Appendix 2 SAMPLE INPUT FILES FOR COMPUTER SIMULATIONS

A2.1 INTRODUCTION

In this appendix, an annotated set of General Utility Lattice Program (GULP, Gale 1997) input files is given. This set was used for the computer simulations presented in Chapters 4 and 5, and could serve as a template for future users of GULP interested in studying the energetics of trace element incorporation into minerals.

The lattice static computer modelling discussed in this thesis consists of two complementary types. First, perfect crystal lattices (i.e. lattices which do not contain any defects) are simulated. Second, one or more trace elements are inserted into these perfect lattices, and the energy difference between perfect and defective lattices is calculated. Sample GULP input files for simulation of perfect and defective lattices are discussed in sections A2.3 and A2.4 respectively. In section A2.2, an explanation is given of the format of the library file, containing the potential parameters used in both types of simulations.

A2.2 POTENTIAL PARAMETERS AND THE LIBRARY FILE

As discussed in Chapters 4 and 5, the simulations use a consistent set of interatomic potential parameters, which quantify the long-range and short-range interactions between the ions in the crystal structure. These interactions can be split into several independent energy terms, which all need to be taken into account for an accurate GULP simulation of any lattice (perfect or defective) to result. Each of these energy terms is described in the so-called library file, called *library.lib*, given in Table A2.1.

TABLE A2.1. GULP library file (‘library.lib’)

```
species
Li core 1.0
O core 0.86902
O shell -2.86902
Na core 1.0
Mg core 2.0
Al core 3.0
Si core 4.0
K core 1.0
Ca core 2.0
Sc core 3.0
Cr core 3.0
Mn core 2.0
Fe core 2.0 #( or 3.0) #
Co core 2.0
Ni core 2.0
Rb core 1.0
Sr core 2.0
Ba core 2.0
La core 3.0
Nd core 3.0
Eu core 2.0 # (or 3.0) #
Gd core 3.0
Ho core 3.0
Yb core 3.0
Lu core 3.0
buckingham
Li   core O shel 262.54   0.3476 0.0    0.0 12.0
O    shel O shel 22736.92 0.1490 27.880 0.0 12.0
Na   core O shel 1266.84  0.3065 0.0    0.0 12.0
Mg   core O shel 1428.50  0.2945 0.0    0.0 12.0
Al   core O shel 1114.90  0.3118 0.0    0.0 12.0
Si   core O shel 1283.91  0.3205 10.654 0.0 12.0
K    core O shel 680.44   0.3798 0.0    0.0 12.0
Ca   core O shel 1090.39  0.3437 0.0    0.0 12.0
Sc   core O shel 1299.40  0.3312 0.0    0.0 12.0
Cr   core O shel 1734.10  0.3010 0.0    0.0 12.0
Mn   core O shel 1007.40  0.3262 0.0    0.0 12.0
Fe   core O shel 1207.59  0.3084 0.0    0.0 12.0 # (2+) #
Fe   core O shel 1102.40  0.3299 0.0    0.0 12.0 # (3+) #
Co   core O shel 1491.70  0.2951 0.0    0.0 12.0
Ni   core O shel 1582.50  0.2882 0.0    0.0 12.0
Rb   core O shel 919.38   0.3772 0.0    0.0 12.0
Sr   core O shel 1375.00  0.3500 0.0    0.0 12.0
Ba   core O shel 931.70   0.3949 0.0    0.0 12.0
La   core O shel 1439.70  0.3651 0.0    0.0 12.0
Nd   core O shel 1379.90  0.3601 0.0    0.0 12.0
Eu   core O shel 1248.50  0.3556 0.0    0.0 12.0 # (2+) #
Eu   core O shel 1358.00  0.3556 0.0    0.0 12.0 # (3+) #
Gd   core O shel 1336.80  0.3551 0.0    0.0 12.0
Ho   core O shel 1350.20  0.3487 0.0    0.0 12.0
Yb   core O shel 1309.60  0.3462 0.0    0.0 12.0
Lu   core O shel 1347.10  0.3430 0.0    0.0 12.0
three-body
Si   core O shel O shel   2.094  109.47 2.0 2.0 3.0
spring
O core O shel 74.923
```

The long-range, electrostatic or Coulombic term is energetically the most important. It describes the sum of all attractive energies U_C between two adjacent ions of charges q_i and q_j as a function of the distance between the cores of the ions (r_{ij}):

$$U_C = \frac{1}{2}\sum\left(\frac{q_i q_j}{r_{ij}}\right) \tag{A2.1}$$

In Eqn. A2.1, the factor 0.5 is inserted to ensure that all ion pairs are counted only once. U_C for individual pairs of atoms can be negative or positive, depending on whether the charges of the ions are opposite or like. The charges q for each element featuring in our simulations are given in lines 2-26 of *library.lib* (Table A2.1), preceded by the key word `species` (line 1). The integral charges are assumed to fully reside in the core of each species, except for oxygen which has a bulk charge of -2.0, divided over a core and a shell. The explanation for this is given below.

The short-range, non-Coulombic term consists of two-body short-range repulsions and attractions. Neighbouring atoms repel each other due to electron cloud overlaps. Pair-wise repulsive energies are described by

$$E_r = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) \tag{A2.2}$$

with A_{ij} and ρ_{ij} constants depending on the ion types, and r_{ij} the interatomic distance. Pairs of neighbouring ions attract each other due to dispersion and covalence (Van der Waals-interactions), through interaction of instantaneous momentary dipoles. The energy associated with this attraction is of the form

$$E_a = -\frac{C_{ij}}{r_{ij}^6} \tag{A2.3}$$

for each pair, with C_{ij} a constant depending on the nature of the two ions of the pair. The net 2-body-term, U_{SR}, is therefore of the form

$$U_{SR} = \frac{1}{2}\sum\left(A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right)-\frac{C_{ij}}{r_{ij}^6}\right) \tag{A2.4}$$

This potential description is called a Buckingham potential. For each cation-oxygen pair used in the simulations, values for A_{ij} (in eV), ρ_{ij} (in Å) and C_{ij} (in eV·Å^6) are listed in lines 28-53 (Table A2.1), preceded by the keyword `buckingham` (line 27). For each cation-oxygen pair, the values of these three constants are followed by the range (in Å) over which the potential is evaluated.

For silicate minerals, U_{SR} alone (which is by nature a central, angle-independent force) has been proven to be insufficient for an accurate description of lattice energies. Angle-dependent (three-body), covalent forces are also important, especially in the case of O-Si-O groups. This covalent term, summed over all O-Si-O groups, is of the form

$$U_{THB} = \sum\left(K_{ijk}\left(\theta_{ijk}-\theta_0\right)^2\right) \tag{A2.5}$$

with K_{ijk} a constant, θ_{ijk} the observed O-Si-O angle and θ_0 the ideal O-Si-O angle. Values of K_{ijk} (in eV rad^{-2}) and θ_0 (in degrees) are given in line 55 of Table A2.1, preceded by the keyword `three-body`. The constants are followed by three additional values which provide GULP with initial values (in Å) of the 2 Si-O distances and the O-O distance in each O-Si-O group, respectively.

Finally, account was taken of the energetic effect of permanent dipole moments, due to polarisable oxygen ions. The shell model of Dick and Overhauser (1958) was used. Oxygen polarisability was simulated by splitting the total charge of each oxygen ion (-2.0) into a positive core (charge +0.86902, line 3 in Table A2.1) and a negative shell (charge –2.86902, line 4 in Table A2.1). Core and shell are linked by a spring ,with spring constant k, and core-shell interaction is quantified using

$$U_{CS} = \sum \frac{1}{2} k x^2 \tag{A2.6}$$

where x is the core-shell separation (in Å). The value used for k (in eV Å^{-2}) is given in line 57 of *library.lib* (Table A2.1), preceded by the keyword `spring`.

A2.3 SIMULATION OF PERFECT LATTICES

As explained in Chapter 4, during simulations of perfect lattices, the atomic positions, and with those the interatomic distances r_{ij}, are varied with the aim of minimising the total internal energy, $U_C + U_{SR} + U_{THB} + U_{CS}$. Table A2.2 gives a sample GULP input file for such a simulation. The first line of the input file consists of a series of GULP keywords. `opti` is used for an energy minimisation with respect to geometrical variables (i.e., lattice vectors), `prop` signals calculation of bulk lattice properties. Minimisation can be performed at constant volume (i.e., unit cell dimensions stay the same as in the input file, with atoms moving within the cell) or at constant pressure (i.e., atomic coordinates and unit cell dimensions are allowed to vary). All simulations in Chapters 4 and 5 were performed at constant pressure, hence the keyword `conp` in line 1 of Table A2.2. Crystal symmetry was turned off after generation of the unit cell with the keyword `nosym`, and `full` was used so that the structure was written out as a full structure rather than a primitive cell. In the case of garnets, the full structure consists of 256 species: 24 X-site cations, 16 Y-site cations, 24 Z-site cations, 96 O cores and 96 O shells)

In order for GULP to simulate perfect crystal lattices, the potential parameters discussed in the previous section are combined with an initial trial structure. This initial structure includes (1) Lattice vectors (lines 2-3, unit cell edges *a, b* and *c* (in Å), and angles α, β, γ (in degrees). The six so-called flags at the end of line 3 define which of these are to be varied during the simulations. (2) Species types and positions (using fractional *x*, *y* and *z* coordinates, lines 4-9) and crystal symmetry (space group, given in lines 10-11).

The potential parameters to be used in the simulation (taken from *library.lib*, discussed in the previous section) are given in line 12.

TABLE A2.2. Sample GULP input file for simulation of perfect mineral lattice (pyrope garnet, $Mg_3Al_2Si_3O_{12}$)

```
Line  Code
1     opti prop conp nosym full
2     cell
3     11.459 11.459 11.459 90. 90. 90. 1 1 1 0 0 0
4     frac
5     Mg  core .125 .000 .250
6     Al  core .000 .000 .000
7     Si  core .375 .000 .250
8     O   core .03285 .05015 .65335
9     O  shell .03285 .05015 .65335
10    space
11    I a 3 d
12    library library.lib
```

A2.4 SIMULATION OF DEFECTIVE LATTICES

The output of simulations for perfect crystal lattices gives the optimised lattice vectors and the total lattice energy of the final structure. As described in Chapter 4, this optimised structure is then used for simulations of defective lattices. In Table A2.3, a sample GULP input file for simulation of defective mineral lattices is given. Keywords in line 1 are similar to those in Table A2.2, but the keyword `prop` is replaced by the keywords `defect` and `regi`, to denote a defect calculation based on the two-region approach (see Chapter 4 for explanation). Unit cell parameters and fractional coordinates of all species, given in lines 2-22, are taken directly from the output of the perfect lattice simulation (which is why there is a difference between the values in Tables A2.2 and Table A2.3, although both are concerned with a simulation of pyrope).

In the defect calculations, the positions of all 256 species are entered in the input file, so that symmetry has already been incorporated. The space group of the resulting structure is therefore 1 (lines 23-24 in Table A2.3). In lines 25-31, details are presented of the insertion of trace elements into the perfect lattice. These include the type and charge of the trace elements (in the sample file La^{3+} and charge-balancing Li^{1+}, lines 25-27), and the defect centres, i.e. the elements in the perfect lattice that are to be replaced (in our case 2 Mg ions, lines 28-29). In lines 30 and 31, the keyword `impurity`, followed by two species names is used to signal the actual replacements. Line 32 gives the radii (in Å) of the inner and outer regions (using the terminology of Catlow and Mackrodt 1982) centered on the defect listed first (i.e. in line 28). Details of this two-region approach are given in Chapter 4. Finally, as in the perfect lattice simulation, a reference to the potential parameters to be used in the simulation (taken from *library.lib*, discussed in section A4.2) is given in line 33. Output of these defect calculations are the initial and final defect energies forming the basis for the data presented in Chapters 4 and 5.

TABLE A2.3. Sample GULP input file for simulation of defective mineral lattice

```
Line  Code
1     opti defect regi conp full
2     cell
3     11.281 11.281 11.281 90. 90. 90. 1 1 1 0 0 0
4     frac
5     Mg1   core     0.625000    0.500000    0.750000
6     Mg2   core     0.750000    0.625000    0.500000
7     Mg    core     0.000000    0.250000    0.125000
8     Mg    core     etc. etc.
9     Al    core     0.750000    0.750000    0.750000
10    Al    core     0.250000    0.250000    0.250000
11    Al    core     0.750000    0.250000    0.250000
12    Al    core     etc. etc.
13    Si    core     0.875000    0.500000    0.750000
14    Si    core     0.375000    0.000000    0.250000
15    Si    core     0.125000    0.000000    0.750000
16    Si    core     etc. etc.
17    O     core     0.031827    0.051913    0.651869
18    O     core     0.531827    0.551913    0.151869
19    O     core     etc. etc.
20    O     shel     0.037262    0.046039    0.656156
21    O     shel     0.537262    0.546039    0.156156
22    O     shel     etc. etc.
23    space
24    1
25    species
26    La core 3.0
27    Li core 1.0
28    centre Mg1 core
29    centre Mg2 core
30    impurity La Mg1
31    impurity Li Mg2
32    size 8.0 14.0
33    library library.lib
```