

DFT calculation of pressure induced phase transition in silicon

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1 Introduction

Under ambient pressure silicon forms a diamond crystal structure and is semiconducting, but at high pressures a phase transition to the metallic β -Sn structure will occur. The aim of this student project is to calculate the transition pressure using the open source program package Quantum ESPRESSO [1]. Quantum ESPRESSO (QE) is a Density Functional Theory (DFT) code that uses a plane wave basis combined with pseudopotentials to calculate the bandstructure of a given crystal. It can be downloaded for free from their website: This includes source files to compile it yourself, but they do in particular also provide **precompiled binaries for Windows**. QE consists of a large collection of programs that perform a variety of different calculations. The program that is used in this project is pw.x (pw.exe on Windows) which performs the plane wave DFT calculation. To help future students to get started with QE quickly, the calculation input files for this project are included and commented, to act as a starting point for other calculations using pw.x. This entire project was realized using QE 5.1.2 on a contemporary Windows laptop and took about 4 CPU hours, showing that simple band structure calculations are within the reach of personal computers.

2 Structure of the input file

To perform a band structure calculation, an input text file must be created that fully specifies the calculation to be performed. To start the calculation, pipe the input file into pw.x and pipe the program output to a text file for further analysis:

```
pw < inputfile.in > outputfile.out
```

The following is an example input file for a single-point calculation of silicon in the diamond structure.

```
&control
  calculation= 'scf'
  prefix= 'SI'
  pseudo_dir = 'C:\develop\QuantumEspresso\pseudo'
  outdir= './tmp/'
  tprnfor = .true.,
  tstress = .true.,
/
&system
 ibrav= 2, celldm(1)=10.1494786191,
 nat= 2, ntyp= 1,
 ecutwfc= 40
/
&electrons
  conv_thr = 1.0D-6
  mixing_beta = 0.4
/
ATOMIC_SPECIES
Si 28.085 Si.pbe-mt_fhi.UPF
ATOMIC_POSITIONS crystal
Si 0.0 0.0 0.0
Si 0.25 0.25 0.25
K_POINTS automatic
16 16 16 0 0 0
```

Note the following formatting details:

- All indentations use whitespaces: Do not use tabulator.
- All linebreaks use the **Unix linebreak** `'\n'`: Even if QE runs on a windows machine, you must not use the windows line terminator `'\r\n'`. If you copy this example into a text file on a Windows machine, open it with a decent plain text editor (e.g. notepad++) and verify that the lines are terminated by `'\n'` only.

All input parameters are documented at http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html. Some key parameters, used in this input file are:

- **calculation**: `'scf'` means self-consistent field and is the starting point for any single point calculation.
- **pseudo_dir**: Specifies the directory where the pseudopotentials for this calculation are stored. Pseudopotentials are effective potentials for the valence electrons. You can download a pseudopotential for almost any atom from the QE website.
- **ibrav**: Type of bravais lattice for your crystal. Since the diamond structure is an fcc lattice with 2 atoms in the basis we specify `ibrav=2` (equals fcc). See the online documentation for all other bravais lattices.
- **nat**: Number of atoms in the primitive unit cell. For diamond there are 2 atoms in the unit cell.
- **celldm(1)**: Lattice constant of the unit cell in atomic units (= bohr radii), not in angstrom.
- **ecutwfc**: Kinetic energy cut off. Implicitly specifies the highest wavenumber to be used in the plane wave expansion by specifying its kinetic energy. Always *test that your calculations have converged* with respect to this parameter.
- **ATOMIC_SPECIES**: Lists all types of atoms that occur in your unit cell with name, atomic mass and pseudopotential filename.
- **ATOMIC_POSITION**: Lists the position of the atoms in the primitive unit cell as multiples of the primitive lattice vectors. (0,0,0) and (0.25,0.25,0.25) are the positions for the diamond structure.
- **K_POINTS**: k-points to evaluate the dispersion relationship. *automatic* will generate a 3D lattice of k-points. To calculate the bandstructure along high symmetry lines you can manually list the desired k points.

The output file contains various results of the calculation, most importantly it contains the total energy. The line containing the total energy is preceded by a `'!'` to allow easy data extraction.

3 Calculation of phase transition

All subsequent calculations were performed using the pseudopotential `Si.pbe-mt_fhi.UPF` obtained from the QE website <http://www.quantum-espresso.org/pseudopotentials>. For the calculation of this phase transition, only the electronic part to the total energy was considered, in particular no phonon contributions were included. Therefore the results are only strictly valid at low temperatures, but comparison to experiments 4 justifies this approach.

3.1 Checking convergence

It is vitally important that all your calculations have converged with respect to the cut-off energy and the number of k points, otherwise all results might be meaningless. To

check for convergence, the same calculation was done with different cut-off energies and number of k-points per dimension and its total energy plotted in Fig. 1.

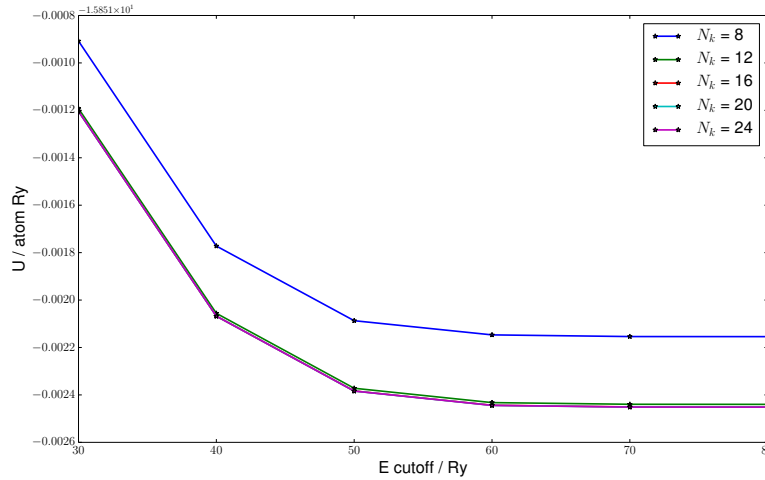


Figure 1: Internal energy of Si in the diamond structure as a function of cutoff energy and number of k points.

Convergence is achieved at $E_{cut} \geq 60$ Ry and $N_k \geq 16$.

3.2 Internal energy over volume

To calculate the phase transition it is necessary to calculate the enthalpy as a function of pressure:

$$H(p) = U(V(p)) + pV \quad (1)$$

Therefore it is necessary to evaluate the internal energy for different unit cell volumes. In the diamond structure the only degree of freedom in the unit cell is the lattice constant a . For the β -Sn phase - which consists of 2 atoms on a tetragonal bravais lattice - two degrees of freedom have to be varied: The lattice constant a as well as the asymmetry ratio c/a . Fig. 2 shows that the internal energy is minimized by $c/a = 0.55$. For both crystal structures the internal energy was evaluated for a range of different volumes, by repeatedly calling pw.x with different lattice constants. Then the enthalpy was calculated for a range of pressures (Eq. 1), and plotted in Fig. 3. At any given pressure, the crystal will occur in the configuration of minimum enthalpy. Fig. 3 shows that at $p = 0$, the diamond structure has the minimum enthalpy, but as pressure increases the enthalpy of the diamond structure rises faster, due to its larger volume, until at around $p = 20$ GPa, the enthalpies are equal. At higher pressures the crystal will transform to the β -Sn configuration.

The pressure at which the phase transition occurs can be directly seen from Fig. 4, which plots H as a function of pressure p . At a pressure of 19.6 GPa the enthalpies of the diamond structure and the β -Sn structure are equal.

Fig. 5 shows the dependance of the unit cell volume on pressure. The derivative of this curve is directly related to the bulk modulus of the crystal. During the transition from the diamond structure to the β -Sn structure, the crystal volume suddenly decreases by 24 %.

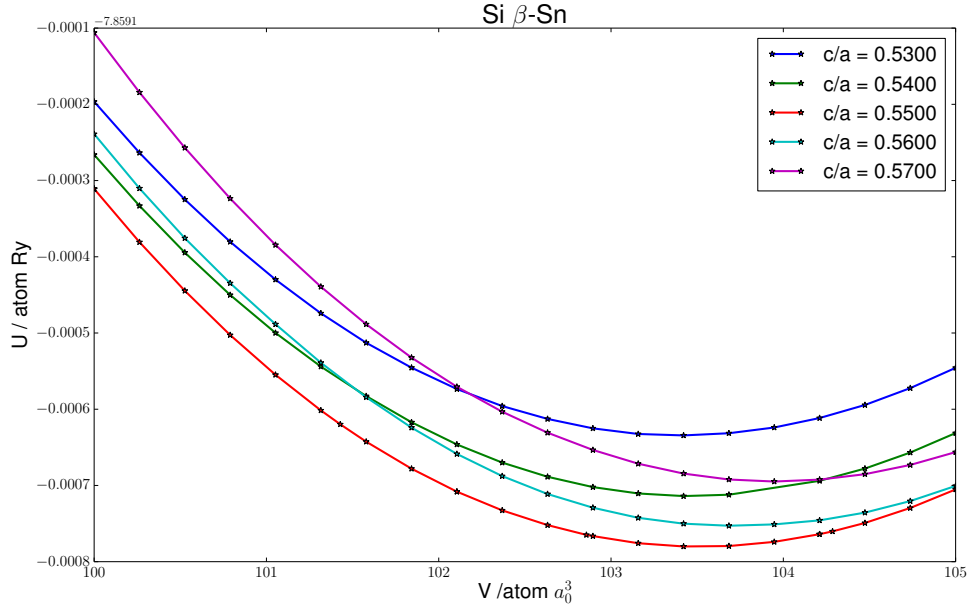


Figure 2: Internal energy of Si in the β -Sn structure as a function of volume and c/a ratio. For all volumes in this range the energy is minimized by $c/a = 0.55$.

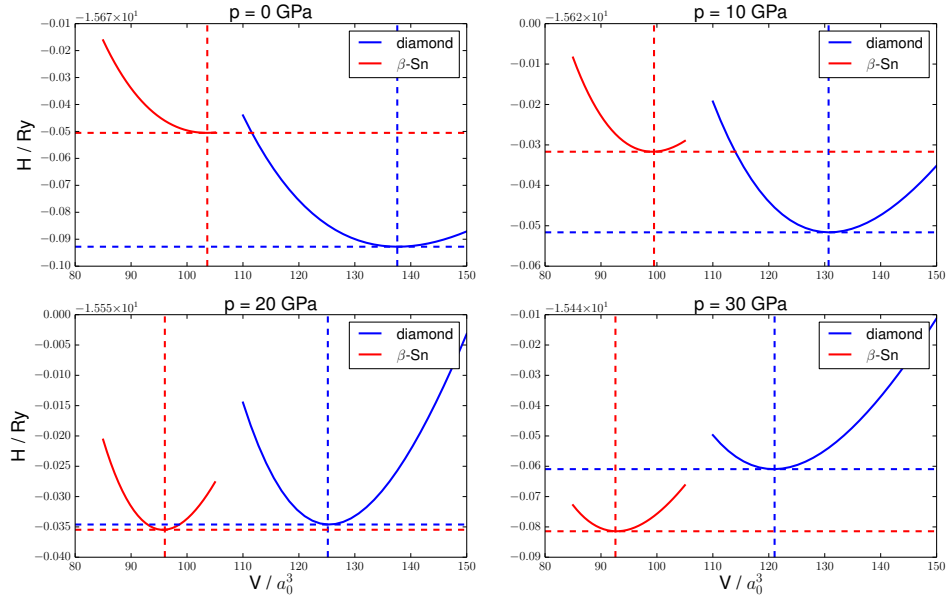


Figure 3: Enthalpy of both crystal structures for various applied pressures as a function of unit cell volume / atom. For low pressures the enthalpy minimum lies on the diamond curve, for high pressures it is found on the β -Sn curve.

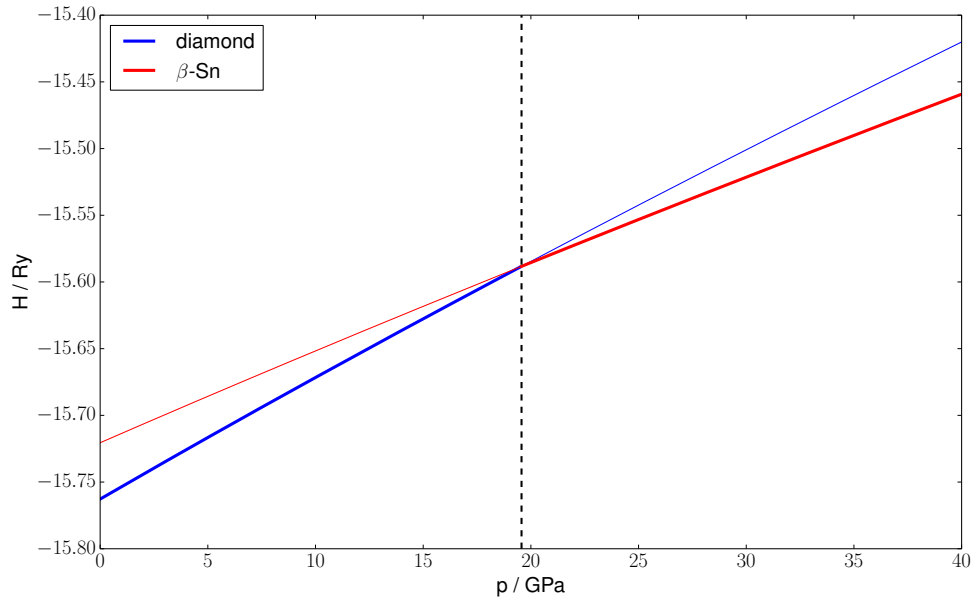


Figure 4: Enthalpy as a function of pressure. The phase transition occurs at 19.6 GPa.

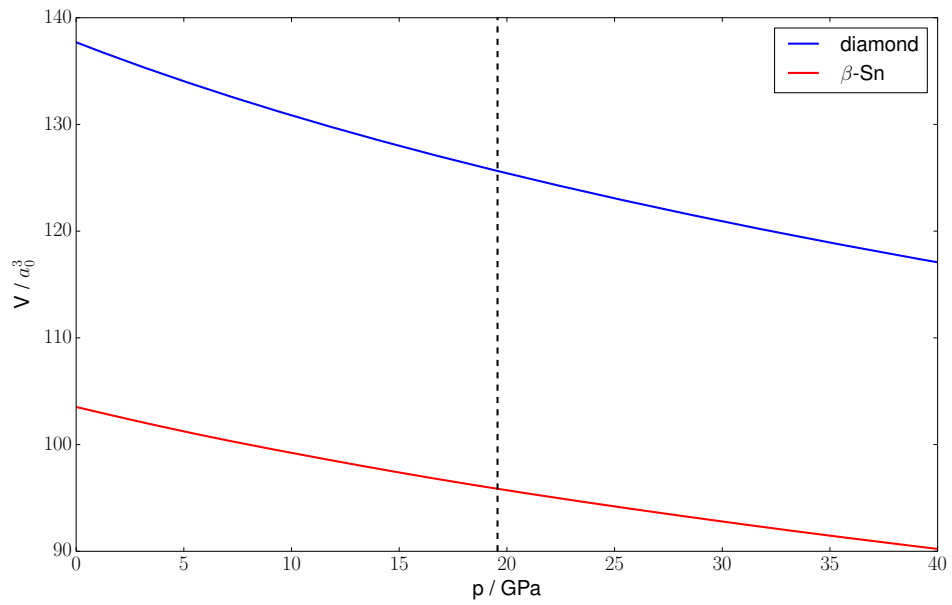


Figure 5: Equation of state for both crystal structures.

At the phase transition (dotted line) the volumes differ by 24 %.

4 Comparison to experimental data

High pressure experiments with Si were performed by Minomura and Drickamer [2]. They found a strong decrease in electrical resistance between 19.5 - 20 GPa (Fig. 6), which is in excellent agreement with the 19.6 GPa obtained by this DFT calculation. The electrical resistance drops sharply because Silicon transforms from a poorly conducting semiconducting material to a well conducting metal.

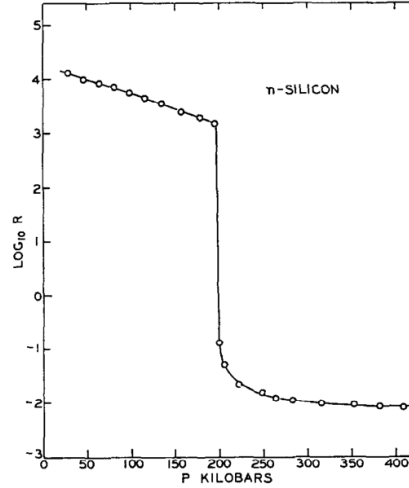


FIG. 1. Resistance vs. pressure—*n*-Silicon.

Figure 6: Plot by Minomura and Drickamer [2]: At 20 GPa (= 200 kBar) Si transforms from the semiconducting diamond structure to the metallic β -Sn structure.

5 Conclusion

The structural phase transition of Si from the diamond phase to the β -Sn phase has been calculated using the DFT package Quantum ESPRESSO. The calculated transition pressure of 19.6 GPa is in excellent agreement with experimental data.

References

- [1] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, “Quantum espresso: a modular and open-source software project for quantum simulations of materials,” *Journal of Physics: Condensed Matter*, vol. 21, no. 39, p. 395502 (19pp), 2009.
- [2] H. G. D. S. Minomura, “Pressure induced phase transitions in silicon, germanium and some iii-v compounds,” *J. Phys. Chem. Solids Pergamon Press*, vol. 23, pp. 451–456, 1962.

6 Appendix

These input files were used for the calculation of the total energy in the diamond and β -Sn phase respectively. Please refer to Sec. 2 for further documentation and important formatting notes for copying these input files.

6.1 Input file for the diamond phase

The following input file is almost identical to the one presented in Sec. 2. Major difference is only the higher accuracy (bigger cut-off energy and larger number of k-points).

```
&control
  calculation= 'scf'
  prefix= 'SI'
  pseudo_dir = 'C:\develop\QuantumEspresso\pseudo'
  outdir= './tmp/'
  tprnfor = .true.,
  tstress = .true.,
/
&system
  ibrav= 2, cellldm(1)=10.1494786191,
  nat= 2, ntyp= 1,
  ecutwfc= 60
/
&electrons
  conv_thr = 1.0D-6
  mixing_beta = 0.4
/
ATOMIC_SPECIES
Si 28.085 Si.pbe-mt_fhi.UPF
ATOMIC_POSITIONS crystal
Si 0.0 0.0 0.0
Si 0.25 0.25 0.25
K_POINTS automatic
24 24 24 0 0 0
```


6.2 Input file for the β -Sn phase

```
&control
  calculation= 'scf'
  prefix= 'SI'
  pseudo_dir = 'C:\develop\QuantumEspresso\pseudo'
  outdir= './tmp/'
  tprnfor = .true.,
  tstress = .true.,
/
&system
  ibrav= 7, celldm(1)=8.85111832357, celldm(3)=0.55,
  nat= 2, ntyp= 1,
  ecutwfc= 60,
  occupations= 'smearing'
  nbnd= 12
  degauss = 0.0001
/
&electrons
  conv_thr = 1.0D-6
  mixing_beta = 0.4
/
ATOMIC_SPECIES
Si 28.085 Si.pbe-mt_fhi.UPF
ATOMIC_POSITIONS crystal
Si 0.0 0.0 0.0
Si 0.5 0.25 -0.25
K_POINTS automatic
24 24 24 0 0 0
```

Major differences - compared to the diamond input - file are:

- **Crystal structure:** β -Sn is a body-centered tetragonal bravais lattice (ibrav=7) with 2 atoms in the unit cell. The ratio c/a is specified as celldm(3).
- **occupations= 'smearing':** Because β -Sn Si is a metal, there are filled states energetically right next to empty states. When the SCF cycle has not yet fully converged, it is not yet clear which states will be filled, and which ones will be empty. Therefore in each SCF iteration different states might be filled, leading to largely different charge densities and problems with convergence. To avoid this problem, also states that are above the Fermi level are being populated (similar to the occupation at $T > 0$, given by the Fermi function). The energy spread (in Ry) around the Fermi level is given by the parameter degauss and should be a small energy to not introduce a large error in total energy.