

An Interatomic Potential-Function Model for Mg, Ca and CaMg Olivines

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Abstract

The structures of Mg(forsterite), Ca and CaMg(monticellite) olivines have been investigated by lattice energy calculations, where the silicate ions are treated as rigid bodies. The lattice energy was approximated to be the sum of electrostatic and repulsive terms. The net charges on the Si and O atoms in the silicate ion and the repulsive radii of the atoms concerned were derived using the two known crystal structures, Mg and Ca olivines, by a least-squares fit. The results are as follows: $q_{\text{O}}(|e|) = -1.569$, $q_{\text{Si}} = +2.276$, $R_{\text{O}} (\text{Å}) = 1.998$, $R_{\text{Mg}} = 1.164$, and $R_{\text{Ca}} = 1.581$. The repulsive interactions of the Si atoms were neglected, since the Si atom would be screened by the outermost four O atoms of the silicate ion. The reliability and the transferability of the potential model presented were tested by the calculation of the energy-minimized structure for CaMg olivine, with the result that the observed structure was very well reproduced.

Introduction

The interatomic potential-function model, assuming fully ionized ions, has recently been used successfully to explain the structures and the properties of silicate minerals (Miyamoto & Takeda, 1980; a list of publications may be found in the article of Brown & Fenn, 1979). However, as pointed out by Brown (1980), the success of these calculations should not be interpreted as indicating that the fully ionized model for silicates is valid. The fully ionized model has too high a charge distribution so that the total electrostatic energy is expected to be too large.

In this paper the structures of Mg(forsterite), Ca and CaMg(monticellite) olivines have been investigated by lattice energy calculations, where the covalency of the Si–O bond is taken into account in treating the silicate ions as rigid bodies and in reducing the net charges on the Si and O atoms from their formal values.

The repulsive radii (Matsui & Watanabé, 1981*a*) and

the net charges on the Si and O atoms in the silicate ion are derived from the two known crystal structures, Mg and Ca olivines, by a least-squares optimization. In order to examine the reliability and the transferability of the potential model presented, we calculate the energy-minimized structure for CaMg olivine, with the result that the observed structure is found to be well reproduced.

Lattice energy calculation

The techniques and the interatomic potential functions employed here have been described previously (Matsui & Watanabé, 1981*a,b*). The lattice energies of Mg(forsterite), Ca and CaMg(monticellite) olivines were approximated to be the sum of electrostatic and repulsive interactions as follows:

$$E = \frac{1}{2} \sum_i \sum_j [q_\alpha q_\beta r_{ij}^{-1} + \frac{1}{12} f (R_\alpha + R_\beta)^{13} r_{ij}^{-12}],$$

where r_{ij} is the interatomic distance between atoms i and j , and q_α and R_α are the net charge and repulsive radius of an atomic species α , respectively. The standard force f was set equal to $1 \text{ kJ Å}^{-1} \text{ mol}^{-1}$ throughout. The dispersion attraction terms were neglected, since these interactions might be only a minor part of the lattice energy for ionic crystals. The summation over i includes one asymmetric unit, and j is summed over all atoms in different ions in the crystal. To facilitate the computation of the Coulomb sum, the convergence-acceleration method (Williams, 1971) was used. The convergence constant K was set equal to 0.12, the direct lattice sum was truncated at 15 Å , and the reciprocal-lattice sum was ignored; the accuracy of E was estimated to be at least 99%.

Derivation of the potential parameters

The silicate ions were treated as rigid bodies, as a first approximation. To deal with the lattice energies of Mg,

Ca and CaMg olivines, the potential parameters require the net charges q and the repulsive radii R for the four atomic species, Mg, Ca, Si and O. Of these the net charges on the Mg and Ca ions were both fixed at $+2|e|$, and the sum $q_{\text{Si}} + 4q_{\text{O}}$ was constrained to equal $-4|e|$. The repulsive interactions for the Si atoms were neglected, since the Si atom would be screened by the outermost four O atoms of the silicate ion. Thus there remain four energy parameters, q_{O} , R_{O} , R_{Mg} and R_{Ca} . These four parameters were derived from the two known crystal structures, Mg olivine (Fujino, Sasaki, Takéuchi & Sadanaga; 1981) and Ca olivine (Czaya, 1971), with a least-squares fit. We minimize the expression

$$F = \sum_i w_i (\partial E / \partial p_i)_{\text{obs}}^2,$$

where p_i are the structural parameters including cell parameters, atomic coordinates, and the rotation of the silicate ion. The space group, the site symmetry, and the cell content of the observed structure were all kept unchanged. The rotation axis of the silicate ion was taken parallel to the c axis through the Si atom. The rotation was taken in radians, and the cell parameters and atomic coordinates in Å. The weighting factors w_i were arbitrarily chosen as $|p_i|^2$ for the cell parameters, $|\text{mean Si-O}|^{-2}$ ($=1.64^{-2}$) for the rotation of the silicate ion, and 1 for the atomic coordinates.

Olivines crystallize in space group $Pbnm$ with $Z = 4$. There exist two crystallographically independent metallic ions, $M(1)$ and $M(2)$, with $M(1)$ lying on a centre of inversion, and $M(2)$ on a mirror plane. For each silicate ion, the Si, O(1) and O(2) atoms lie on a mirror plane, and the O(3) atom on a general position. The structural parameters employed as observed quantities, for one structure, are the three cell parameters, a , b and c , the two atomic coordinates, X and Y , for both the $M(2)$ and the silicate ions, and the rotation angle, θ , for the silicate ion. Thus from the two structures a total of 16 observations is available. The minimization of F was performed with the *SIMPLEX* method (Nelder & Mead, 1965). The initial values for q_{O} , R_{O} , R_{Mg} and R_{Ca} were arbitrarily chosen in the ranges -0.86 – $-0.99|e|$, 1.67 – 1.73 Å, 0.95 – 1.10 Å, and 1.40 – 1.44 Å, respectively. The optimized values of the potential parameters obtained are listed in Table 1. The net charges on the Si and O atoms can be compared to those obtained by accurate single-crystal X-ray data for Mg olivine [$+2.11(3)|e|$ for Si, -1.29 – $-1.52(7)|e|$ for O from the EDR (effective distribution radii) method, and $1.8(1)|e|$ for Si, -1.6 – $-1.9(1)|e|$ for O from the $L1$ method; Fujino *et al.*, 1981], and the relative magnitudes of the repulsive radii follow the expected trend: $R_{\text{Mg}} < R_{\text{Ca}} < R_{\text{O}}$. It is to be noted that the R_{Ca} value of 1.581 Å is almost identical to that obtained from the crystal structure of α -calcium formate (1.591 Å; Matsui & Watanabé, 1981a), in spite of the different

Table 1. *Optimized values of the potential parameters*

	$q(e)$	R (Å)
O	-1.569	1.998
Si	$+2.276$	Neglected*
	$(= -4 - 4 \times q_{\text{O}})^*$	
Mg	$+2^\dagger$	1.164
Ca	$+2^\dagger$	1.581

* See text.

† Fixed.

environment of the Ca^{2+} ions in the two crystals: the Ca^{2+} ions in Ca olivine are surrounded by the six O atoms from silicate ions at distances of 2.311 – $2.388(8)$ Å for Ca(1), and 2.286 – $2.442(8)$ Å for Ca(2) (Czaya, 1971), and the Ca^{2+} ions in α -calcium formate are surrounded by the seven O atoms from formate ions at distances of 2.321 – $2.561(1)$ Å (Watanabé & Matsui, 1978).

Energy-minimized structure for CaMg olivine

The reliability and the transferability of the potential parameters obtained were tested by the calculation of the energy-minimized structure for CaMg olivine. Starting from the neighbourhoods of the observed structure (Onken, 1965), the calculated lattice energy E was minimized by changing structural parameters, where the space group, the site symmetry, and the cell content of the observed structure were all kept unchanged, and each silicate ion was taken as a rigid body having Td symmetry with $\text{Si-O} = 1.64$ Å, based on the mean value reported for olivines. Structural parameters to be optimized are eight in number, including three cell parameters, two atomic coordinates for both the Ca^{2+} ion and the Si atom, as the reference atom of the silicate ion, and one rotation angle of the silicate ion. The rotation axis of the silicate ion is taken as the same as that in the previous section. The minimization was carried out with the *SIMPLEX* method (Nelder & Mead, 1965). The results are listed in Table 2, which includes the observed and calculated values with their differences. Table 2 also lists the unit-cell volume and the fractional coordinates of the O atoms for the sake of comparison. The agreement between the observed and energy-minimized structures is quite satisfactory. The errors of the lattice parameters are in the range 2–5%, and that of the volume only 0.2%. The mean discrepancy of the fractional coordinates between the observed and energy-minimized structures is 0.005, with the worst discrepancy of 0.022 occurring in the x coordinates of the Si atom. Octahedral distortions of the Mg and Ca sites in the observed structure are very well reproduced as can be seen in Table 3. The Mg–O and Ca–O distances for the energy-minimized structure are

arranged in the order of Mg—O(2) < Mg—O(3) < Mg—O(1) and Ca—O(3'') < Ca—O(2) < Ca—O(3) < Ca—O(1), respectively. The same is true for the observed structure. The maximum deviation of the M^{2+} —O distances is only 0.02 Å for Mg—O and 0.04 Å for Ca—O. For each of the Mg and Ca octahedra, the O—O distances are also correctly ordered by the energy minimization, with the shortest for the shared edge between an octahedron and tetrahedron, and the longest for the unshared edges.

In conclusion, the present potential-function model for Mg, Ca and CaMg olivines has been proved to be very effective in deriving crystal structures. However, it should be remarked that the silicate ions were treated as rigid bodies throughout, and that the present model can be applied only for silicates containing separate SiO_4^{4-} groups. We hope to extend the method to other more complex silicates.

Table 2. Comparison between observed and energy-minimized structures for CaMg olivine

The cell parameters come from Onken (1965), and the fractional coordinates from Brown's (1970) re-refinement of data from Onken. [The coordinates of O(2) are the transforms of those of Brown: $x' = \frac{1}{2} - x, y' = -\frac{1}{2} + y$.]

	obs	calc	obs - calc
Cell parameters (Å) and volume (Å ³)			
<i>a</i>	4.822 (1)*	4.598	0.22
<i>b</i>	11.108 (3)	11.462	-0.35
<i>c</i>	6.382 (2)	6.500	-0.12
<i>V</i>	341.8 (2)	342.6	-0.8
Rotation angle (°)			
θ†	—	56.83	
Fractional coordinates			
<i>x</i> (Ca)	0.9770 (2)	0.9708	0.006
<i>y</i> (Ca)	0.2767 (1)	0.2728	0.004
<i>x</i> (Si)	0.4101 (2)	0.3885	0.022
<i>y</i> (Si)	0.0811 (1)	0.0778	0.003
<i>x</i> [O(1)]	0.7447 (6)	0.7449‡	-0.000
<i>y</i> [O(1)]	0.0777 (3)	0.0725	0.005
<i>x</i> [O(2)]	0.2535 (6)	0.2574	-0.004
<i>y</i> [O(2)]	-0.0516 (3)	-0.0553	0.004
<i>x</i> [O(3)]	0.2729 (4)	0.2758	-0.003
<i>y</i> [O(3)]	0.1472 (2)	0.1469	0.000
<i>z</i> [O(3)]	0.0452 (4)	0.0440	0.001

* Estimated standard errors referring to the last decimal place.

† For the rotation angle of the silicate ion, there is no explicit comparison between the observed and energy-minimized structures since the sizes of the silicate ion in these two structures are different.

‡ The coordinates of the O atoms are calculated from the following formula:

$$\begin{pmatrix} ax \\ by \\ cz \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} + \begin{pmatrix} ax(Si) \\ by(Si) \\ cz(Si) \end{pmatrix}$$

where *X*, *Y* and *Z* are the internal coordinates (Å) of each O atom with $X = 1.64 \text{ Å} \times \cos(109.47^\circ/2) (= LC)$, $Y = 1.64 \text{ Å} \times \sin(109.47^\circ/2) (= LS)$, $Z = 0$ for O(1); $X = LC$, $Y = -LS$, $Z = 0$ for O(2); $X = -LC$, $Y = 0$, $Z = -LS$ for O(3).

Table 3. Comparison of the M^{2+} —O distances (Å) between observed and energy-minimized structures for CaMg olivines

Observed values are from Brown (1970).

	obs	calc	obs - calc
Mg octahedron			
[2]* Mg—O(1)	2.194 (2)†	2.170	0.02
[2] Mg—O(2)	2.091 (2)	2.108	-0.02
[2] Mg—O(3)	2.120 (2)	2.127	-0.01
⟨Mg—O⟩	2.135 (1)	2.135	0.00
[2] O(1)—O(3)‡	2.966 (4)	2.912	0.05
[2] O(1)—O(3')	3.132 (4)	3.160	-0.03
[2] O(1)—O(2)‡	2.844 (5)	2.775	0.07
[2] O(1)—O(2')	3.206 (2)	3.256	-0.05
[2] O(2)—O(3')	3.336 (4)	3.281	0.06
[2] O(2)—O(3)§	2.569 (4)	2.678	-0.11
⟨O—O⟩	3.009 (2)	3.010	-0.00
Ca octahedron			
[1] Ca—O(1)	2.478 (3)	2.520	-0.04
[1] Ca—O(2)	2.309 (4)	2.333	-0.02
[2] Ca—O(3)	2.411 (3)	2.417	-0.01
[2] Ca—O(3'')	2.289 (2)	2.303	-0.01
⟨Ca—O⟩	2.364 (1)	2.382	-0.02
[2] O(1)—O(3'')	3.593 (4)	3.744	-0.15
[2] O(1)—O(3)‡	2.966 (4)	2.912	0.05
[2] O(2)—O(3)	3.595 (4)	3.670	-0.08
[2] O(2)—O(3''')	3.147 (4)	3.060	0.09
[1] O(3)—O(3')§	2.615 (5)	2.678	-0.06
[2] O(3)—O(3'')	3.371 (4)	3.346	0.03
[1] O(3'')—O(3''')	3.771 (5)	3.822	-0.05
⟨O—O⟩	3.311 (1)	3.330	-0.02

* The numbers in brackets refer to the multiplicity of the bond.

† Estimated standard errors referring to the last decimal place.

‡ O—O edge shared between two octahedra.

§ O—O edge shared between an octahedron and tetrahedron.

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