

## Crystal Structure and Elastic Constants of $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> under High Pressure Simulated from a Potential Model

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### Abstract

A computational model based on energy minimization has been developed for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>. The potential energy of the model includes Coulomb and repulsive interactions between non-bonded atoms as well as bond-distance-stretching energy terms for Si-O distances and bond-angle-bending energy terms for O-Si-O angles. Some of the energy parameters are treated as common to  $\alpha$ - and  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>, and are obtained by varying these parameters until both the calculated atmospheric-pressure structure and the elastic constants of  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub> agree as closely as possible with the experimental ones. Other necessary energy parameters for the modeling of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> are derived to reproduce the observed atmospheric-pressure structure of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>. The potential model obtained is successfully used for the calculation of the elastic constants of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>. Subsequently, the model is applied to the simulation of crystal structures of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> under high pressure. The pressure derivatives of the elastic constants of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> are also evaluated using the model. The present model is compared with a recently proposed one for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>.

### Introduction

Three polymorphs of Mg<sub>2</sub>SiO<sub>4</sub> [olivine ( $\alpha$ ), modified spinel ( $\beta$ ) and spinel ( $\gamma$ )], are major constituents of the earth's mantle. It is therefore important to understand their crystal structures and physical properties and how they change with pressure.

Modeling of these polymorphs in terms of potential-energy calculations has been performed by Miyamoto & Takeda (1980, 1984), Catti (1981, 1982), Matsui & Matsumoto (1982), Catlow & Parker (1982), Price & Parker (1984), and Matsui & Busing (1984*a*). Matsui & Busing (1984*a, b*) emphasized that a realistic model of the mineral should be obtained so as to reproduce not only the observed crystal structure but also the experimental elastic properties; they showed that two early models for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub> (Miyamoto & Takeda, 1980; Matsui & Matsumoto, 1982) succeeded in reproducing the observed atmospheric-pressure

structure fairly well; however, they failed to reproduce the experimental elastic constants.

Horiuchi & Sawamoto (1981) have determined the crystal structure of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> by single-crystal X-ray analysis. Recently Sawamoto, Weidner, Sasaki & Kumazawa (1984) have measured elastic constants of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> by Brillouin spectroscopy.

The purpose of this paper is to derive a reasonable computational model for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>, which can be further applied to the simulation of the crystal structures under high pressure as well as to the prediction of the pressure dependencies of the elastic constants.

During the preparation of this manuscript, a paper on a similar modeling for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> came to our notice (Price, Parker & Yeomans, 1985). It is worthwhile to compare the present results with those reported by Price *et al.* because they have used a somewhat different model.

### Potential-energy model

#### Crystal-lattice energy

The crystal-lattice energy is assumed to be the sum of the non-bonded and covalently bonded energy terms:

$$W_{\text{cryst}} = W_{\text{non-bond}} + W_{\text{covalent bond}} \quad (1)$$

The non-bonded energy used in this study is represented by an atom-atom potential of the form:

$$W_{\text{non-bond}} = 1/(2Z) \sum_i \sum_j \{ q_i q_j r_{ij}^{-1} + f(B_i + B_j) \times \exp [(A_i + A_j - r_{ij})/(B_i + B_j)] \}, \quad (2)$$

where  $r_{ij}$  is the distance between atoms  $i$  and  $j$ , and  $Z$  is the number of formula units per cell. The first term represents the Coulomb energy between atoms with net charges  $q_i$  and  $q_j$ , and the second term describes the repulsive interaction in a form suggested by Gilbert (1968). Here  $f$  is a standard force of  $4.184 \text{ kJ mol}^{-1} \text{ \AA}^{-1}$ ,  $A_i$  and  $A_j$  are repulsive radii, and  $B_i$  and  $B_j$  are the softness parameters of the atoms concerned. The summation over  $i$  includes one unit cell and  $j$  is summed over all atoms in the crystal except those which are bonded directly to the atom  $i$ .

The covalently bonded energy,  $W_{\text{covalentbond}}$ , includes bond-distance-stretching energy terms for Si–O distances of the type:

$$V(d) = \frac{1}{2}K_d(d - d_0)^2, \quad (3)$$

and bond-angle-bending potentials for O–Si–O angles of the type:

$$V(\alpha) = \frac{1}{2}K_\alpha(\alpha - \alpha_0)^2. \quad (4)$$

Here  $d$  and  $\alpha$  are the calculated bond distance and angle for a structural model,  $d_0$  and  $\alpha_0$  are the unstrained distance and angle, and  $K_d$  and  $K_\alpha$  are the force constants for the distance and angle, respectively. Bond-angle-bending potentials for Si–O–Si angles were neglected in this study.

#### Derivation of energy parameters

Before obtaining a potential for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>, we first derived a set of energy parameters for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>, because the potential should be transferable so that one set of energy parameters for atoms or groups of atoms can be used to construct potential functions for the other system. Crystals of  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub> consist of Mg ions and isolated SiO<sub>4</sub> groups. Matsui & Busing (1984a) presented a potential model for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>, where they treated the SiO<sub>4</sub> ions as rigid bodies and assumed the net charges on the Mg ions to be +2 |e|. We extended their potential by using a flexible SiO<sub>4</sub> model and by relaxing the net charges on the Mg ions. The required energy parameters were derived so as to reproduce both the experimental atmospheric-pressure structure (Fujino, Sasaki, Takéuchi & Sadanaga, 1981) and the elastic constants (Graham & Barsch, 1969; Kumazawa & Anderson, 1969) of  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>, using a method similar to that described by Matsui & Busing (1984a). We will designate the model thus developed for  $\alpha$ -MgSiO<sub>4</sub> as the *MM1* potential.

The optimized energy parameters in the *MM1* potential are listed in Table 1. The resulting net charges are  $q_{\text{Mg}} = +1.57$ ,  $q_{\text{Si}} = +1.604$  and  $q_{\text{O}} = -1.186$  |e|. Fujino *et al.* (1981) have made an accurate X-ray diffraction analysis for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>, and obtained net charges of  $q_{\text{Mg}(1)} = +1.76$ ,  $q_{\text{Mg}(2)} = +1.74$ ,  $q_{\text{Si}} = +2.11$ ,  $q_{\text{O}(1)} = -1.52$ ,  $q_{\text{O}(2)} = -1.29$  and  $q_{\text{O}(3)} = -1.40$  |e|. McLarnan, Hill & Gibbs (1979) have carried out semi-empirical molecular-orbital (CNDO/2) calculations on a tetrahedral–octahedral cluster modeled from the arrangement in  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>, and presented  $q_{\text{Mg}(1)} = +1.38$ ,  $q_{\text{Mg}(2)} = +1.31$ ,  $q_{\text{Si}} = +0.86$ ,  $q_{\text{O}(1)} = -0.74$ ,  $q_{\text{O}(2)} = -0.82$  and  $q_{\text{O}(3)} = -0.81$  |e|. The values of net charges on atoms in the *MM1* potential (Table 1) lie between the values obtained from these two groups. The optimized value of the force constant of the Si–O bond,  $3.43 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ , may be comparable with that derived by a molecular-orbital calculation for

Table 1. Energy parameters used for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub> (*MM1*) and  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> (*MM2*)

	<i>MM1</i>	<i>MM2</i>
Non-bonded interactions		
$q_{\text{Mg}}$ ( e )	+1.570	+1.570
$q_{\text{Si}}$ ( e )	+1.604	+1.3195
$q_{\text{O}}$ (non-bridging) ( e )	-1.186	-1.111
$q_{\text{O}}$ (bridging) ( e )	—	-0.730
$q_{\text{O}}[\text{O}(1)]$ ( e )	—	-1.523
$A_{\text{Mg}}$ (Å)	1.036	1.036
$A_{\text{O}}$ (non-bridging) (Å)	1.775	1.775
$A_{\text{O}}$ (bridging) (Å)	—	1.727
$A_{\text{O}}[\text{O}(1)]$ (Å)	—	1.795
$B_{\text{Mg}}$ (Å)	0.052	0.052
$B_{\text{O}}$ (Å)	0.150	0.150
Bond-distance stretching		
$K_d$ (Si–O) ( $10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ )	3.43	3.43
$d_0$ (non-bridging Si–O) (Å)	1.442	1.442
$d_0$ (bridging Si–O) (Å)	—	1.556
Bond-angle bending		
$K_\alpha$ (O–Si–O) ( $\text{kJ mol}^{-1} \text{ deg}^{-2}$ )	0.075	0.075
$\alpha_0$ (O–Si–O) (deg)	109.47	109.47

orthosilicic acid, Si(OH)<sub>4</sub> ( $4.00 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ ; Gibbs, Meagher, Newton & Swanson, 1981), and also with that obtained by a lattice-dynamics calculation for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub> ( $2.38 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ ; Iishi, 1978). The softness parameter of the Mg ion was optimized to be 0.052 Å, and is almost identical to that derived by using alkaline-earth halide crystals (0.0528 Å; Yuen, Murfitt & Collin, 1974).

The *MM1* potential was then successfully applied to the calculations of the atmospheric-pressure structure, and the elastic constants and their pressure derivatives for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>. Tables 2 and 3 show comparisons of the calculated structure and elastic properties with those obtained from experiments. The calculations were made with the computer program *WMIN* (Busing, 1981), using the technique described by Busing & Matsui (1984).

Next we applied the *MM1* potential to the modeling of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>. Crystals of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> are orthorhombic with space group *Imma* and eight formula units per cell (Horiuchi & Sawamoto, 1981). The structure is based on a cubic closest-packed array of O atoms with Si and Mg atoms occupying tetrahedral and octahedral sites, respectively. The structure contains isolated Si<sub>2</sub>O<sub>7</sub> groups formed by two SiO<sub>4</sub> tetrahedra sharing an O atom. As shown in Fig. 1, there exist three different kinds of O atoms, the bridging O atom O(2), the non-bridging O atoms O(3) and O(4), and O atom O(1) which is not bonded to the Si atom. Therefore, different values for each  $q_{\text{O}}$  and  $A_{\text{O}}$  were used for these three types of O atoms, although the same value of  $B_{\text{O}}$  was assumed for all three. Repulsive interactions of the Si atoms were neglected. The nine energy parameters,  $q_{\text{Mg}}$ ,  $A_{\text{Mg}}$ ,  $B_{\text{Mg}}$ ,  $A_{\text{O}}$ (non-bridging),  $B_{\text{O}}$ ,  $K_d$ (Si–O),  $d_0$ (non-bridging Si–O),  $K_\alpha$ (O–Si–O) and  $\alpha_0$ (O–Si–O), were treated as common to  $\alpha$ - and  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> and were

Table 2. Comparison between observed and calculated structures for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>

	Observed*	Calculated
<b>Lattice</b>		
<i>a</i> (Å)	4.753	4.744
<i>b</i> (Å)	10.190	10.355
<i>c</i> (Å)	5.978	6.058
<i>V</i> (Å <sup>3</sup> )	289.6	297.6
<b>Mg-O distances (Å)</b>		
†[2] Mg(1)-O(1)	2.084	2.087
[2] -O(2)	2.068	2.078
[2] -O(3)	2.131	2.127
(Mg(1)-O)	2.094	2.097
[1] Mg(2)-O(1)	2.177	2.229
[1] -O(2)	2.045	2.076
[2] -O(3)	2.066	2.086
[2] -O(3')	2.210	2.263
(Mg(2)-O)	2.129	2.167
<b>Si-O distances (Å)</b>		
[1] Si-O(1)	1.614	1.634
[1] -O(2)	1.655	1.646
[2] -O(3)	1.637	1.638
(Si-O)	1.636	1.639
<b>O-Si-O angles (°)</b>		
[1] O(1)-Si-O(2)	114.3	113.5
[2] O(1)-Si-O(3)	116.1	115.2
[2] O(2)-Si-O(3)	101.8	102.5
[1] O(3)-Si-O(3')	104.8	106.4

\* From Fujino *et al.* (1981).

† Numbers in square brackets refer to the multiplicity of the bonds.

all fixed at the values in the *MM1* potential developed for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>. The net charge on Si was calculated by the requirement of charge neutrality. The other six energy parameters,  $q_{\text{O}}$ (non-bridging),  $q_{\text{O}}$ (bridging),  $q_{\text{O}}[\text{O}(1)]$ ,  $A_{\text{O}}$ (non-bridging),  $A_{\text{O}}$ (bridging) and  $d_{\text{O}}$ (bridging Si-O), were derived using *WMIN* to optimize the energy parameters with respect to the observed crystal structure at atmospheric pressure (Horiuchi & Sawamoto, 1981). We will call the potential model for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> thus obtained the *MM2* model, which is given in Table 1. Both the repulsive radii and the absolute values of the net charges determined for the three types of O atoms are in the

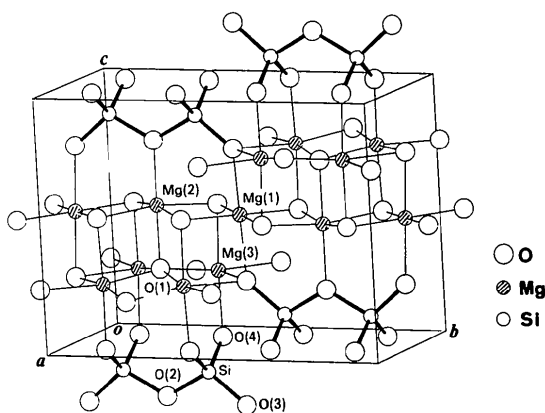


Fig. 1. Part of the crystal structure of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> drawn using the program *ORTEPII* (Johnson, 1976).

Table 3. Observed and calculated elastic constants,  $c_{ij}$ (TPa), and their pressure derivatives (dimensionless) for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>

<i>ij</i>	$c_{ij}$		$\partial c_{ij}/\partial P$	
	Observed*	Calculated	Observed*	Calculated
11	0.329	0.317	8.4	8.0
22	0.200	0.196	6.2	7.6
33	0.236	0.241	6.4	6.4
44	0.067	0.050	2.1	3.7
55	0.081	0.077	1.7	1.9
66	0.081	0.068	2.3	3.3
12	0.065	0.076	4.5	5.8
13	0.069	0.088	4.5	4.9
23	0.073	0.079	3.8	4.3
<i>K</i> †	0.131	0.138	5.2	5.8

\* Average of values from Graham & Barsch (1969) and Kumazawa & Anderson (1969).

† *K*: bulk modulus calculated from Voigt approximation.

expected order, with the values for bridging O smallest and for O(1), which is not bonded to Si, largest.

### Model of Price, Parker & Yeomans

Quite recently, Price, Parker & Yeomans (1985) have presented a computational model for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>. They have described two different models: one is based on a fully ionic potential and the other is a partially ionic model. Of these we selected the latter model (*P4a* potential), because it produced both the observed structure and the elastic constants better than the former model. The crystal-lattice energy of the *P4a* potential is represented as the sum of non-bonded interactions between atoms, using equation (2), and covalent-bond energy terms with a Morse potential of the form

$$V_{ij}(r) = D_{ij} \{ \exp[-2E_{ij}(r-r_0)] - 2 \exp[-E_{ij}(r-r_0)] \}, \quad (5)$$

where  $r$  is the calculated distance, and  $r_0$ ,  $D_{ij}$  and  $E_{ij}$  are the energy parameters to describe the covalent character of the Si-O bond. Bond-angle-bending energies were neglected. The required energy parameters were derived by a least-squares fitting to the X-ray-determined structure of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> (Horiuchi & Sawamoto, 1981), in which some parameters were fixed at values presented by Price & Parker (1984) for the modeling of  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>.

The energy parameters in the *P4a* potential are listed in Table 4. A characteristic of the *P4a* potential is that the O ions are much harder than the Si and Mg ions, with mean  $B_{\text{O}} = 0.07$ ,  $B_{\text{Si}} = 0.17$  and mean  $B_{\text{Mg}} = 0.19$  Å which is contrary to the general feature that in an isoelectric series of closed-shell ions the anions are softer than the cations (Butterfield & Carlson, 1972; Ida, 1976).

The *P4a* potential includes more energy parameters for the non-bonded interactions than the *MM2* potential. In contrast to the *MM2* potential having

Table 4. Energy parameters in the *P4a* potential for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> reported by Price, Parker & Yeomans (1985)

Non-bonded interactions			
$q_{Mg(1)}, q_{Mg(3)}$ ( e )	+1.726	$A_O(\text{non-bridging})$ (Å)	1.4745
$q_{Mg(2)}$ ( e )	+1.715	$A_O(\text{bridging})$ (Å)	1.4858
$q_{Si}$ ( e )	+1.380	$A_O[O(1)]$ (Å)	1.6060
$q_O(\text{non-bridging})$ ( e )	-1.208	$B_{Mg(1)}, B_{Mg(3)}$ (Å)	0.1969
$q_O(\text{bridging})$ ( e )	-0.740	$B_{Mg(2)}$ (Å)	0.1731
$q_O[O(1)]$ ( e )	-1.665	$B_{Si}$ (Å)	0.1706
$A_{Mg(1)}, A_{Mg(3)}$ (Å)	1.6297	$B_O(\text{non-bridging})$ (Å)	0.0568
$A_{Mg(2)}$ (Å)	1.5397	$B_O(\text{bridging})$ (Å)	0.0655
$A_{Si}$ (Å)	1.0763	$B_O[O(1)]$ (Å)	0.0833
Morse potential for Si-O			
$D(\text{non-bridging Si-O})$ (kJ mol <sup>-1</sup> )	430.8	$r_0$ (Å)	1.63
$D(\text{bridging Si-O})$ (kJ mol <sup>-1</sup> )	250.8	$E$ (Å <sup>-1</sup> )	1.975

Table 5. Observed and calculated structural data for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>

	Observed*	<i>P4a</i>	<i>MM2</i>
$a$ (Å)	5.698	5.695	5.696
$b$ (Å)	11.438	11.508	11.515
$c$ (Å)	8.257	8.381	8.365
$V$ (Å <sup>3</sup> )	537.7	549.3	548.7
$z[Mg(2)]$	0.9701	0.9598	0.9648
$y[Mg(3)]$	0.1276	0.1290	0.1286
$y[Si]$	0.1198	0.1173	0.1195
$z[Si]$	0.6168	0.6134	0.6151
$z[O(1)]$	0.2166	0.2109	0.2106
$z[O(2)]$	0.7164	0.7034	0.7110
$y[O(3)]$	0.9900	0.9890	0.9893
$z[O(3)]$	0.2558	0.2564	0.2578
$x[O(4)]$	0.2615	0.2600	0.2614
$y[O(4)]$	0.1225	0.1210	0.1224
$z[O(4)]$	0.9925	0.9931	0.9928

\* From Horiuchi &amp; Sawamoto (1981).

the same energy parameters for the Mg ions, the *P4a* potential was developed by treating the Mg(2) ion and the other Mg ions separately. In the *MM2* potential the same value of  $B_O$  was assumed for the three types of O atoms; on the other hand, in the *P4a* potential different values of  $B_O$  were used for these three O atoms. Furthermore, the non-bonded interactions between Si and adjacent O atoms were omitted and these interactions were represented using the quadratic potential of form (3) for the *MM2* potential, while the non-bonded interactions between these Si and O atoms were included in addition to the Morse potential of form (5) for the *P4a* potential.

#### Reliability of the potential model

In order to test the reliability of the *MM2* model we calculated the crystal structure and elastic constants at atmospheric pressure for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> based on the *MM2* potential, using *WMIN* (Busing, 1981). The results of the calculations are listed in Tables 5, 6 and 7 for the structural data, bond distances and angles, and elastic constants, respectively, together

Table 6. Observed and calculated bond distances (Å) and angles (°) for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>

	Observed*	<i>P4a</i>	<i>MM2</i>
Mg-O distances			
†[2] Mg(1)-O(3)	2.115	2.153	2.160
[4] -O(4)	2.046	2.034	2.051
[1] Mg(2)-O(1)	2.035	2.104	2.057
[1] -O(2)	2.095	2.149	2.123
[4] -O(4)	2.093	2.115	2.105
[2] Mg(3)-O(1)	2.016	2.018	2.022
[2] -O(3)	2.123	2.151	2.146
[2] -O(4)	2.128	2.155	2.154
$I\ddagger$		0.030	0.022
Si-O distances			
[1] Si-O(2)	1.701	1.703	1.704
[1] -O(3)	1.638	1.639	1.643
[2] -O(4)	1.632	1.633	1.632
$I\ddagger$		0.001	0.003
O-Si-O angles			
[1] O(2)-Si-O(3)	111.1	112.0	111.6
[2] -O(4)	104.5	102.6	104.1
[2] O(3)-Si-O(4)	111.7	112.5	111.9
[1] O(4)-Si-O(4')	112.8	113.7	112.8
$I\ddagger$		1.3	0.3
Si-O-Si angle			
[1] Si-O(2)-Si'	122.2	127.4	123.8

\* From Horiuchi &amp; Sawamoto (1981).

† Same as in Table 2.

‡  $I = [\sum (p_{\text{obs}} - p_{\text{calc}})^2 / n]^{1/2}$ , where  $p$  and  $n$  are the parameters and number of parameters respectively.Table 7. Observed and calculated elastic constants,  $c_{ij}$  (TPa), for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>

$c_{ij}$	Observed*	<i>P4a</i>	<i>MM2</i>
11	0.360	0.382	0.389
22	0.383	0.363	0.374
33	0.273	0.302	0.271
44	0.112	0.080	0.091
55	0.118	0.090	0.107
66	0.098	0.108	0.101
12	0.075	0.140	0.124
13	0.110	0.123	0.124
23	0.105	0.127	0.118
$I\ddagger$		0.33	0.24
$K$	0.177	0.203	0.196

\* From Sawamoto *et al.* (1984).†  $I = \{[\sum (p_{\text{obs}} - p_{\text{calc}}) / p_{\text{obs}}]^2 / n\}^{1/2}$ , where  $p$  and  $n$  are the parameters and number of parameters respectively.

with the reported values using the *P4a* potential, for comparison. Tables 6 and 7 also give root-mean-square deviations between observed and calculated values for the *MM2* and *P4a* potentials.

As can be seen in Tables 5 and 6, the *MM2* model reproduces the observed structure fairly well, and the accuracy of the *MM2* model is slightly better than that of the *P4a* model, in spite of the *MM2* potential being constructed with fewer energy parameters than the *P4a* potential as described before. Root-mean-square deviations in the Mg-O distances, Si-O distances and O-Si-O angles, and the mismatch in the Si-O-Si angle are 0.030, 0.001 Å, 1.3 and 5.2° respectively for the *P4a* model, and 0.022, 0.003 Å, 0.3 and 1.6° respectively for the *MM2* model (Table 6).

It should be noted that the energy parameters were derived to fit the observed structure in the two models; on the other hand, the experimental elastic constants were not included as observational quantities in either work and, therefore, the elastic constants are more useful for checking purposes than the crystal structure. In addition to this the accuracy of a potential is critically tested by its ability to reproduce elasticity data more than the crystal structure, because the calculated structure simply depends on the position of the potential minimum, while the elastic properties depend on the curvature (second derivatives) of the potential (Born & Huang, 1962).

When the calculated elastic constants, based on the two models, are compared with those from experiment, it appears that the *MM2* potential is better than the *P4a* potential, with root-mean-square deviations relative to the experimental values of 0.33 for *P4a* and 0.24 for *MM2*. This superiority of the *MM2* potential over the *P4a* potential may arise from the softness parameters of the atoms used in the two works [with the O ions being much softer than the Mg ions for the *MM2* potential (Table 1), but much harder than the Mg ions for the *P4a* potential (Table 4)], or may be the result of including the bond-angle-bending terms for the O–Si–O angles in the *MM2* potential.

### Effects of pressure

$\beta$ - $\text{Mg}_2\text{SiO}_4$  is an important constituent of the earth's mantle and, therefore, it is most desirable to characterize the effects of pressure on the crystal structure and on the elastic constants. So far, the lattice parameters of  $\beta$ - $\text{Mg}_2\text{SiO}_4$  have been measured up to 10 GPa, using X-ray powder diffraction analysis (Mizukami, Ohtani, Kawai & Ito, 1975). Experimental pressure dependencies have not been reported for the detailed crystal structure or for the elastic constants.

The success of the *MM2* potential in reproducing the observed atmospheric-pressure structure as well as the elastic constants for  $\beta$ - $\text{Mg}_2\text{SiO}_4$  encouraged us to apply the model to the calculations of the pressure dependencies of the structure and elastic constants. The crystal structure and elastic constants of  $\beta$ - $\text{Mg}_2\text{SiO}_4$  at hydrostatic pressures of +2.5 and –2.5 GPa\* were calculated using the technique described by Busing & Matsui (1984), and then their pressure derivatives at zero pressure were obtained from averages of the differences in the parameters at –2.5 GPa and zero pressure and at zero pressure and +2.5 GPa. Table 8 lists the resultant compressibilities of the lattice parameters, interatomic distances and bond angles. The volume compressibility and the

Table 8. Calculated compressibilities ( $\text{TPa}^{-1}$ ) of the lattice parameters, interatomic distances and bond angles for  $\beta$ - $\text{Mg}_2\text{SiO}_4$

Parameter, $p$	$-(1/p)(\partial p/\partial P)$
Lattice	
$a$	1.32*
$b$	1.47*
$c$	2.42*
$V$	5.21*
Mg–O distances	
†[2] Mg(1)–O(3)	3.57
[4] –O(4)	1.51
(Mg(1)–O)	2.20
[1] Mg(2)–O(1)	1.70
[1] –O(2)	4.33
[4] –O(4)	1.78
(Mg(2)–O)	2.19
[2] Mg(3)–O(1)	1.55
[2] –O(3)	2.16
[2] –O(4)	2.67
(Mg(3)–O)	2.13
Si–O distances	
[1] Si–O(2)	0.57
[1] –O(3)	0.67
[2] –O(4)	0.70
(Si–O)	0.66
O–Si–O angles	
[1] O(2)–Si–O(3)	0.34
[2] –O(4)	–0.17
[2] O(3)–Si–O(4)	–0.09
[1] O(4)–Si–O(4')	0.18
Si–O–Si angle	
Si–O(2)–Si'	1.16

\* Compressibilities calculated using the experimental elastic constants (Sawamoto *et al.*, 1984) are 1.73, 1.63, 2.34 and 5.70  $\text{TPa}^{-1}$  for  $a$ ,  $b$ ,  $c$  and  $V$ , respectively.

† See Table 2.

linear compressibilities of  $a$ ,  $b$  and  $c$ , calculated using the experimental elastic constants (Sawamoto *et al.*, 1984), are 5.70, 1.73, 1.63 and 2.34  $\text{TPa}^{-1}$ , respectively, in reasonable agreement with our calculated values of 5.21, 1.32, 1.47 and 2.42  $\text{TPa}^{-1}$ , respectively. This agreement gives us some confidence for the calculated pressure derivatives of the interatomic distances and bond angles listed in Table 8.

The Mg–O bonds are predicted to be much more compressible than the Si–O bonds, with the mean compressibilities of the Mg–O and Si–O distances being 2.17 and 0.66  $\text{TPa}^{-1}$ , respectively. This is consistent with the experimental results obtained from high-pressure single-crystal X-ray analyses for forsterite ( $\alpha$ - $\text{Mg}_2\text{SiO}_4$ ; Hazen, 1976) and diopside ( $\text{CaMgSi}_2\text{O}_6$ ; Levien & Prewitt, 1981*a*) where the Mg octahedra are significantly softer than the Si tetrahedra. The Si–O–Si angle is calculated to be much more flexible with pressure than the O–Si–O angles, with the compressibility of the Si–O–Si angle being 1.2  $\text{TPa}^{-1}$ ; in contrast, the compressibilities of the O–Si–O angles range from –0.2 to +0.3  $\text{TPa}^{-1}$ , again in accordance with the experimental results

\* A positive value for the hydrostatic pressure implies compression; a negative value implies tension.

Table 9. Calculated pressure derivatives of the elastic constants (dimensionless) for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>

<i>ij</i>	$\partial c_{ij}/\partial P$	<i>ij</i>	$\partial c_{ij}/\partial P$
11	6.7	66	2.8
22	7.1	12	5.5
33	11.4	13	3.2
44	0.9	23	4.2
55	0.6	K	5.7

obtained from high-pressure single-crystal X-ray analyses for  $\alpha$ -quartz (SiO<sub>2</sub>; d'Amour, Denner & Schulz, 1979; Levien, Prewitt & Weidner, 1980), diopside (CaMgSi<sub>2</sub>O<sub>6</sub>; Levien & Prewitt, 1981a), and coesite (SiO<sub>2</sub>; Levien & Prewitt, 1981b) where, in each substance, on average, the Si-O-Si angle changes with pressure more than the O-Si-O angle.

The predicted pressure derivatives of the elastic constants are given in Table 9. It should be recalled that the *MM2* potential for  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> was developed by transferring the *MM1* potential derived in advance for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>, and the *MM1* potential succeeded rather well in reproducing not only the observed elastic constants for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub> but also their pressure derivatives, as can be seen in Table 3. As the *MM2* potential also produced the experimental elastic constants of  $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub> well (Table 7), the accuracies of the calculated pressure derivatives of the elastic constants, based on the *MM2* potential, may be expected to be of a similar order as those for  $\alpha$ -Mg<sub>2</sub>SiO<sub>4</sub>.

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## References

- AMOUR, H. D., DENNER, W. & SCHULZ, H. (1979). *Acta Cryst.* B35, 550-555.
- BORN, M. & HUANG, K. (1962). *Dynamical Theory of Crystal Lattices*. Oxford: Clarendon Press.
- BUSING, W. R. (1981). *WMIN*. Report ORNL-5747. Oak Ridge National Laboratory, Tennessee.
- BUSING, W. R. & MATSUI, M. (1984). *Acta Cryst.* A40, 532-538.
- BUTTERFIELD, C. & CARLSON, E. H. (1972). *J. Chem. Phys.* 56, 4907-4911.
- CATLOW, C. R. A. & PARKER, S. C. (1982). *Computer Simulation of Solids*, edited by C. R. A. CATLOW & W. C. MACKRODT, pp. 222-242. New York: Springer-Verlag.
- CATTI, M. (1981). *Phys. Chem. Miner.* 7, 20-25.
- CATTI, M. (1982). *J. Phys. Chem. Solids*, 43, 1111-1118.
- FUJINO, K., SASAKI, S., TAKÉUCHI, Y. & SADANAGA, R. (1981). *Acta Cryst.* B37, 513-518.
- GIBBS, G. V., MEAGHER, E. P., NEWTON, M. D. & SWANSON, D. K. (1981). *Structure and Bonding in Crystals*. Vol. I, edited by M. O'KEEFFE & A. NAVROTSKY, pp. 195-225. New York: Academic Press.
- GILBERT, T. L. (1968). *J. Chem. Phys.* 49, 2640-2642.
- GRAHAM, E. K. & BARSCH, G. R. (1969). *J. Geophys. Res.* 74, 5949-5960.
- HAZEN, R. M. (1976). *Am. Mineral.* 61, 1280-1293.
- HORIUCHI, H. & SAWAMOTO, H. (1981). *Am. Mineral.* 66, 568-575.
- IDA, Y. (1976). *Phys. Earth Planet. Inter.* 13, 97-104.
- IISHI, K. (1978). *Am. Mineral.* 63, 1198-1208.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KUMAZAWA, M. & ANDERSON, O. L. (1969). *J. Geophys. Res.* 74, 5961-5972.
- LEVIEN, L. & PREWITT, C. T. (1981a). *Am. Mineral.* 66, 315-323.
- LEVIEN, L. & PREWITT, C. T. (1981b). *Am. Mineral.* 66, 324-333.
- LEVIEN, L., PREWITT, C. T. & WEIDNER, D. J. (1980). *Am. Mineral.* 65, 920-930.
- MCLARNAN, T. J., HILL, R. J. & GIBBS, G. V. (1979). *Aust. J. Chem.* 32, 949-959.
- MATSUI, M. & BUSING, W. R. (1984a). *Phys. Chem. Miner.* 11, 55-59.
- MATSUI, M. & BUSING, W. R. (1984b). *Am. Mineral.* 69, 1090-1095.
- MATSUI, M. & MATSUMOTO, T. (1982). *Acta Cryst.* A38, 513-515.
- MIYAMOTO, M. & TAKEDA, H. (1980). *Geochem. J.* 14, 243-248.
- MIYAMOTO, M. & TAKEDA, H. (1984). *Am. Mineral.* 69, 711-718.
- MIZUKAMI, S., OHTANI, A., KAWAI, N. & ITO, E. (1975). *Phys. Earth Planet. Inter.* 10, 177-182.
- PRICE, G. D. & PARKER, S. C. (1984). *Phys. Chem. Miner.* 10, 209-216.
- PRICE, G. D., PARKER, S. C. & YEOMANS, J. (1985). *Acta Cryst.* B41, 231-239.
- SAWAMOTO, H., WEIDNER, D. J., SASAKI, S. & KUMAZAWA, M. (1984). *Science*, 224, 749-751.
- YUEN, P. S., MURFITT, R. M. & COLLIN, R. L. (1974). *J. Chem. Phys.* 61, 2383-2393.