

## On the computer modeling of diopside: Toward a transferable potential for silicate minerals

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### ABSTRACT

The crystal structure and elastic properties of diopside,  $\text{CaMgSi}_2\text{O}_6$ , have been calculated by a lattice-energy-minimization procedure using a model that incorporates explicit terms for the covalent Si–O bond, including an O–Si–O bond-bending interaction; a shell-model interaction for the  $\text{O}^{2-}$  ions; short-range, exponential repulsive interactions between the oxygen atoms and the Ca and Mg cations; and Coulomb interactions. The parameters for this model were taken from various sources in the literature and were deliberately not optimized for diopside, yet the model reproduces many of the features of the observed crystal structure. These include the unit-cell parameters, the detailed Mg and Ca coordination, the silicate chain structure, and the Si–O bond lengths for both dangling and bridging bonds. The calculated values of the elastic constants are in reasonable agreement with experimental measurements. The model does better than some alternative models that have been reported, suggesting that its main features should be included in a general transferable potential for systems with tetrahedrally coordinated Si. The fact that the parameters of the model were transferred from other studies indicates that they are close to their optimum values for a truly transferable model.

### INTRODUCTION

A number of recent papers (e.g., Catlow and Mackrodt, 1982; Catlow et al., 1982; Leinenweber and Navrotsky, 1988; Matsui and Busing, 1984a, 1984b; Post and Burnham, 1986; Price and Parker, 1984; Price et al., 1987a, 1987b; Saunders et al., 1984) have dealt with the problem of developing models for interatomic forces in silicate minerals. These have each contributed toward the general goal of obtaining a model that incorporates interactions involving the common elements O, Si, Al, Mg, Ca, Fe, Na, K, etc. and that can be applied to most mineral structures. This is the concept of transferability. If this goal could be achieved, it would lead to spectacular progress in the study of the microscopic properties and behavior of minerals, encompassing equilibrium properties, phase equilibria, kinetic behavior, and defect properties, to name but a few. A successful model would enable the study of those properties and systems that are very difficult or even impossible to study using conventional experimental techniques. It is primarily this reason that has motivated most of the recent efforts in this field.

The development of transferable models for minerals is a mirror reflection of the study of molecular crystallography of the past two decades (e.g., Williams and Houpt, 1986). In the latter case, the development of realistic transferable potentials for molecular crystals containing the atoms C, H, N, O, Cl, F, etc. has meant that modeling techniques can now be routinely applied to most molecular systems. The primary applications have been in the study of phase equilibrium and dynamic proper-

ties, and the methods have also been extensively applied to the studies of proteins, polymers, and other macromolecular systems. This work has illustrated one of the main advantages of having a reliable transferable model, namely that it is possible to apply this model to a new system with some confidence that it will be realistic. Although it is often possible to develop a new model for any new case, the use of a transferable model ensures that the properties being studied have not automatically been built into the model from the start. The best transferable potentials for molecular crystals were obtained empirically by fitting the potential parameters to the crystal structures of a wide range of systems (Williams and Houpt, 1986) rather than by concentrating on individual structures.

In the case of molecular systems, the basic forms of the transferable model functions were established before the main development work was undertaken. But in the case of mineral structures, this essential groundwork has yet to be developed to the point where a consensus view of the main necessary features of such a model has emerged. Therefore, it is unlikely that a large-scale calculation of transferable model potentials at the present time will yield appropriate dividends. Instead, the next stage is to apply the present available models to a range of systems in order to obtain information about the relative roles of different features of the models. It will then be possible to follow the work on molecular systems and calculate transferable model potentials for aluminosilicate minerals by empirical fitting to a database of mineral structures.

Whether or not parameters for a model potential are determined phenomenologically or from *ab initio* calculations, the essential form of any model is chosen from more general considerations. Most of the work to date has fallen somewhere between two limiting cases. The first is the purely ionic case, in which the only interactions included in the model are electrostatic and short-range repulsive interactions (see, for example, Post and Burnham 1986). The second takes an extreme view of the covalent Si–O bond as a perfectly rigid bond and models all other interactions as in the ionic case. An example of this is the model of Matsui and Busing (1984a) for forsterite. Subsequent studies of forsterite (Price and Parker, 1984; Price et al., 1987a, 1987b) and diopside (Post and Burnham, 1986; Matsui and Busing, 1984b) have shown that neither of these extreme cases are entirely adequate and that any realistic model will lie between these limiting cases. For example, Price and Parker (1984) showed that a more realistic model for forsterite that is able to reproduce both structural and elastic properties must include an explicit Si–O interaction representative of the covalent bond.

Saunders et al. (1984) developed a very successful model for quartz that included O–Si–O bond-bending interactions in addition to explicit Si–O covalent interactions. The Si–O interactions were modeled using an empirical function of the form

$$V(r) = -Ar^{-6} + B \exp(-r/c), \quad (1)$$

where  $r$  is the interionic distance. A similar function was used to model O···O interactions, which effectively included both the effects of nearest-neighbor short-range interactions and the longer-range van der Waals interactions. The O–Si–O bond-bending interaction was modeled using a harmonic interaction of the form

$$V(\theta) = (1/2)k(\theta - \theta_0)^2, \quad (2)$$

where  $\theta$  is the bond angle. It was found empirically that a similar potential for Si–O–Si bonds was unnecessary. Electrostatic interactions were included, assuming formal ionic charges. Polarization effects were modeled using a shell model for the O<sup>2-</sup> ions, where the interaction between the shell and core is represented by

$$V(d) = (1/2)Kd^2 \quad (3)$$

and where  $d$  is the separation distance between the centers of the core and shell. The interactions involving the O<sup>2-</sup> ion described above (Eqs. 1–2) used the position of the shell as the interaction center. Further details of the parameterization of this model are given by Saunders et al. (1984).

Price et al. (1987a, 1987b) added a short-range exponential repulsive interaction of the form

$$V(r) = B \exp(-r/c) \quad (4)$$

for Mg···O interactions and applied this model to forsterite. The agreement between calculated and observed structural and dynamic properties was encouraging, giv-

ing better results than all previous models. More recently, Jackson and Catlow (1988) applied extensions of this basic model to zeolite structures with some success. The parameters for additional short-range repulsive interactions have either been obtained empirically or taken from the modified electron gas (MEG) calculations of Post and Burnham (1986).

The results of these studies suggest that this extension of the model by Saunders et al. (1984) for quartz may represent a successful route to the development of a general transferable model for minerals. Accordingly I have modeled a number of complex mineral structures that are of interest for the work of our laboratory in an attempt to draw some general conclusions concerning the transferability of this model; general details will be presented elsewhere. One of the systems studied is diopside, CaMgSi<sub>2</sub>O<sub>6</sub>, which deserves detailed consideration in its own right for two related reasons. First, a number of previous attempts to model the diopside structure have already been reported (Catlow et al., 1982; Matsui and Busing, 1984b; Post and Burnham, 1986), with varying success. A detailed comparison between the results of different models will therefore serve to highlight their contrasting behavior. Second, unlike many minerals, the pyroxene structure represents a very real challenge to the modeler because it is not related to a simple close-packed structure; this in part is why diopside has been the subject of previous studies. A detailed study of the application of any new model to diopside will hence serve as an excellent test of its transferability. The main aim of this paper therefore is to assess the application of the extended quartz model described above to the diopside structure. The results of this study should point toward ways in which this particular model can be developed into a general transferable scheme and should also suggest appropriate modifications.

## METHOD

The values of the parameters in the model potential used in this study are given in Table 1. The parameters for the Si···O and O···O interactions (Eqs. 1–2) were taken directly from the work of Saunders et al. (1984) on quartz; these are the same as used in other simulations (Price et al., 1987a, 1987b; Jackson and Catlow, 1988). The charges on the O<sup>2-</sup> core and shell and the spring constant  $K$  of Equation 3 were also taken from Saunders et al. (1984). The parameters for the Ca···O short-range interactions (Eq. 4) were taken from the MEG calculations of Post and Burnham (1986), and those for the Mg···O interactions were the same as used by Price et al. (1987a, 1987b) in their study of forsterite. The reason for this latter choice was simply to emphasize the transferable nature of these parameters. In fact it is probable that the exact choice of the set of consistent potential parameters for these short-range interactions will make little difference. Figure 1a compares the distance dependence of the Mg···O potential used in this study with the sets of potentials proposed by Post and Burnham (1984);

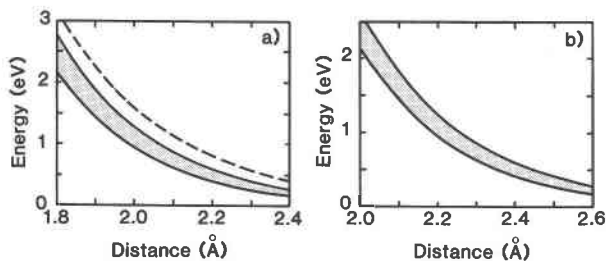


Fig. 1. (a) Calculated Mg···O short-range energy as a function of ionic separation, as given in Equation 4. The functions given by the different parameters of Post and Burnham (1986) lie in the patterned area. The dashed curve shows the function used by Price et al. (1987a, 1987b), which is used in the present study. (b) Calculated Ca···O short-range energy. The functions given by Post and Burnham (1986) lie within the patterned area. The function used in this study lies in the middle of this area.

the first and second derivatives of the potential are very close for all models. Similarly, the range of models for Ca···O proposed by Post and Burnham (1984) also all have very similar derivatives (Fig. 1b). The full set of parameters used in this calculation is given in Table 1.

The calculations were performed using the lattice-energy minimization program THBREL, which is a recent version of CASCADE (Catlow and Mackrodt, 1982). This was specifically written to handle bond-bending interactions and shell-model effects. The lattice-relaxation procedure used in this program follows the standard Newton minimization technique. THBREL also calculates the full elastic-constant tensor directly. The calculations were performed on a Microvax 2000.

The reference crystal structure of diopside used in this study was that determined by Clark et al. (1969) at 24 °C. The elastic constants of diopside have been measured by Levien et al. (1979). No attempt has been made to use these data to modify the potentials used in this study, since this would be outside the spirit of this exercise.

## RESULTS

The results of the lattice-energy calculations are most easily presented in a series of tables (Tables 2–5) where they are compared with experimental values. The cell parameters and the fractional atomic coordinates are given

in Table 2. The unit-cell lengths are consistently shorter than the observed cell lengths by between 1.7 and 3.0%. This discrepancy is much smaller than was obtained using ionic models (Catlow et al., 1982; Post and Burnham, 1986) and is slightly better than the best model of Matsui and Busing (1984b). It is encouraging that the discrepancies are of the same sign and of roughly the same size for each of the cell lengths. The calculated monoclinic cell angle differs from the observed angle by only 1.65°. This agreement is also much better than for the ionic models. The calculated fractional coordinates given in Table 2 do not differ significantly from those measured experimentally.

One point that needs to be noted before discussing bond lengths in detail is that the equilibrium core-shell separation distances are 0.126, 0.142, and 0.096 Å for the three independent O<sup>2-</sup> ions, respectively. This size of separation is usual for this model. However, it raises an ambiguity when it comes to a consideration of bond lengths, which reflects two possible ways of interpreting this separation. On one hand, the separation can be viewed as a real effect, so that the position of the core can be considered to be identical to the atomic position given by X-ray diffraction. In this case, the fact that the shell position is used as the center for all the short-range interactions resembles the coupling between ionic polarization and these interactions. On the other hand, the displacement of the core relative to the shell can be interpreted as a simple, but unrealistic, representation of an induced dipole moment since the displacement is much smaller than a typical interionic distance. In this case, the position of the shell would be interpreted as the actual ion position, since it is the interaction center. In the discussion of bond geometry given below, I leave this issue open by referring to both interpretations of the actual bond length.

The Si–O bond lengths are given in Table 3. The bond lengths calculated using the O<sup>2-</sup> core positions are close to the actual bond lengths, but those calculated using the O<sup>2-</sup> shell positions are shorter than the observed values. The discrepancy is smallest for the bonds involving the bridging atoms [O(3)]. Particularly encouraging is the fact that the differences between the bridging bond lengths and the dangling bond lengths are reproduced by the model, even though identical interactions were used for

TABLE 1. Parameters used in the model for diopside as defined by Eqs. 1–4

$A(\text{Si}\cdots\text{O}) = 10.6616$	$B(\text{Si}\cdots\text{O}) = 1283.9$	$c(\text{Si}\cdots\text{O}) = 0.3205$
$A(\text{O}\cdots\text{O}) = 27.88$	$B(\text{O}\cdots\text{O}) = 22764.0$	$c(\text{O}\cdots\text{O}) = 0.1490$
	$B(\text{Mg}\cdots\text{O}) = 1428.5$	$c(\text{Mg}\cdots\text{O}) = 0.2945$
	$B(\text{Ca}\cdots\text{O}) = 6958.3$	$c(\text{Ca}\cdots\text{O}) = 0.2516$
$k = 2.09724$	$\theta_0 = 109.47$	
$K = 74.9204$		
$q(\text{Si}) = 4e$	$q(\text{Mg}) = 2e$	$q(\text{Ca}) = 2e$
$q(\text{O core}) = 0.8482e$	$q(\text{O shell}) = -2.8482e$	

Note: Energy units are eV, distances are in Å, and angles are in degrees.

**TABLE 2.** Calculated and observed crystal structure of diopside

	Present results	Experimental results*
<i>a</i> (Å)	9.5848	9.746
<i>b</i> (Å)	8.6365	8.899
<i>c</i> (Å)	5.1355	5.251
$\beta$ (°)	103.98	105.63
Si <i>x</i>	0.2840	0.2862
<i>y</i>	0.0983	0.0933
<i>z</i>	0.2317	0.2293
O1 (core) <i>x</i>	0.1135	0.1156
<i>y</i>	0.0962	0.0873
<i>z</i>	0.1426	0.1422
O1 (shell) <i>x</i>	0.1270	
<i>y</i>	0.0961	
<i>z</i>	0.1481	
O2 (core) <i>x</i>	0.3594	0.3611
<i>y</i>	0.2558	0.2500
<i>z</i>	0.3297	0.3180
O2 (shell) <i>x</i>	0.3548	
<i>y</i>	0.2407	
<i>z</i>	0.3207	
O3 (core) <i>x</i>	0.3571	0.3505
<i>y</i>	0.0175	0.0176
<i>z</i>	0.9982	0.9953
O3 (shell) <i>x</i>	0.3473	
<i>y</i>	0.0152	
<i>z</i>	0.9977	
Mg <i>x</i>	0	0
<i>y</i>	0.9065	0.9082
<i>z</i>	0.25	0.25
Ca <i>x</i>	0	0
<i>y</i>	0.3069	0.3015
<i>z</i>	0.25	0.25

\* Clark et al. (1969).

these two types of bonds. The ionic calculations of Post and Burnham (1984) were unable to reproduce this feature. The calculated intratetrahedron O···O bond lengths and O–Si–O bond angles are compared with experiment in Table 3. The agreement is reasonable although the bond lengths calculated using the shell positions are consistently shorter than the observed values. The calculated

**TABLE 3.** Calculated and measured bond lengths (Å) and angles (°) within the SiO<sub>3</sub> chains

	Calculated using O <sup>2-</sup> shell positions	Calculated using O <sup>2-</sup> core positions	Observed*
Si–O(1)	1.4615	1.5869	1.602
Si–O(2)	1.4257	1.5654	1.585
Si–O(3)	1.6368	1.6797	1.664
Si–O(3)	1.6713	1.7033	1.687
Mean	1.5488	1.6338	1.635
O(1)–Si–O(2)	118.81	117.75	118.2
O(1)–Si–O(3)	108.44	111.58	110.3
O(1)–Si–O(3)	112.17	114.86	109.9
O(2)–Si–O(3)	112.42	110.50	109.7
O(2)–Si–O(3)	101.12	100.57	103.6
O(3)–Si–O(3)	102.56	99.69	104.0
Si–O(3)–Si	137.0	130.96	135.8
O3C1–O3C2–O3C1	168.34	166.53	166.4

\* Clark et al. (1969).

**TABLE 4.** Calculated and measured Mg···O and Ca···O bond lengths (Å)

	Calculated using O <sup>2-</sup> shell positions	Calculated using O <sup>2-</sup> core positions	Observed*
Mg–O(1)	2.1782	2.1124	2.16
Mg–O(1)	2.1118	2.0470	2.06
Mg–O(2)	2.0890	1.9861	2.05
Mean	2.1264	2.0485	2.08
Mg–Mg	3.0334		3.10
Ca–O(1)	2.3191	2.2555	2.36
Ca–O(2)	2.3416	2.3157	2.35
Ca–O(3)	2.4782	2.4499	2.56
Ca–O(3)	2.6502	2.5776	2.72
Mean	2.4473	2.3997	2.50

\* Clark et al. (1969).

values of the O3C1–O3C2–O3C1 angle (following the nomenclature of Burnham et al., 1967) are given in Table 3 also. This angle is close to the experimental value but cannot be reproduced by the ionic model of Post and Burnham (1986). The chain structure is determined by this angle, and this result shows that the model has correctly reproduced this important feature of the diopside structure.

The calculated Mg–O, Mg–Mg, and Ca–O distances are presented in Table 4. The distances calculated using the shell positions are all consistent with the observed values to within 3% in all cases, and the differences are only slightly larger when the core positions are used. The model has therefore correctly reproduced the detailed Mg and Ca coordinations remarkably well. This is much better than for the ionic models of Catlow et al. (1983) and Post and Burnham (1986); it was this aspect of the diopside structure that these ionic models were unable to reproduce.

The calculated elastic constants are compared with the experimental measurements in Table 5. In general, the model overestimates the values by up to 0.55 Mbar, with an average discrepancy of 0.22 Mbar.

## DISCUSSION

The results presented above show that this model has simulated the crystal structure of diopside reasonably well.

**TABLE 5.** Calculated and measured elastic constants (Mbar)

	Calculated	Observed*
<i>C</i> <sub>11</sub>	2.78	2.23
<i>C</i> <sub>22</sub>	1.95	1.71
<i>C</i> <sub>33</sub>	2.55	2.35
<i>C</i> <sub>44</sub>	0.60	0.74
<i>C</i> <sub>55</sub>	0.69	0.67
<i>C</i> <sub>66</sub>	0.97	0.66
<i>C</i> <sub>12</sub>	1.26	0.77
<i>C</i> <sub>13</sub>	1.06	0.81
<i>C</i> <sub>23</sub>	0.83	0.57
<i>C</i> <sub>15</sub>	0.18	0.17
<i>C</i> <sub>25</sub>	0.15	0.07
<i>C</i> <sub>35</sub>	0.66	0.43
<i>C</i> <sub>46</sub>	0.09	0.07

\* Levien et al. (1979).

The elastic constants are not reproduced so well, but nevertheless the calculated values are of the correct order of magnitude. What should be borne in mind is the fact that no part of the model potential has been optimized for diopside. The level of agreement between the calculated and observed properties therefore reflects the transferable nature of the model. Because the present model has not been optimized for diopside, it is not surprising that it does have some deficiencies, but the success of the model suggests that these deficiencies might be removed by slight adjustment of some of the parameter values. This statement is supported by the fact that the model of Matsui and Busing (1984b) for diopside, which was specifically optimized by fitting to the structural and elastic properties of diopside, gives better agreement with the elastic properties. Their model also included bond-bending interactions and specific Si-O covalent-bond interactions.

The comparison between the results of this paper and the previous studies of diopside using ionic models (Catlow et al., 1982; Post and Burnham, 1986) has shown that the ionic approach does not work as well as a model that contains covalent effects. The two ionic models failed to reproduce the cation ( $Mg^{2+}$ ,  $Ca^{2+}$ ) coordination, whereas this feature was successfully modeled using the present approach. The fact that the  $Mg \cdots O$  and  $Ca \cdots O$  potentials are very similar to those of one of the ionic models (Post and Burnham, 1986) demonstrates that the failings of these ionic models do not follow from inadequate parameterization.

The main conclusion of this work is that the present model contains the necessary features for a model of the pyroxene structures, namely specific covalent-bond interactions, bond-bending interactions, and shell-model effects. Since the parameters were taken from other sources, it can also be concluded that this model represents a very good starting point for a transferable potential that might be expected to work for a wide range of silicate minerals with tetrahedral Si-O coordination. I anticipate that it will also be appropriate for systems with tetrahedral Al-O coordination, and my preliminary calculations for structures such as cordierite tend to confirm this view. It is encouraging that these results have confirmed the transferability of the short-range repulsive parameters for  $Mg \cdots O$  and  $Ca \cdots O$  interactions that were obtained from MEG calculations (Post and Burnham, 1986).

The parameters for Si-O and  $O \cdots O$  interactions were obtained from fitting to the structure and elastic properties of quartz (Saunders et al., 1984). It is therefore unreasonable to expect that they will automatically be appropriate for other systems. Nevertheless, the present calculations and those of other workers (Price et al., 1987a, 1987b; Jackson and Catlow, 1988) have shown that the Si-O parameters can be transferred to other systems and give reasonable results. It would therefore be expected that if these parameters were optimized using a range of mineral structures, they would give even more accurate results. The deficiencies highlighted in this study suggest

that the Si-O potential parameters could be improved. Alternatively, it is likely that the use of formal charges can be faulted. If the ionic charge values were reduced, the electrostatic attractions would also be reduced, the Si-O bond length would be expected to increase, the cell volume would increase, and the model crystal would be elastically softer. One approach to tackling this problem might be to introduce a scale factor for the ionic charges as suggested by Leinenweber and Navrotsky (1988), in which all the formal ionic charges are reduced by a single scale factor. Some support for this idea comes from the model of Matsui and Busing (1984b) and from my additional independent calculations for diopside, which have shown that optimum values of charges for the different oxygen ions are roughly the same, independent of environment. Such a scale parameter may be sample dependent and not transferable; this is the experience with molecular systems. But if this is so, the application of the transferable model to any system will require the optimization of only one parameter in a linear function.

I have argued in this paper that the present model will give a starting point for a transferable potential that will be better than ionic models used by other workers. I have also argued that it would probably not be of long-term value to attempt to optimize this model using only the results of the present study. Instead, the model parameters should be obtained by fitting to a wide range of aluminosilicate mineral structures, in exactly the same way that the models for molecular crystals discussed in the introduction were developed (Williams and Houpt, 1986). The first stage in this work is the more general analysis of the application of the present model to a number of different mineral structures. This has been carried out, and the results will be presented elsewhere. However, as noted in the introduction, structures such as pyroxenes, which are not related to a simple close-packing of oxygens, will be crucial in the general analysis; this is why I have concentrated on modeling diopside in this paper.

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