American Mineralogist, Volume 69, pages 1090–1095, 1984

Calculation of the elastic constants and high-pressure properties of diopside, $CaMgSi_2O_6$[1]

MASANORI MATSUI[2] AND WILLIAM R. BUSING

Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Abstract

A computational model has been developed which describes the structure of the pyroxene mineral diopside, $CaMgSi_2O_6$, at the atomic level. The best model for the one-dimensional silicate chains permits all bond angles and the bond distances along the chain to vary. The crystal energy of the model is calculated from Coulomb, near-neighbor repulsion, bond-angle bending, and bond stretching terms. Minimizing this energy with respect to 16 structural variables, including the lattice parameters, yields a structure which reproduces the observed one reasonably well. Elastic constants were calculated which also agree well with experiment. Calculations for the model have been repeated at a simulated pressure of 50 kbar, and pressure derivatives of the elastic constants have been obtained. Calculated pressure derivatives of the lattice parameters, bond distances, and bond angles are in rough agreement with those observed experimentally. Two other models, with more constraints on the silicate chains, did not reproduce the elastic constants satisfactorily.

Introduction

The development of computational models for structures of minerals at the atomic level is an important step toward the goal of predicting the high-pressure properties of mantle materials. Properties of interest include crystal structures, elastic constants, rates of defect formation, and diffusion constants of these substances. Much effort has been directed recently to the modeling of the orthosilicate Mg_2SiO_4 in its olivine and spinel forms (Myamoto and Takeda, 1980; Catti, 1981, 1982; Matsui and Matsumoto, 1982; Price and Parker, 1984; Matsui and Busing, 1984). The orthosilicates are relatively simple in that they are composed of isolated SiO_4 groups coordinated to the various cations. In the present paper we extend this work to diopside, $CaMgSi_2O_6$, a representative of the somewhat more complicated pyroxene minerals, in which the silicate groups form one-dimensional infinite chains. Pyroxenes are important mantle materials which occur as stable phases in many types of igneous rock.

A computational model of a crystal consists of a description of the structure, expressions for calculating the energy of this structure, and a way of minimizing the calculated energy by adjusting the structural variables. Recently Busing and Matsui (1984) have described ways of simulating the application of external forces to these models. Such forces can be hydrostatic pressure, normal or shearing stresses, or various combinations of these. The elastic constants at any pressure can thus be calculated. In previous work (Matsui and Busing, 1984) we have emphasized that for a model to be realistic the energy parameters should be selected to reproduce not only the crystal structures but also the elastic constants of the materials of interest. The purpose of this paper is to describe the development of models for diopside based on our earlier model for the olivine forsterite. We will show that our final model reproduces the structure and elastic constants of the mineral reasonably well. We will use this model to calculate the structural changes at high pressure and to predict the pressure derivatives of the elastic constants.

Other efforts to model the pyroxene minerals have been reported recently (Catlow et al., 1982; Parker, 1983). However, these authors used fully ionic descriptions, somewhat different from those which we will present.

Crystal structure of diopside

The atomic arrangement in diopside was first determined by Warren and Bragg (1928), and recently careful refinements have been made from X-ray (Levien and Prewitt, 1981) and neutron-diffraction studies (Rossi et al., 1982). The structure is illustrated in Figure 1.

The crystal is monoclinic with space group *C*2/*c* and four $CaMgSi_2O_6$ units per cell. The Ca and Mg ions each occupy sites on 2-fold axes parallel to **b** (perpendicular to the page in the figure). One kind of Si atom and three kinds of O atoms are located in general positions. The O

---

[1] Research sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

[2] Present Address: Chemical Laboratory, Kanazawa Medical University, Uchinada, Ishikawa-ken 920–02, Japan.

0003–004X/84/1112–1090$02.00

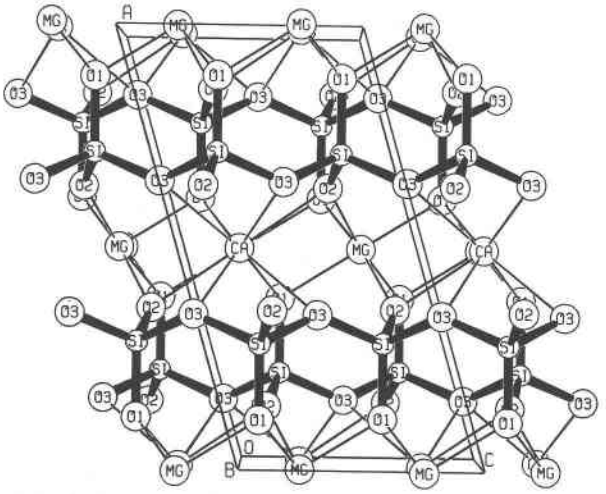

Fig. 1. The crystal structure of diopside. Pairs of one-dimensional silicate chains overlap each other in this view down the **b** axis.

atoms are arranged about the Si atoms to form tetrahedral SiO_4 groups, and these are linked to each other through the O3 atoms to form one-dimensional chains parallel to the **c**-axis. Each tetrahedral group is related to its neighbors in the chain by the *c*-glide plane, which is parallel to the page in the figure.

These silicate chains are stacked together to form layers parallel to the **b**, **c** plane. The silicate layers are held together by intermediate layers of cations. Each Mg ion is octahedrally coordinated to six O atoms of the silicate chains, and each Ca is coordinated less regularly to eight O atoms. Table 1 lists the lattice parameters and some interatomic distances and bond angles for the observed structure.

Three models for diopside

Three kinds of models were tried for diopside with different constraints on the silicate chains. Two of these were eventually abandoned, because, although they predicted the crystal structure reasonably well, they could not be made to reproduce the observed elastic compliance constants. We will describe all three of these models, but we will present detailed results only for the most successful one. All calculations were made with computer program WMIN (Busing, 1981).

Because we had obtained good results in modeling forsterite with rigid SiO_4 groups (Matsui and Busing, 1984), we chose a similar model for our first attempt to fit diopside. The silicate chains were assumed to be composed of rigid SiO_4 moieties sharing common O3 atoms. The only flexibility in the chain arises from the variable Si–O3–Si angles. We designate this as the RT (rigid tetrahedra) model.

Structural variables for the RT model include the four lattice parameters, *a*, *b*, *c*, and β, and two *y*-coordinates for the Ca and Mg ions. The silicate chain is permitted to translate with two degrees of freedom in the *x* and *z* directions, but one of the two rotation angles of the SiO_4 groups is related to the lattice parameter *c* in order to maintain the *c*-glide symmetry. The model thus has a total of nine structural variables.

As we shall describe below, this RT model proved to be much too stiff, especially along the **c**-axis, the direction of the chains.

Table 1. Observed and calculated lattice parameters, interatomic distances, and bond angles for diopside at atmospheric pressure

Parameter	Obs*	Calc**	Calc-Obs
Lattice			
a	9.75	9.60	-0.15
b	8.92	9.43	0.51
c	5.25	5.28	0.03
β	105.9	106.2	0.3
V	439.1	458.5	19.4
Intra-chain distances			
Si-O(1C1)†	1.60	(1.60)††	
Si-O(2C1)	1.59	(1.59)	
Si-O(3C1)	1.67	1.68	0.01
Si-O(3C2)	1.69	1.67	-0.02
<Si-O>	1.64	1.63	0.01
Si-Si	3.11	3.15	0.04
O(1C1)-O(2C1)	2.74	2.75	0.01
O(1C1)-O(3C1)	2.68	2.67	-0.01
O(1C1)-O(3C2)	2.69	2.64	-0.05
O(2C1)-O(3C1)	2.66	2.69	0.03
O(2C1)-O(3C2)	2.58	2.57	-0.01
O(3C1)-O(3C2)	2.64	2.66	0.02
<O-O>	2.67	2.66	-0.01
Intra-chain angles			
O(1C1)-Si-O(2C1)	118.2	119.3	1.1
O(1C1)-Si-O(3C1)	110.3	108.8	-1.5
O(1C1)-Si-O(3C2)	109.9	107.6	-2.3
O(2C1)-Si-O(3C1)	109.7	110.9	1.2
O(2C1)-Si-O(3C2)	103.6	104.1	0.5
O(3C1)-Si-O(3C2)	104.0	105.0	1.0
Si-O(3)-Si	135.8	140.3	4.5
Mg octahedron distances			
M(1)-O(1A1,B1)	2.12	2.24	0.12
M(1)-O(1A2,B2)	2.06	2.02	-0.04
M(1)-O(2C1,D1)	2.05	2.09	0.04
<M(1)-O>	2.08	2.12	0.04
M(1)-M(1)	3.10	3.23	0.13
O(1A1)-O(1B1)	2.78	2.76	-0.02
O(2C1)-O(2D1)	2.98	2.79	-0.19
O(1A1)-O(2C1)	3.02	3.34	0.32
O(1A1)-O(1A2)	3.05	3.12	0.07
O(1A2)-O(2C1)	2.88	2.93	0.05
O(1A2)-O(2D1)	2.97	2.98	0.02
O(1A1)-O(1B2)	2.81	2.79	-0.02
<O-O>	2.94	2.99	0.05
Ca polyhedron distances			
M(2)-O(1A1,B1)	2.36	2.43	0.07
M(2)-O(2C2,D2)	2.35	2.32	-0.03
M(2)-O(3C1,D1)	2.56	2.70	0.14
M(2)-O(3C2,D2)	2.72	2.77	0.05
<M(2)-O>	2.50	2.55	0.05

*Levien and Prewitt (1981). Distances are in Å, and angles are in degrees.

**Calculated values are for the CS model.

†Notation is that of Burnham *et al.* (1967) as used by Levien and Prewitt (1981).

††Parentheses indicate quantities which were not varied.

At this point we felt that the Si–O bond lengths should be rather insensitive to external forces, an idea supported by the results of high pressure studies of forsterite by Hazen (1976) and by similar work on diopside by Levien and Prewitt (1981). We, therefore, developed a model for the silicate chains in which all Si–O distances remain constant, but all bond angles are variable. The constraints required to maintain the *c*-glide symmetry of this model are complicated but possible within the framework of program WMIN. The resulting chain has eight degrees of freedom, and, with the four lattice parameters and two cation coordinates, produces a model with 14 structural variables. We will call this the VA (variable angle) model.

Although the agreement between the observed and calculated elastic constants for the VA model is much better than that for the RT model, it is still not completely satisfactory.

Our final model uses a less complicated description of the silicate chains in which the Si–O3 bridging distances are also assumed to be variable. Parameters of the chain include three translations each for the Si and O3 atoms. Atoms O1 and O2 rotate about Si, each with two degrees of freedom, so that the Si–O1 and Si–O2 distances remain constant. The structural variables then include these 10 for the silicate chain, two cation coordinates, and the four lattice parameters, for a total of 16 variables. This will be known as the CS (chain stretching) model.

In retrospect we realize that the structure would probably be better described by a model with all Si–O distances variable, but we did not have time to treat a fourth model during the period of this collaboration.

Potential energy expressions

For each of the models, the nonbonded interaction energy was computed from the potential function

$$V(r_{ij}) = q_i q_j r_{ij}^{-1} + f(B_i + B_j) \exp[(A_i + A_j - r_{ij})/(B_i + B_j)], \quad (1)$$

where the first term represents the Coulomb energy for pairs of atoms or ions with charges q_i and q_j, and the second term expresses the near-neighbor repulsion in a form suggested by Gilbert (1968). Here f is a standard force of 1 kcal mol^{-1} $Å^{-1}$, A_i and A_j are related to the atomic radii, and B_i and B_j are softness parameters of the atoms involved. In calculating the energy of the model, terms computed from (1) are included for all nonbonded contacts except those between geminal atoms of the silicate chain (i.e., two atoms bonded to the same atom).

The same repulsion parameters A and B were used for all three models, and these are listed in Table 2. The values for Mg and O were taken from our work on forsterite (Matsui and Busing, 1984), and parameters for Ca were derived similarly from the structure of the synthetic olivine γ-Ca_2SiO_4 (Czaya, 1971). Repulsion terms for Si atoms are omitted, as these atoms have no nonbonded near neighbors.

Charges q(Mg) and q(Ca) on the cations are fixed at +2 proton units. Partial charges q(O1) and q(O2) are constrained to be equal, but q(O3) for the bridging oxygen atom is treated separately. Finally q(Si) is constrained to make the structure have a net charge of zero. The oxygen charges were adjusted separately for each of the three models, and those for the CS model are given in Table 2.

A bond-angle bending potential of the form

$$V(\alpha) = (k_\alpha/2)(\alpha - \alpha_0)^2 \quad (2)$$

is included for the Si–O3–Si angle in all three models. Here α is the calculated angle; and the unstrained value, α_0, and the force constant, k_α, are energy parameters to be determined. The VA and CS models also include energy terms of the same form for the O–Si–O angles. The same value of k_α is assumed for all O–Si–O angles, but three separate values of α_0 were assigned to angles O1–Si–O2, O3–Si–O3, and O3–Si–O1 or O3–Si–O2.

For the CS model it is also necessary to include a bond stretching term

$$V(d) = (k_d/2)(d - d_0)^2 \quad (3)$$

for the variable Si–O3 distances. Here d is the calculated bond distance; and the unstrained value, d_0, and the force constant, k_d, are energy parameters of the model.

Determining the energy parameters

The general procedure used for determining the energy parameters of a model was to fix the repulsion parameters A and B and the cation charges q(Ca) and q(Mg) as described above. Certain other quantities were set arbitrarily at trial values. The remaining parameters were then adjusted by the least-squares procedure of program WMIN, based on the observed crystal structure. Using the resulting values for the energy parameters, the energy of the model was then minimized with respect to the structural variables. A reasonable fit to the observed structure was usually obtained. Normal stresses on the model were then simulated, as described by Busing and Matsui (1984), and certain of the elastic constants s_{ij} were determined and compared with the observed values. The entire procedure was repeated several times with modified values of the trial parameters, finally using interpolation to select values which give the best agreement for both the structure and the elastic constants.

When this procedure was used for the RT mode, reasonably good agreement was obtained for the crystal structure, but the calculated compliance constants were always too small, indicating that the models are too stiff. This was especially true of s_{33}, which measures compliance along the chain. We found it impossible to increase s_{33} above 26% of its observed value.

The VA model is considerably better in this regard, producing reasonable structures and a calculated value of s_{33} as large as 79% of the observed value. The overall agreement of the observed and calculated elastic constants for this model was still not very good, however.

Table 2. Potential energy parameters used for the CS model

Parameter	Value*	Parameter	Value*
A(Mg)	1.552	α_0(Si-O3-Si)	169.00
A(Ca)	1.833	α_0(O3-Si-O1,2)	109.18
A(O)	1.791	α_0(O3-Si-O3)	101.47
		α_0(O1-Si-O2)	117.47
B(Mg)	0.0538		
B(Ca)	0.0711	k_α(Si-O3-Si)	0.0220
B(O)	0.2500	k_α(O-Si-O)	0.0730
q(Mg,Ca)	2.000	d_0(Si-O3)	1.786
q(Si)	1.425		
q(O1,2)	-1.260	k_d(Si-O3)	724.0
q(O3)	-0.905		

*Lengths are in A, charges in electrons, angles in degrees, and force constants in kcal mol^{-1} deg^{-2} or kcal mol^{-1} A^{-2}.

The chain-stretching model

The difficulties with the RT and VA models were eliminated by the use of the CS model, which has more degrees of freedom and more energy parameters than the earlier models, and the remainder of this paper will be concerned with this model. Listed in Table 2 are its final energy parameters, which were determined in the following way.

The repulsion parameters and cation charges were again fixed at values derived earlier. The unstrained angles α_0(O–Si–O) were arbitrarily fixed at the values given in the table. Several sets of trial values were chosen for k_d(Si–O3), k_α(O–Si–O), and k_α(Si–O3–Si). For each such trial, parameters d_0(Si–O3), α_0(Si–O3–Si), q(O1,2), and q(O3) were determined by least squares, the structure was adjusted to minimum energy, and the elastic compliance constants were computed. Linear interpolation was then used to select trial parameters which would best reproduce s_{11}, s_{22}, and s_{33}, and the remaining parameters were again determined by least squares.

Minimizing the energy of this model produces the calculated structure with lattice parameters, interatomic distances, and bond angles as listed in Table 1. The agreement with the observed structure is fairly good. Although the calculated *b* is 5.7% too large, the other lattice parameters are off by less than 1.5%, and the β angle is correct to 0.3°. Interatomic distances within the silicate chains are well reproduced, the largest discrepancy being 0.05Å, but the Si–O3–Si angle is calculated 4.5° too large.

In the Mg and Ca coordination shells the largest discrepancy in O · · · O distances is 0.32Å, indicating that the calculated translation of the silicate chains with respect to each other is not quite correct, but this is also partly a result of the increased *b* parameter.

Elastic compliance constants were calculated, as described by Busing and Matsui (1984), by applying normal stresses σ_1, σ_2, and σ_3, and shear stresses σ_5 of ± 10 kbar to the model and readjusting the structure. Linear interpolation was used to obtain compliance constants at zero stress. No change in the crystal symmetry is produced by these stresses.

In order to compute the remaining tensor elements, shear stresses σ_4 and σ_6 of 2.5 kbar and 5 kbar were applied. These stresses cause the crystal to become triclinic, and it is necessary to reduce the symmetry to $C\bar{1}$. The number of structural variables then increases from 16 to 32. Compliance constants at zero stress were obtained by parabolic extrapolation.

The precision of these numerical calculations can readily be checked, because each off-diagonal tensor element s_{ij} ($i \neq j$) is calculated in two ways, from stresses σ_i and σ_j. These checks show that the present results are good to about three significant figures.

Although it is the compliance constants s_{ij} which are computed by this method, we will follow the customary usage and report the stiffness coefficients c_{ij} obtained by inverting the matrix. These calculated quantities are given in Table 3 together with the observed values of Levien et al. (1979). In general the agreement is quite good, considerably better for example than the results reported for enstatite (Parker, 1983, p. 74).

Effects of pressure

Because the properties of pyroxene minerals at high pressures are of great interest, we applied a simulated hydrostatic pressure of 50 kbar to the CS model for diopside. This was done by using the techniques described by Busing and Matsui (1984), and the energy of the model was minimized to obtain the modified structure, slightly different from the structure calculated for zero pressure. Additional normal and shear stresses were then applied to the model and the compliance constants at

Table 3. Observed and calculated elastic constants and bulk modulus K for diopside, and their calculated pressure derivatives

ij	Obs* c_{ij}	Calc c_{ij}	Calc-Obs	Calc** $\partial c_{ij}/\partial P$
11	2.23	2.10	-0.13	5.0
22	1.71	1.66	-0.05	7.5
33	2.35	2.42	0.07	4.7
44	0.74	0.80	0.06	2.5
55	0.67	0.70	0.03	1.3
66	0.66	0.58	-0.08	2.4
12	0.77	0.64	-0.13	5.9
13	0.81	0.87	0.06	4.6
23	0.57	0.72	0.15	4.1
15	0.17	0.26	0.09	-1.0
25	0.07	0.11	0.04	-1.6
35	0.43	0.49	0.06	-0.7
46	0.073	0.092	0.019	1.0
K	1.08	1.05	-0.03	6.2†

*Levien et al. (1979), Mbar.
**Dimensionless.
†Observed value is 4.8 (Levien et al., 1979).

Table 4. Observed and calculated pressure derivatives of the lattice parameters, interatomic distances, and bond lengths in diopside

Parameter, p	Obs* ∂p/∂P	Calc ∂p/∂P
Lattice		
a	-2.57(7)	-3.07
b	-2.94(4)	-3.18
c	-1.32(3)	-1.25
β	-10.2(5)	-14.1
V	-347(7)	-373
Intra-chain distances		
Si-0(1C1)**	-0.21(8)	(0)
Si-0(2C1)	-0.07(4)	(0)
Si-0(3C1)	-0.10(8)	-0.20
Si-0(3C2)	-0.17(8)	-0.18
<Si-0>	-0.14(3)	-0.09
Si-Si	-0.64(1)	-0.72
0(1C1)-0(2C1)	-0.29(13)	-0.09
0(1C1)-0(3C1)	-0.13(11)	-0.05
0(1C1)-0(3C2)	-0.05(22)	-0.12
0(2C1)-0(3C1)	-0.15(4)	-0.11
0(2C1)-0(3C2)	-0.03(6)	-0.04
0(3C1)-0(3C2)	-0.53(2)	-0.52
<0-0>	-0.18(4)	-0.16
Intra-chain angles		
0(1C1)-Si-0(2C1)	-5(4)	-6
0(1C1)-Si-0(3C1)	5(6)	6
0(1C1)-Si-0(3C2)	13(7)	2
0(2C1)-Si-0(3C1)	-3(3)	3
0(2C1)-Si-0(3C2)	8(5)	6
0(3C1)-Si-0(3C2)	-19(2)	-12
Si-0(3)-Si	-35(3)	-36
Mg octahedron distances		
M(1)-0(1A1,B1)	-0.83(10)	-1.67
M(1)-0(1A2,B2)	-0.42(17)	-0.17
M(1)-0(2C1,D1)	-0.77(6)	-0.79
<M(1)-0>	-0.66(6)	-0.87
M(1)-M(1)	-1.12(2)	-1.55
0(1A1)-0(1B1)	-1.06(14)	-1.49
0(2C1)-0(2D1)	-0.44(12)	-0.83
0(1A1)-0(2C1)	-1.54(5)	-2.22
0(1A1)-0(1A2)	-0.73(5)	-1.19
0(1A2)-0(2C1)	-0.97(4)	-0.86
0(1A2)-0(2D1)	-1.10(20)	-0.83
0(1A1)-0(1B2)	-0.60(18)	-1.11
<0-0>	-0.92(4)	-1.23
Ca polyhedron distances		
M(2)-0(1A1,B1)	-0.57(6)	-0.70
M(2)-0(2C2,D2)	-0.35(19)	-0.17
M(2)-0(3C1,D1)	-0.43(11)	-0.41
M(2)-0(3C2,D2)	-2.17(10)	-2.01
<M(2)-0>	-0.89(7)	-0.82

*From a least-squares fit to the data of Levien and Prewitt (1981). Units are Å Mbar^{-1}, Å^3 Mbar^{-1}, or deg Mbar^{-1}. The figures in parentheses are the standard errors of the least significant digit given.

**Notation is that of Burnham et al. (1967) as used by Levien and Prewitt (1981).

high pressure were obtained. These were converted to stiffness coefficients, and the derivatives $\partial c_{ij}/\partial P$, which were calculated numerically, are listed in Table 3. Although the experimental values of these individual derivatives have not been reported, Levien et al. (1979) did observe $\partial K/\partial P$, the pressure derivative of the bulk modulus, to be 4.8, in rough agreement with our calculated value of 6.2, lending some credibility to our calculated derivatives.

Levien and Prewitt (1981) have reported the results of careful structure refinements based on X-ray data taken at five pressures from one atmosphere to 53 kbar. Although there are some discrepancies between our calculated structure and their observations, we would expect the calculated pressure derivatives of the various parameters to be comparable to those observed. Since the parameters tabulated by Levien and Prewitt show some scatter, we have obtained observed pressure derivatives by fitting a straight line to each of their quantities as a function of pressure. We used the method of least squares, weighting each observation according to its reported standard error. The resulting derivatives are reported in Table 4 with standard errors based on either the reported standard errors or the error of fit, whichever is larger.

Also tabulated are the derivatives calculated numerically from the CS model. These were obtained simply from the differences in the parameters calculated at zero pressure and at 50 kbar. The observed and calculated derivatives agree roughly, although, in general, the agreement is not so good as would be expected from the standard errors. Again, the agreement is better for distances and angles within a silicate chain than for distances from one chain to another. In any case, we regard this rough agreement as further indication that our model is approximately correct and that it is a reasonable starting point for further improvements.

References

Burnham, C. W., Clark, J. R., Papike, J. J., and Prewitt, C. T. (1967) A proposed crystallographic nomenclature for clinopyroxene structures. Zeitschrift für Kristallographie, 125, 109–119.

Busing, W. R. (1981) WMIN, a computer program to model molecules and crystals in terms of potential energy functions. U. S. National Technical Information Service, ORNL–5747.

Busing, W. R. and Matsui, M. (1984) The application of external forces to computational models of crystals. Acta Crystallographica.

Catlow, C. R. A., Thomas, J. M., Parker, S. C., and Jefferson, D. A. (1982) Simulating silicate structures and the structural chemistry of pyroxenoids. Nature, 295, 658–662.

Catti, M. (1981) The lattice energy of forsterite. Charge distribution and formation enthalpy of the SiO_4^{4-} ion. Physics and Chemistry of Minerals, 7, 20–25.

Catti, M. (1982) Atomic charges in Mg_2SiO_4 (forsterite), fitted to thermoelastic and structural properties. Journal of the Physics and Chemistry of Solids, 43, 1111–1118.

Czaya, R. (1971) Refinement of the structure of γ-Ca_2SiO_4. Acta Crystallographica, B27, 848–849.

Gilbert, T. L. (1968) Soft-sphere model for closed-shell atoms and ions. Journal of Chemical Physics, 49, 2640–2642.

Hazen, R. M. (1976) Effects of temperature and pressure on the crystal structure of forsterite. American Mineralogist, 61, 1280–1293.

Levien, L. and Prewitt, C. T. (1981) High-pressure structural study of diopside. American Mineralogist, 66, 315–323.

Levien, L., Weidner, D. J., and Prewitt, C. T. (1979) Elasticity of diopside. Physics and Chemistry of Minerals, 4, 105–133.

Matsui, M. and Busing, W. R. (1984) Computational modeling of the structure and elastic constants of the olivine and the spinel forms of Mg_2SiO_4. Physics and Chemistry of Minerals, 11, 55–59.

Matsui, M. and Matsumoto, T. (1982) An interatomic potential function model for Mg, Ca, and CaMg olivines. Acta Crystallographica, A38, 513–515.

Miyamoto, M. and Takeda, H. (1980) An interpretation of the structures of mantle minerals at high pressure in terms of interionic forces. Geochemical Journal, 14, 243–248.

Parker, S. C. (1983) Computer modelling of minerals. Ph.D. Thesis, University College, London.

Price, G. D. and Parker, S. C. (1984) Computer simulations of the structural and physical properties of the olivine and spinel polymorphs of Mg_2SiO_4. Physics and Chemistry of Minerals, 10, 209–216.

Rossi, G., Ghose, S., and Busing, W. R. (1982) Diopside, $CaMgSi_2O_6$: Refinement of the crystal structure by x-ray and neutron diffraction and preliminary observations on charge density distribution. (abstr.) Geological Society of America Abstracts with Programs, 14, 603.

Warren, B. and Bragg, W. L. (1928) XII. The structure of diopside, $CaMg(SiO_3)_2$. Zeitschrift für Kristallographie, 69, 168–193.

Manuscript received, January 9, 1984;
accepted for publication, July 12, 1984.