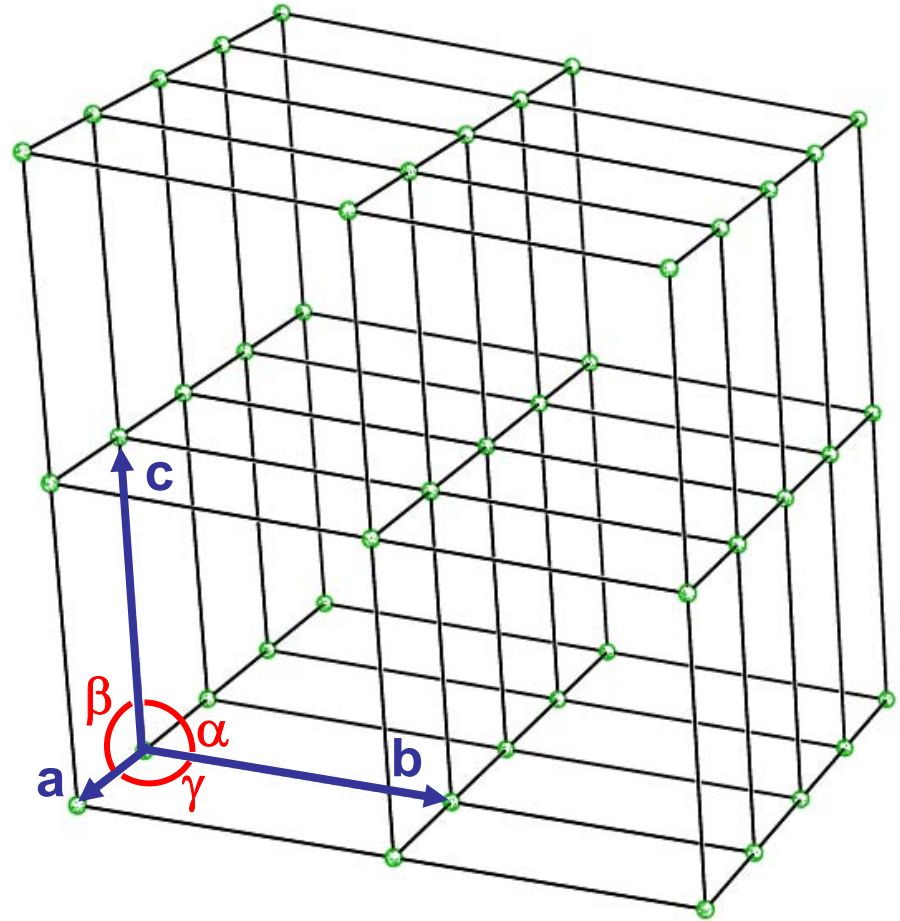


Going 3D

A crystal is a three dimensional periodic discontinuum. It consists of identical “bricks” called unit cells, which form a three-dimensional lattice.

The unit cell is defined by the axes a , b , and c , and the three angles α , β , γ , which form a right-handed system.



Courtesy of George M. Sheldrick. Used with permission.

Volume of the unit cell V :

$$V = abc [1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma]^{1/2}$$

The Unit Cell

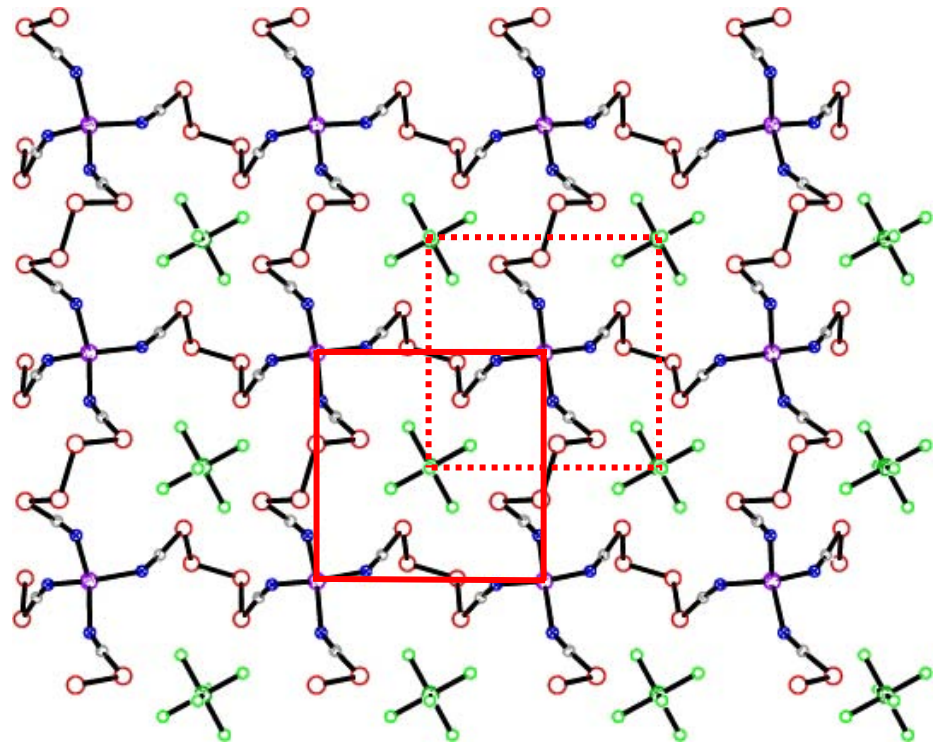
The unit cell is the smallest unit that can generate the entire crystal structure only by means of translation in three dimensions.

Within each unit cell there may be several symmetry related copies of the asymmetric unit but in general those are oriented differently.

Even though in the structure of NaCl there is an atom at every corner of the unit cell, such an arrangement is rather rare.

If the structure is centrosymmetric, the unit cell is chosen so that its origin lies on an inversion center.

Else: conformity with other symmetry elements (see Volume A *International Tables for Crystallography*).



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Crystallographic Conventions

Unit cell: Right handed system $a, b, c, \alpha, \beta, \gamma$

Triclinic system: $a \leq b \leq c$

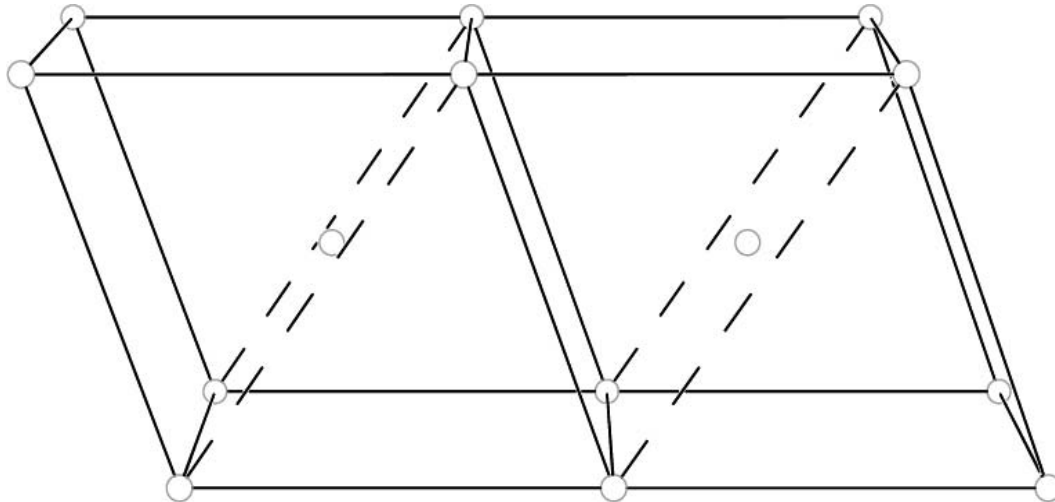
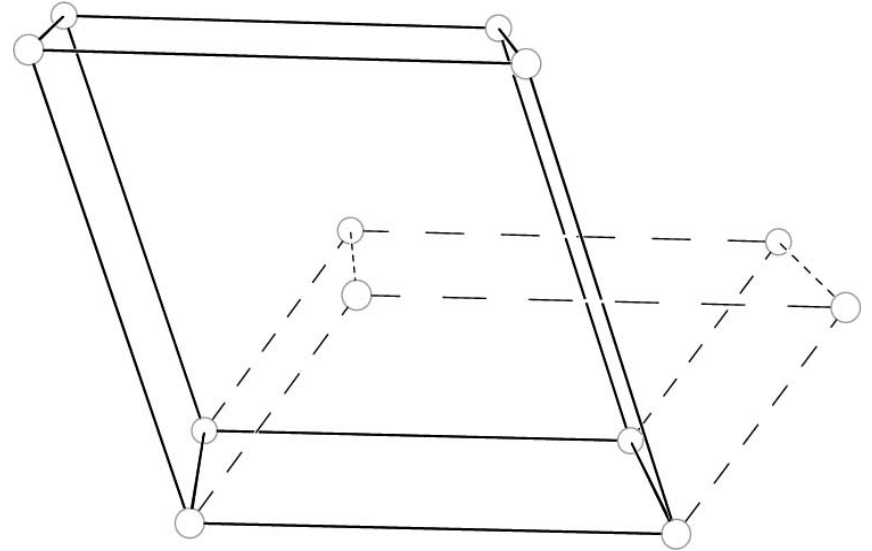
The monoclinic angle is β with $\beta \geq 90^\circ$. This makes b the unique axis in the monoclinic system.

In the tetragonal, trigonal and hexagonal systems, c is the unique axis.

Unconventional Lattices

E.g.: **Monoclinic B** can always be transformed into **monoclinic P**, with half the unit cell volume.

Monoclinic I can always be transformed into **monoclinic C** with the same unit cell volume.



That is why the list of the 14 Bravais lattices does not include **monoclinic B** nor **monoclinic I** nor several other unconventional lattices.

Space Groups

Instead of 17 in two dimensions, in 3D there are 230 different ways of combining symmetry elements with translation and lattice centering: the 230 space groups.

Atomic Coordinates

The coordinates of the atoms within a unit cell are given as $0 \leq x < 1$, $0 \leq y < 1$ und $0 \leq z < 1$. Thus distance between two atoms $x_1y_1z_1$ and $x_2y_2z_2$ is:

$$d = (x_2 - x_1)a + (y_2 - y_1)b + (z_2 - z_1)c \quad \text{oder} \quad d = a\Delta x + b\Delta y + c\Delta z$$

The x , y , and z coordinates are also used to describe symmetry operations:

If there is an atom on the place x, y, z

$x+1, y, z$ is the equivalent atom in the next unit cell in x -direction (a cell axis).

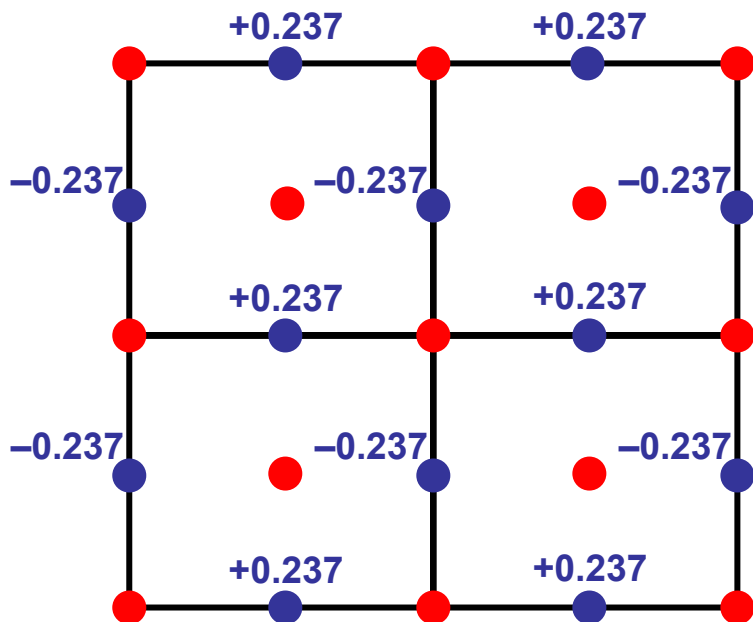
$-x, -y, -z$ is generated by an inversion center at $0, 0, 0$.

Red Modification of PbO

Tetragonal with $a = b = 3.98 \text{ \AA}$, $c = 5.02 \text{ \AA}$. Two formula units per unit cell.

Pb @ 0, 0.5, 0.273 and 0.5, 0, 0.763

O @ 0, 0, 0 and 0.5, 0.5, 0



Projection of 4 unit cells along
the c axis. O: ● Pb: ●

Pb is surrounded by 4 atoms (square pyramid); O is tetrahedrally coordinated by 4 Pb atoms.

The shortest Pb-O distance is
 $\Delta x = 0.5$, $\Delta y = 0.0$, $\Delta z = 0.237$

$$d = [(0.5 \times 3.98)^2 + (0.237 \times 5.02)^2]^{1/2} = 2.32 \text{ \AA}$$

Some Definitions

Symmetry Operation: An operation that leads to superimposition of an object on itself.

Symmetry Element: An imaginary geometric entity (line, point, plane) about which a symmetry operation takes place.

Unit cell: The smallest unit that can generate the entire crystal structure only by means of translation in three dimensions.

Asymmetric unit: The minimum unit from which the structure can be generated by symmetry operations.

Lattice: A rule of translation.

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5.069 Crystal Structure Analysis
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