This document explains how to use Quantum ESPRESSO (QE) interfaced with Phonopy to determine the phonon spectra of hexagonal Silicon. Under extreme conditions, Si in the cubic diamond phase (d-Si) transforms into a hexagonal wurtzite crystal, known as lonsdaleite (2H).

The QE package itself has a force constants calculation environment based on Density Functional Perturbation Theory (DFPT) for phonon calculations. However, this document provides a step-by-step explanation of how to calculate phonon-phonon interaction and related properties using phonopy interfaced with QE. Phonopy uses the finite displacement and supercell approach to determine the phonon spectra of any given material.

Background Information

In equilibrium, the forces on all atoms in a crystal are zero. When an atom is displaced, this generates a restoring force on the atom itself and generates forces on all other atoms as well. Analysis of the forces associated with a systematic set of displacements provides a series of phonon frequencies. First-principles phonon calculations with a finite displacement method can be made in this way. The properties of phonon can be calculated from the dynamical matrix, which is determined by force constants.

Every calculation done with phonopy starts with a supercell with some displaced phonon atom. Finite atomic displacement distance is set as specified value when creating supercells with displacements. The default displacement amplitude is 0.01Å (0.02bohr).

For this task, install both the Quantum Espresso and phonopy codes on your computer. For Quantum espresso, one can just install the quantum mobile package on a virtualbox machine while phonopy can be best installed using conda on the terminal.

```
conda install -c atztogo phonopy
```

Structure of lonsdaleite Silicon

Hexagonal Silicon (Lonsdaleite) has a space group $P6_3/mmc$ and lattice vectors: a=$a(1,0,0)$, b=$a(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0)$ and c=$a(0,0,N\sqrt{\frac{2}{3}})$ where N is the number of layers in the hexagonal closed pack unit cell. Download from a crystallographic database a file that contains a full specification of the crystal structure of silicon in the hexagonal wurtzite structure at room temperature. This file has the so-called cif-format, a common crystal structure definition format that is human-readable as well as machine-readable.

```
wget http://aflow.org/CrystalDatabase/CIF/AB_hP4_186_b_b.cif
```

- Edit cif by changing all element to Si.
- Convert cif to a QE input file using the cif2cell tool.

```
cif2cell AB_hP4_186_b_b.cif -p quantum-espresso -o Si.hcp.in
```

```
_aflow_Pearson 'hP4'

_symmetry_space_group_name_Hall "P 6c -2c"
_symmetry_space_group_name_H-M "P 63 m c"
_symmetry_Int_Tables_number 186

_cell_length_a    3.82270
_cell_length_b    3.82270
_cell_length_c    6.26070
_cell_angle_alpha 90.00000
_cell_angle_beta  90.00000
_cell_angle_gamma 120.00000

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
2 x-y,x,z+1/2
3 -y,x-y,z
4 -x,-y,z+1/2
5 -x+y,-x,z
6 y,-x+y,z+1/2
7 -x+y,y,z
8 -x,-x+y,z+1/2
9 -y,-x,z
10 x-y,-y,z+1/2
11 x,x-y,z
12 y,x,z+1/2

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
Si1  Si1   2 b 0.33333 0.66667 0.37480 1.00000
Si2  Si2   2 b 0.33333 0.66667 0.00000 1.00000
```

Figure 1: Edited cif file

```
#*******************************************************************************
#*                    Generated by cif2cell 1.2.10 2020-07-06 2:45             *
#*    T. Bjorkman, Comp. Phys. Commun. 182, 1183-1186 (2011). Please cite generously.   *
#*                                                                             *
#*                                (Wurtzite)                                   *
#* Erich H. Kisi and Margaret M. Elcombe, Acta Crystallographica C 45, 1867-1870 (1989) *
#*******************************************************************************

&SYSTEM
  ibrav = 0
  A =    3.82270
  nat = 4
  ntyp = 1
/
CELL_PARAMETERS {alat}
  0.866025403784439  -0.500000000000000   0.000000000000000
  0.000000000000000   1.000000000000000   0.000000000000000
  0.000000000000000   0.000000000000000   1.637769116069794
ATOMIC_SPECIES
  Si   28.08500  Si_PSEUDO
ATOMIC_POSITIONS {crystal}
Si   0.333333333333333   0.666666666666667   0.374800000000000
Si   0.666666666666667   0.333333333333333   0.874800000000000
Si   0.333333333333333   0.666666666666667   0.000000000000000
Si   0.666666666666667   0.333333333333333   0.500000000000000
```

Figure 2: QE input file

Convergence testing

Convergence testing for basis set size, kmesh sampling and supercell size. Phonopy gives a default displacement distance of 0.02 a.u (bohr) in creating supercells. Phonopy uses a single point displacement to determine force constants, so it is important for the displacements to be in the harmonic region. The displacement must be large enough for the force amplitude

to overcome the noise levels, but not so large that anharmonic terms become noticeable. The way to test this is to plot $\frac{F}{x}$ against x (where x is the displacement distance), and inspect for which values of x the force constant becomes independent of the displacement (seen as a "plateau").

For this work, we adopted a $3\times3\times4$ supercell for the hcp Silicon unit cell and a displacement amplitude of 0.04385 bohr.

The Phonopy Workflow

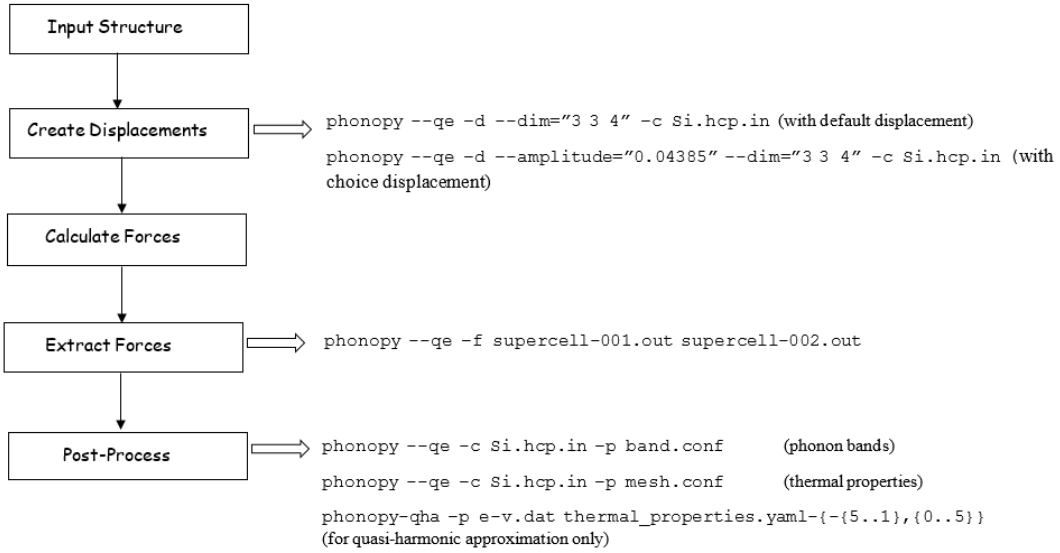

Figure 3: Workflow

Details of input files for Phonopy

band.conf

DIM = 3 3 4
BAND = 0.00 0.00 0.00 0.50 0.00 0.00 0.33 0.33 0.00 0.00 0.00 0.00 0.00 0.00 0.50 0.50 0.00 0.50 0.33 0.33 0.50 0.00 0.00 0.50 0.50 0.00 0.00 0.33 0.33 0.00
BAND_LABELS = \Gamma M K \Gamma A L H A M K
EIGENVECTORS = .TRUE.

mesh.conf

DIM = 3 3 4
MESH = 35 35 35
TPROP = .TRUE.
TMIN = 0
TMAX = 1000
TSTEP = 10

dos.conf

DIM = 3 3 4
MP = 35 35 35
GAMMA_CENTER = .TRUE.

e_v.dat

73.58538206 -2542.690187
75.16733351 -2542.791450
76.77179673 -2542.867604
78.39893077 -2542.920207
80.04889468 -2542.950749
81.72184751 -2542.960651
83.41794830 -2542.951263
85.13735609 -2542.923828
86.88022994 -2542.879702
88.64672889 -2542.819986
90.43701199 -2542.745776

NOTE: The volume and energy from QE must be converted to Å and eV respectively.

band-pdos.conf

ATOM_NAME = Si
DIM = 3 3 4
MP = 35 35 35
BAND = 0.00 0.00 0.00 0.50 0.00 0.00 0.33 0.33 0.00 0.00 0.00 0.00 0.00 0.00 0.50 0.50 0.00 0.50 0.33 0.33 0.50 0.00 0.00 0.50 0.50 0.00 0.00 0.33 0.33 0.00
BAND_LABELS = \Gamma M K \Gamma A L H A M K
DOS = .TRUE.
PDOS = 1 3, 2 4

NOTE: Details of each line is available on the phonopy website

Command line for plotting

Plot phonon bands

To plot the phonon bands, you need to prepare a band.conf file (see above)

```
phonopy --qe -c Si.hcp.in -p band.conf
```

To save a copy band in pdf format (ie band.pdf)

```
phonopy --qe -c Si.hcp.in -p -s band.conf
```

Alternatively, you can use an auxiliary tool available in phonopy to plot the bands

```
phonopy-bandplot band.yaml
```

If you desire to save a text file of the data which can be plotted with gnuplot

```
phonopy-bandplot --gnuplot band.yaml
```

Plot DOS and PDOS

To plot the density of states, you need an input file dos.conf (see above)

```
phonopy --qe -c dos.conf -p Si.hcp.in
```

To plot the band and project DOS side by side, you need the band-pdos.conf input (see above)

```
phonopy --qe -c band-pdos.conf -p Si.hcp.in
```

Plot Gruneisen Parameter

```
phonopy-gruneisen --qe orig plus minus --dim="3 3 4" --band="0.00 0.00 0.00  0.50 0.00 0.00  0.33 0.33 0.00  0.00 0.00 0.00  0.00 0.00 0.50  0.50 0.00 0.50  0.33 0.33 0.50  0.00 0.00 0.50  0.50 0.00 0.00  0.33 0.33 0.00" -p -c Si.hcp.in
```

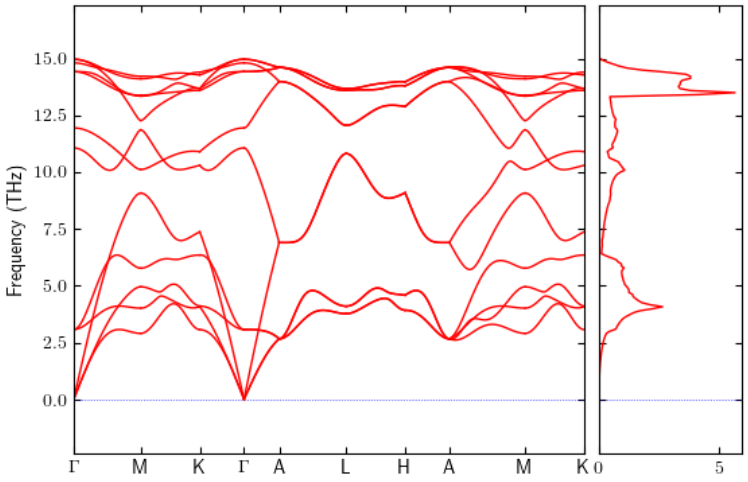

Figure 4: Phonon bands and DOS of Si Lonsdaleite

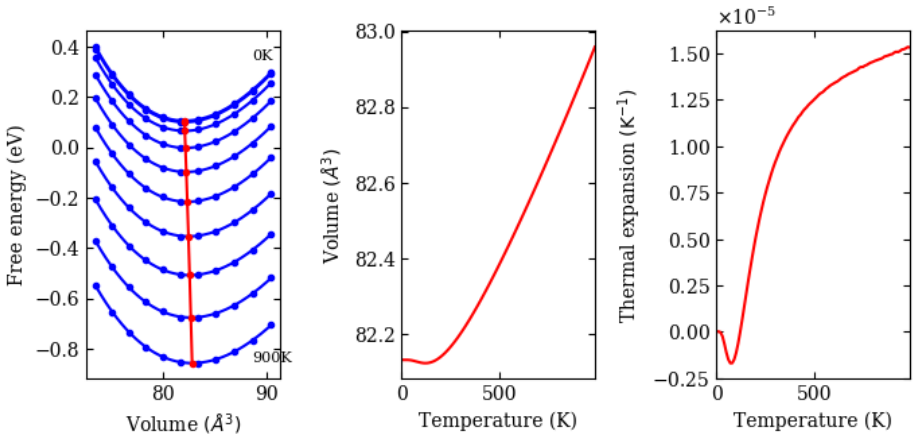

Figure 5: Lonsdaleite

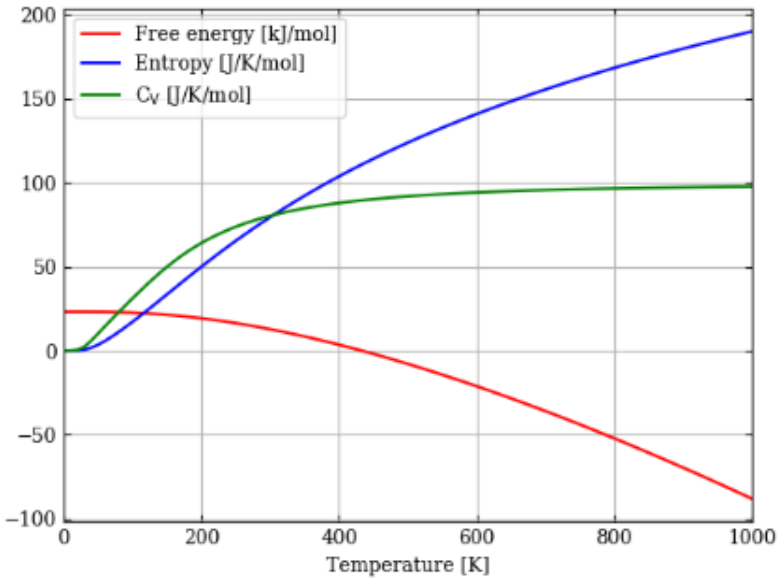

Figure 6: Specfic heat

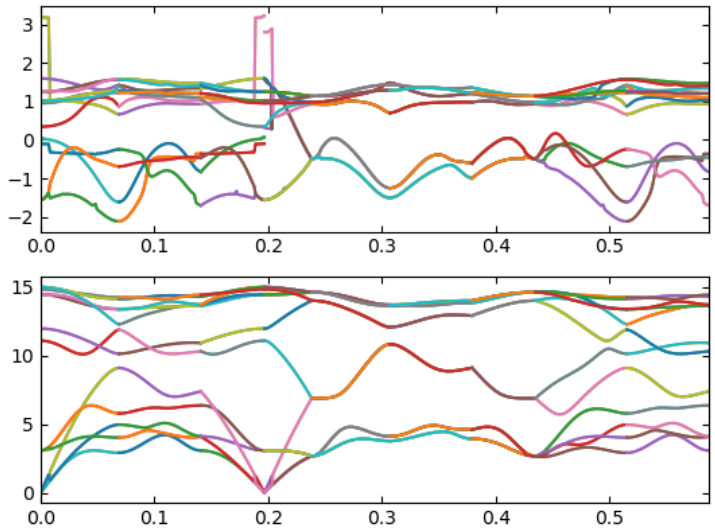

Figure 7: Phonon dispersion and mode Gruneisen parameter for 2H Silicon

APPENDIX

Reference https://phonopy.github.io/phonopy/qe.html

Run a simple calculation

1. Download cif

```
(base) max@qmobile:~/PHONON$ wget http://aflow.org/CrystalDatabase/CIF/AB_hP4_186_b_b.cif
--2020-09-30 13:16:56--  http://aflow.org/CrystalDatabase/CIF/AB_hP4_186_b_b.cif
Resolving aflow.org (aflow.org)... 184.168.235.1
Connecting to aflow.org (aflow.org)|184.168.235.1|:80... connected.
HTTP request sent, awaiting response... 301 Moved Permanently
Location: http://aflow.org/prototype-encyclopedia/CIF/AB_hP4_186_b_b.cif [following]
--2020-09-30 13:16:56--  http://aflow.org/prototype-encyclopedia/CIF/AB_hP4_186_b_b.cif
Reusing existing connection to aflow.org:80.
HTTP request sent, awaiting response... 200 OK
Length: 1405 (1.4K) [chemical/x-cif]
Saving to: 'AB_hP4_186_b_b.cif'

AB_hP4_186_b_b.cif                      100%[=============================================================================
================>]   1.37K  --.-KB/s    in 0s

2020-09-30 13:16:57 (74.3 MB/s) - 'AB_hP4_186_b_b.cif' saved [1405/1405]
```

2. Edit and convert cif to QE input file using any tool of your choice – cif2cell, cif2qe.sh (available on PW/tool directory of the QE package), Quantum ESPRESSO input generator and structure visualizer on materialscloud.org

   NOTE: Only ibrav = 0 type representation of crystal structure is supported.

```
(base) max@qmobile:~/PHONON$ ls
AB_hP4_186_b_b.cif  cif2qe.sh
(base) max@qmobile:~/PHONON$ vi AB_hP4_186_b_b.cif
(base) max@qmobile:~/PHONON$ ./cif2qe.sh AB_hP4_186_b_b > Si.hcp.in
(base) max@qmobile:~/PHONON$ ls
AB_hP4_186_b_b.cif  cif2qe.sh  Si.hcp.in
(base) max@qmobile:~/PHONON$
```

3. Perform all convergence testing for basis set size, kmesh sampling and supercell size.

4. Create supercells with displacements with `--qe` option of phonopy

   NOTE: A unit has to be specified for CELL_PARAMETERS and ATOMIC_POSITIONS in the QE input file.

Using the default amplitude displacement of phonopy and a $3 \times 3 \times 4$ supercell.

For Lonsdaleite, a displacement amplitude of 0.04385 bohr obtained by plotting Force against displacement is used.

A perfect $3 \times 3 \times 4$ supercell (supercell.in) and four $3 \times 3 \times 4$ supercells (supercell-xxx.in) of the conventional unit cell written in Si.hcp.in are created. In addition, phonopy_disp.yaml file is created.

5. Add necessary setting information to the supercell-xxx.in files.

   NOTE: A file "header.in" is specially made for this example and this file is found in same directory as the supercell-xxx files.

```
(base) max@qmobile:~/PHONON$ ls
AB_hP4_186_b_b.cif  phonopy_disp.yaml  supercell-001.in  supercell-004.in
cif2qe.sh           script             supercell-002.in  supercell.in
header.in           Si.hcp.in          supercell-003.in
(base) max@qmobile:~/PHONON$ cat header.in
&control
  calculation = 'scf',
  prefix = 'Si'
  outdir='./tmp'
  pseudo_dir = '.',
  tstress = .true.
  tprnfor = .true.
  verbosity = 'low'

 /
&system
  ibrav = 0
  nat   = 144
  ntyp  = 1
  ecutwfc = 75
/
&electrons
  mixing_beta = 0.7
  conv_thr =  1.0d-8

/

K_POINTS automatic
  5  5  3  0  0  0

(base) max@qmobile:~/PHONON$
```

   Execute the bash script which adds content of header.in to the supercell-xxx files and also rename them to si-xxx.in.

```
(base) max@qmobile:~/PHONON$ ls
AB_hP4_186_b_b.cif  cif2qe.sh  header.in  phonopy_disp.yaml  script.sh  Si.hcp.in  supercell-001.in  supercell-002.in
  supercell-003.in  supercell-004.in  supercell.in
(base) max@qmobile:~/PHONON$ cat script.sh
#!/bin/bash
for i in {001,002,003,004} ; do cat header.in supercell-$i.in >| si-$i.in; done



(base) max@qmobile:~/PHONON$ ./script.sh
(base) max@qmobile:~/PHONON$ ls
AB_hP4_186_b_b.cif  phonopy_disp.yaml  si-002.in  Si.hcp.in         supercell-003.in
cif2qe.sh           script.sh          si-003.in  supercell-001.in  supercell-004.in
header.in           si-001.in          si-004.in  supercell-002.in  supercell.in
(base) max@qmobile:~/PHONON$
```

6. Execute QE-PW supercell calculations to obtain force on atoms.

   NOTE: The .out files are the output of the Pwscf calculations and are supposed to contain the forces on atoms calculated by Pwscf.

```
(base) max@qmobile:~/PHONON$ ls
AB_hP4_186_b_b.cif  phonopy_disp.yaml  si-002.in  Si.hcp.in                      supercell-002.in  supercell.in
cif2qe.sh           script.sh          si-003.in  Si.pbe-n-kjpaw_psl.1.0.0.UPF  supercell-003.in
header.in           si-001.in          si-004.in  supercell-001.in               supercell-004.in
(base) max@qmobile:~/PHONON$ mpirun -np 2 ~/../../usr/local/bin/pw.x < si-001.in > si-001.out &
[1] 4078
(base) max@qmobile:~/PHONON$
```

7. Create FORCE_SETS that is used by phonopy.

```
(base) max@qmobile:~/PHONON$ ls
AB_hP4_186_b_b.cif  script.sh   si-002.out  si-004.out                    supercell-002.in  tmp
cif2qe.sh           si-001.in   si-003.in   Si.hcp.in                     supercell-003.in
header.in           si-001.out  si-003.out  Si.pbe-n-kjpaw_psl.1.0.0.UPF  supercell-004.in
phonopy_disp.yaml   si-002.in   si-004.in   supercell-001.in              supercell.in
(base) max@qmobile:~/PHONON$ phonopy --qe -f si-001.out si-002.out si-003.out si-004.out
                     _
  _ __   | |__    ___    _ __     ___    _ __   _   _
 | '_ \  | '_ \  / _ \  | '_ \   / _ \  | '_ \ | | | |
 | |_) | | | | | (_) | | |_) | | (_) | | |_) | |_| |
 | .__/  |_| |_|  \___/  |_.__/   \___/  | .__/ \__, |
 |_|                                     |_|    |___/
                                           2.6.1

Python version 3.6.9
Spglib version 1.14.1

Calculator interface: qe
Displacements were read from "phonopy_disp.yaml".
1. Drift force of "si-001.out" to be subtracted
 -0.00000000   0.00000000  -0.00000000
2. Drift force of "si-002.out" to be subtracted
 -0.00000000   0.00000000   0.00000000
3. Drift force of "si-003.out" to be subtracted
  0.00000000  -0.00000000   0.00000000
4. Drift force of "si-004.out" to be subtracted
  0.00000000  -0.00000000  -0.00000000
FORCE_SETS has been created.
                     _
   ___   _ __      __| |
  / _ \ | '_ \    / _` |
 |  __/ | | | |  (_| |
  \___| |_| |_|\__,_|

(base) max@qmobile:~/PHONON$
```

8. Prepare the band.conf and save in the same directory

```
(base) max@qmobile:~/PHONON$ cat band.conf
DIM = 3 3 4
BAND = 0.00 0.00 0.00   0.50 0.00 0.00   0.33 0.33 0.00  0.00 0.00 0.00  0.00 0.00 0.50   0.50 0.00 0.50
 0.33 0.33 0.50  0.00 0.00 0.50   0.50 0.00 0.00  0.33 0.33 0.00
BAND_LABELS = $\Gamma$  M   K  $\Gamma$  A   L   H   A   M   K
EIGENVECTORS = .TRUE.
FMIN = 0
FMAX = 20
(base) max@qmobile:~/PHONON$
```

9. Plot phonon bands

```
(base) max@qmobile:~/PHONON$ phonopy --qe -c Si.hcp.in -p band.conf
  _
 | |__   ___  _ __   ___   _ __  _   _
 | '_ \ / _ \| '_ \ / _ \ | '_ \| | | |
 | | | | (_) | | | | (_) || |_) | |_| |
 |_| |_|\___/|_| |_|\___(_) .__/ \__, |
                          |_|    |___/
                                 2.6.1

Python version 3.6.9
Spglib version 1.14.1

Calculator interface: qe
Crystal structure was read from "Si.hcp.in".
Unit of length: au
Band structure mode
Settings:
  Supercell: [3 3 4]
Spacegroup: Cmcm (63)
Use -v option to watch primitive cell, unit cell, and supercell structures.

Forces and displacements were read from "FORCE_SETS".
Computing force constants...
Max drift of force constants: -0.000125 (zy) 0.000000 (xx)

Reciprocal space paths in reduced coordinates:
[ 0.000  0.000  0.000] --> [ 0.500  0.000  0.000]
[ 0.500  0.000  0.000] --> [ 0.330  0.330  0.000]
[ 0.330  0.330  0.000] --> [ 0.000  0.000  0.000]
[ 0.000  0.000  0.000] --> [ 0.000  0.000  0.500]
[ 0.000  0.000  0.500] --> [ 0.500  0.000  0.500]
[ 0.500  0.000  0.500] --> [ 0.330  0.330  0.500]
[ 0.330  0.330  0.500] --> [ 0.000  0.000  0.500]
[ 0.000  0.000  0.500] --> [ 0.500  0.000  0.000]
[ 0.500  0.000  0.000] --> [ 0.330  0.330  0.000]
```