

1 Linux introduction

Linux is *the* main tool for scientific computation. Virtually all important scientific software is available for the Linux OS, usually in form of plain source code, so it can be compiled for your specific hardware in order to run highly optimized. This is a crucial point since physical or chemical computations can easily take several days to weeks or even months. It is therefore necessary that users of such computer programs are familiar with the basic commands on the so called “command line”, i.e. a terminal where commands can be entered in.

In this computer course, we will first restrict to the visual interface that is installed on your computers, which is the Gnome desktop.

- Read additional infos PDF!
- Power on your lab computer, switch to Linux, use Gnome, navigate, create folders etc.

2 Revision: Model of crystal structures

In solid state physics, probably the most essential concept is the one of crystalline systems. The main property of a crystal is its symmetry. Virtually all other physical properties can be deduced from it. From a mathematical point of view, crystallography is basically nothing but applied group theory.

In this course, we want to have a look at some specific types of crystals which are highly symmetric and thus easy and quick to compute. But first some recap of what you should already know. Think about the Diamond structure:

1. What basic crystal lattice is behind this structure? What else can you tell about that crystal?

Solution: fcc with basis $[(0, 0, 0), (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})]$

2. What other compounds that crystallize in this system do you know?

Solution: C, Si, Ge

3. Are there any other important basic structures that you know of?

Solution:

- Sphalerit/Zincblende: same as diamond but two different atoms in basis
- Wurzit (ZnS): hexagonal lattice (ABA stacking) with basis $[(0, 0, 0), (\frac{1}{3}, \frac{2}{3}, \frac{1}{2})]$
- Rocksalt/Halite (NaCl): fcc lattice with basis $[(0, 0, 0), (\frac{1}{2}, 0, 0)]$
- Caesium Chloride (CsCl): simple cubic (sc) with basis $[(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})]$
- Graphite: hexagonal with carbon atoms in two layers
 $A = [(0, 0, 0), (\frac{2}{3}, \frac{1}{3}, 0)]$ and $B = [(0, 0, \frac{1}{2}), (\frac{2}{3}, \frac{1}{3}, \frac{1}{2})]$

4. How many atoms does the fcc, bcc and diamond unit cell contain? Draw them (without basis)!

Solution:

Conventional fcc unit cell:

- corner atoms: $8 \times \frac{1}{8} = 1$
- face atoms: $6 \times \frac{1}{2} = 3$
- $\sum = 4$

Conventional bcc unit cell:

- corner atoms: $8 \times \frac{1}{8} = 1$
- center atoms: 1
- $\sum = 2$

Each primitive unit cell contains only 1 single lattice point per definition and consequently the same number of atoms as there are elements in the basis.

Since the diamond structure is fcc plus basis with 2 atoms, there are $2 \times 4 = 8$ atoms in the conventional cell and 2×1 in the primitive cell.

5. What is the difference between a conventional and a primitive cell? How can the primitive fcc cell be built in terms of the crystal axes of the conventional fcc cell? What changes for bcc?

Solution:

The conventional cell is chosen in a way to reflect the full symmetry of the crystal lattice and help with visualization. It often contains more than one lattice point and can be larger than the primitive cell. By contrast, the primitive cell is the smallest possible unit that can be used to build the entire lattice by translation. It contains exactly one lattice point by definition (not to be confused with one atom!) and has minimum volume.

There can be different choices for primitive cells which may differ in shape or orientation, although mathematically they are all equivalent and enclose the same volume. Their choice depend on the convenience for certain type of calculations or for highlighting particular symmetries or properties of the crystal. A special unique primitive cell is the Wigner-Seitz cell. It is the region of space closer to a given lattice point than to any other lattice point. The lattice point consequently lies exactly in its center.

For our purposes however, it is convenient to work with primitive cells whose geometric shapes can be associated with a set of primitive lattice vectors $\{\mathbf{a}_i\}$ such that they form a parallelepiped (see Fig. 1). For fcc and bcc, these sets are given by the following equations¹:

$$\mathbf{a}_i^{\text{fcc}} = \frac{a}{2} \sum_{j=1}^3 (1 - \delta_{ij}) \mathbf{e}_j = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 - \mathbf{a}_i \quad (1)$$

$$\mathbf{a}_i^{\text{bcc}} = \frac{a}{2} \sum_{j=1}^3 (1 - 2\delta_{ij}) \mathbf{e}_j = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 - 2\mathbf{a}_i \quad (2)$$

i. e.

$$\mathbf{a}_1^{\text{fcc}} = \frac{a}{2} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}, \quad \mathbf{a}_2^{\text{fcc}} = \frac{a}{2} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \quad \mathbf{a}_3^{\text{fcc}} = \frac{a}{2} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \quad (3)$$

and

$$\mathbf{a}_1^{\text{bcc}} = \frac{a}{2} \begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix}, \quad \mathbf{a}_2^{\text{bcc}} = \frac{a}{2} \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix}, \quad \mathbf{a}_3^{\text{bcc}} = \frac{a}{2} \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix}. \quad (4)$$

6. What can you tell about the edge length and the volume of the primitive cell in relation to the lattice constant, which is defined as the edge length of the conventional cell?

Solution:

In general, the following formula applies for any unit cell, primitive or not:

$$V_{\text{cell}} = (\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3 = \det \begin{pmatrix} | & | & | \\ \mathbf{a}_1 & \mathbf{a}_2 & \mathbf{a}_3 \\ | & | & | \end{pmatrix} \quad (5)$$

¹In different text books the order of these primitive vectors may be chosen differently. For instance, Ashcroft [1, §4] uses the same order we employ in Eqs. (3) and (4), whereas in Kittel [2, §1], the indices are cyclically rotated.

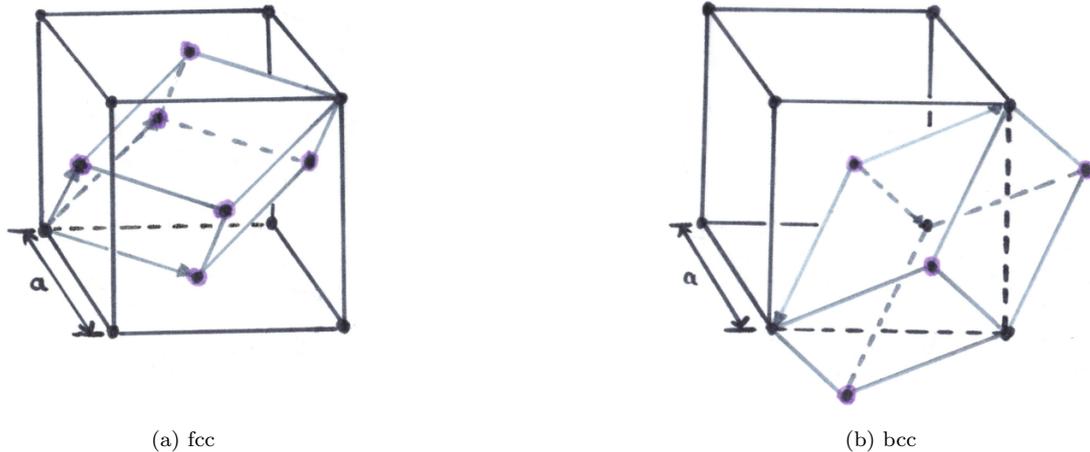


Figure 1: Primitive and conventional unit cells for fcc and bcc. For fcc, the primitive lattice vectors form a rhombohedron, whereas for bcc it remains a general parallelepiped.

The edge length is simply the magnitude of the lattice vectors $|\mathbf{a}_i|$. An overview of crystal properties of simple, body-centered and face-centered cubic lattices is given in Table 1.

	Simple	Body-centered	Face-centered
Volume conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Packing fraction	$\frac{\pi}{6} \approx 52.4\%$	$\frac{\sqrt{3}\pi}{8} \approx 68\%$	$\frac{\sqrt{2}\pi}{6} \approx 74\%$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$\frac{\sqrt{3}a}{2} \approx 0.866a$	$\frac{a}{\sqrt{2}} \approx 0.707a$
Number of second neighbors	12	6	6
Second-neighbor distance	$\sqrt{2}a$	a	a

Table 1: Characteristics of cubic lattices. Nearest-neighbor distance is equal to the edge length of the primitive cell. Packing fraction is the maximum proportion of the available volume that could theoretically be filled with hard spheres, i. e. “volume occupied by atoms” divided by “volume of unit cell”.

3 Crystals and their visualization

Compared to purely (group) theoretical approaches, in computational physics it is often necessary to first study new systems visually. We usually use one of these tools for that purpose:

- VESTA, XCrysDen, ASE-gui, jMol, ovito (and others)

Before we can look at a crystal structure, we first have to find a description of the crystal setup. A standardized format for that kind of information is given with CIF - the Crystallographic Information File format. The details of this format are not so important, but we will have a short look at the content of such a file nevertheless.

Choose a material:

Diamond	Zincblende	Rocksalt
C, Si, Ge	ZnS, GaAs, AlP, SiC	NaCl, LiF

Tasks:

- Download a Crystallographic Information File (CIF) for your system:
 - Inorganic Crystal Structure Database: <https://icsd.fiz-karlsruhe.de> (only accessible from within university network or via demo account)
 - Crystallography Open Database: <http://www.crystallography.net>
- Open the file in VESTA (pre-installed on pool computers) and have a look at the 3D model.
- Identify atom positions and species.
Solution: Check output or summary tab at bottom
- Find lattice constants and space group.
Solution: Check output or summary tab at bottom
- Extend the view to a 4x4x4 grid of unit cells. Look at the crystal from different perspectives, try to detect familiar symmetries, then undo the changes.
Solution: Objects → Boundary... → Ranges of fractional coordinates
- Identify symmetry equivalent atoms using Wyckoff positions and compare with Bilbao Server results for your space group:
Bilbao Server | Bilbao Server - Wyckoff Positions | Bilbao Server - SG 227 with Cell Choice 1
Solution: Have a look at the VESTA output and compare with bilbao server:
 - Edit → Edit Data → Unit Cell → Remove symmetry
 - Edit → Edit Data → Structure Parameters
- Try different options under Edit → Bonds... (Ctrl+B), in particular the “Do not search atoms beyond the boundary” setting.
- Reduce Boundaries to 0.09 (Ctrl+Shift+B).
- Convert conventional into primitive cell and verify it has the correct volume.
Edit → Edit Data → Unit Cell → Transform... → Rotation Matrix P

Solution:

In order to find the change-of-basis matrix we need to express the new base vectors $\{\mathbf{e}'_i\}$ in terms of the old ones $\{\mathbf{e}_i\}$:

$$\begin{aligned} \mathbf{e}'_1 &= P_{11} \mathbf{e}_1 + P_{21} \mathbf{e}_2 + P_{31} \mathbf{e}_3 \\ \mathbf{e}'_2 &= P_{12} \mathbf{e}_1 + P_{22} \mathbf{e}_2 + P_{32} \mathbf{e}_3 \\ \mathbf{e}'_3 &= P_{13} \mathbf{e}_1 + P_{23} \mathbf{e}_2 + P_{33} \mathbf{e}_3 \end{aligned} \quad (6)$$

The required transformation matrix is then simply given by the coefficients P_{ij} ,

$$P = \begin{pmatrix} | & | & | \\ \mathbf{e}'_1 & \mathbf{e}'_2 & \mathbf{e}'_3 \\ | & | & | \end{pmatrix}. \quad (7)$$

For fcc and bcc, the transformation matrices read

$$P_{\text{fcc}} = \frac{1}{2} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}, \quad P_{\text{bcc}} = \frac{1}{2} \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}. \quad (8)$$

Volume ratios should be 1:4 for fcc and 1:2 for bcc, cf. Table 1.

Wyckoff Positions of Group 227 (*Fd-3m*) [origin choice 1]

Multiplicity	Wyckoff letter	Site symmetry	Coordinates						
			(0,0,0) + (0,1/2,1/2) + (1/2,0,1/2) + (1/2,1/2,0) +						
192	i	1	(x,y,z)	(-x,-y+1/2,z+1/2)	(-x+1/2,y+1/2,-z)	(x+1/2,-y,-z+1/2)			
			(z,x,y)	(z+1/2,-x,-y+1/2)	(-z,-x+1/2,y+1/2)	(-z+1/2,x+1/2,-y)			
			(y,z,x)	(-y+1/2,z+1/2,-x)	(y+1/2,-z,-x+1/2)	(-y,-z+1/2,x+1/2)			
			(y+3/4,x+1/4,-z+3/4)	(-y+1/4,-x+1/4,-z+1/4)	(y+1/4,-x+3/4,z+3/4)	(-y+3/4,x+3/4,z+1/4)			
			(x+3/4,z+1/4,-y+3/4)	(-x+3/4,z+3/4,y+1/4)	(-x+1/4,-z+1/4,-y+1/4)	(x+1/4,-z+3/4,y+3/4)			
			(z+3/4,y+1/4,-x+3/4)	(z+1/4,-y+3/4,x+3/4)	(-z+3/4,y+3/4,x+1/4)	(-z+1/4,-y+1/4,-x+1/4)			
			(-x+1/4,-y+1/4,-z+1/4)	(x+1/4,y+3/4,-z+3/4)	(x+3/4,-y+3/4,z+1/4)	(-x+3/4,y+1/4,z+3/4)			
			(-z+1/4,-x+1/4,-y+1/4)	(-z+3/4,x+1/4,y+3/4)	(z+1/4,x+3/4,-y+3/4)	(z+3/4,-x+3/4,y+1/4)			
			(-y+1/4,-z+1/4,-x+1/4)	(y+3/4,-z+3/4,x+1/4)	(-y+3/4,z+1/4,x+3/4)	(y+1/4,z+3/4,-x+3/4)			
			(-y+1/2,-x,z+1/2)	(y,x,z)	(-y,x+1/2,-z+1/2)	(y+1/2,-x+1/2,-z)			
			(-x+1/2,-z,y+1/2)	(x+1/2,-z+1/2,-y)	(x,z,y)	(-x,z+1/2,-y+1/2)			
			(-z+1/2,-y,x+1/2)	(-z,y+1/2,-x+1/2)	(z+1/2,-y+1/2,-x)	(z,y,x)			
			96	h	.2	(1/8,y,-y+1/4)	(7/8,-y+1/2,-y+3/4)	(3/8,y+1/2,y+3/4)	(5/8,-y,y+1/4)
						(-y+1/4,1/8,y)	(-y+3/4,7/8,-y+1/2)	(y+3/4,3/8,y+1/2)	(y+1/4,5/8,-y)
(y,-y+1/4,1/8)	(-y+1/2,-y+3/4,7/8)	(y+1/2,y+3/4,3/8)				(-y,y+1/4,5/8)			
(1/8,-y+1/4,y)	(3/8,y+3/4,y+1/2)	(7/8,-y+3/4,-y+1/2)				(5/8,y+1/4,-y)			
(y,1/8,-y+1/4)	(y+1/2,3/8,y+3/4)	(-y+1/2,7/8,-y+3/4)				(-y,5/8,y+1/4)			
(-y+1/4,y,1/8)	(y+3/4,y+1/2,3/8)	(-y+3/4,-y+1/2,7/8)				(y+1/4,-y,5/8)			
96	g	.m				(x,x,z)	(-x,-x+1/2,z+1/2)	(-x+1/2,x+1/2,-z)	(x+1/2,-x,-z+1/2)
						(z,x,x)	(z+1/2,-x,-x+1/2)	(-z,-x+1/2,x+1/2)	(-z+1/2,x+1/2,-x)
						(x,z,x)	(-x+1/2,z+1/2,-x)	(x+1/2,-z,-x+1/2)	(-x,-z+1/2,x+1/2)
			(x+3/4,x+1/4,-z+3/4)	(-x+1/4,-x+1/4,-z+1/4)	(x+1/4,-x+3/4,z+3/4)	(-x+3/4,x+3/4,z+1/4)			
			(x+3/4,z+1/4,-x+3/4)	(-x+3/4,z+3/4,x+1/4)	(-x+1/4,-z+1/4,-x+1/4)	(x+1/4,-z+3/4,x+3/4)			
			(z+3/4,x+1/4,-x+3/4)	(z+1/4,-x+3/4,x+3/4)	(-z+3/4,x+3/4,x+1/4)	(-z+1/4,-x+1/4,-x+1/4)			
48	f	2.m m	(x,0,0)	(-x,1/2,1/2)	(0,x,0)	(1/2,-x,1/2)			
			(0,0,x)	(1/2,1/2,-x)	(3/4,x+1/4,3/4)	(1/4,-x+1/4,1/4)			
			(x+3/4,1/4,3/4)	(-x+3/4,3/4,1/4)	(3/4,1/4,-x+3/4)	(1/4,3/4,x+3/4)			
32	e	.3m	(x,x,x)	(-x,-x+1/2,x+1/2)	(-x+1/2,x+1/2,-x)	(x+1/2,-x,-x+1/2)			
			(x+3/4,x+1/4,-x+3/4)	(-x+1/4,-x+1/4,-x+1/4)	(x+1/4,-x+3/4,x+3/4)	(-x+3/4,x+3/4,x+1/4)			
16	d	-.3m	(5/8,5/8,5/8) (3/8,7/8,1/8) (7/8,1/8,3/8) (1/8,3/8,7/8)						
16	c	-.3m	(1/8,1/8,1/8) (7/8,3/8,5/8) (3/8,5/8,7/8) (5/8,7/8,3/8)						
8	b	-43m	(1/2,1/2,1/2) (1/4,3/4,1/4)						
8	a	-43m	(0,0,0) (3/4,1/4,3/4)						

Figure 2: Wyckoff positions for space group 227 (origin choice 1) as displayed on the Bilbao Crystallographic Server.

10. Reproduce the original conventional cell

Solution:

We need to invert the change-of-basis matrix. Let's use python for the task.

```

1 # load numpy module and enable shortcut 'np'
2 import numpy as np
3 # load invert function from linear algebra submodule
4 from numpy.linalg import inv
5
6 # create numpy array and fill with transformation matrix for fcc
7 A = np.full((3, 3), 0.5) - 0.5 * np.identity(3)
8 # or alternatively
9 A = np.array([[0, 0.5, 0.5], [0.5, 0, 0.5], [0.5, 0.5, 0]])
10 # invert matrix
11 B = inv(A)

```

We obtain the following inverted matrices:

$$P_{\text{fcc}}^{-1} = \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}, \quad P_{\text{bcc}}^{-1} = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}. \quad (9)$$

Convert primitive cell back to conventional cell via

1. Edit → Edit Data → Unit Cell → Remove symmetry
2. Transform... → Rotation Matrix P → enter inverse matrix

11. Run the `spglib_wyckoff.py` script. Compare its output with the cell parameters, atom positions and Wyckoff positions with data from VESTA and Bilbao Server. What is the purpose of the ICT standardized cell?

Solution:

ICT standardized cell defines (amongst other properties) a specific cell origin and cell choice according to conventions established by the International Tables for Crystallography (ICT) in order to provide a consistent and standardized framework for describing crystal structures. This standardization helps in comparing different crystals and their properties.

References

- [1] Neil W. Ashcroft and N. David Mermin. *Solid State Physics*. New York: Cengage Learning Emea, Jan. 1976. ISBN: 978-0-03-083993-1.
- [2] Charles Kittel. *Introduction to solid state physics*. 8th ed. Hoboken, NJ: Wiley, 2005. ISBN: 978-0-471-41526-8.