Point defects in silicate minerals studied using empirical potentials

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About Silicate Minerals

- Most abundant rock-forming minerals on Earth
- Geology, Planetary Sciences
- Found in Asteroids
  - Olivine
  - Orthopyroxene
Our Silicate Minerals

- **Olivine**: \((\text{Mg, Fe})_2\text{SiO}_4\)
  - Forsterite: 100% Mg
  - Fayalite: 100% Fe

- **Orthopyroxene**: \((\text{Mg, Fe})\text{SiO}_3\)
  - Enstatite: 100% Mg
  - Ferrosilite: 100% Fe
Structure of Olivine $M_2SiO_4$

- Orthorhombic
- Forsterite $Mg_2SiO_4$
- Fayalite $Fe_2SiO_4$
- Two metal sites
- Fe prefers M1 site
Structure of Orthopyroxene

(Mg, Fe)SiO$_3$

- Enstatite: 100% Mg
- Ferrosilite: 100% Fe
- Two metal sites
- Fe also prefers M1 site
Optical Properties

- Dependent on Magnesium-Iron concentration
- Iron’s valence electrons leads to smaller band gap
Point Defects

- Defects that occur on a single lattice point
  - Substitutional defects
    - Replaces an host atom with an impurity atom
- Vacancy defects
  - Removal of one atom
  - Schottky defects
    - Removal of 2 charge neutral atoms
Space Weathering

- Creates point defects
- Micrometeorite impacts
- Solar-wind sputtering
- Interactions with cosmic rays
Finite Size Effects

Small System
Mg1O3

Larger System
Mg1O3
Empirical Potentials

- A method of measuring lattice energies and mechanical properties of a crystal structure with respect to the atomic positions and interactions

\[ \Phi_{12}(r) = A \exp(-Br) - \frac{C}{r^6} \] **Buckingham Potential**

\[ V(r) - D_e = D_e(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}) \] **Morse Potential**
About Empirical Potentials

- Works well with large systems where DFT would take too long
- Not as accurate as DFT
- e.g. Coulomb, Buckingham, Morse, and Lennard-Jones

\[ U(r) = \frac{z_i z_j e^2}{r} + D_{ij} \left[ \left\{ 1 - e^{-a_{ij}(r-r_0)} \right\}^2 - 1 \right] + \frac{C_{ij}}{r^{12}} \]

Pedone's potential
This Application of Empirical Potentials

- Relaxation of crystal structures
- Fe substitution in olivine silicates
- Schottky Defects

<table>
<thead>
<tr>
<th>Olivine</th>
<th>Fe1</th>
<th>Fe2</th>
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<tbody>
<tr>
<td>Pedone gulp large</td>
<td>-8300.038193</td>
<td>-8300.07427</td>
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<tr>
<td>Pedone fit gulp large</td>
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<td>Pedone fit gulp small</td>
<td>-9571.866503</td>
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</tbody>
</table>

Fe substitution into olivine in both small and large unit cells
Mechanical Properties of Relaxed Structures

- Relaxed olivine and orthopyroxene silicates
- Referenced empirical potentials of olivine and orthopyroxene calculations from academic articles

Results
- Lattice parameters (a, b, c)
- Elastic Constants
- Bulk Modulus
- Shear Modulus
- Young's Modulus
Schottky Defects

- Metals on M1 or M2 sites and oxygen removed
- The energies were compared
- Most favored: Mg1-O1
- Least favored: Mg2-O2

<table>
<thead>
<tr>
<th>Mg 1 removed</th>
<th>distance from Mg 1</th>
<th>Schottky Energy</th>
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<tbody>
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<table>
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</table>
Glass

- Heated up Olivine and Orthopyroxene solid crystal structures to 5000K
- Solid crystals $\rightarrow$ Liquid crystals
- Slowly cooled liquid crystals into glass (annealing)

Forsterite Liquid at 5000 K
Future Work

- Bigger cell sizes
- Further study optical properties
- Properties of olivine as function of iron content