

# **Ab initio thermodynamics of MgSiO<sub>3</sub> perovskite at high pressures and temperatures**

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Using quantum-mechanical simulations based on density-functional perturbation theory, we address the problem of stability of MgSiO<sub>3</sub> perovskite to decomposition into MgO and SiO<sub>2</sub> at pressures and temperatures of the Earth's lower mantle. We show that MgSiO<sub>3</sub> perovskite (and its post-perovskite phase) is more stable than the mixture of oxides throughout the pressure-temperature regime of the Earth's mantle. Structural stability and lattice dynamics of phases in the system MgO-SiO<sub>2</sub> are discussed. © 2005 American Institute of Physics. [DOI: 10.1063/1.1869973]

## **I. INTRODUCTION**

It is widely believed that (Mg,Fe)SiO<sub>3</sub> perovskite is the most abundant mineral in the Earth's lower mantle (probably ~75 Vol %) and in the Earth as a whole (~40 Vol %). Crucial to this statement is the thermodynamic stability of perovskite relative to decomposition into the oxides MgO and SiO<sub>2</sub>. This stability has been suggested in many studies,<sup>1-6</sup> but has been doubted by some researchers.<sup>7-10</sup> The reason for this experimental controversy could be due to the development of large temperature gradients, deviatoric stresses, and possible incongruent melting in some studies, or MgSiO<sub>3</sub> perovskite may indeed have a limited field of stability relative to component oxides.

In fact, many ternary oxides and silicates break down into simple oxides at high pressure. For instance, it is well established (experiment,<sup>11,12</sup> theory<sup>13</sup>) that Al<sub>2</sub>SiO<sub>5</sub> breaks down into the mixture of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> above 11 GPa. A more complicated picture is established for MgAl<sub>2</sub>O<sub>4</sub> (experiment,<sup>14,15</sup> theory<sup>16</sup>): MgAl<sub>2</sub>O<sub>4</sub> spinel, stable at low pressures, breaks down into MgO and Al<sub>2</sub>O<sub>3</sub> at 15 GPa, but at >25 GPa MgAl<sub>2</sub>O<sub>4</sub> becomes stable in the calcium ferrite (CaFe<sub>2</sub>O<sub>4</sub>) structure. If MgSiO<sub>3</sub> perovskite were to decompose into its component oxides, this would have dramatic consequences for the structure and dynamics of the Earth. First, there would be a seismic discontinuity splitting the lower mantle into two different regions. Although several small seismic discontinuities have been reported at various depths within the lower mantle (see, e.g., Ref. 17), all of them are rather weak and might not be global. If decomposition did take place, it could introduce a barrier to mantle convection, a major factor for the dynamics of our planet.

Given the problems of performing high pressure and temperature experiments, the use of the complementary quantum-mechanical simulation approach is attractive. Early

Hartree-Fock-based calculations at 0 K (Ref. 18) found that MgSiO<sub>3</sub> perovskite is thermodynamically more stable than the oxides above 25 GPa. It was assumed, however, that SiO<sub>2</sub> is present in the stishovite structure, however, both experiment<sup>19-23</sup> and theory<sup>19,20,24-27</sup> showed that a series of other SiO<sub>2</sub> structures are stable above 50 GPa. Two interesting technical details were reported:<sup>18</sup> (i) the calculations of structural stability are extremely sensitive to the quality of the Gaussian basis set used and (ii) pure Hartree-Fock theory is not sufficient for this problem, and an account of electron correlation is needed.

The first attempt to include the effect of temperature and post-stishovite polymorphs of silica on the stability of MgSiO<sub>3</sub>-perovskite was undertaken in Ref. 28. The effects of temperature were incorporated using lattice dynamics simulations based on a parametrical interatomic potential. Contrary to Ref. 18, these authors claimed that at high temperatures the decomposition of MgSiO<sub>3</sub> perovskite (into MgO and  $\alpha$ -PbO<sub>2</sub>-structured phase of SiO<sub>2</sub>) does occur, though at higher pressures than in the experiments carried out by the same group.<sup>8,9</sup> From their calculations it appeared that decomposition is favored by the entropy, but disfavored by the enthalpy.

Calculations reported here are based on density functional theory<sup>29,30</sup> within the local density approximation<sup>31</sup> and the generalized gradient approximation (GGA),<sup>32</sup> and include electron correlation self-consistently, although still approximately. The use of density-functional perturbation theory<sup>33-36</sup> allowed us to take into account thermal effects within a quantum-mechanical framework, without the need to use interatomic potentials or any other more approximate methods. Finally, we also consider the effect of the established high-pressure polymorphs of SiO<sub>2</sub> (stishovite, CaCl<sub>2</sub>-,  $\alpha$ -PbO<sub>2</sub>-, and pyrite-structured phases) and the phase diagram of SiO<sub>2</sub> (Ref. 27) on the problem.

Recently, a post-perovskite phase of MgSiO<sub>3</sub> was independently discovered by two groups<sup>4,5</sup> and confirmed in a

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separate experimental investigation.<sup>6</sup> This phase is stable at conditions of the D'' layer (lowermost ~150 km of the mantle). In calculations reported here we only consider directly the perovskite polymorph for MgSiO<sub>3</sub>. The main conclusion of this work (only reinforced by the recently reported stability of the post-perovskite phase at higher pressures) is that MgSiO<sub>3</sub> (in perovskite and post-perovskite structures) remains thermodynamically stable with respect to decomposition throughout the Earth's lower mantle.

## II. COMPUTATIONAL METHODOLOGY

Our static as well as lattice dynamics results were obtained with the use of the ABINIT code,<sup>37</sup> a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL <http://www.abinit.org>), based on pseudopotentials and plane waves. It relies on an efficient fast Fourier transform algorithm<sup>38</sup> for the conversion of wave functions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate gradient method,<sup>39</sup> and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential.<sup>40</sup> Technical details on the computation of responses to atomic displacements and homogeneous electric fields can be found in Ref. 35, and the subsequent computation of dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants was described in Ref. 36. The local density approximation (LDA) (Ref. 31) was used for the exchange correlation. The pseudopotentials used are of the Troullier–Martins type,<sup>41</sup> fully nonlocal and including partial core corrections;<sup>42</sup> the core radii are 0.766 Å for O (1s<sup>2</sup> core), 1.105 Å for Si (1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup> core), and 1.371 Å for Mg (1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup> core). The plane wave kinetic energy cutoff of 40 hartree enabled convergence to within 0.02–0.03 eV per C atom for the total energy, more than an order of magnitude better for the energy differences, and within 0.05 GPa for the pressure. The Monkhorst–Pack<sup>43</sup> meshes used for sampling of the Brillouin zone were 4 × 4 × 2 (for MgSiO<sub>3</sub> perovskite, 20 atoms in the unit cell), 4 × 4 × 4 (for α-PbO<sub>2</sub>- and pyrite-structured phases of SiO<sub>2</sub>, 12 atoms in the unit cell), 4 × 4 × 6 (for stishovite and CaCl<sub>2</sub>-structured phases of SiO<sub>2</sub>, 6 atoms in the unit cell), and 8 × 8 × 8 (for MgO, 2 atoms in the unit cell). Lattice dynamical calculations relied on the computed values of the dielectric constants, Born effective charges, and short-range force constants calculated on 2 × 2 × 2 grids for MgSiO<sub>3</sub> perovskite (this corresponds to a full set of force constants in a supercell with 160 atoms) and α-PbO<sub>2</sub>- and pyrite-structured phases of SiO<sub>2</sub> (equivalent to 96-atom supercells), 2 × 2 × 3 for stishovite and CaCl<sub>2</sub>-structured phases of SiO<sub>2</sub> (equivalent to 72-atom supercells), and 4 × 4 × 4 for MgO (equivalent to a 128-atom supercell). Having both the long-range (given by Born charges and dielectric constants) and short-range contributions to force constants, we constructed dynamical matrices at very dense Brillouin-zone meshes, from the diagonalization of which we obtained phonon densities of states and vibrational thermodynamic functions (for these, we typically used ~10<sup>7</sup> frequencies), e.g.,

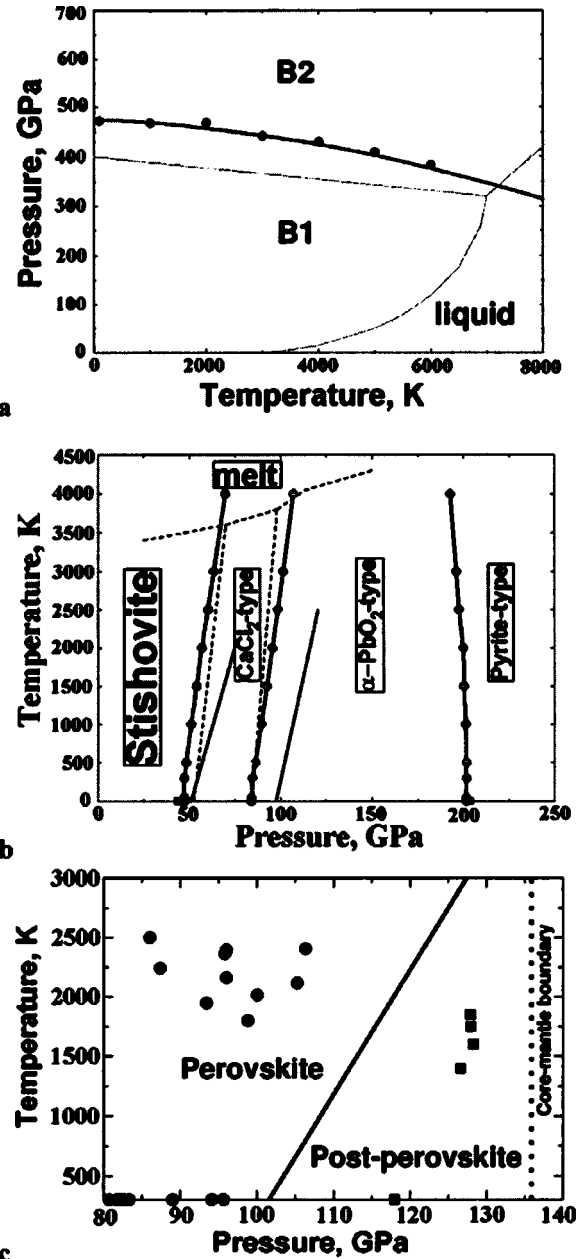


FIG. 1. High-pressure phase diagrams of (a) MgO, (b) SiO<sub>2</sub>, (c) MgSiO<sub>3</sub>. (a) Theoretical results of Oganov *et al.* [black line with solid circles (Ref. 48)] and Strachan *et al.* [gray lines (Ref. 49)], (b) Theory [solid lines with circles (Ref. 27)], experiment [solid lines (Refs. 22 and 23)], interpretation of shock-wave data [dashed lines (Ref. 50)], (c) Theory (Ref. 5) and experiment [circles (Ref. 51), squares (Ref. 5)]. Adapted from Refs. 5, 27, and 48.

$$F = E_0 + \int_0^{\omega_{\max}} \frac{1}{2} \hbar \omega g(\omega) d\omega + k_B T \times \int_0^{\omega_{\max}} \ln \left[ 1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right) \right] g(\omega) d\omega. \quad (1)$$

One can easily obtain the Gibbs free energy

$$G = F + PV = F - \left( \frac{\partial F}{\partial V} \right)_T V, \quad (2)$$

since  $P = -(\partial F / \partial V)_T$ . To perform differentiation, at each temperature thermal contributions to the Helmholtz free energy

TABLE I. Equations of state of phases in the MgO-SiO<sub>2</sub> system: theory and experiment.

	$V_0$ (Å <sup>3</sup> )	$K_0$ (GPa)	$K'_0$
MgO			
Theory <sup>a</sup>	76.2	168.7	4.258
Expt. <sup>b</sup>	74.7	160.2	3.99
Stishovite			
Theory <sup>a</sup>	46.3	318.3	4.373
Expt. <sup>c</sup>	46.9	312.9	4.8
$\alpha$ -PbO <sub>2</sub> type phase of SiO <sub>2</sub>			
Theory <sup>a</sup>	91.1	324.4	4.233
Expt.	...	...	...
Pyrite-type phase of SiO <sub>2</sub>			
Theory <sup>a</sup>	87.0	344.8	4.313
Expt.	...	...	...
MgSiO <sub>3</sub> perovskite			
Theory <sup>a</sup>	163.3	261.4	4.032
Expt. <sup>d</sup>	162.3	259.5	3.69

<sup>a</sup>All theoretical equations of state are in the Vinet form (Refs. 44 and 45).

<sup>b</sup>Third-order Birch–Murnaghan equation of state at 300 K (Ref. 52).

<sup>c</sup>Third-order Birch–Murnaghan equation of state at 300 K (Ref. 53).

<sup>d</sup>Third-order Birch–Murnaghan equation of state at 300 K (Ref. 54).

were fitted by third-order polynomials of volume, the static  $E_0(V)$  were fitted by the Vinet function.<sup>44,45</sup> The approach outlined above corresponds to the quasiharmonic approximation, i.e., phonon frequencies are assumed to be independent of temperature at fixed volume. For MgO the effects beyond this approximation (collectively known as intrinsic anharmonic effects) have been studied in Ref. 46 using *ab initio* molecular dynamics simulations; general analysis was presented in Ref. 47. Based on these studies, we expect that at pressures and temperatures of interest intrinsic anharmonic contribution to the free energy of decomposition is very small relative to other terms.

### III. RESULTS

Figure 1 shows the calculated phase diagrams of MgO, SiO<sub>2</sub>, and MgSiO<sub>3</sub> from our previous works.<sup>5,27,48</sup> While MgO does not exhibit polymorphism, both SiO<sub>2</sub> and MgSiO<sub>3</sub> undergo phase transitions in the pressure range of the Earth's mantle. These phase transitions are taken into account in our present calculations.

To illustrate the accuracy of our simulations, in Table I we give Vinet equation of state parameters of these phases in

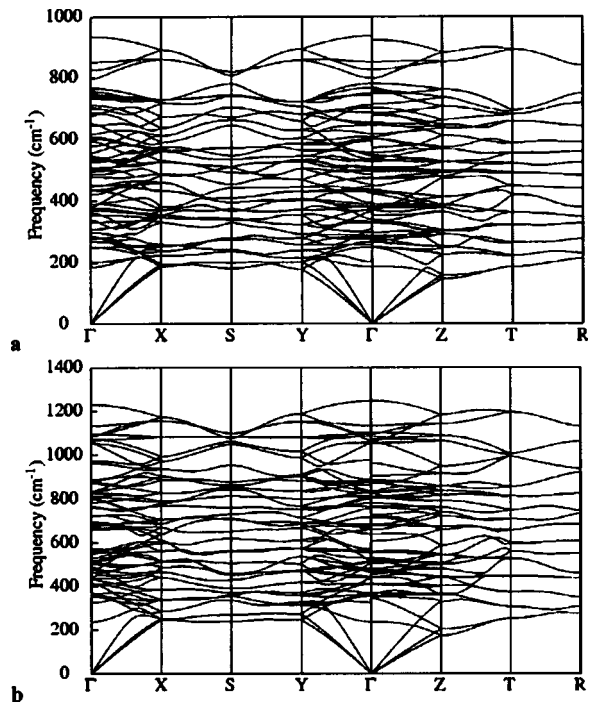


FIG. 2. Phonon dispersion curves of MgSiO<sub>3</sub> perovskite (a) at 0 GPa, (b) at 100 GPa.  $\Gamma=[0;0;0]$ ,  $X=[1/2;0;0]$ ,  $S=[1/2;1/2;0]$ ,  $Y=[0;1/2;0]$ ,  $Z=[0;0;1]$ ,  $T=[0;1/2;1/2]$ ,  $R=[1/2;1/2;1/2]$ . (*Pbnm* setting).

comparison with experiment, and in Table II comparison between theoretical and experimental thermodynamic properties at ambient conditions. Figures 2–4 show phonon dispersion curves, which agree well with available experimental data (detailed comparison with experimental data for these phases is discussed in Refs. 48 and 58–61—results of these studies are very similar or identical to those reported here). Several features of these phonon dispersion curves are worth mentioning.

(1) In noncubic phases, polar modes have discontinuities at the  $\Gamma$  point.

(2) Structural pseudosymmetry of MgSiO<sub>3</sub> perovskite and of the CaCl<sub>2</sub>-type phase leads to pseudosymmetry of phonon dispersions, e.g., in X-S-Y sections.

(3) None of the phases of SiO<sub>2</sub> display soft modes at zero pressure. Consequently, these phases may be quenchable - except for the CaCl<sub>2</sub>-type phase, which becomes identical to stishovite at the point of second-order transition at 44 GPa and below. This would be especially interesting for not-yet-synthesized pyrite-type SiO<sub>2</sub>, a potential superhard material.

TABLE II. Thermodynamic properties (heat capacity  $C_V$  and entropy  $S$ ) of phases in the MgO-SiO<sub>2</sub> system: theory and experiment (0 GPa, 300 K).

	MgO periclase		SiO <sub>2</sub> stishovite		MgSiO <sub>3</sub> perovskite	
	Theory	Expt.	Theory	Expt.	Theory	Expt.
$C_V$ (J mol <sup>-1</sup> K <sup>-1</sup> )	36.58	36.87 <sup>a</sup>	41.3	42.2 <sup>b</sup>	80.73	77.3
$S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	26.81	27.13 <sup>a</sup>	24.6	25.9 <sup>b</sup>	57.14	57.2 <sup>c</sup>

<sup>a</sup>Data of Ref. 55,  $C_V$  recalculated from reported  $C_p$ .

<sup>b</sup>Recalculated using data from Ref. 56.

<sup>c</sup>Data of Ref. 57,  $C_V$  recalculated from reported  $C_p$ .

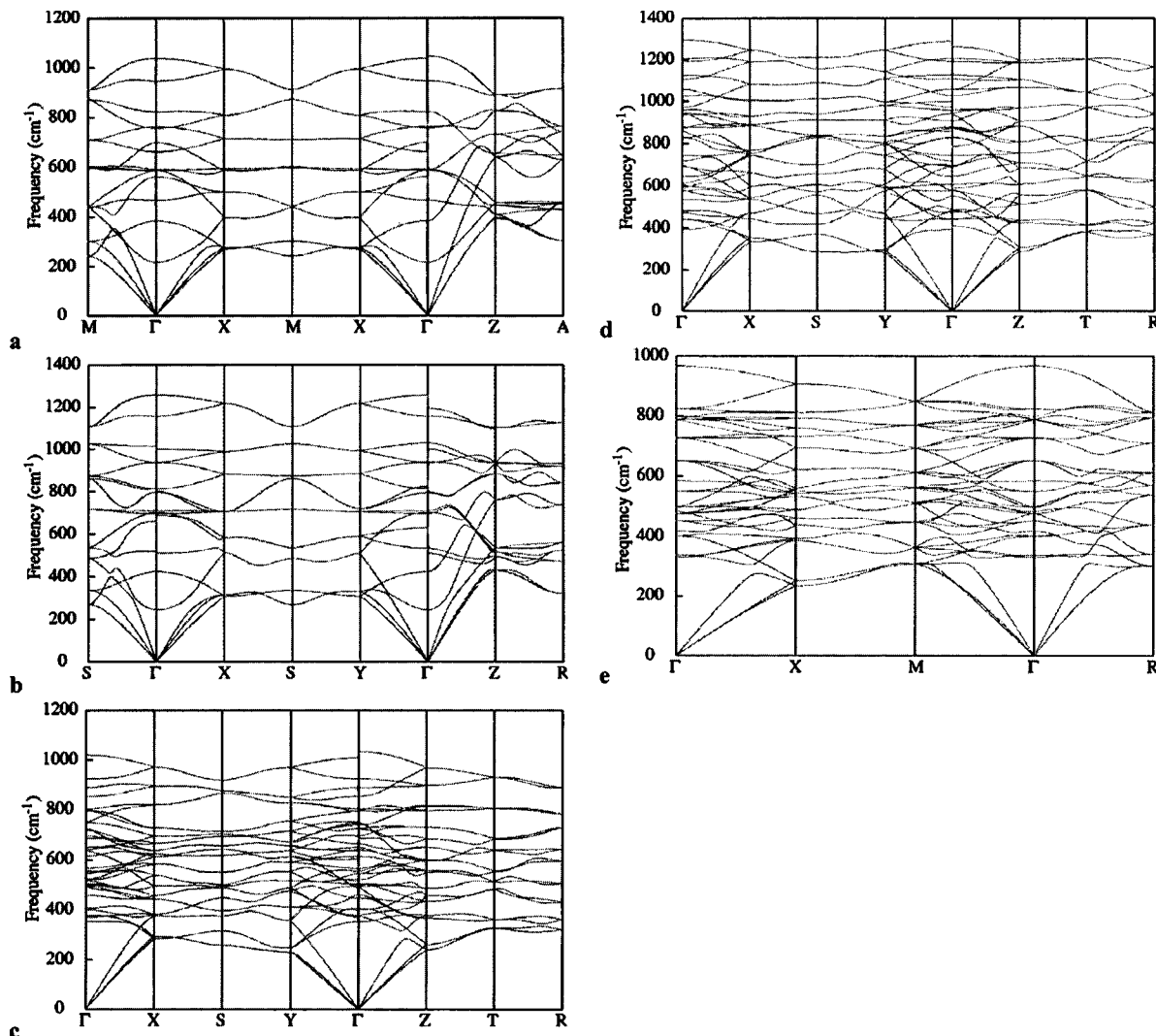


FIG. 3. Phonon dispersion curves of SiO<sub>2</sub> polymorphs: (a) stishovite at 0 GPa, (b) CaCl<sub>2</sub>-type phase at 70 GPa, (c)  $\alpha$ -PbO<sub>2</sub> type phase at 0 GPa, (d)  $\alpha$ -PbO<sub>2</sub> type phase at 100 GPa (e) pyrite-type phase at 0 GPa. Stishovite:  $M=[1/2;1/2;0]$ ,  $\Gamma=[0;0;0]$ ,  $X=[1/2;0;0]$ ,  $Z=[0;0;1]$ ,  $A=[1/2;1/2;1/2]$ . CaCl<sub>2</sub>-type phase:  $S=[1/2;1/2;0]$ ,  $\Gamma=[0;0;0]$ ,  $X=[1/2;0;0]$ ,  $Y=[0;1/2;0]$ ,  $Z=[0;0;1]$ ,  $R=[1/2;1/2;1/2]$ .  $\alpha$ -PbO<sub>2</sub> type phase:  $\Gamma=[0;0;0]$ ,  $X=[1/2;0;0]$ ,  $S=[1/2;1/2;0]$ ,  $Y=[0;1/2;0]$ ,  $Z=[0;0;1]$ ,  $T=[0;1/2;1/2]$ ,  $R=[1/2;1/2;1/2]$ . Pyrite-type phase:  $\Gamma=[0;0;0]$ ,  $X=[1/2;0;0]$ ,  $M=[1/2;1/2;0]$ ,  $R=[1/2;1/2;1/2]$ .

The calculated Gibbs free energy of decomposition is shown in Fig. 5. One can see that it increases with both pressure and temperature and remains positive at all  $P$ - $T$  conditions of the lower mantle (1500–4200 K, 24–136 GPa). In other words, MgSiO<sub>3</sub> perovskite is stable to decomposition at all lower-mantle pressures and temperatures and becomes increasingly more stable as pressure and temperature increase.

It is well known that the LDA underestimates phase transition pressures, whereas the GGA tends to slightly overestimate them.<sup>13,62</sup> Furthermore, the use of pseudopotentials is an approximation. To check the accuracy of our pseudopotential LDA calculations, we have calculated the relative enthalpies of MgSiO<sub>3</sub> perovskite and the MgO+SiO<sub>2</sub> mixture by using the GGA<sup>32</sup> and the all-electron projector augmented wave (PAW) method<sup>63,64</sup> as implemented in the VASP code.<sup>65</sup> It is encouraging that the results (Fig. 6) of these calculations are in excellent agreement with our pseudopotential LDA calculations (Fig. 5).

In fact, just from the static enthalpy of decomposition one could conclude that decomposition is unlikely. One could estimate the entropy of decomposition from a simple formula,<sup>66</sup> which can be more generally written as

$$\Delta S = \bar{\gamma} C_V \frac{\Delta V}{V} + 3 \sum_i n_i R \ln \sqrt{\frac{v_i}{v_{0i}}}, \quad (3)$$

where  $\bar{\gamma}$  is the average Grüneisen parameter ( $1.15 \pm 0.08$  for MgO and MgSiO<sub>3</sub>) perovskite,<sup>46,67,68</sup>  $C_V$  the isochoric heat capacity ( $3nR$  in the classical quasiharmonic case),  $R$  the gas constant,  $\Delta V/V$  the relative volume change (1.34% from our *ab initio* calculations at 100 GPa),  $n_i$  number of cations of the  $i$ th type, and  $v_i/v_{0i}$  ratios of their coordination numbers in the final and initial states, respectively. From Eq. (2), at 100 GPa we obtain the high-temperature entropy of decomposition  $\Delta S = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}$ , in excellent agreement with *ab initio* estimates ( $-5.23 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and suggesting that vibrational entropy stabilizes perovskite against decomposition.

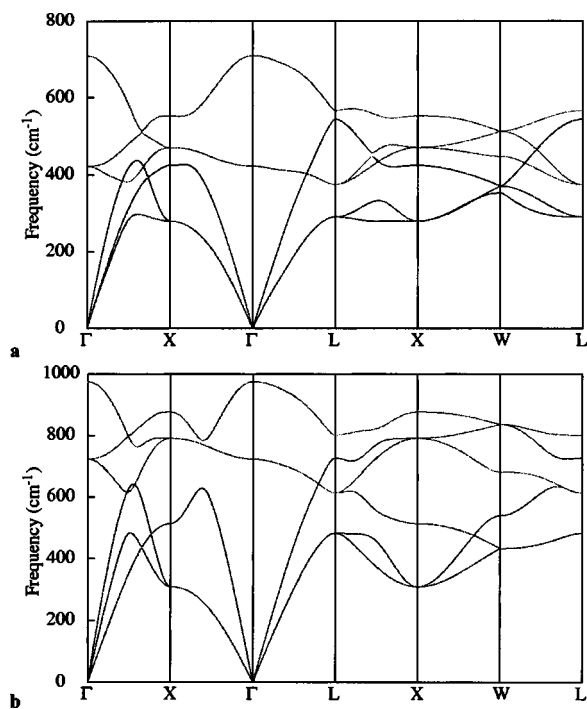


FIG. 4. Phonon dispersion curves of MgO (a) at 0 GPa (b) at 100 GPa. Drawn along  $\Gamma[000]-X[1/2;1/2;1]/X[1/2;1/2;0]-\Gamma[000]-L[1/2;1/2;1/2]-X[1/2;1/2;0]-W[1/2;1/4;3/4]-L[1/2;1/2;1/2]$ .

#### IV. DISCUSSION

In our calculations we assumed completely ordered structures. However, in SiO<sub>2</sub> polymorphs at high-temperatures Si atoms could be disordered over the octahedral voids of the hexagonal close packing of oxygens (the so called Fe<sub>2</sub>N structure—Ref. 69). Recently, Prakapenka *et al.*<sup>70</sup> found this structure experimentally in SiO<sub>2</sub> and GeO<sub>2</sub>, but it was metastable. In any case, even the maximum possible entropy of disorder (in this case,  $k_B \ln 2 = 5.76 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is not nearly sufficient to destabilize perovskite and reverse the sign of  $\Delta G_{\text{decomp}} \approx 50 \text{ kJ mol}^{-1}$  at lower-mantle conditions (temperatures of well over 8000 K would be needed to achieve this). We conclude, therefore, that at all pressure-temperature conditions of the Earth's

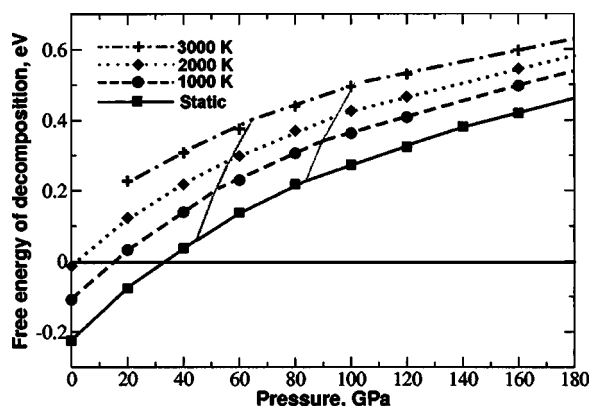


FIG. 5. Free energy of decomposition: MgSiO<sub>3</sub> → MgO + SiO<sub>2</sub>. Gray lines show pressures of phase transitions in SiO<sub>2</sub> at each temperature. Pseudopotential LDA results. Thin solid lines separate regions of stability of different SiO<sub>2</sub> phases. All lines are guides to the eye.

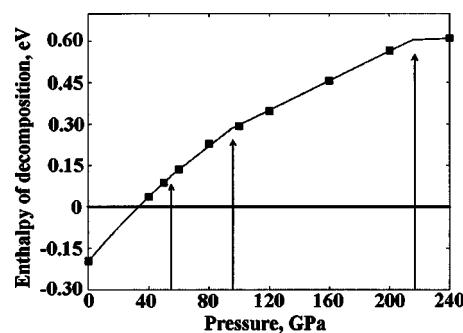


FIG. 6. Enthalpy of decomposition: MgSiO<sub>3</sub> → MgO + SiO<sub>2</sub>. PAW GGA results. PAW potentials had the following parameters:  $1s^2 2s^2$  core (radius 1.058 Å) for Mg,  $1s^2 2s^2 2p^6$  core (1.005 Å radius) for Si  $1s^2$  core (radius 0.804 Å) for O. The plane wave kinetic energy cutoff of 500 eV was used, together with Brillouin zone sampling grids similar to those described in Sec. II.

lower mantle MgSiO<sub>3</sub> perovskite is stable relative to decomposition into oxides. Thus our conclusions support the experimental results of Refs. 1 and 3–6, but not those of Ref. 7–9. Serghiou *et al.*<sup>2</sup> argued that decomposition could be due to large temperature gradients in the experiments where decomposition was observed, Murakami *et al.*<sup>4</sup> invoked the possibility of melting, apparently meaning incongruent melting of the sample due to poor control of temperature and its gradients. However, in thermodynamic equilibrium decomposition would not occur.

For a multicomponent system like the Earth's mantle, one has additional thermodynamic parameters—the chemical potentials of Mg<sup>2+</sup> and of the major impurities, Fe<sup>3+</sup>, Al<sup>3+</sup>, Fe<sup>2+</sup>. However, our results obtained for pure MgSiO<sub>3</sub> should be relevant to the lower mantle, where significant amounts of Fe<sup>3+</sup>, Al<sup>3+</sup>, Fe<sup>2+</sup> are incorporated into perovskite. Among the impurity ions, only Fe<sup>2+</sup> is expected to be partitioned into the oxides (MgO) stabilizing the mixture of oxides against perovskite. We note, however, that in perovskite with a composition realistic for the lower mantle, ~65% of all Fe is present as Fe<sup>3+</sup>, not Fe<sup>2+</sup> (Ref. 71) and partitioning of Fe<sup>3+</sup> and Al<sup>3+</sup> into perovskite should be much stronger than partitioning of Fe<sup>2+</sup> into magnesiowüstite. For the latter, there have been numerous experimental studies (e.g., Refs. 72–77). Though consensus is still lacking, most of these studies show some degree of preference of Fe<sup>2+</sup> for magnesiowüstite, but  $K$  is of the order of 1, consistent with the finding of Ref. 78 that crystal field stabilization energies of Fe<sup>2+</sup> are nearly the same in MgSiO<sub>3</sub> perovskite and magnesiowüstite.

Since MgSiO<sub>3</sub> is more stable than MgO + SiO<sub>2</sub> and Mg/Si > 1 in pyrolite mantle, no free SiO<sub>2</sub> is expected in the bulk of the lower mantle. One might expect free SiO<sub>2</sub> only in silica-rich subducted slabs. In any case, recent theoretical<sup>27</sup> and experimental<sup>22,23</sup> studies show that SiO<sub>2</sub> phases are unlikely to be important mantle-forming minerals as  $P$ - $T$  conditions of phase transitions in SiO<sub>2</sub> do not match any seismic discontinuities known in the mantle.<sup>17</sup> We conclude, therefore, that MgSiO<sub>3</sub> polymorphs (perovskite and post-perovskite) in the lower mantle are stable with respect to decomposition, and are likely to make up a significant proportion of all lower mantle assemblages.

## ACKNOWLEDGMENTS

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- <sup>1</sup>G. Serghiou, A. Zerr, and R. Boehler, *Science* **280**, 2093 (1998).
- <sup>2</sup>G. Serghiou, A. Zerr, and R. Boehler, *Science* **285**, 983a (1999).
- <sup>3</sup>S. H. Shim, T. S. Duffy, and G. Y. Shen, *Science* **293**, 2437 (2001).
- <sup>4</sup>M. Murakami, K. Hirose, K. Kawamura, N. Sata, and Y. Ohishi, *Science* **304**, 855 (2004).
- <sup>5</sup>A. R. Oganov and S. Ono, *Nature (London)* **430**, 445 (2004).
- <sup>6</sup>S.-H. Shim, T. S. Duffy, R. Jeanloz, and G. Shen, *Geophys. Res. Lett.* **31**, L10603 (2004).
- <sup>7</sup>C. Meade, H. K. Mao, and J. Z. Hu, *Science* **268**, 1743 (1995).
- <sup>8</sup>S. K. Saxena, L. S. Dubrovinsky, P. Lazor, Y. Cerenius, P. Häggkvist, M. Hanfland, and J. Hu, *Science* **274**, 1357 (1996).
- <sup>9</sup>S. K. Saxena, L. S. Dubrovinsky, P. Lazor, and J. Z. Hu, *Eur. J. Mineral.* **10**, 1275 (1998).
- <sup>10</sup>L. S. Dubrovinsky, S. K. Saxena, and S. Rekhi, *Science* **285**, 983a (1999).
- <sup>11</sup>L.-G. Liu, *Earth Planet. Sci. Lett.* **24**, 224 (1974).
- <sup>12</sup>M. W. Schmidt, S. Poli, P. Comodi, and P. F. Zanazzi, *Am. Mineral.* **82**, 460 (1997).
- <sup>13</sup>A. R. Oganov and J. P. Brodholt, *Phys. Chem. Miner.* **27**, 430 (2000).
- <sup>14</sup>T. Irifune, K. Fujino, and E. Ohtani, *Nature (London)* **349**, 409 (1991).
- <sup>15</sup>N. Funamori, R. Jeanloz, and J. Nguyen, *J. Geophys. Res.* **103**, 20813 (1998).
- <sup>16</sup>M. Catti, *Phys. Chem. Miner.* **28**, 729 (2001).
- <sup>17</sup>L. Vinnik, M. Kato, and H. Kawakatsu, *Geophys. J. Int.* **147**, 41 (2001).
- <sup>18</sup>Ph. D'Arco, G. Sandrone, R. Dovesi, E. Apra, and V. R. Saunders, *Phys. Chem. Miner.* **21**, 285 (1994).
- <sup>19</sup>K. J. Kingma, R. E. Cohen, R. J. Hemley, and H.-K. Mao, *Nature (London)* **374**, 243 (1995).
- <sup>20</sup>L. S. Dubrovinsky, S. K. Saxena, P. Lazor, R. Ahuja, O. Eriksson, J. M. Wills, and B. Johansson, *Nature (London)* **388**, 362 (1997).
- <sup>21</sup>L. S. Dubrovinsky, N. A. Dubrovinskaya, S. K. Saxena, F. Tutti, S. Rekhi, T. LeBihan, G. Shen, and J. Hu, *Chem. Phys. Lett.* **333**, 264 (2001).
- <sup>22</sup>S. Ono, K. Hirose, M. Murakami, and M. Isshiki, *Earth Planet. Sci. Lett.* **197**, 187 (2002).
- <sup>23</sup>M. Murakami, K. Hirose, S. Ono, and Y. Ohishi, *Geophys. Res. Lett.* **30**, 1207 (2003).
- <sup>24</sup>R. E. Cohen, in *High Pressure Research in Mineral Physics: Application to Earth and Planetary Science*, edited by M. H. Manghanani and Y. Syono (American Geophysical Union, Washington, D.C., 1992), pp. 425–432.
- <sup>25</sup>B. B. Karki, M. C. Warren, L. Stixrude, G. J. Ackland, and J. Crain, *Phys. Rev. B* **55**, 3465 (1997); **56**, 2884(E) (1997).
- <sup>26</sup>D. M. Teter, R. J. Hemley, G. Kresse, and J. Hafner, *Phys. Rev. Lett.* **80**, 2145 (1998).
- <sup>27</sup>A. R. Oganov, M. J. Gillan, and G. D. Price, *Phys. Rev. B* **71**, 064104 (2005).
- <sup>28</sup>L. S. Dubrovinsky, S. K. Saxena, R. Ahuja, and B. Johansson, *Geophys. Res. Lett.* **25**, 4253 (1998).
- <sup>29</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- <sup>30</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- <sup>31</sup>J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- <sup>32</sup>Y. Wang and J. P. Perdew, *Phys. Rev. B* **44**, 13298 (1991).
- <sup>33</sup>S. Baroni, P. Gianozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987).
- <sup>34</sup>S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Gianozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- <sup>35</sup>X. Gonze, *Phys. Rev. B* **55**, 10337 (1997).
- <sup>36</sup>X. Gonze and C. Lee, *Phys. Rev. B* **55**, 10355 (1997).
- <sup>37</sup>X. Gonze, J.-M. Beuken, R. Caracas, *Comput. Mater. Sci.* **25**, 478 (2002).
- <sup>38</sup>S. Goedecker, *SIAM J. Sci. Comput. (USA)* **18**, 1605 (1997).
- <sup>39</sup>M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
- <sup>40</sup>X. Gonze, *Phys. Rev. B* **54**, 4383 (1996).
- <sup>41</sup>N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- <sup>42</sup>S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
- <sup>43</sup>H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- <sup>44</sup>P. Vinet, J. Ferrante, J. R. Smith, and J. H. Rose, *J. Phys. C* **19**, L467 (1986).
- <sup>45</sup>P. Vinet, J. H. Rose, J. Ferrante, and J. R. Smith, *J. Phys.: Condens. Matter* **1**, 1941 (1989).
- <sup>46</sup>A. R. Oganov and P. I. Dorogokupets, *Phys. Rev. B* **67**, 224110 (2003).
- <sup>47</sup>A. R. Oganov and P. I. Dorogokupets, *J. Phys.: Condens. Matter* **16**, 1351 (2004).
- <sup>48</sup>A. R. Oganov, M. J. Gillan, and G. D. Price, *J. Chem. Phys.* **118**, 10174 (2003).
- <sup>49</sup>A. Strachan, T. Çağın, and W. A. Goddard III, *Phys. Rev. B* **60**, 15084 (1999).
- <sup>50</sup>J. A. Akins and T. J. Ahrens, *Geophys. Res. Lett.* **29**, 1394 (2002).
- <sup>51</sup>S. Ono, Y. Ohishi, and K. Mibe, *Am. Mineral.* **89**, 1480 (2004).
- <sup>52</sup>S. Speziale, C.-S. Zha, T. S. Duffy, R. J. Hemley, and H.-K. Mao, *J. Geophys. Res.* **106**, 515 (2001).
- <sup>53</sup>W. R. Panero, L. R. Benedetti, and R. Jeanloz, *J. Geophys. Res., [Solid Earth]* **B108**, 2015 (2003).
- <sup>54</sup>G. Fiquet, A. Dewaele, D. Andrault, M. Kunz, and T. Le Bihan, *Geophys. Res. Lett.* **27**, 21 (2000).
- <sup>55</sup>R. A. Robie and B. S. Hemingway, *U. S. Geol. Surv. Bull.* **2131**, 461 (1995).
- <sup>56</sup>M. Akaogi, H. Yusa, K. Shiraishi, and T. Suzuki, *J. Geophys. Res.* **100**, 22337 (1995).
- <sup>57</sup>M. Akaogi and E. Ito, *Geophys. Res. Lett.* **20**, 105 (1993).
- <sup>58</sup>C. Lee and X. Gonze, *Phys. Rev. Lett.* **72**, 1686 (1994).
- <sup>59</sup>O. Schütt, P. Pavone, W. Windl, K. Karch, and D. Strauch, *Phys. Rev. B* **50**, 3746 (1994).
- <sup>60</sup>B. B. Karki, R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, *Phys. Rev. B* **62**, 14750 (2000).
- <sup>61</sup>B. B. Karki, R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, *Phys. Rev. B* **61**, 8793 (2000).
- <sup>62</sup>A. Zupan, P. Blaha, K. Schwarz, and J. P. Perdew, *Phys. Rev. B* **58**, 11266 (1998).
- <sup>63</sup>P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- <sup>64</sup>G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- <sup>65</sup>G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- <sup>66</sup>V. S. Urusov, *Theoretical Crystal Chemistry* (Moscow State University Press, Moscow, 1987), p. 275.
- <sup>67</sup>A. R. Oganov, J. P. Brodholt, and G. D. Price, *Nature (London)* **411**, 934 (2001).
- <sup>68</sup>A. R. Oganov, J. P. Brodholt, and G. D. Price, *Earth Planet. Sci. Lett.* **184**, 555 (2001).
- <sup>69</sup>L.-G. Liu, W. A. Bassett, and J. Sharry, *J. Geophys. Res.* **83**, 2301 (1978).
- <sup>70</sup>V. P. Prakapenka, G. Shen, L. S. Dubrovinsky, M. L. Rivers, and S. R. Sutton, *J. Phys. Chem. Solids* **65**, 1537 (2004).
- <sup>71</sup>D. J. Frost, C. Liebske, F. Langenhorst, C. A. McCammon, R. G. Tronnes, and D. C. Rubie, *Nature (London)* **428**, 409 (2004).
- <sup>72</sup>I. Martinez, Y. B. Wang, F. Guyot, R. C. Liebermann, and J. C. Doukhan, *J. Geophys. Res.* **102**, 5265 (1997).
- <sup>73</sup>H.-K. Mao, G. Shen, and R. J. Hemley, *Science* **278**, 2098 (1997).
- <sup>74</sup>B. J. Wood, *Earth Planet. Sci. Lett.* **174**, 341 (2000).
- <sup>75</sup>D. Andrault, *J. Geophys. Res.* **106**, 2079 (2001).
- <sup>76</sup>S. E. Kesson, H. S. O'Neill, and J. M. G. Shelley, *Phys. Earth Planet. Inter.* **131**, 295 (2002).
- <sup>77</sup>D. J. Frost and F. Langenhorst, *Earth Planet. Sci. Lett.* **199**, 227 (2002).
- <sup>78</sup>H. Keppler, C. A. McCammon, and D. C. Rubie, *Am. Mineral.* **79**, 1215 (1994).