Lecture 2:

short repetition (primitive cells lattice planes and Miller indices)

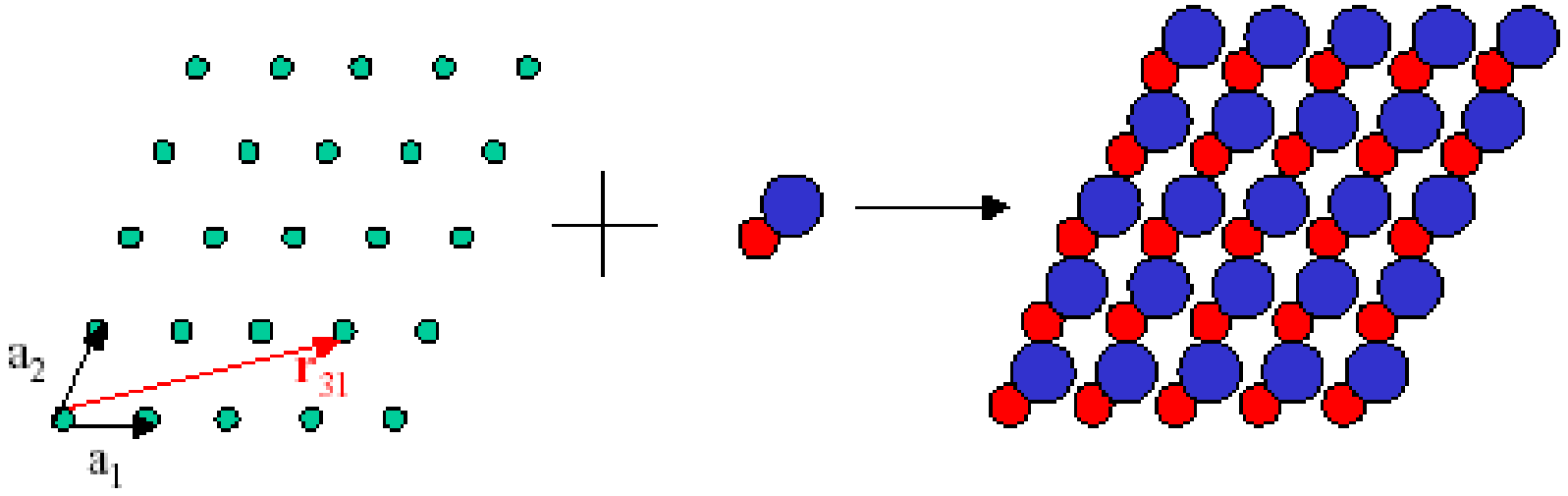
distance between lattice planes

x-ray diffraction

reciprocal space

Crystal structure I

- In bulk, many solids are crystalline.
- Have discrete translational and rotational symmetries.
- Real-space structure is periodic - repetitions of a single *unit cell*.
- Smallest unit cell that gives full structure: *primitive unit cell*
- Can describe structure by a *lattice* and a *basis*.



Lattice Planes and Miller Indices

Atoms or ions in lattices can be thought of as being connected by lattice planes. Each plane is a representative member of a parallel set of equally spaced planes.

A family of crystallographic planes is always uniquely defined by three indices, h, k, l, (Miller indices) usually written (h, k, l)

The Miller indices are defined by $h = \frac{1}{X}, k = \frac{1}{Y}, l = \frac{1}{Z}$

X, Y, Z are the intersections of one plane with on a, b, c respectively

Note - plane // to axis, intercept = ∞ and $1/\infty = 0$

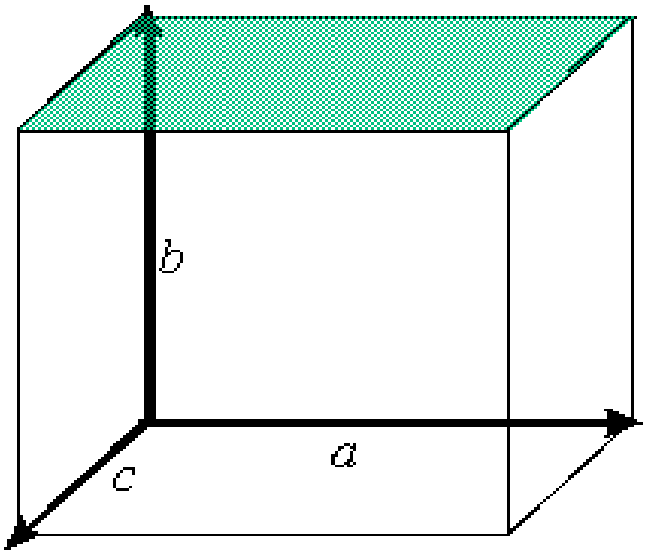
$(0kl)$ x

$(h0l)$ **family of lattice planes parallel to** y

$(hk0)$ z

How to Determine Miller Indices

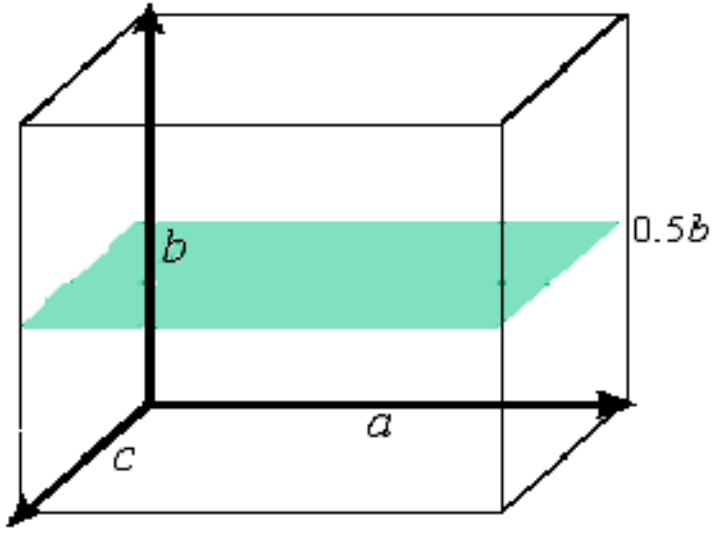
1.



- Intercepts are $\infty, 1, \infty$
- Miller indices of the plane are:

$$\left(\frac{1}{\infty}\frac{1}{1}\frac{1}{\infty}\right) = (010)$$

2.



- Intercepts are $\infty, 1/2, \infty$
- Miller indices of the plane are:

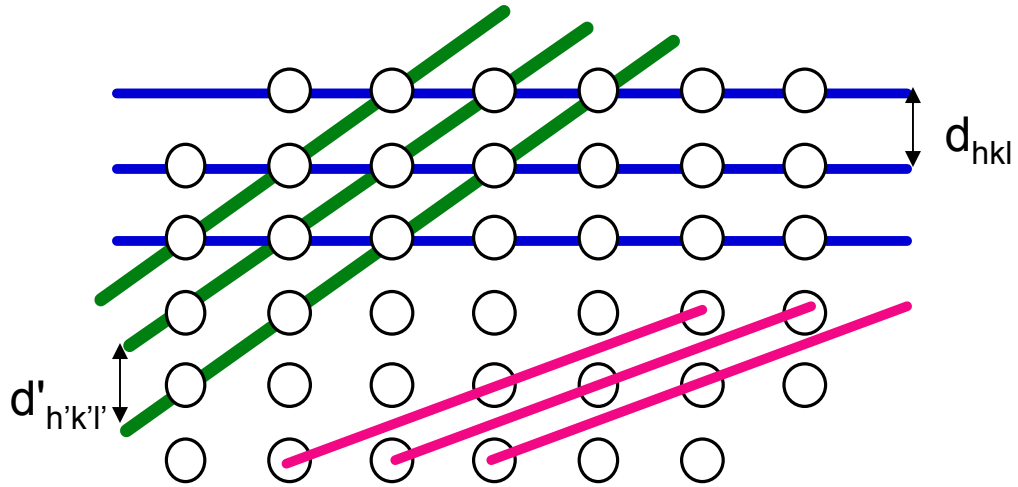
$$\left(\frac{1}{\infty}\frac{1}{1/2}\frac{1}{\infty}\right) = (020)$$

Inter-Planar Spacing, d_{hkl}, and Miller Indices

The inter-planar spacing ($\mathbf{d_{hkl}}$) between crystallographic planes belonging to the same family (h,k,l) is denoted ($\mathbf{d_{hkl}}$)

Distances between planes defined by the same set of Miller indices are unique for each material

2D



Inter-planar spacings can be measured by x-ray diffraction (Bragg's Law)

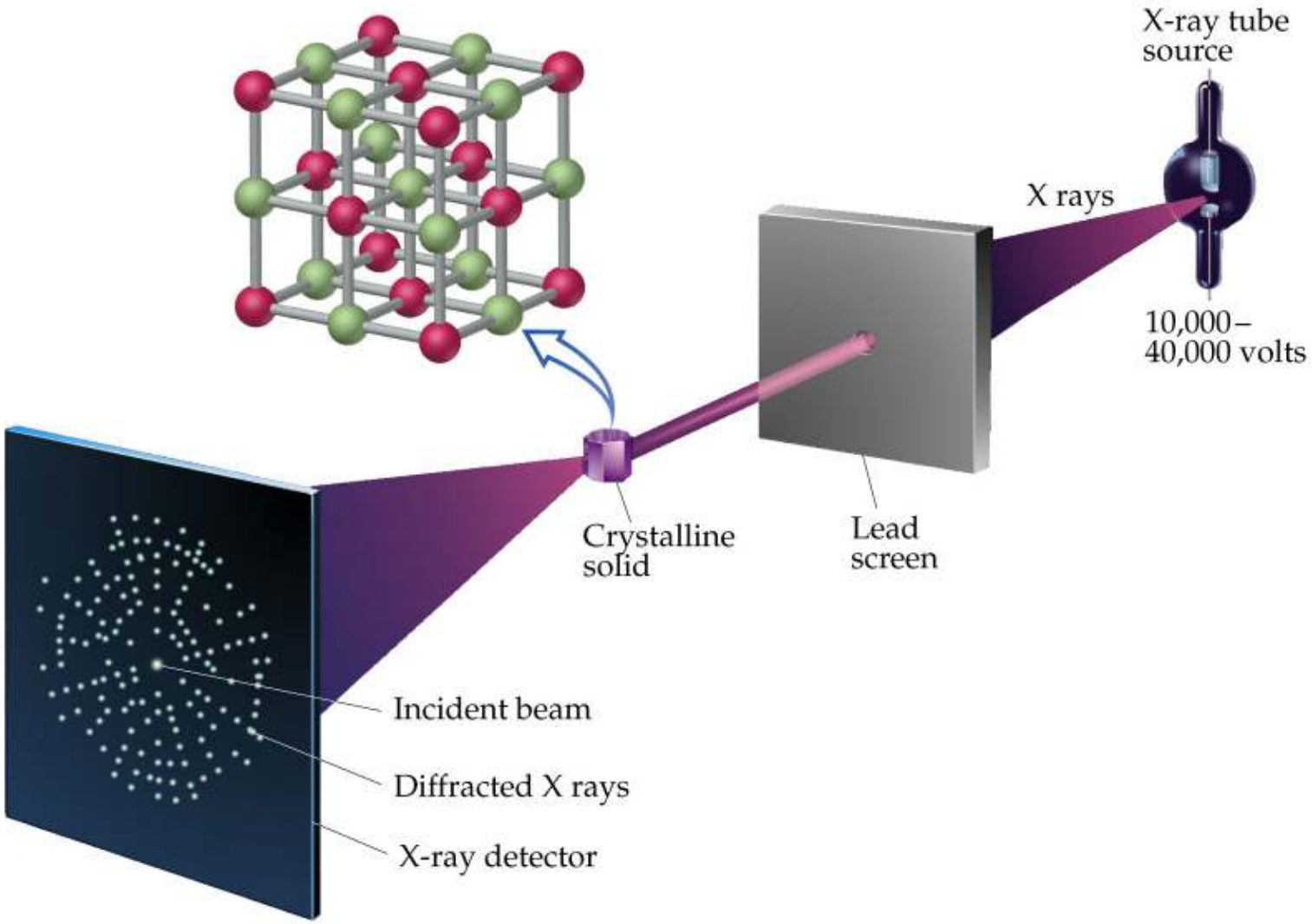
The lattice parameters *a, b, c* of a unit cell can then be calculated

The relationship between d and the lattice parameters can be determined geometrically and depends on the crystal system

Crystal system	**d_{hkl}, lattice parameters and Miller indices**
Cubic	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

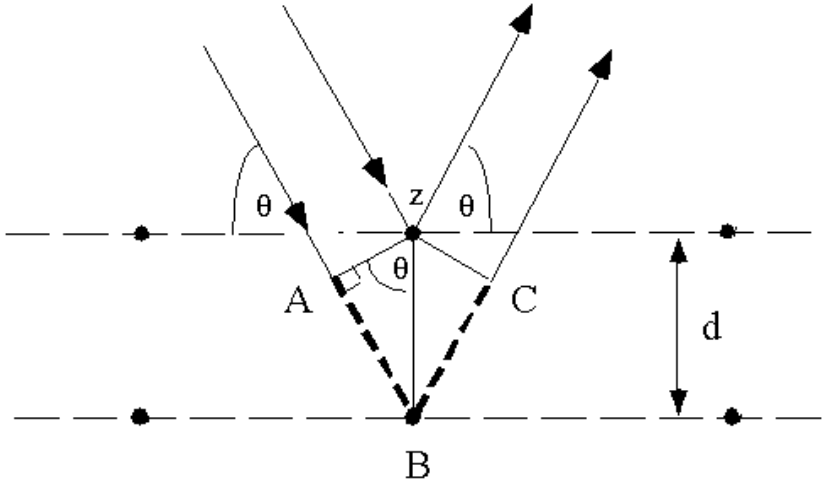
The expressions for the remaining crystal systems are more complex

The angles at which x-rays are diffracted depends on the distance between adjacent layers of atoms or ions. X-rays that hit adjacent layers can add their energies constructively when they are “in phase”. This produces dark dots on a detector plate



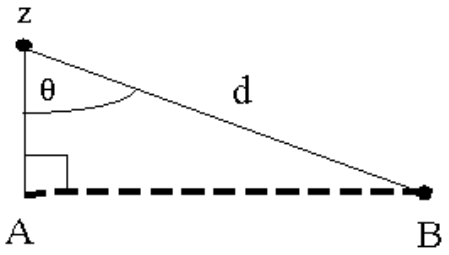
Derivation of Bragg's Law

Bragg's Law can be derived using simple geometry by considering the distances traveled by two parallel X-rays reflecting from adjacent planes. The X-ray hitting the lower plane must travel the extra distance AB and BC. To remain in phase with the first X-ray, this distance must be a multiple of the wavelength thus:



$n\lambda = AB+BC = 2AB$
(since the two triangles are identical)

The distance AB can be expressed in terms of the interplanar spacing (d) and incident angle (θ) because d is the hypotenuse of right triangle *zAB* shown at right.



$\sin(\theta) = AB/d$ thus $AB = d \sin(\theta)$

Therefore:
$n\lambda = 2\ d \sin(\theta)$

Reflection (signal) only occurs when conditions for constructive interference between the beams are met

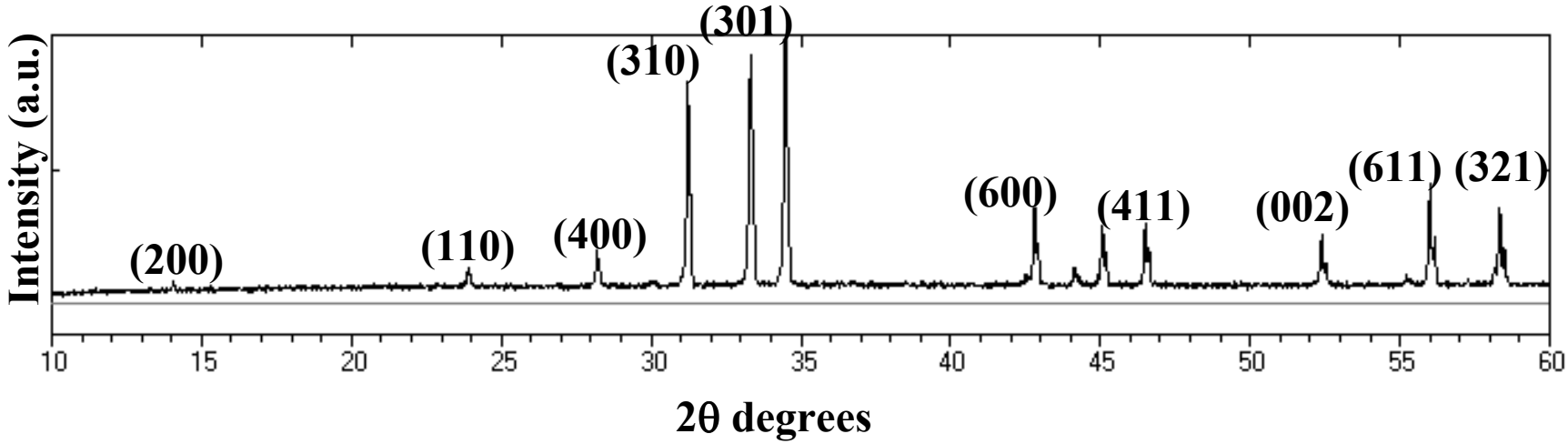
These conditions are met when the difference in path length equals an integral number of wavelengths, *n*. The final equation is the BRAGG'S LAW

$$n\lambda = 2d\sin\theta$$

Data are collected by using x-rays of a known wavelength. The position of the sample is varied so that the angle of diffraction changes

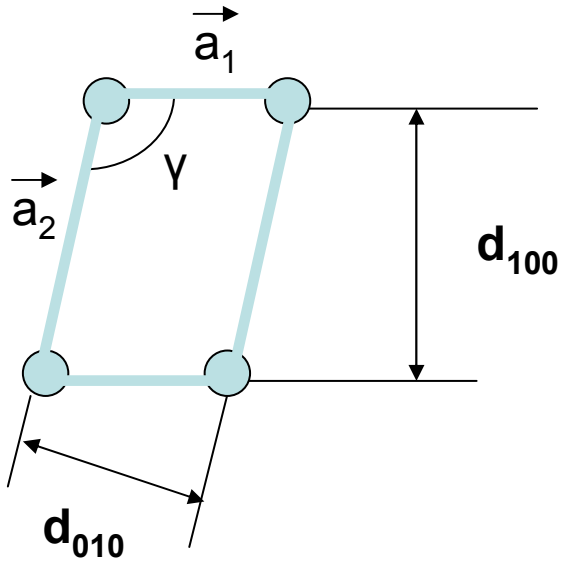
When the angle is correct for diffraction a signal is recorded

With modern x-ray diffractometers the signals are converted into peaks



Reciprocal Lattice

Because of the reciprocal nature of d spacings and θ from Bragg's Law, the pattern of the diffraction we observe can be related to the crystal lattice by a mathematical construct called the *reciprocal lattice*. In other words, the pattern of X-ray reflections makes a lattice that we can use to gain information about the crystal lattice.



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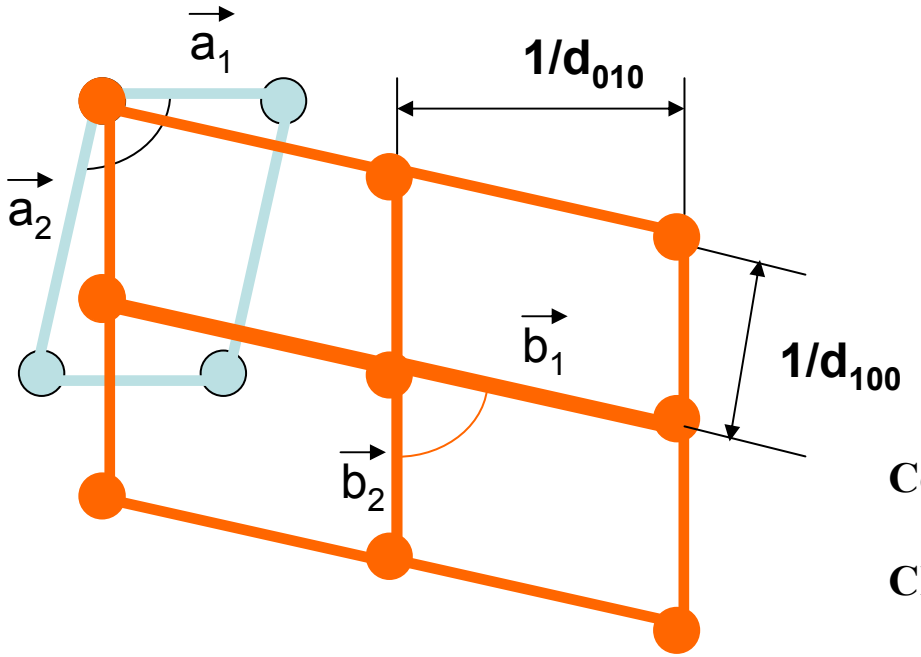


Constructing the reciprocal lattice

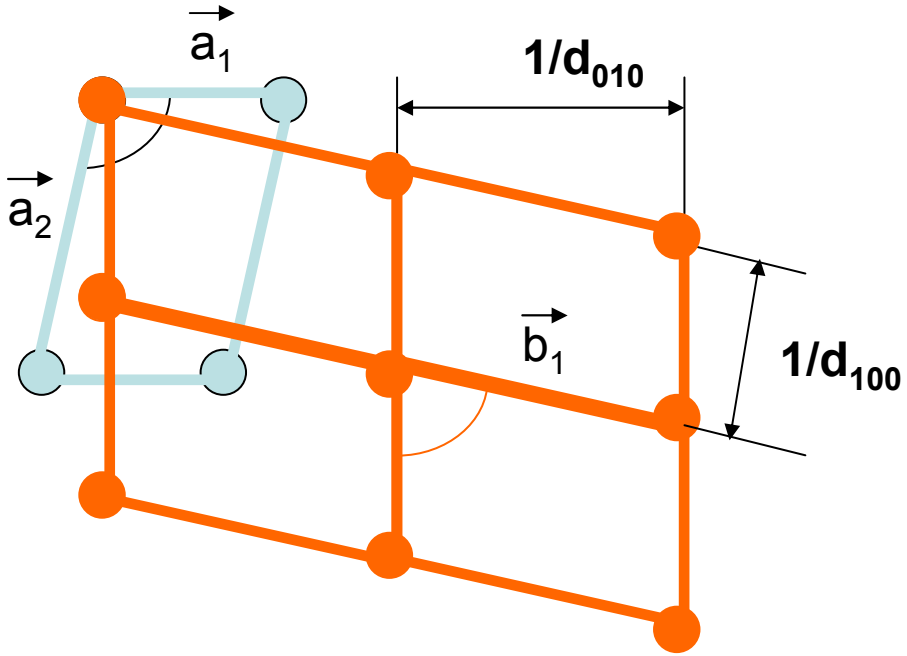
Choose a point to be the origin in the crystal lattice.

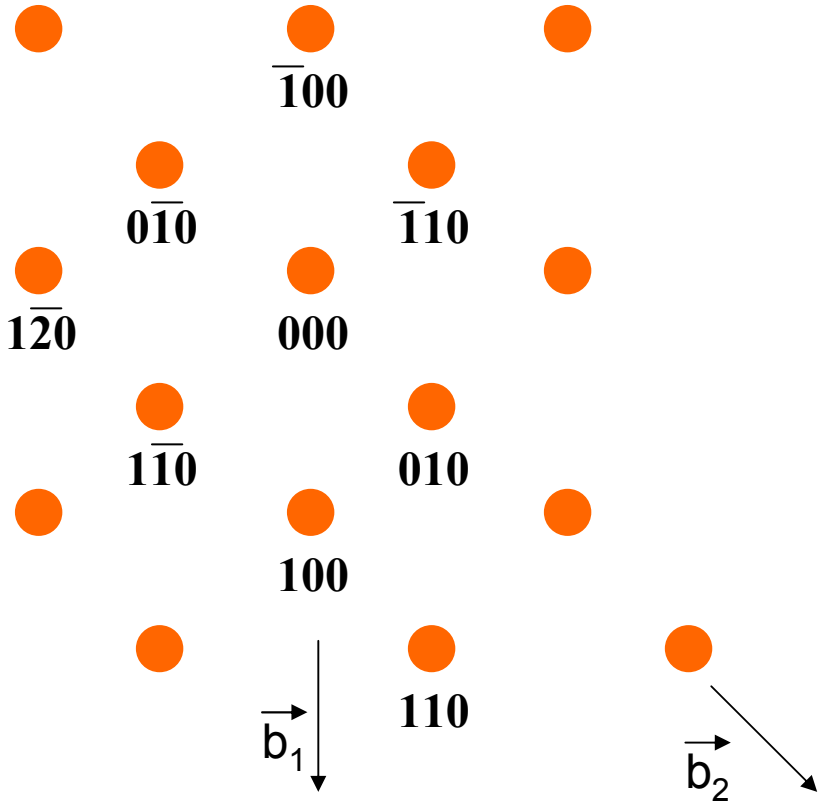
Let the vector normal to a set of lattice planes in the real lattice radiate from that origin point such that the distance of the vector is thereciprocal of the d spacing for each family of planes. i.e. the vector for the plane (hkl) has a distance of 1/d(hkl) (or, more generallyK/d(hkl)).

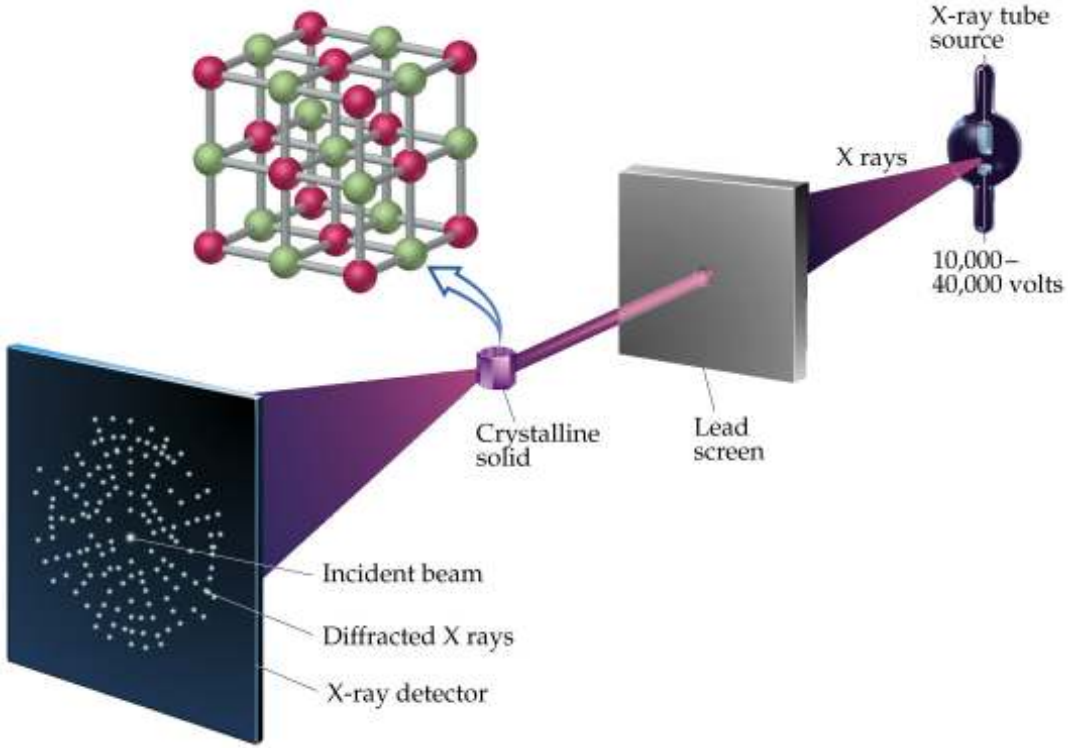
Repeat for all real lattice planes.

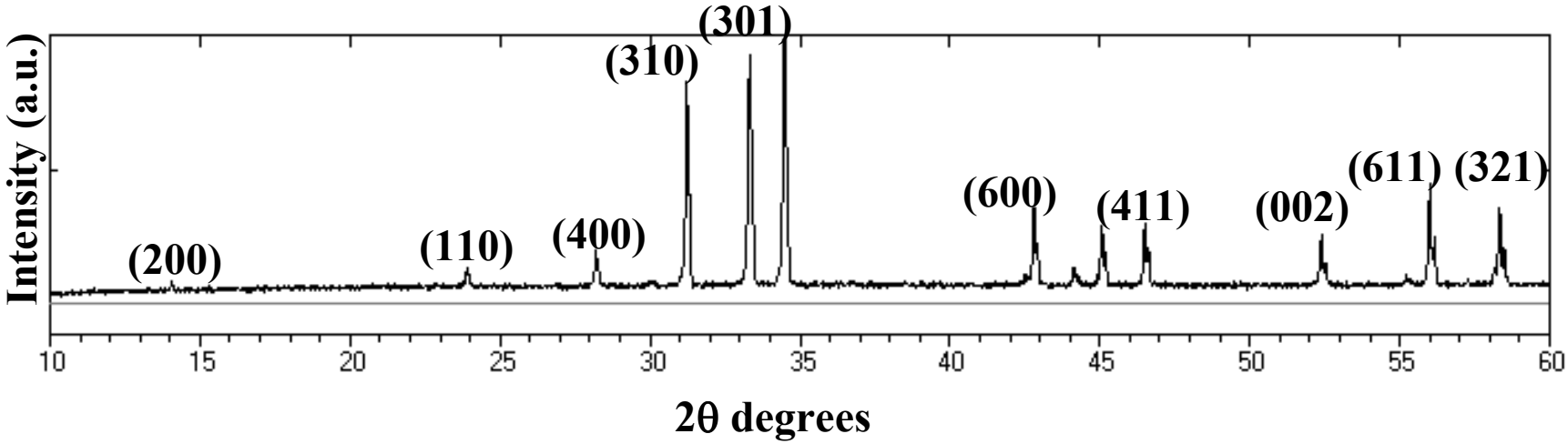
Reciprocal Lattice

This procedure constructs a reciprocal lattice in which each lattice point corresponds to the reflection that is generated by a particular family of planes. This lattice can easily be indexed by assigning the proper (hkl) value to each lattice point.






X-ray tube source
X rays
10,000–40,000 volts
Crystalline solid
Lead screen
Incident beam
Diffracted X rays
X-ray detector


Intensity (a.u.)
(200)
(110)
(400)
(310)
(301)
(600)
(411)
(002)
(611)
(321)
10
15
20
25
30
35
40
45
50
55
60
2θ degrees