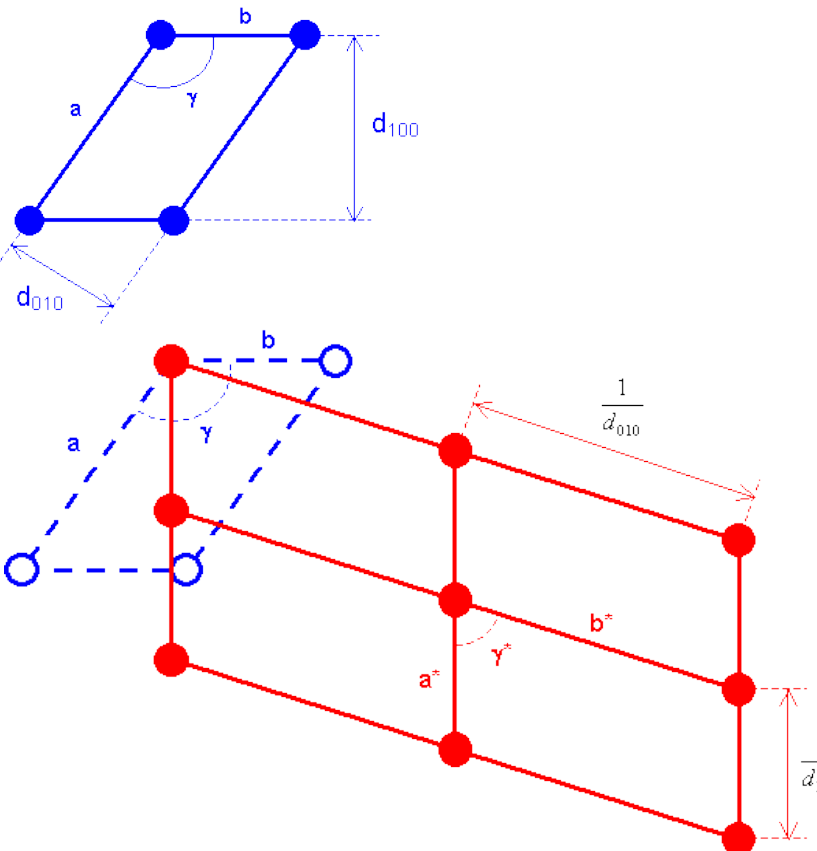# The Reciprocal Lattice

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.

The reciprocal lattice is constructed as follows:

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

2. Let the vector normal to a set of lattice planes in the real lattice (i.e. [hkl]) radiate from that origin point such that the distance of the vector is the reciprocal of the d spacing for each family of planes. i.e. the vector for the family of planes (hkl) has an orientation of [hkl] and a distance of $1/d_{(hkl)}$ (or, more generally $K/d_{(hkl)}$).

3. Repeat step 2 for all real lattice planes.

The Reciprocal Lattice

This procedure constructs a reciprocal lattice (RL) 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.
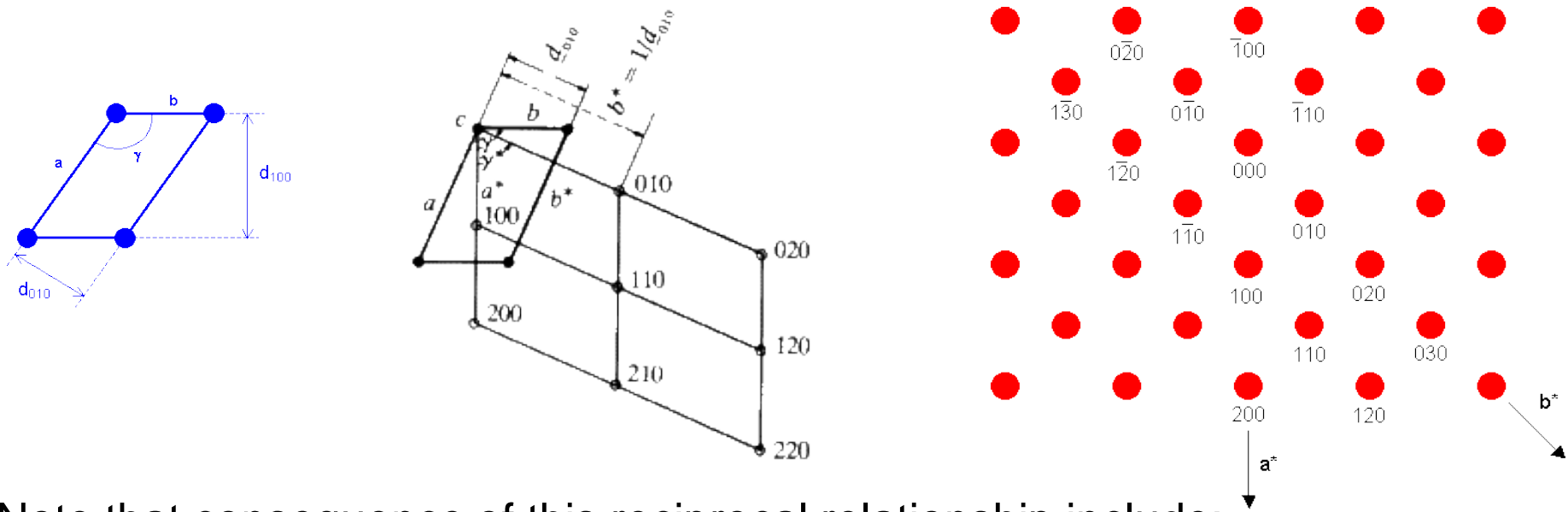
Note that consequence of this reciprocal relationship include:

-Large d spacings correspond to small spacings in the RL – this is an important feature that must be considered during data collection.

- Obtuse angles in the real lattice correspond to obtuse angles in the RL

The Reciprocal Lattice

For those of you who are comfortable with vectors, here is how the reciprocal lattice is built:

Note that:
$a \cdot a^* = 1$ (etc. – this is the reciprocal part)
$a \cdot b^* = 0$ (etc. – the vectors are orthogonal in this geometry)

Thus the reciprocal lattice can be represented by vectors of the form:

$\mathbf{R}hkl = ha^* + kb^* + lc^*$,
$|\mathbf{R}hkl| = K / dhkl$

where h, k, and l are the indices of sets of planes in the crystal, and K can assume the value of 1, λ, or $2\pi\lambda$, depending on the user's convention (crystallography, solid-state physics, etc). In later discussions, K will be assumed to have a value of 1. K is shown in the relations below for completeness.

Thus the individual lattice vectors have the following definitions:

$a^* = K (b \times c) / (a \cdot (b \times c))$ $a = (b^* \times c^*) / K (a^* \cdot (b^* \times c^*))$
$b^* = K (c \times a) / (b \cdot (c \times a))$ $b = (c^* \times a^*) / K (b^* \cdot (c^* \times a^*))$
$c^* = K (a \times b) / (c \cdot (a \times b))$ $c = (a^* \times b^*) / K (c^* \cdot (a^* \times b^*))$

$\cos\alpha^* = (\cos\beta \cos\gamma - \cos\alpha) /(\sin\beta \sin\gamma)$ $\cos\alpha = (\cos\beta^* \cos\gamma^* - \cos\alpha^*) /(\sin\beta^* \sin\gamma^*)$
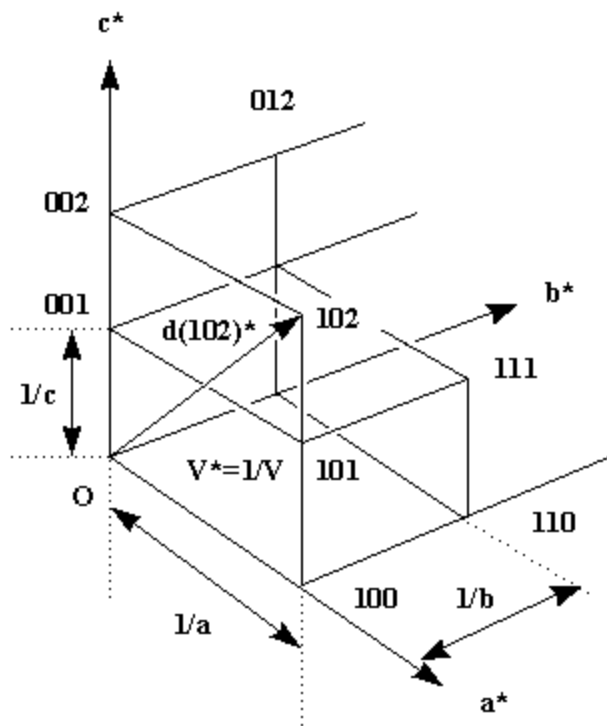$\cos\beta^* = (\cos\alpha \cos\gamma - \cos\beta) /(\sin\alpha \sin\gamma)$ $\cos\beta = (\cos\alpha^* \cos\gamma^* - \cos\beta^*) /(\sin\alpha^* \sin\gamma^*)$
$\cos\gamma^* = (\cos\alpha \cos\beta - \cos\gamma) /(\sin\alpha \sin\beta)$ $\cos\gamma = (\cos\alpha^* \cos\beta^* - \cos\gamma^*) /(\sin\alpha^* \sin\beta^*)$

$V = a \cdot b \times c = 1/V^* = abc \sqrt{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2 \cos\alpha \cos\beta \cos\gamma)}$
$V^* = a^* \cdot b^* \times c^* = 1/V = a^*b^*c^* \sqrt{(1 - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^* + 2 \cos\alpha^* \cos\beta^* \cos\gamma^*)}$

The Reciprocal Lattice

Some of the important relationships between the real lattice and the reciprocal lattice (in non-vector notation) are summarized here. Note that K = 1 in these equations.

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

$$a^* = V^{-1}bc\sin\alpha$$

$$b^* = V^{-1}ac\sin\beta$$

$$c^* = V^{-1}ab\sin\gamma$$

$$V^* = V^{-1}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \text{(orthogonal)}$$

$$\frac{1}{d^2} = \frac{4}{3}\cdot\frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2} \quad \text{(hexagonal)}$$

$$\frac{1}{d^2} = \frac{\left(\frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{l^2}{c^2}\sin^2\gamma + \frac{2kl}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{2hl}{ac}(\cos\alpha\cos\gamma - \cos\beta) + \frac{2hk}{ab}(\cos\alpha\cos\beta - \cos\gamma)\right)}{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)} \quad \text{(triclinic)}$$

The presence of translational symmetry elements and centering in the real lattice causes some series of reflections to be absent – we will deal with this in more detail when we look at structure factors.

The presence of systematic absences can be understood in a simple way from Bragg's Law. If a set of lattice planes occupy a position such that they reflect X-rays completely out-of-phase with another set of lattice planes, then no reflection will be observed. I.e. although the Bragg condition is satisfied for the sets of planes in question, the destructive interference "extinguishes" the reflection. This situation only arises if there are translational symmetry elements or centering in the crystal lattice.
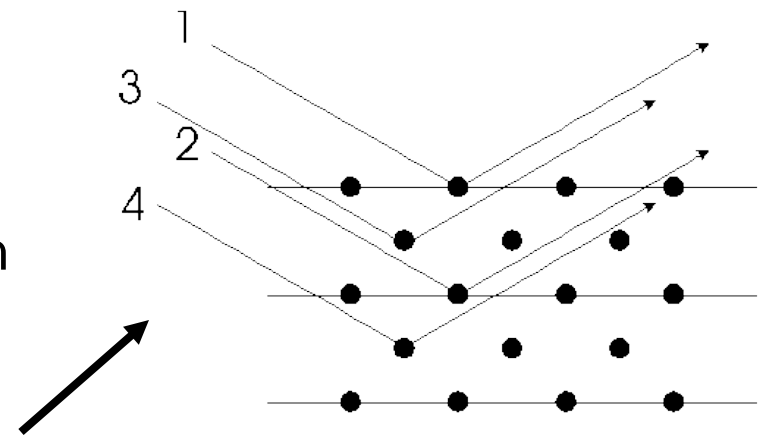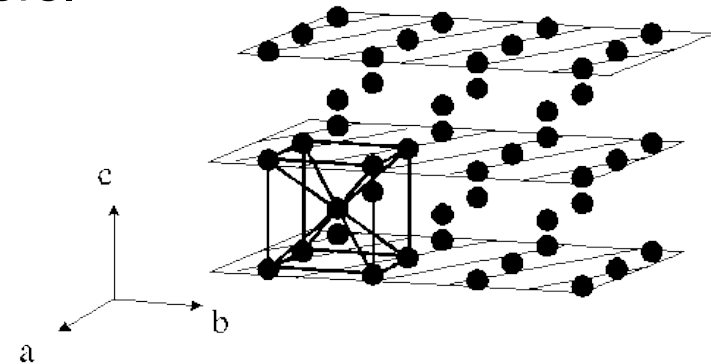
e.g. the (001) reflection in a cubic *I* lattice (BCC) is absent.
Consider the additional path lengths vs. beam "1":
For "2" it is $2d \sin(\theta)$; for "3" it is $2(d/2) \sin(\theta)$, thus the rays from "3" will be exactly out-of-phase with those of "2" and no reflection will be observed.

These systematic absences (or "*systematic extinctions*") thus indicate the presence of centering and/or specific symmetry elements in the lattice and provide us with information about the space group of the crystal. Note that in the *International Tables*, the "limiting conditions" for reflections are reported – this is the opposite of a systematic absence – so be careful in interpreting the information. Note that the conditions for reflections or absences are reported as simple equations in which "n" indicates any integer.

E.g. if for reflections of the type (h00), $h = 2n + 1$ are absent (this means that if h is odd, then the reflection will not be observed)
Conversely, this means that the limiting condition for such reflections to be observed is: for (h00), $h = 2n$ (i.e. reflections are only observed when h is even)
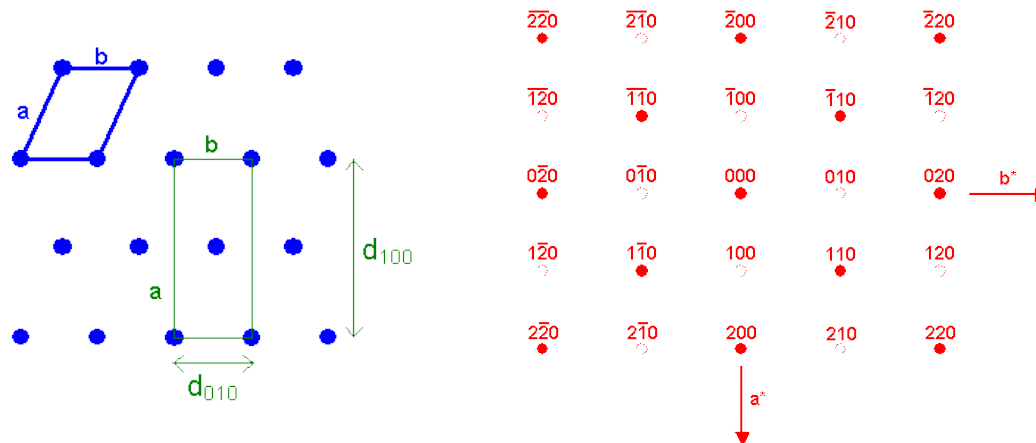
E.g. for *C* centered cells, such as the one pictured above, (hkl) reflections are systematically absent when: $h + k = 2n + 1$ (if the sum of h and k is odd)

Because certain symmetry elements cause absences that supersede those caused by other elements, it is necessary to search for the presence of symmetry elements in the following order: first search for unit cell centering, then for glide planes, then for screw axes.

The reason for this becomes apparent upon examination of the conditions listed below – note there are some more conditions that are found in the hand-out for today.

Symmetry Element	reflection	absence conditions
A centered Lattice (A)	hkl	$k+l = 2n+1$
B centered Lattice (B)		$h+l = 2n+1$
C centered Lattice (C)		$h+k = 2n+1$
face-centered Lattice (F)	hkl	$h+k = 2n+1$
		$h+l = 2n+1$
		$k+l = 2n+1$
Body centered Lattice (I)	hkl	$h+k+l = 2n+1$

Systematic Absences

Symmetry Element			reflection	absence conditions

Glide Perpendicular to *a*

translation	b/2	(b)	0kl	$k = 2n+1$
	c/2	(c)		$l = 2n+1$
	b/2+c/2	(n)		$k+l = 2n+1$
	b/4+c/4	(d)		$k+l = 4n+1$

Glide Perpendicular to *b*

translation	a/2	(a)	h0l	$h = 2n+1$
	c/2	(c)		$l = 2n+1$
	a/2+c/2	(n)		$h+l = 2n+1$
	a/4+c/4	(d)		$h+l = 4n+1$

Glide Perpendicular to *c*

translation	a/2	(a)	hk0	$h = 2n+1$
	b/2	(c)		$k = 2n+1$
	a/2+b/2	(n)		$h+k = 2n+1$
	a/4+b/4	(d)		$h+k = 4n+1$

| 2_1-fold screw		a	h00	$h = 2n+1$
4_2-fold screw along		b	0k0	$k = 2n+1$
6_3-fold screw		c	00l	$l = 2n+1$

Overall, the combination of the symmetry of the reciprocal lattice and the presence or absence of certain types of reflections is used to determine the space group of the crystal lattice. In practice, the identification of systematic absences is done by the collection software on the diffractometer and you will rarely have to look at the results yourself. Note that in many cases the systematic absences are not enough to differentiate between alternative space groups (e.g. *Cc* and *C2/c*) so one must solve the structures and assess the final results using statistical methods. We will look at this and also examine systematic absences in the context of structure factors later in the course.
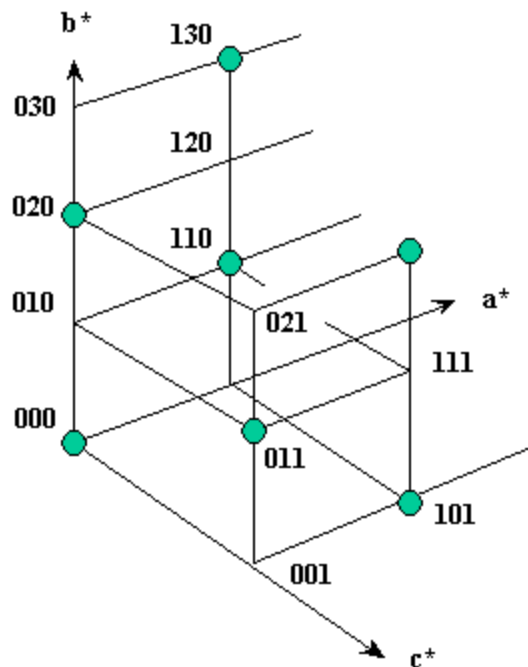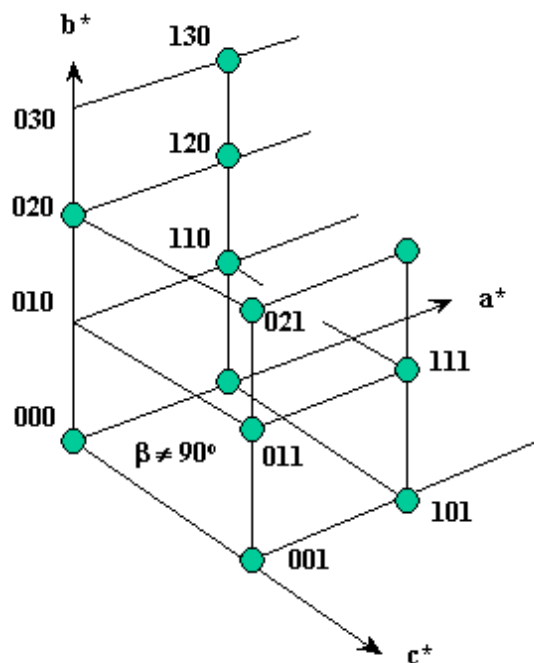
Remember that reciprocal lattices are 3-dimensional and you might have to look in different layers to find the absences.

The Ewald Sphere

We have constructed the reciprocal lattice (RL) in terms of the reciprocal d-spacings, $1/d_{hkl}$, another utility of this lattice in terms of crystallography is made apparent by the Ewald sphere, which tells us the angle at which each family of planes will diffract!

Consider a circle of radius r, with points X and Y lying on the circumference.
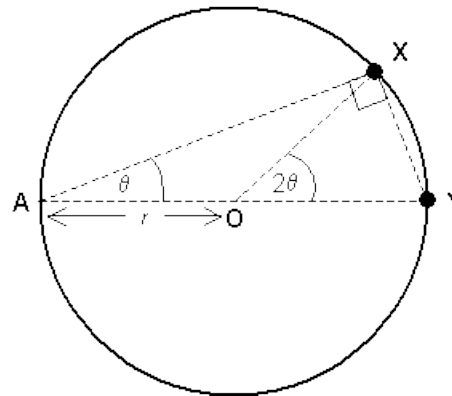
If the angle XAY is defined as θ, then the angle XOY will be 2θ by geometry and $\sin(\theta) = XY/2r$

If this geometry is constructed in reciprocal space, then it has some important implications.

The radius can be set to $1/\lambda$, where λ is the wavelength of the X-ray beam.

If Y is the 000 reciprocal lattice point, and X is a general point hkl, then the distance XY is $1/d_{hkl}$

Thus: $\sin(\theta) = (1/d_{hkl})/(2/\lambda)$ or, rearranged: $\lambda = 2 d_{hkl} \sin(\theta)$, and Bragg's law is satisfied!

This means that when a lattice point intersects the Ewald sphere, the reflection corresponding to that family of planes will be observed and the diffraction angle will be apparent. The step-by-step construction and initial use of a Ewald sphere is described on the web site (http://www.doitpoms.ac.uk/tlplib/reciprocal_lattice/ewald.php).
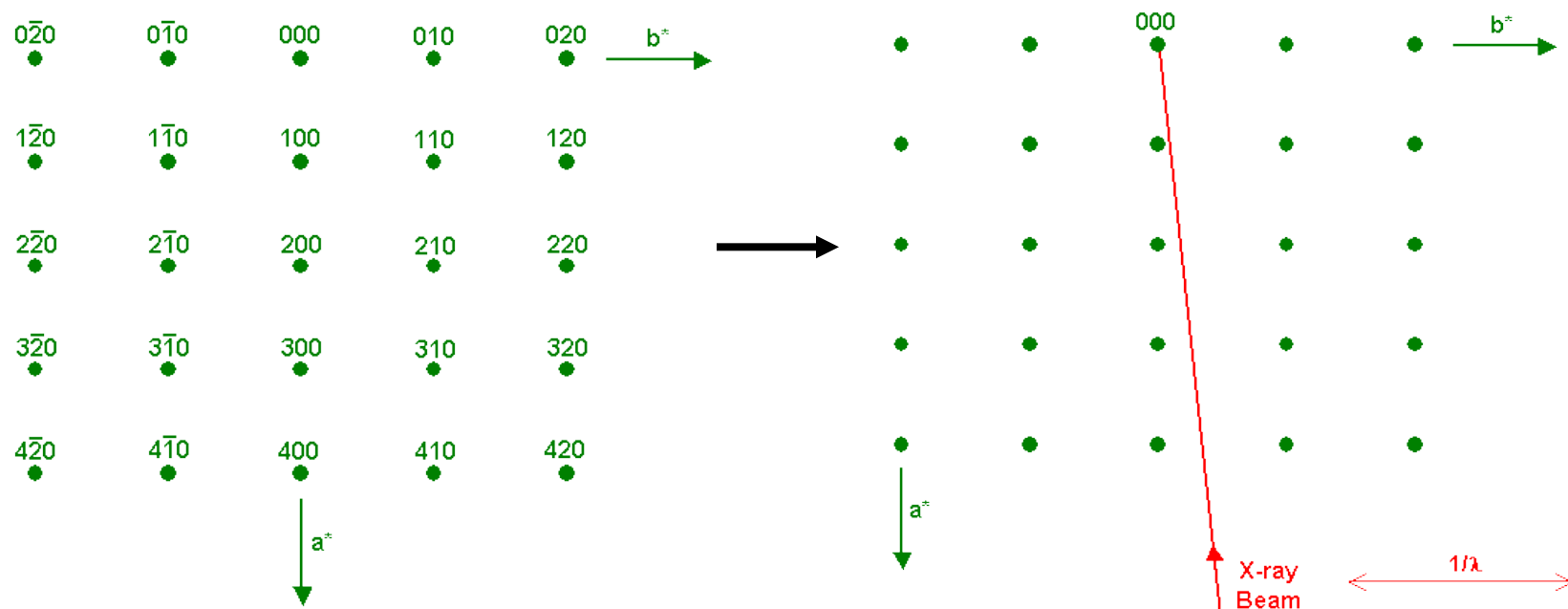
Starting with an indexed reciprocal lattice, an incident X-ray beam must pass through the origin (000) point, corresponding to the direct undiffracted beam of X-rays.
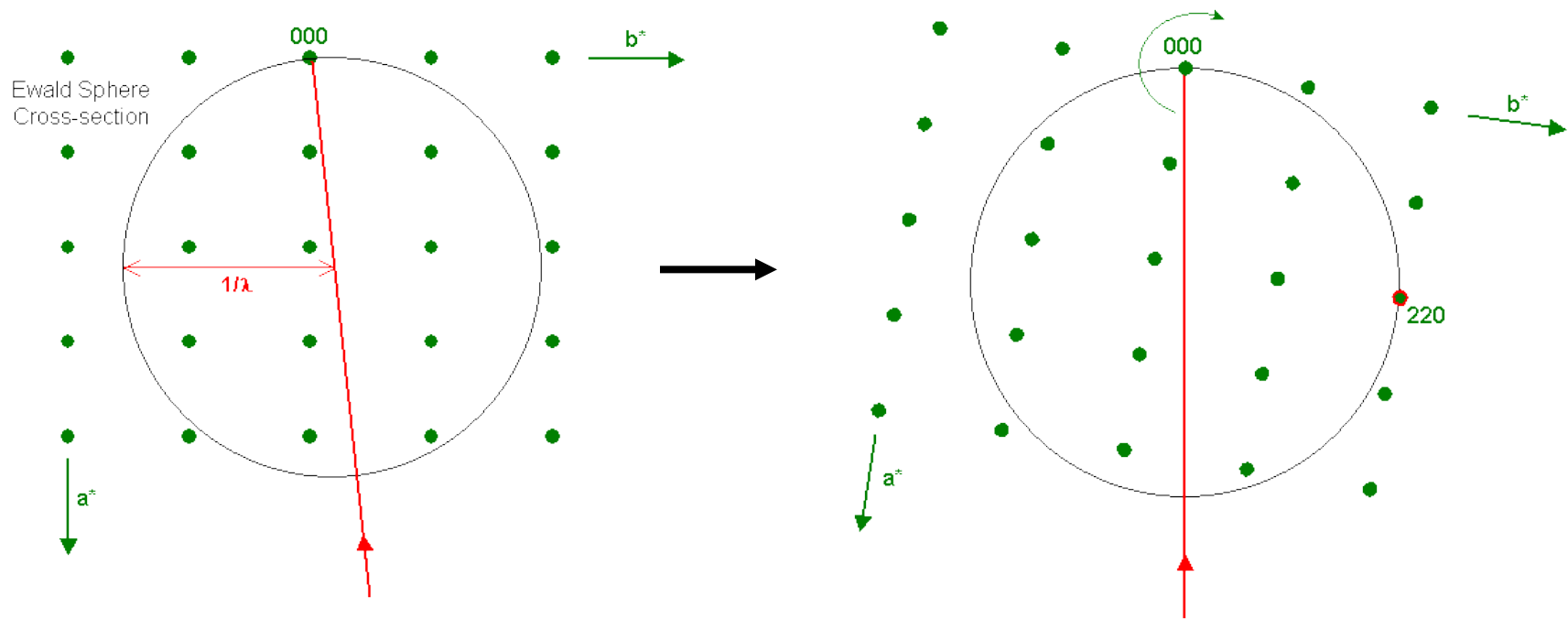
The Ewald sphere for this case is defined by making a sphere of radius $1/\lambda$ having its diameter on the X-ray beam that intersects the origin point. In the diagram on the left, no other RL points are on the surface of the sphere so the Bragg condition is not satisfied for any of the families of planes. To observe reflections, the reciprocal lattice must be rotated until an RL point contacts the surface of the sphere. Note: it would be easier to rotate the sphere on paper, but in practice, we rotate the crystal lattice and the RL.
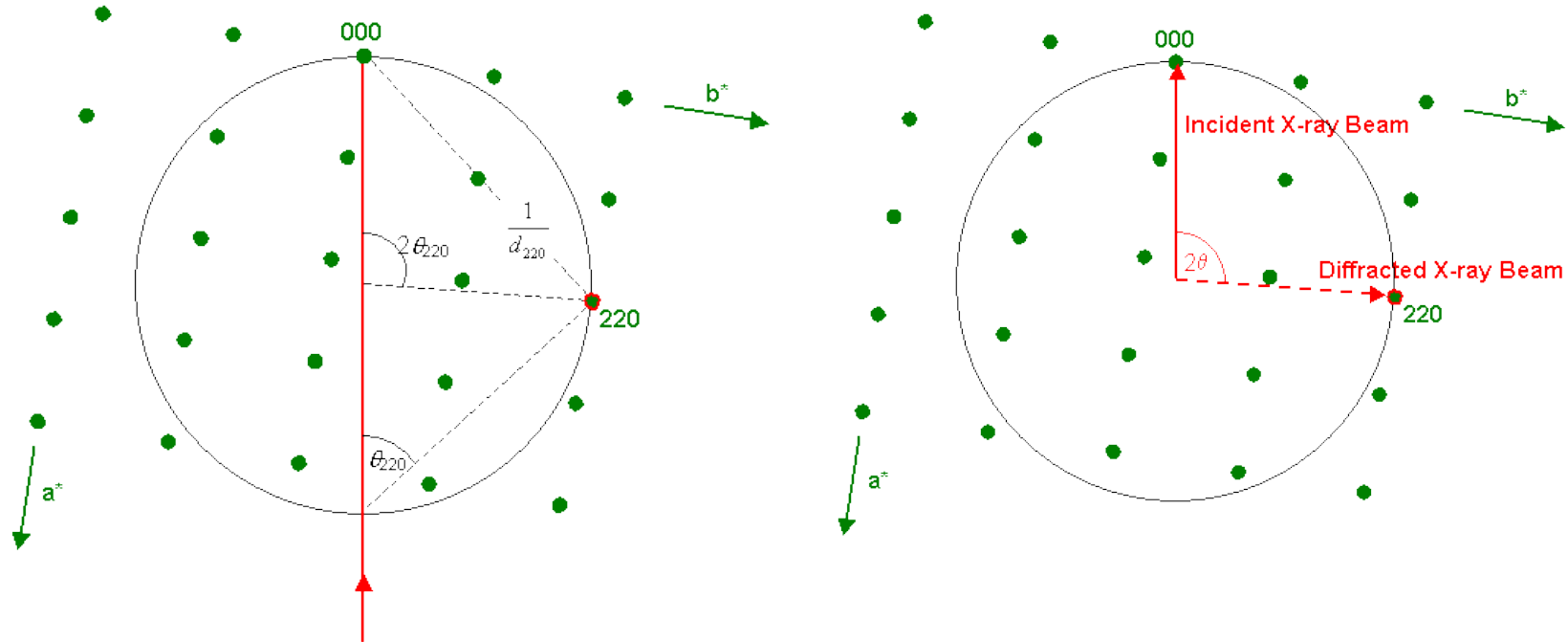
The Ewald Sphere

When a reciprocal lattice point intersects the Ewald sphere, a reflection will occur and can be observed at the 2θ angle of the inscribed triangle. To be able to collect as many different reflections as possible, it is thus necessary to be able to rotate the reciprocal lattice to a great extent…

You can see how this works at: http://www.doitpoms.ac.uk/tlplib/reciprocal_lattice/ewald.php

Our need to rotate the crystal in numerous ways to bring all of the families of planes into reflection (i.e. to make RL point intersect with the Ewald sphere) explains the design of the goniometer portion of the diffractometer. The 4-circles of the goniometer allows the crystal to be rotated in virtually any direction while remaining in the X-ray beam. The labels for each of the goniometer axes (ϕ, χ, ω, and θ) are indicated on the diagram below. Note that there are different designs (such as the Kappa geometry) that accomplish the same task.
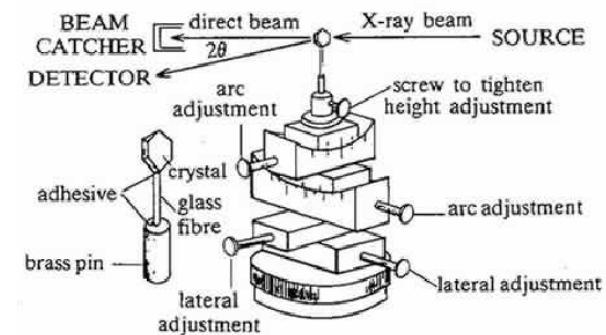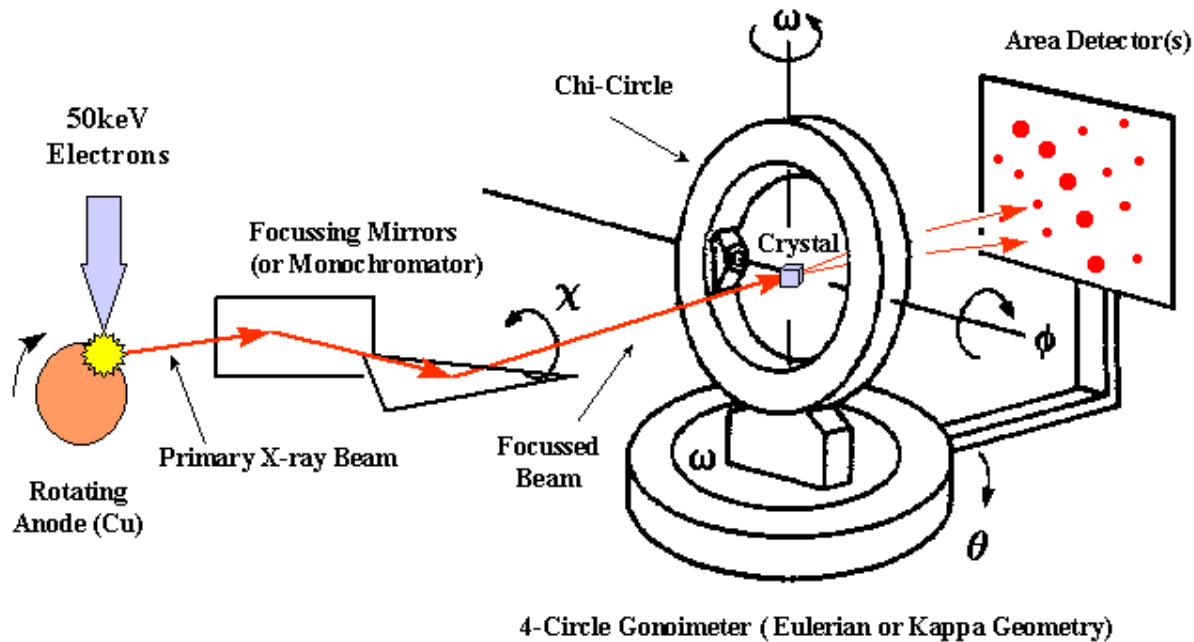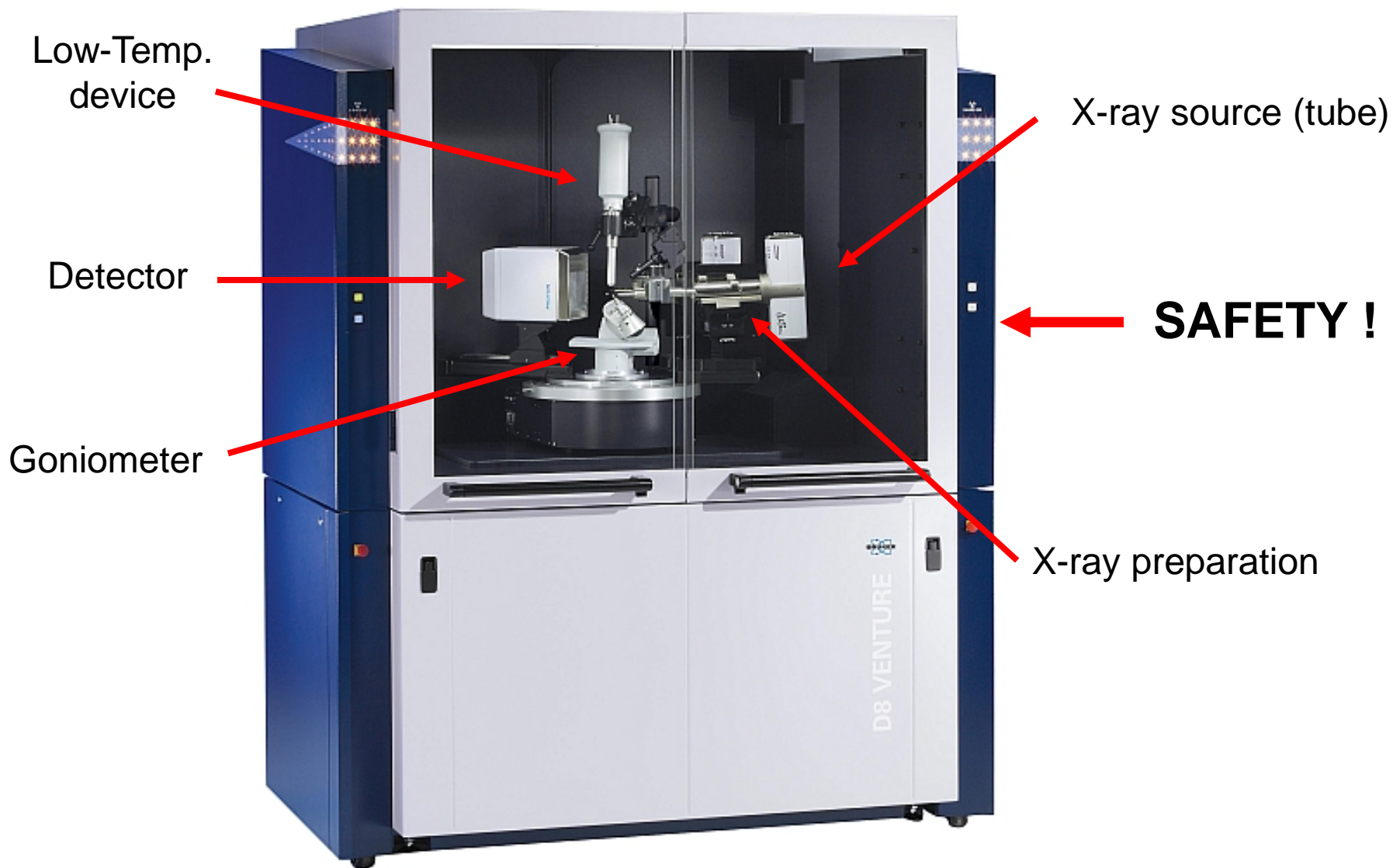

4-Circle Goniometer (Eulerian or Kappa Geometry)

Fig. 23.

A Bruker D8 Venture Diffractometer

Low-Temp. device

X-ray source (tube)

Detector

SAFETY !

Goniometer

X-ray preparation

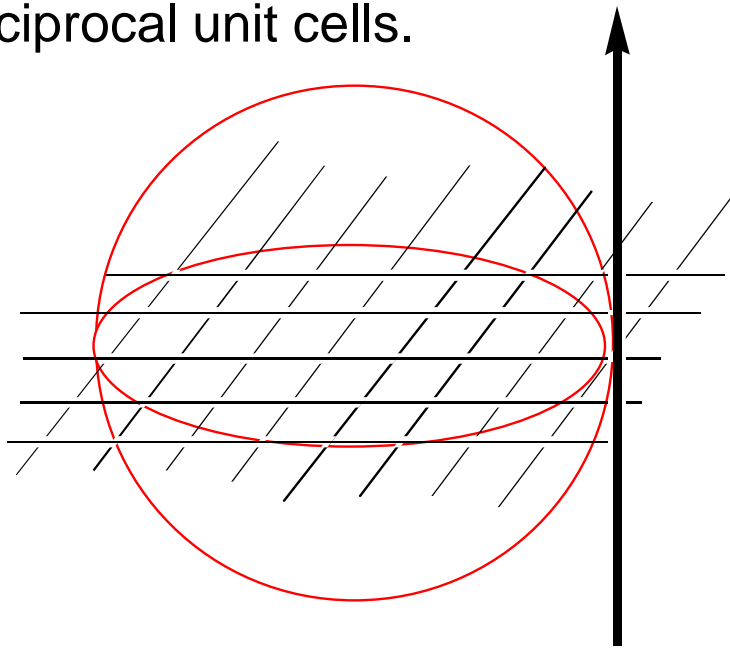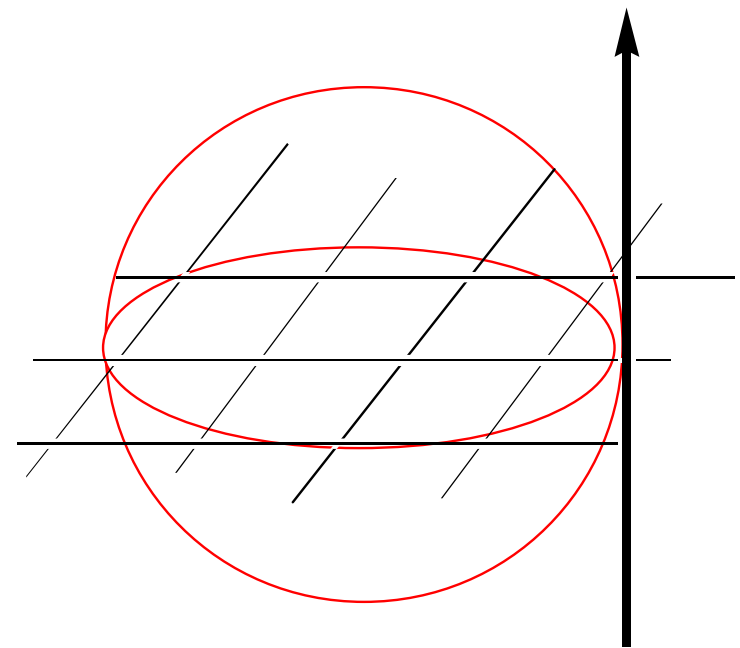# The Ewald Sphere

If one rotates the Ewald sphere completely about the (000) reciprocal lattice point in all three dimensions, the larger sphere (of radius $2/\lambda$) contains all of the reflections that it is possible to collect using that wavelength of X-rays. This construction is known as the "Limiting sphere" and it defines the complete data set. Any reciprocal lattice points outside of this sphere can not be observed. Note that the shorter the wavelength of the X-radiation, the larger the Ewald sphere and the more reflections may be seen (in theory).
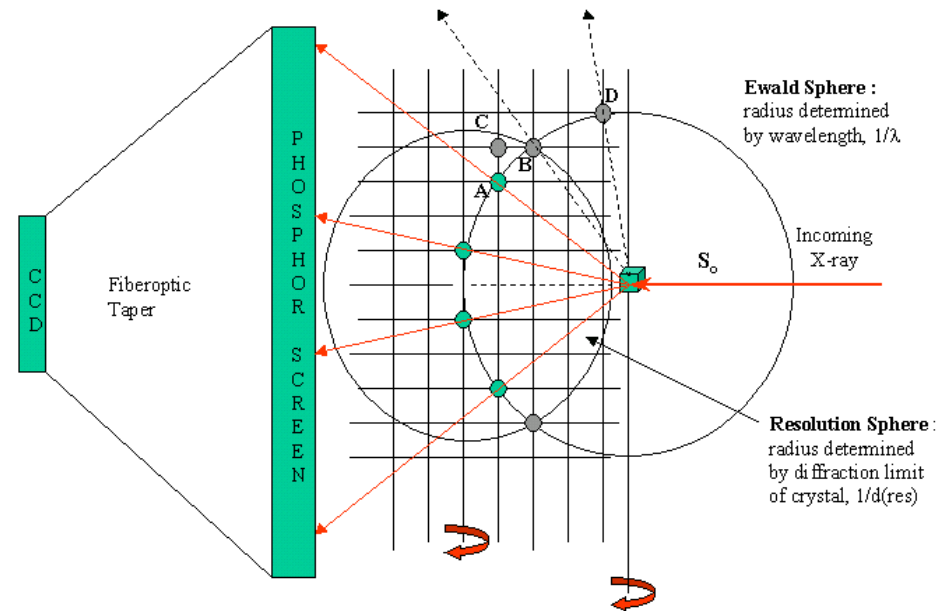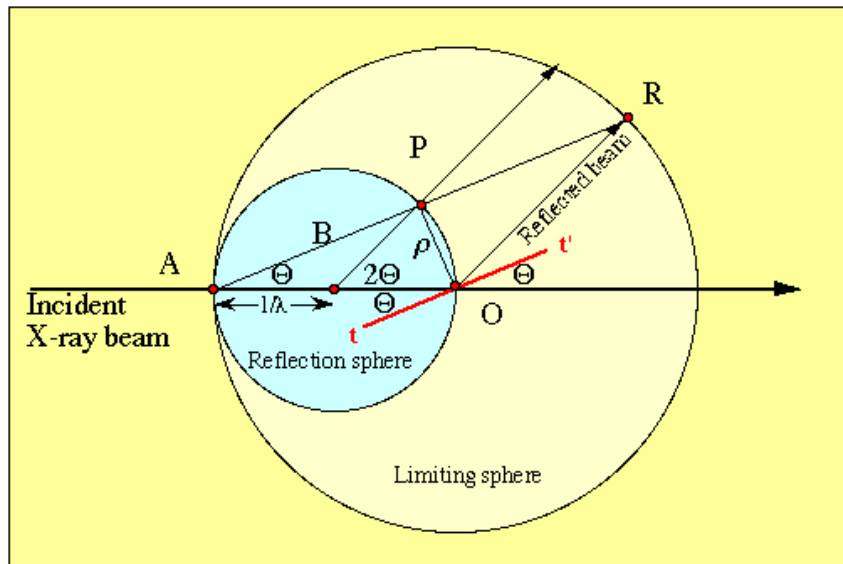
The limiting sphere will hold roughly $(4/3\pi r^3/ V^*)$ lattice points. Since $r = 2/\lambda$, this equates to around $(33.5/ V^*\lambda^3)$ or $(33.5 V/\lambda^3)$ reflections. For an orthorhombic cell with a volume of 1600Å^3, this means $CuK\alpha$ can give around 14,700 reflections while $MoK\alpha$ would give 152,000 reflections.

The Ewald Sphere

Remember that the reciprocal lattice can also be defined in terms of the wavelength of the X-radiation (by setting K = λ). In such a construction, the Ewald sphere remains the same size, having a radius of 1 ($\lambda \cdot 1/\lambda = 1$), independent of the wavelength. Such pictures show the increased number (and density) of reflections for the shorter wavelength radiation. As noted previously, this means that longer wavelength radiation might be necessary to resolve individual reflections for crystals with large unit cells and small reciprocal unit cells.

short λ long λ

To see many of these effects, get XrayView (http://phillips-lab.biochem.wisc.edu/software.html).