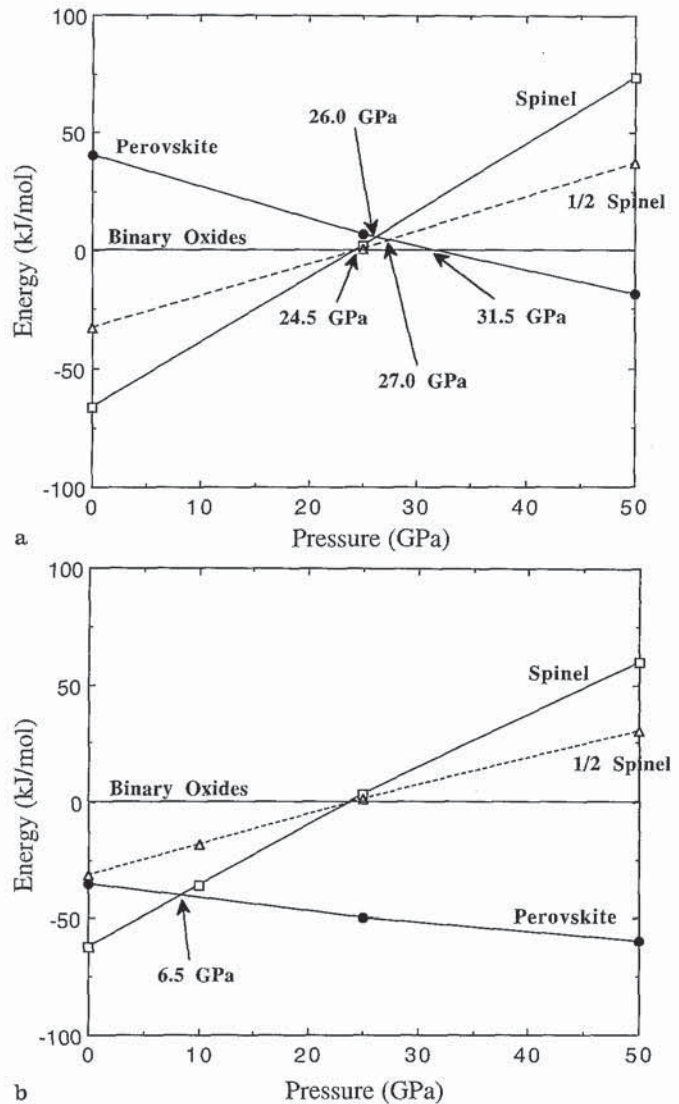


Fig. 2. Enthalpies of phases as a function of pressure, relative to the binary oxides (stishovite and periclase), calculated by the PEG method (2a), and the MEG method (2b)

The PEG results are in good agreement with extrapolations to zero temperature of experimental results, using the data of Gasparik (1992). These extrapolations find the spinel to perovskite phase transition to occur at 27.4 GPa for the Mg_2SiO_4 stoichiometry and 27.7 GPa for the MgSiO_3 stoichiometry. The extrapolations also find that the two-oxide assemblage becomes the most stable form in the pressure range 26.7 GPa to 28.0 GPa, although there is no pressure range of stability for the two oxide phases at the higher temperatures at which the experiments are carried out (these extrapolations find the two-oxide assemblage to be stable in this pressure range relative to *all* magnesium silicate phases, including majorite and ilmenite).

The MEG results are given in Fig. 2b; the agreement with the experimental extrapolations is poor. For the Mg_2SiO_4 stoichiometry, the spinel to perovskite phase transition occurs at 6.5 GPa, and for the MgSiO_3 stoichiometry the perovskite phase is more stable than the spinel phase at all pressures! Also in contrast to the PEG

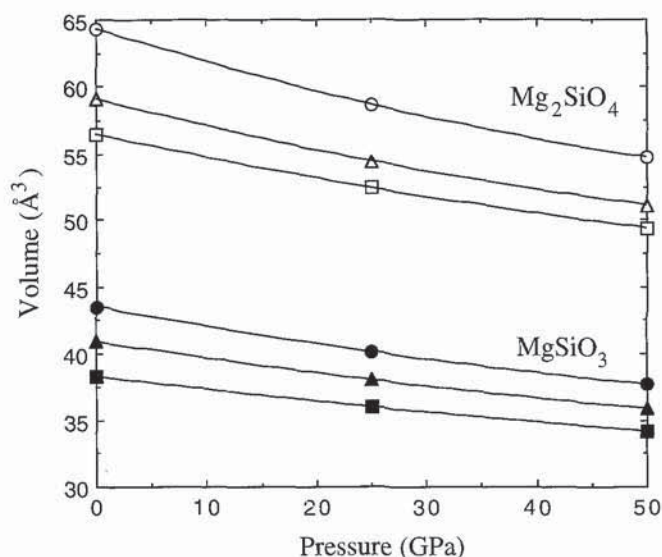


Fig. 3. Volumes of phases as a function of pressure. *Open circles:* spinel; *Open triangles:* stishovite + 2periclase; *Open squares:* perovskite + periclase; *Filled circles:* $\frac{1}{2}$ (spinel + stishovite); *Filled triangles:* stishovite + periclase; *Filled squares:* perovskite

model and the experimental extrapolations, the MEG model finds that the two-oxide assemblage is less stable than the perovskite or spinel phases at all pressures. The improved results for the PEG model with respect to the MEG model can be attributed to the additional stabilization of the spinel and stishovite structures relative to the perovskite and periclase structures due to the inclusion of induction and covalent bonding effects; our analyses of the charge distributions obtained with the PEG model showed that the anions are significantly more distorted in spinel and stishovite than in perovskite (Lacks and Gordon 1993a).

The calculated volumes of the phases as a function of pressure are shown in Fig. 3. The volume decreases accompanying the spinel to perovskite phase transitions in the Mg_2SiO_4 and MgSiO_3 stoichiometries are 11% (6 \AA^3) and 10%, (4 \AA^3) respectively, which agree well with the values of 9% and 8% obtained from the experimentally derived equation of state data of Fei et al. (1991) and extrapolated zero-temperature transition pressures from Gasparik (1992).

Conclusions

Incorporating induction and covalent effects in the electron gas model, by allowing the anions to distort from spherical symmetry, leads to more accurate transition pressures for phase transitions from spinel phases to perovskite phases in magnesian silicates. The spherical ion MEG model underestimates the transition pressures by 20–30 GPa, while the PEG model, which incorporates the induction and covalent effects, calculates the transition pressures to within 2 GPa. In allowing the anions to distort, the spinel phases are stabilized relative to the perovskite phase, leading to higher transition pressures. This observation agrees with our analyses of the charge

distributions obtained with the PEG model, in which we found that the anions are significantly more distorted in spinel and stishovite than in perovskite (Lacks and Gordon 1993a). We also found a significant improvement with the PEG model over the MEG model in the calculation of phase transitions in silica (Lacks and Gordon 1993c).

The PEG model finds a pressure range in which the two oxides are the most stable assemblage at zero temperature. This has not been directly investigated experimentally because the experiments are carried out at high temperatures at which the two-oxide assemblage is no longer stable. However, this two oxide stability field is suggested by extrapolations of experimental results to zero temperature (Gasparik 1992).

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