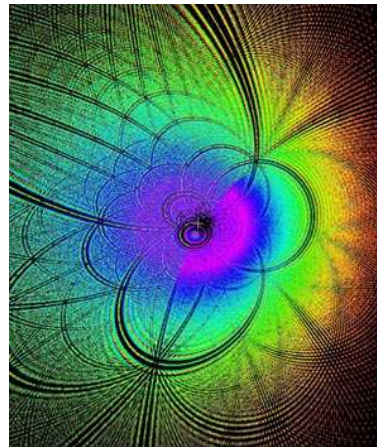
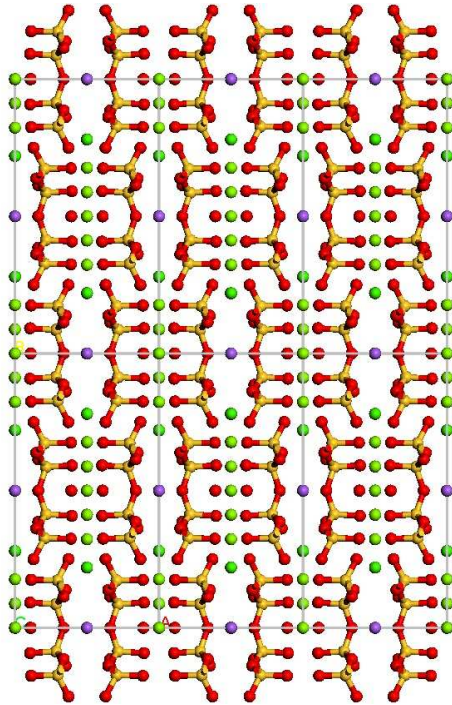


CRYSTAL STRUCTURE AND SCATTERING EXPERIMENTS

Chris J. Pickard



HOW CAN WE TELL WHERE THE ATOMS ARE?



Amphibole

- We have seen the rich variety of bonding and structures that collections of atoms can adopt
- But how can we ever know where the atoms actually are?
- We must experimentally probe the structural information

POSSIBLE EXPERIMENTAL PROBES



*Hit something
and see what it, or the probe, does*

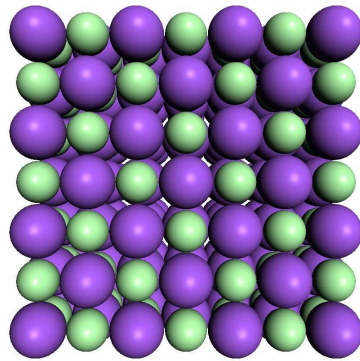
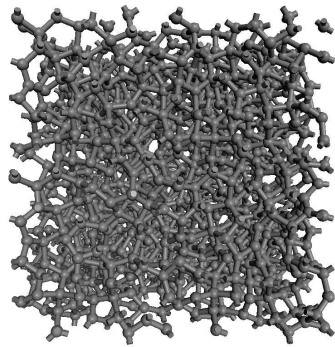
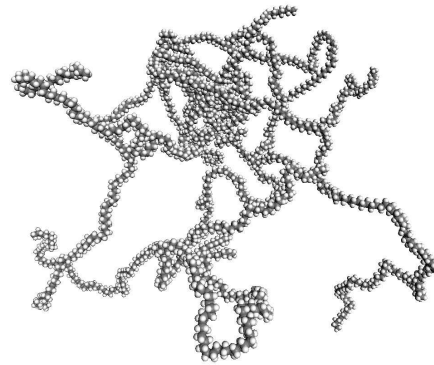
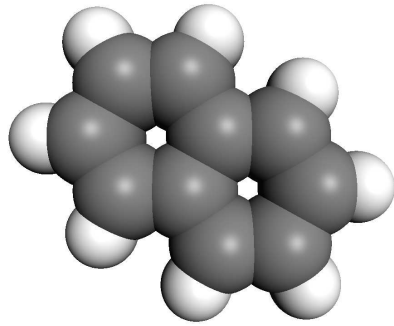
SCATTERING



A scattering experiment: The European Synchrotron Radiation Facility

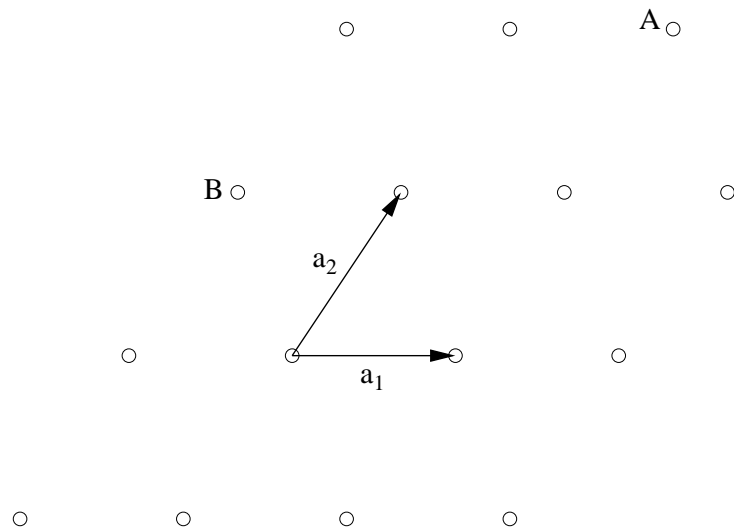
- Probe atomic structure by “bouncing” particles off it, and measuring changes in momentum etc.
- May be X-ray, neutron or electron scattering and elastic or inelastic
- X-ray and neutron facilities are massive pieces of scientific infrastructure

CRYSTAL LATTICES



- In order to interpret the scattering experiments we need a model of where the atoms *might* be
- There are simply too many atoms in a solid for each's coordinates to be determined
- For crystalline solids we introduce the concept of a *Bravais lattice*

THE BRAVAIS LATTICE

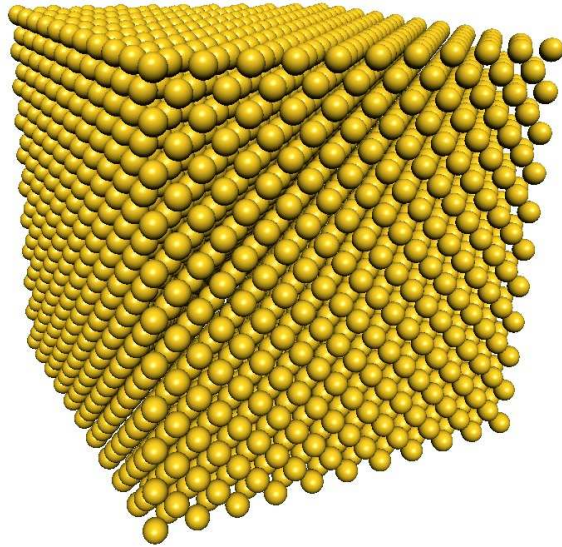


A 2D Bravais Lattice

$$\mathbf{A} = \mathbf{a}_1 + 2\mathbf{a}_2 \text{ and } \mathbf{B} = -\mathbf{a}_1 + \mathbf{a}_2$$

- The Bravais lattice describes the underlying periodic structure: *not* the crystal structure itself
- An infinite array which looks identical if viewed from any point
- $\mathbf{R} = \sum_i n_i \mathbf{a}_i$, n_i are all integers, and \mathbf{a}_i are not in the same plane
- The *primitive* vectors \mathbf{a}_i generate or span the lattice

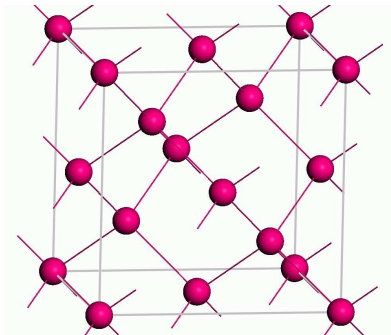
FINITE CRYSTALS



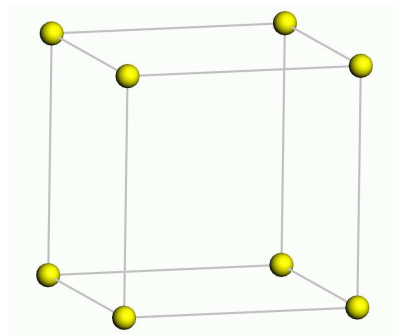
Gold crystallite

- All points are equivalent in a Bravais lattice: it must be infinite, but real crystals are finite
- Finite size effects, or surface effects, may not be important: the Bravais lattice is a useful approximation
- It can be useful to consider a finite portion: $\mathbf{R} = \sum_i n_i \mathbf{a}_i, 0 \leq n_i < N_i$

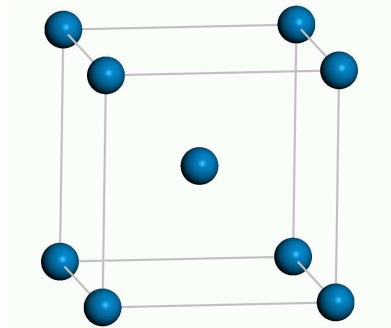
COORDINATION NUMBER



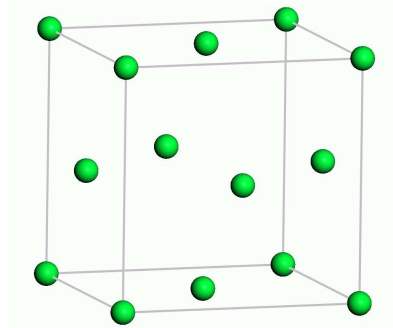
Diamond: 4



Simple Cubic: 6



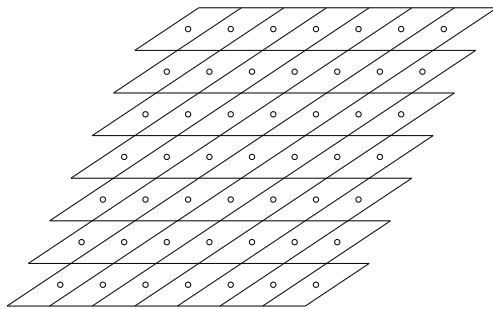
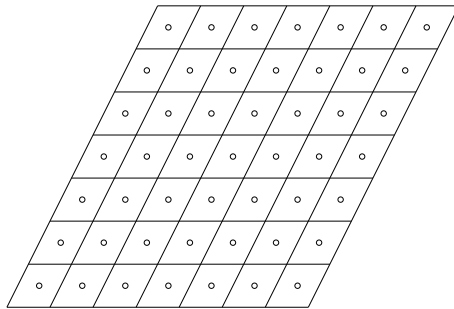
BCC: 8



FCC: 12

- The Bravais lattice points closest to a given point are the nearest neighbours
- Because the Bravais lattice is periodic, all points have the same number of nearest neighbours or *coordination number*. It is a property of the lattice
- Can be extended to arrays of points that are not Bravais lattices (the diamond lattice is not a Bravais lattice)

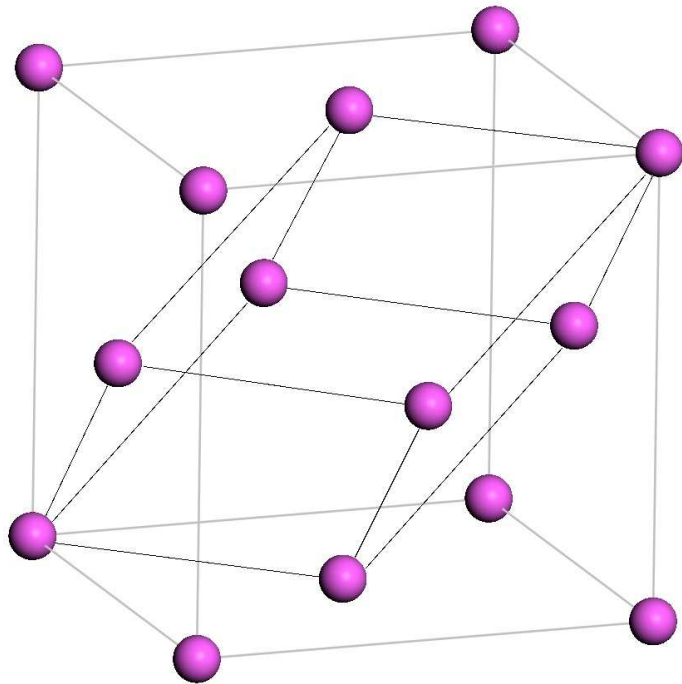
PRIMITIVE UNIT CELL



Two choices

- Volume which when translated by all vectors in Bravais lattice just fills space
- Not uniquely defined
- The set of points $\mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3$, $0 \leq x_i < 1$ is an obvious choice
- Does not display the full symmetry of the lattice

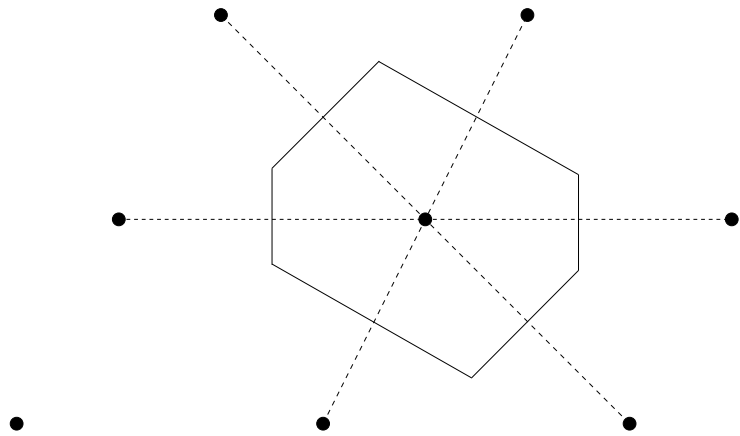
THE CONVENTIONAL UNIT CELL



FCC Bravais lattice

- A *unit cell* just fills space when translated through a subset of Bravais lattice vectors
- The *conventional* unit cell is chosen to be larger than the primitive cell, but with the full symmetry of the Bravais lattice
- The size of the conventional cell is given by the *lattice constants* – a single a in this case

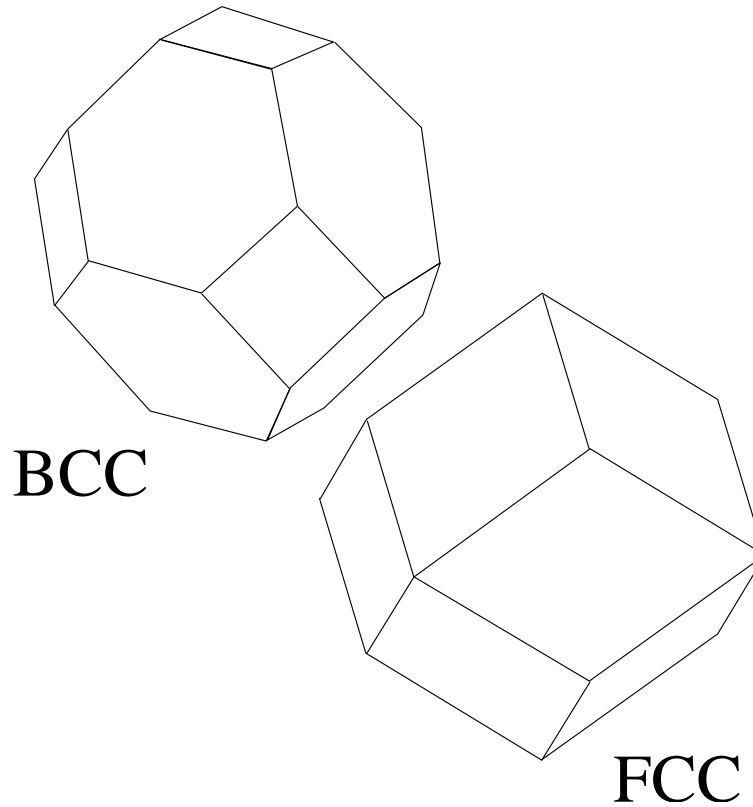
THE WIGNER-SEITZ PRIMITIVE CELL



Wigner-Seitz cell for a 2D lattice

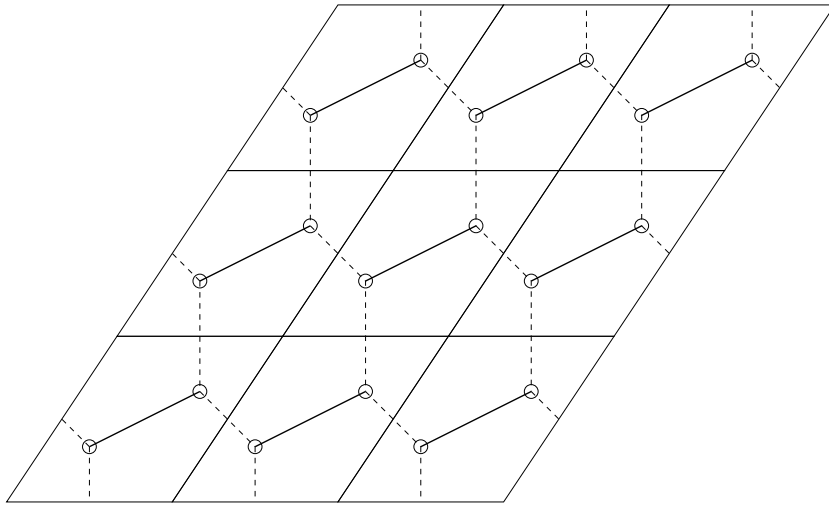
- The Wigner-Seitz cell is a primitive cell with the full symmetry of the Bravais lattice
- Constructed by selecting a lattice point and taking the volume closer to that point than any others
- Algorithm: draw lines from the lattice point to all others, bisect each line with a plane and take the smallest polyhedron containing the point

THE WIGNER-SEITZ PRIMITIVE CELL



Wigner-Seitz cells for BCC and FCC 3D lattices

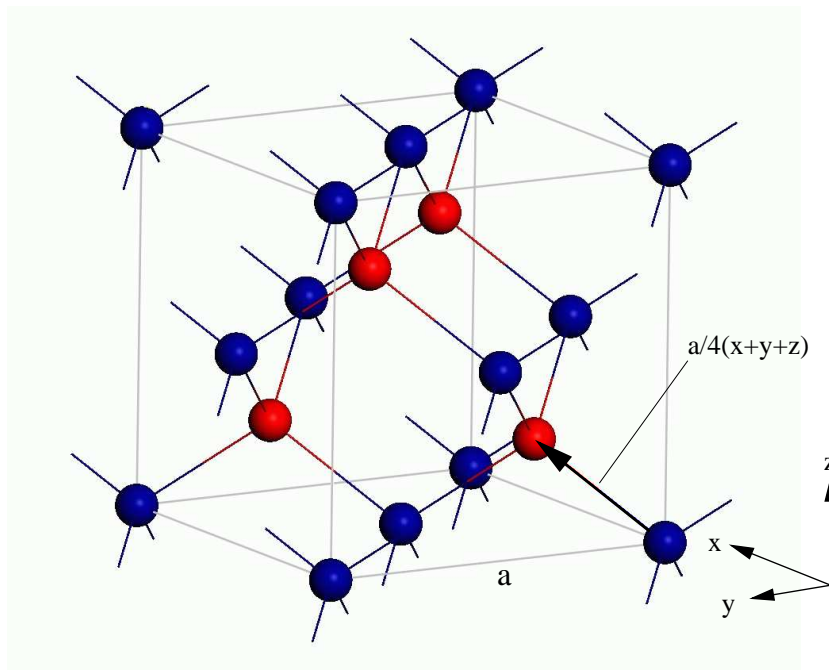
CRYSTAL STRUCTURE



*2D Bravais lattice with
two point basis*

- A *crystal structure* is a *basis*, or physical unit, translated by each vector of the Bravais lattice
- Also known as a “lattice with a basis”
- A *monatomic* Bravais lattice has a basis consisting of a single atom
- A Bravais lattice is a lattice with a basis when a non-primitive cell is chosen

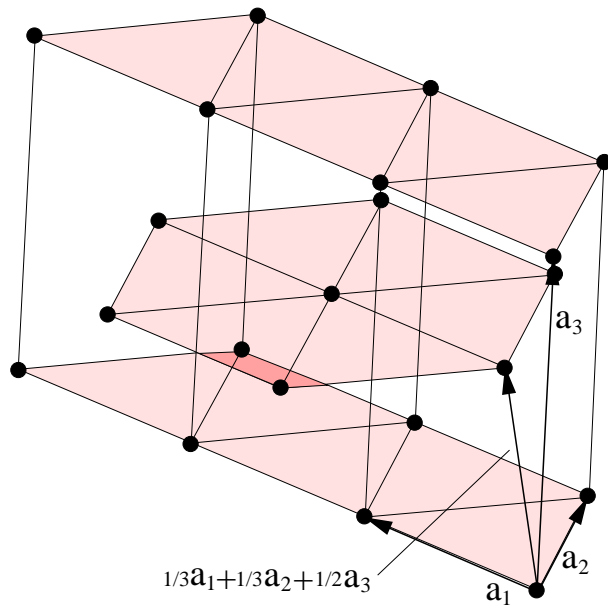
THE DIAMOND STRUCTURE



Conventional cubic cell

- Two interpenetrating FCC Bravais lattices, displaced by $1/4$ length of body diagonal
- FCC cubic lattice with two-point basis: $\mathbf{0}$ and $a/4(\mathbf{x}+\mathbf{y}+\mathbf{z})$
- The diamond lattice is not a Bravais lattice
- Zincblende structure with two species

HEXAGONAL CLOSE PACKING



Hexagonal close packed crystal structure

- The hexagonal close packed (HCP) structure is not a Bravais lattice
- Many pure elements (about 30) crystallise in this way
- The HCP structure consists of two interpenetrating simple hexagonal Bravais lattices
- Other stackings are possible: ...ABCABC... is FCC

THE RECIPROCAL LATTICE

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

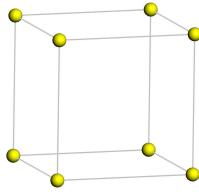
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}$$

- The *reciprocal lattice* arises from the relationship between the Bravais lattice and plane waves, $e^{i\mathbf{k}\cdot\mathbf{r}}$
- For certain \mathbf{k} the plane waves will have the periodicity of the lattice. These are the points of the reciprocal lattice \mathbf{K} and $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$
- The reciprocal lattice is a Bravais lattice, and the reciprocal lattice of the reciprocal lattice is the original *direct lattice*

SOME EXAMPLES

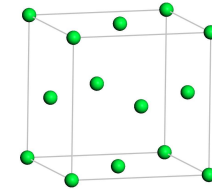


$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \mathbf{a}_2 = a\hat{\mathbf{y}}, \mathbf{a}_3 = a\hat{\mathbf{z}}$$

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}, \mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}$$

$$\mathbf{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}$$

The Simple Cubic Bravais Lattice



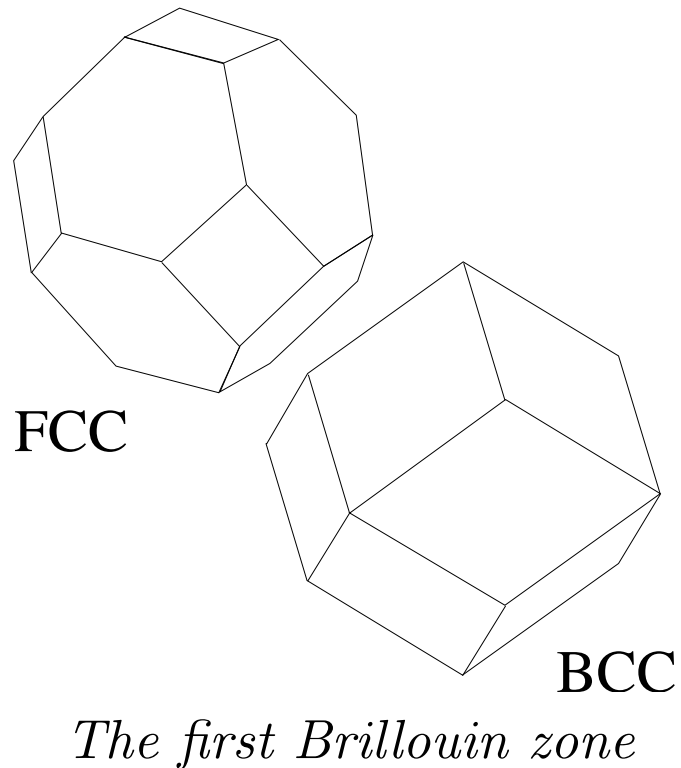
$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

$$\mathbf{b}_1 = \frac{4\pi}{a} \frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \mathbf{b}_2 = \frac{4\pi}{a} \frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}})$$

$$\mathbf{b}_3 = \frac{4\pi}{a} \frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

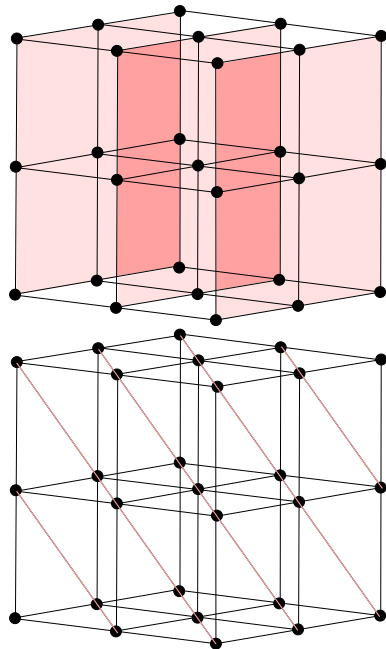
The FCC Bravais Lattice

THE FIRST BRILLOUIN ZONE



- The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice
- Higher Brillouin zones exist, and are important in the theory of electronic levels in a periodic potential
- Take care: the first BZ of a FCC lattice is the Wigner-Seitz primitive cell of the BCC lattice (and vice versa)

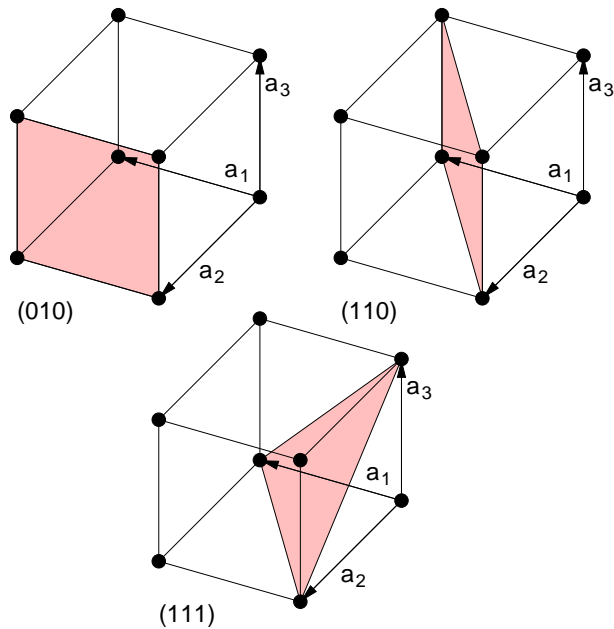
LATTICE PLANES



Two families of lattice planes in a simple cubic Bravais lattice

- Families of lattice planes can be classified in terms of the reciprocal lattice
- For any reciprocal lattice vector \mathbf{K} there is a family of planes normal to \mathbf{K} and separated by a distance d
- The length of the shortest reciprocal lattice vector parallel to \mathbf{K} is $\frac{2\pi}{d}$

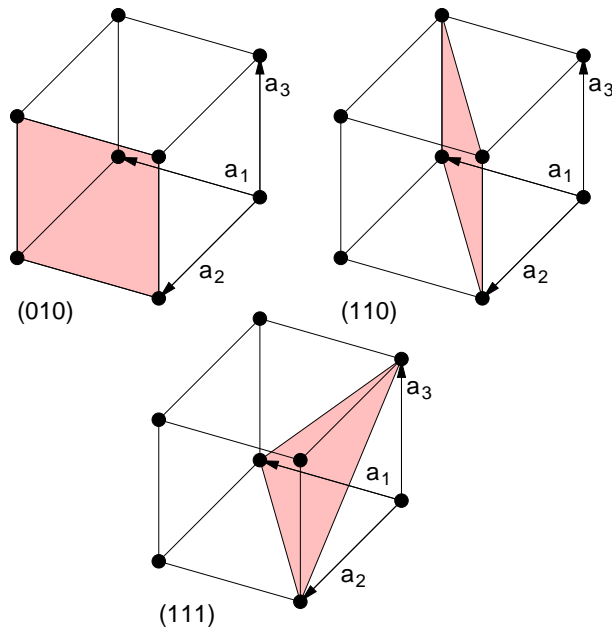
MILLER INDICES



Lattice planes and Miller indices in a simple cubic Bravais lattice

- The reciprocal lattice provides a convenient way to label lattice planes
- The *Miller indices* are the coordinates of the shortest reciprocal lattice vector normal to the plane
- A plane with Miller indices h,k,l is normal to $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$
- h,k,l are integers with no common factor

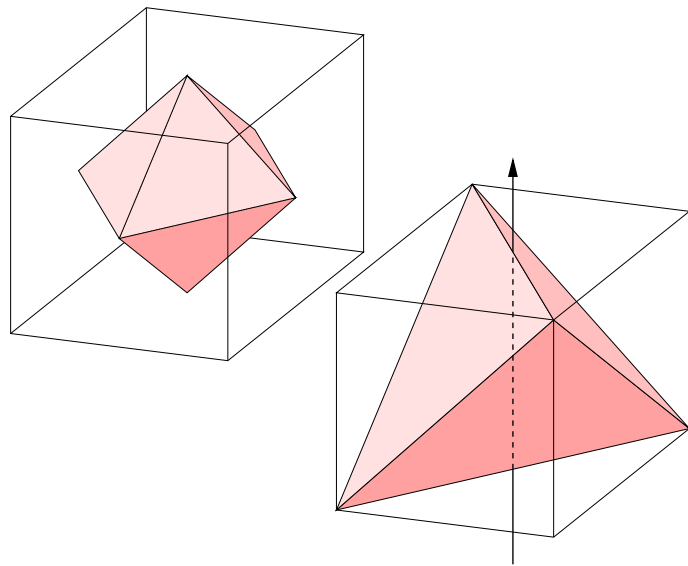
SPECIFYING DIRECTIONS: SOME CONVENTIONS



Lattice planes and Miller indices in a simple cubic Bravais lattice

- Lattice planes: $(h, k, l) \rightarrow (hkl)$ with $-n \rightarrow \bar{n}$ e.g. $(2, -1, 4) \rightarrow (2\bar{1}4)$
- Directions in the direct lattice: use square brackets e.g. $[111]$
- Planes equivalent by symmetry: (100) , (010) , and (001) are equivalent in a cubic crystal, and we write $\{100\}$
- For directions: $[100]$, $[010]$, $[001]$, $[\bar{1}00]$, $[0\bar{1}0]$, $[00\bar{1}] \rightarrow \langle 100 \rangle$

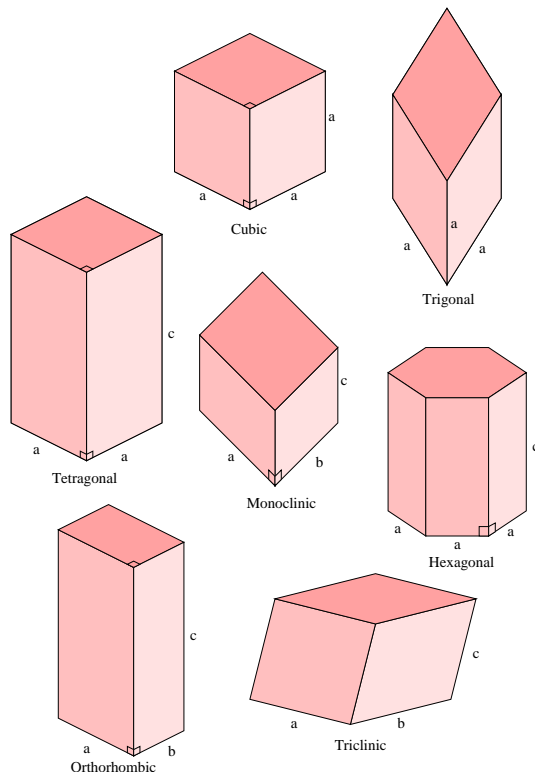
BEYOND TRANSLATIONAL SYMMETRY IN CRYSTALS



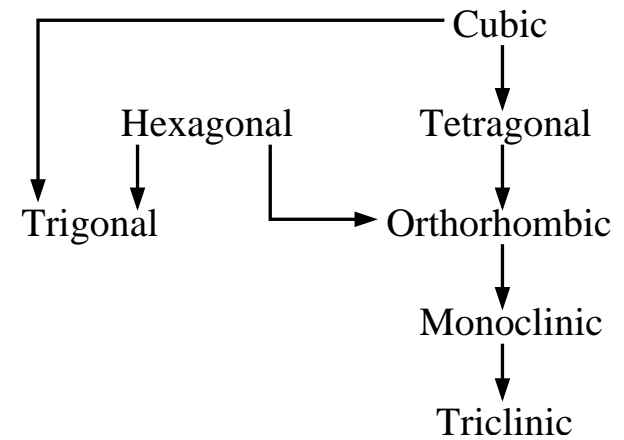
The symmetries of a cube are identical to an octahedron, but not a tetrahedron

- There can be other symmetries in addition to translational symmetry
- The subject of crystallography systematises the classification of these different symmetries
- The number of possibilities can be shown to be finite for crystals, and have been enumerated

SEVEN CRYSTAL SYSTEMS AND FOURTEEN BRAVAIS LATTICES



The Seven Crystal Systems



Hierarchy of Symmetries

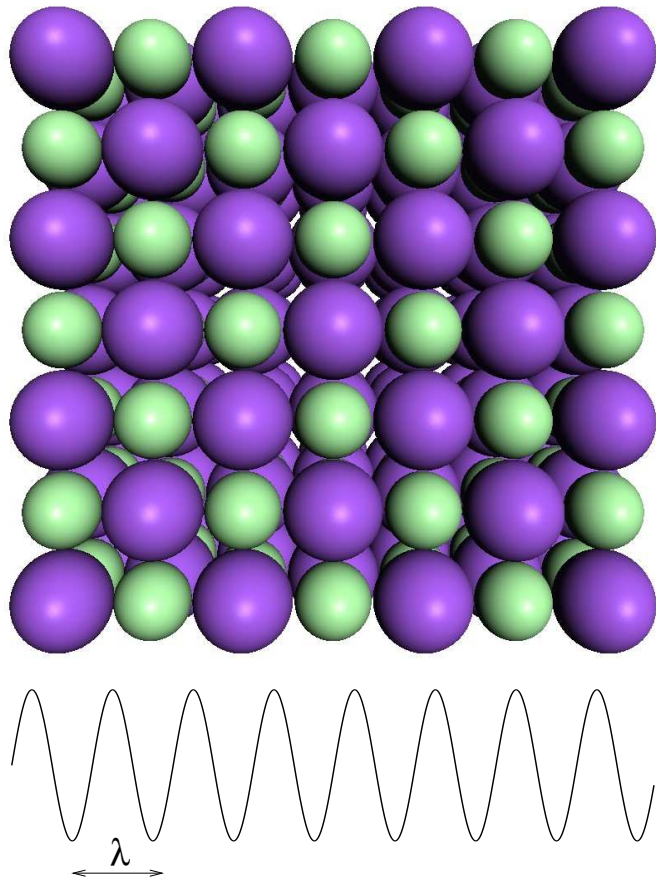
- e.g. the cubic crystal system includes the simple cubic, BCC and FCC Bravais lattices

POINT AND SPACE GROUPS OF BRAVAIS LATTICES AND CRYSTAL STRUCTURES

	Bravais Lattice <i>(basis of spherical symmetry)</i>	Crystal Structure <i>(basis of arbitrary symmetry)</i>
Number of point groups	7 <i>(crystal systems)</i>	32 <i>(crystallographic point groups)</i>
Number of space groups	14 <i>(Bravais lattices)</i>	230 <i>(space groups)</i>

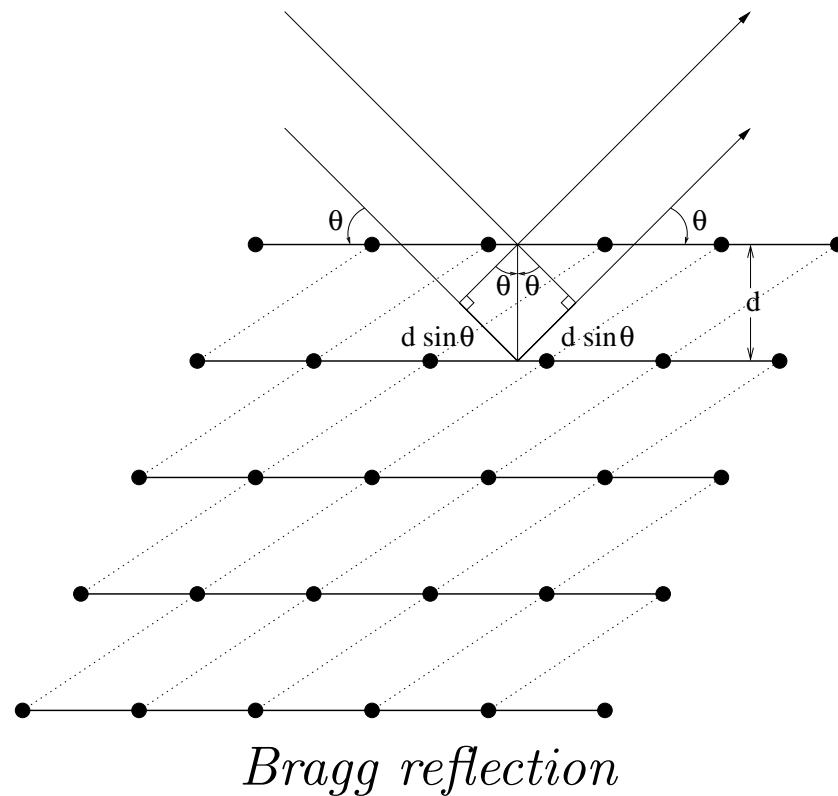
- Adding a basis considerably complicates the situation
- *Nonsymmorphic* groups account for many of the 230: these contain *screw axes* and *glide planes*
- Schönflies (e.g. D_{6h}) and International (e.g. $6/mmm$) notations exist

STRUCTURE DETERMINATION BY X-RAY DIFFRACTION



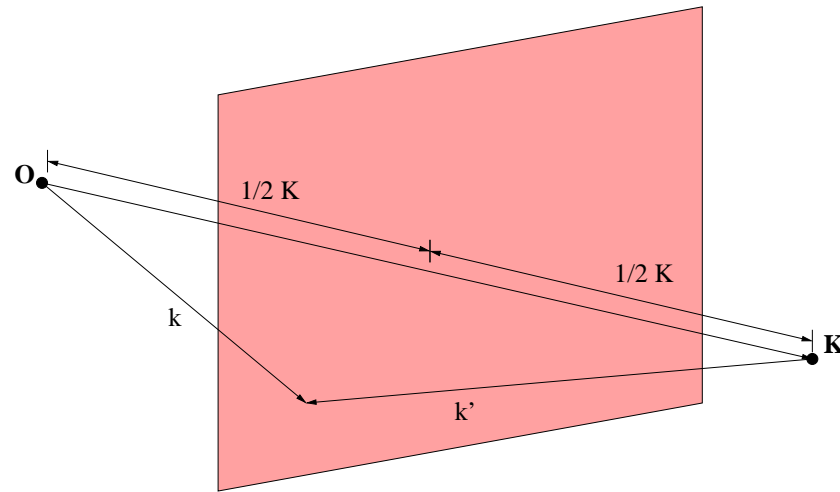
- Atoms are separated by distances of the order of Angstroms (10^{-8}cm): the wavelength must be comparable
- We need X-rays: $\hbar\omega = \frac{hc}{10^{-8}\text{cm}} 12.3 \times 10^3 \text{eV}$
- We now consider how the scattering of X-rays from rigid periodic arrays of ions reveals their structure

THE BRAGG FORMULATION



- W.L. Bragg considered crystals to be made up of parallel planes of atoms
- The diffraction peak occurs if 1) X-rays reflect *specularly* from the atoms in a plane and 2) the X-rays from successive planes constructively interfere
- The diffraction condition is $n\lambda = 2d\sin\theta$, and n is the *order* of the reflection

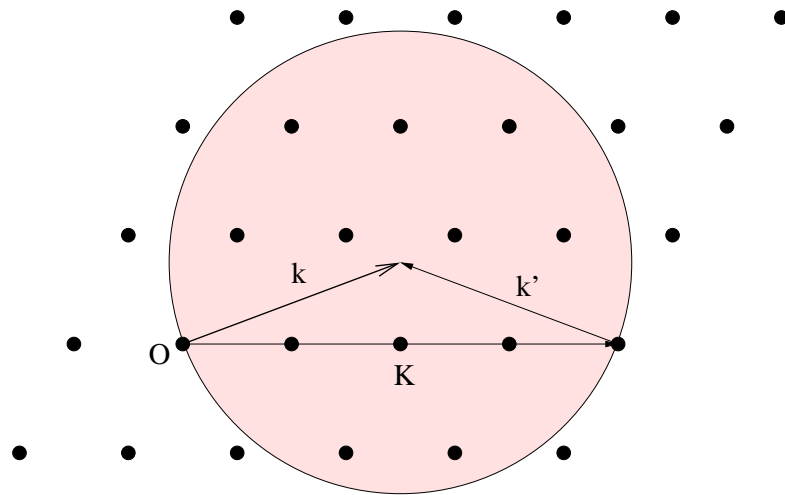
THE VON LAUE FORMULATION



The Laue Condition

- The crystal is considered to be made up of identical microscopic objects at \mathbf{R} , which reradiate in all directions
- The Laue condition: constructive interference occurs if $\mathbf{K} = \mathbf{k} - \mathbf{k}'$ is a reciprocal lattice vector
- No assumption that crystal contains lattice planes is made or that the reflection is specular
- The von Laue picture is equivalent to the Bragg picture

THE EWALD SPHERE



The Ewald Construction

- Given an incident wave vector \mathbf{k} , draw a sphere centered on the origin \mathbf{O}
- If a reciprocal lattice vector \mathbf{K} lies on the surface, a diffraction peak will be observed, and \mathbf{k}' is the Bragg reflected ray
- In general, this is not the case (hence “peak”)

EXPERIMENTAL METHODS

- Laue
 - Use a non-monochromatic beam (from λ_0 to λ_1)
 - All \mathbf{K} between the two Ewald spheres will be seen
- Rotating Crystal
 - A monochromatic beam is used
- The direction of \mathbf{k} is varied by rotating the crystal
- Powder or Debye-Scherrer
 - The randomly oriented crystallites effectively rotate the crystal, and vary the axis of rotation

STRUCTURE AND ATOMIC FORM FACTORS

$$S_{\mathbf{K}} = \sum_{j=1}^n e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

The Structure Factor

- There can be forbidden reflections for lattices with a basis

$$S_{\mathbf{K}} = \sum_{j=1}^n f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

$$f_j(\mathbf{K}) = -\frac{1}{e} \int d\mathbf{r} e^{i\mathbf{K}\cdot\mathbf{r}} \rho(\mathbf{r})$$

The Atomic Form Factor

- Modulates the intensities of the diffraction peaks
- Can be used analytically
- Some species are more visible than others