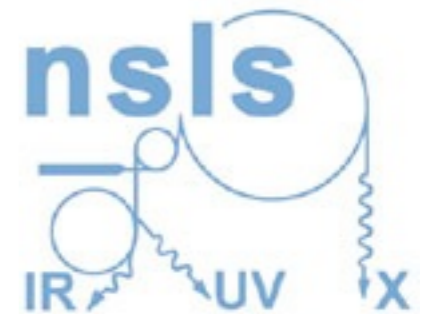
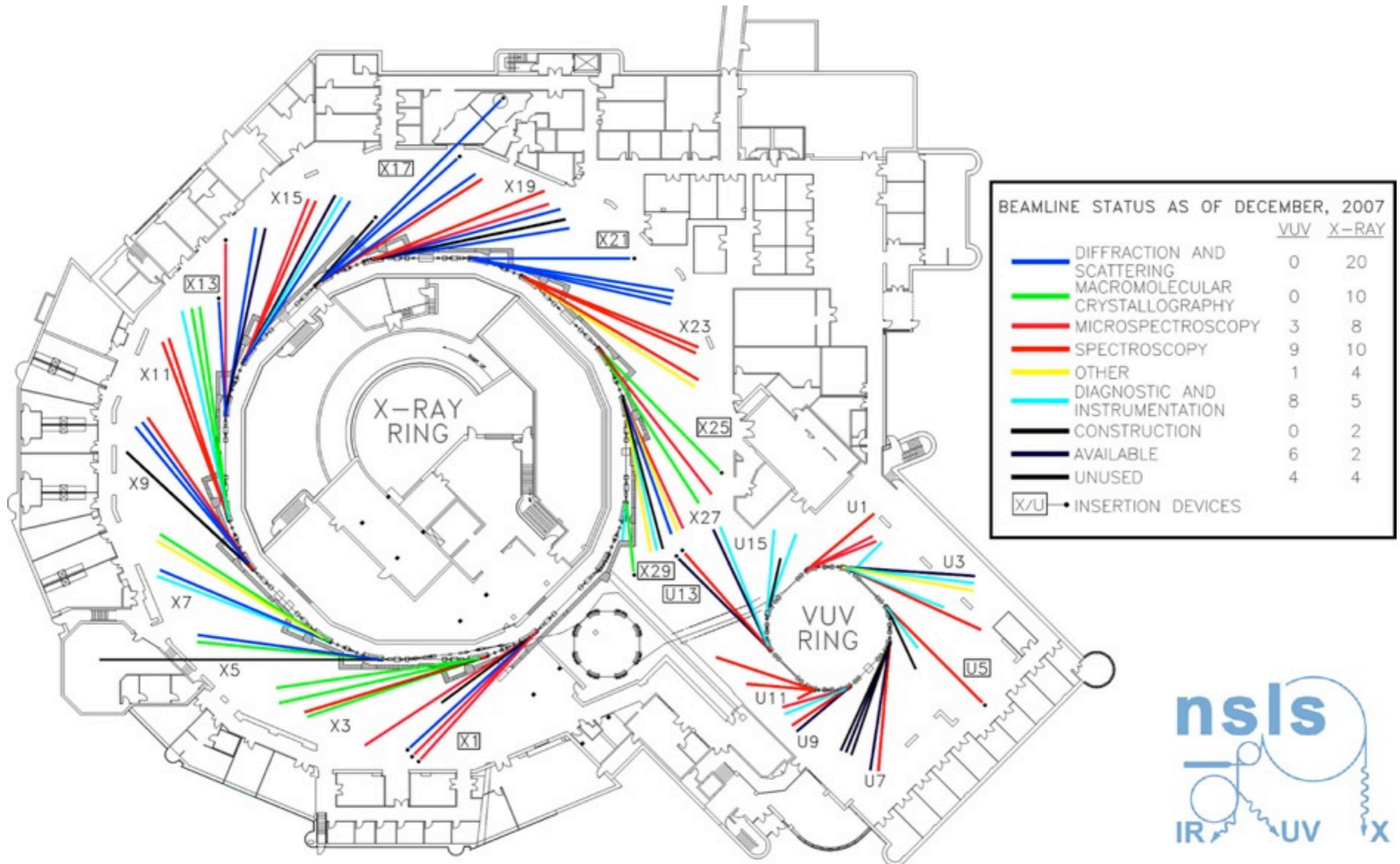


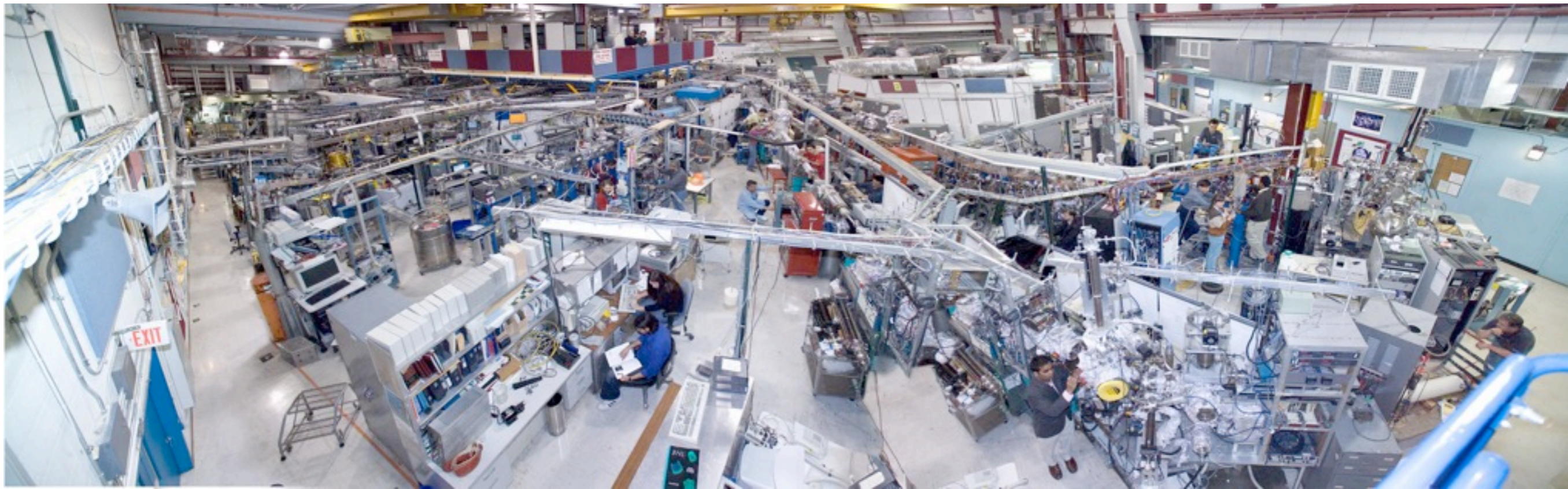
X-ray Crystallography

III

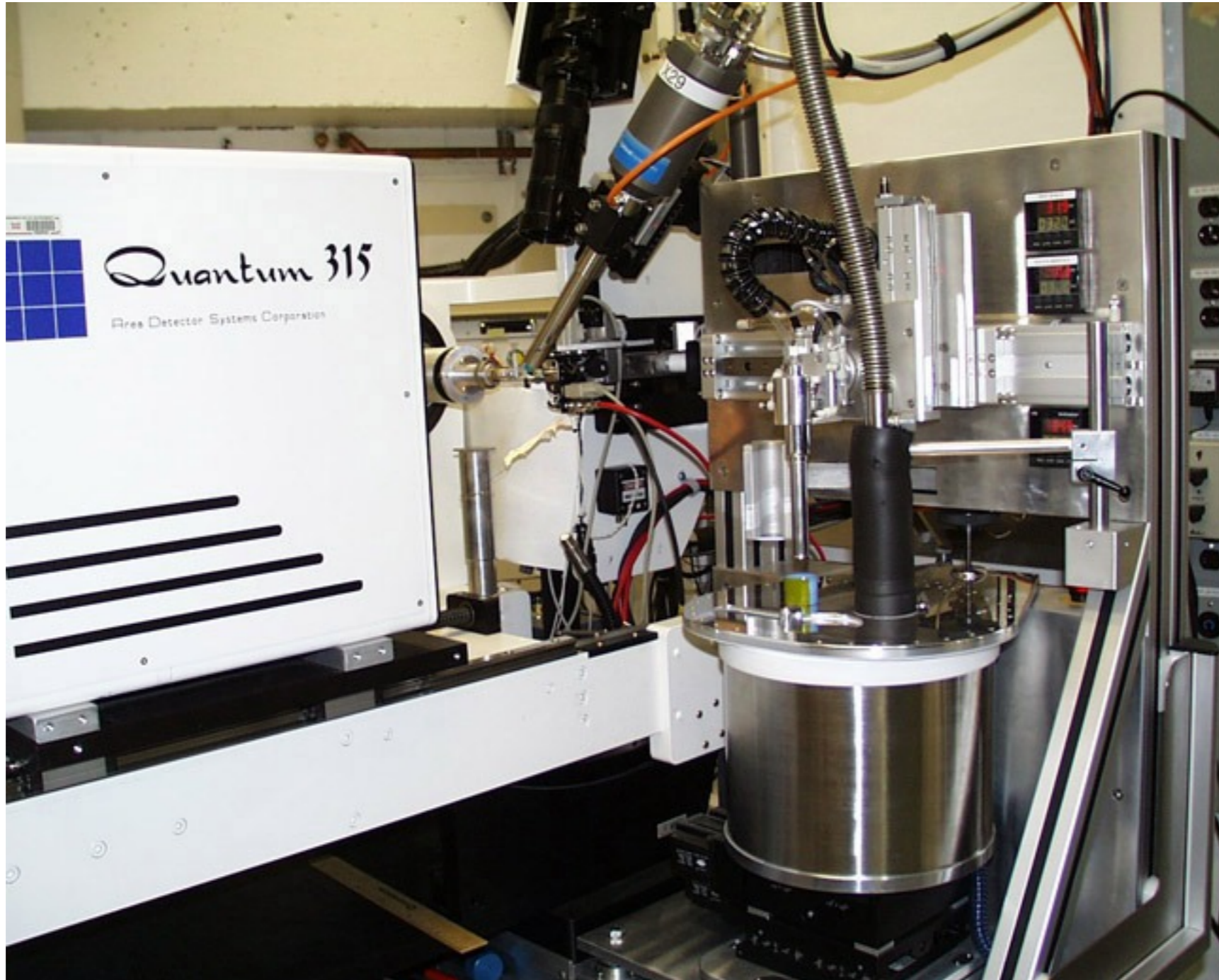
National Synchrotron Light Source

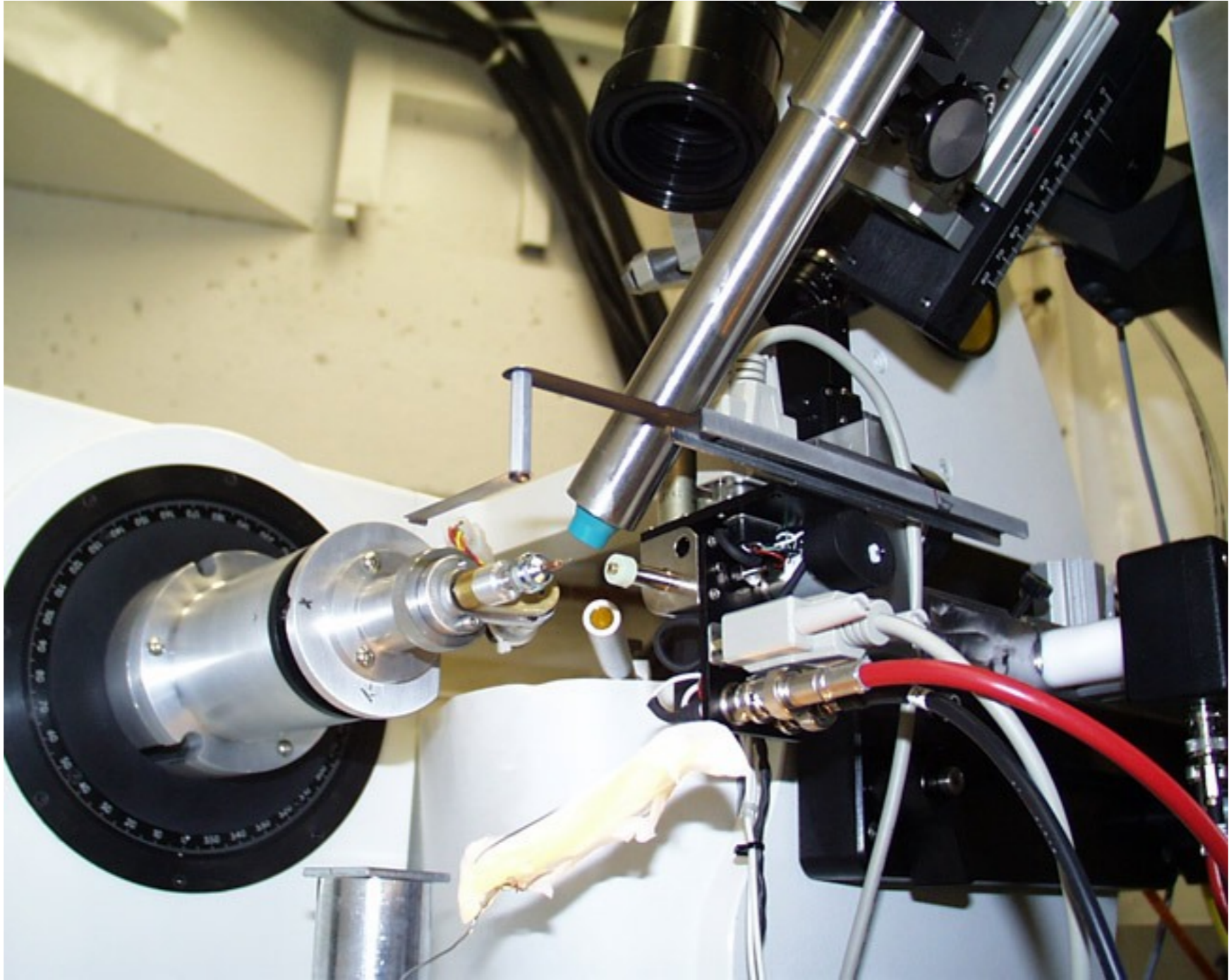


Experimental Floor at NSLS

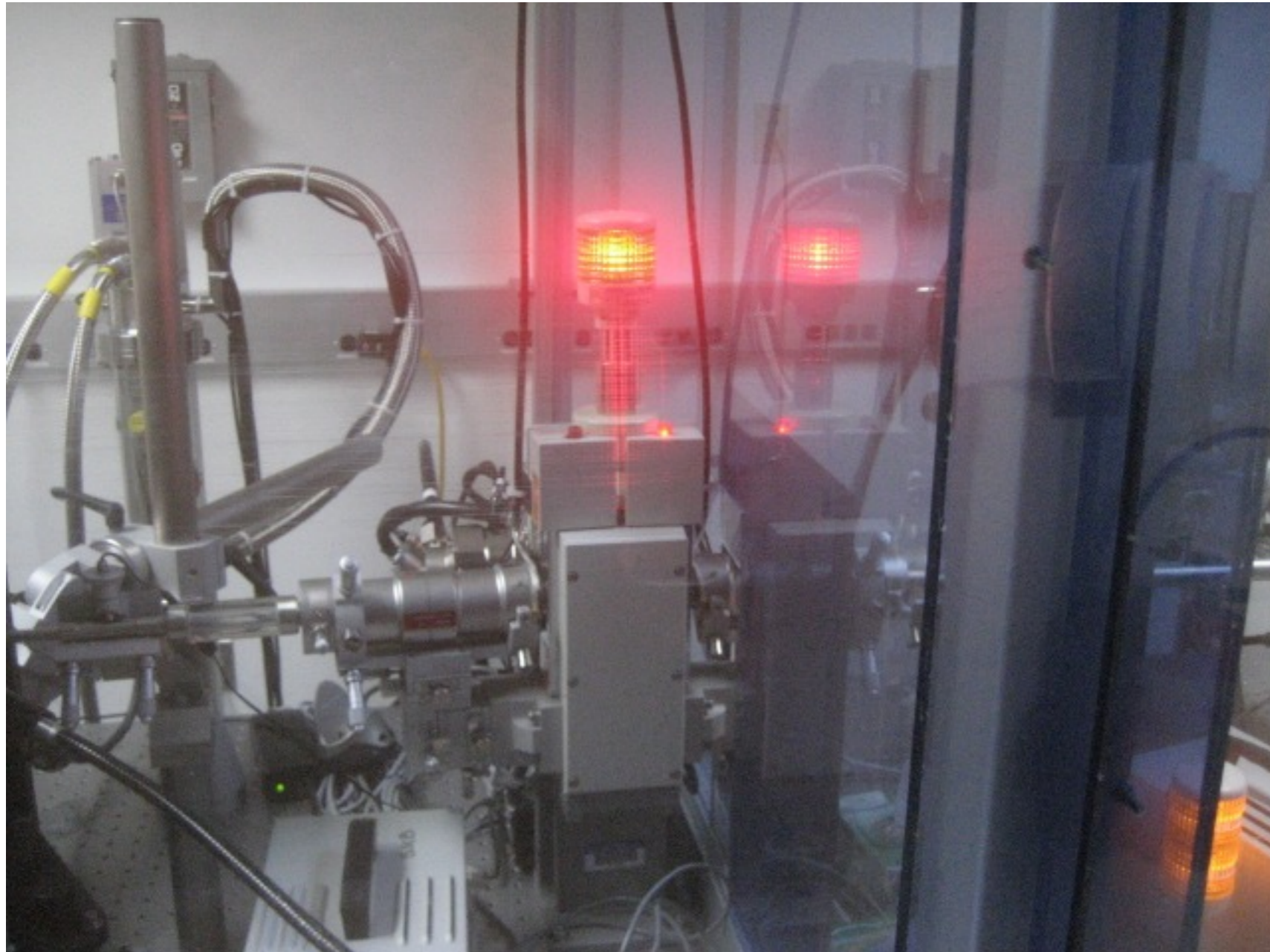


X29 Beamline NSLS

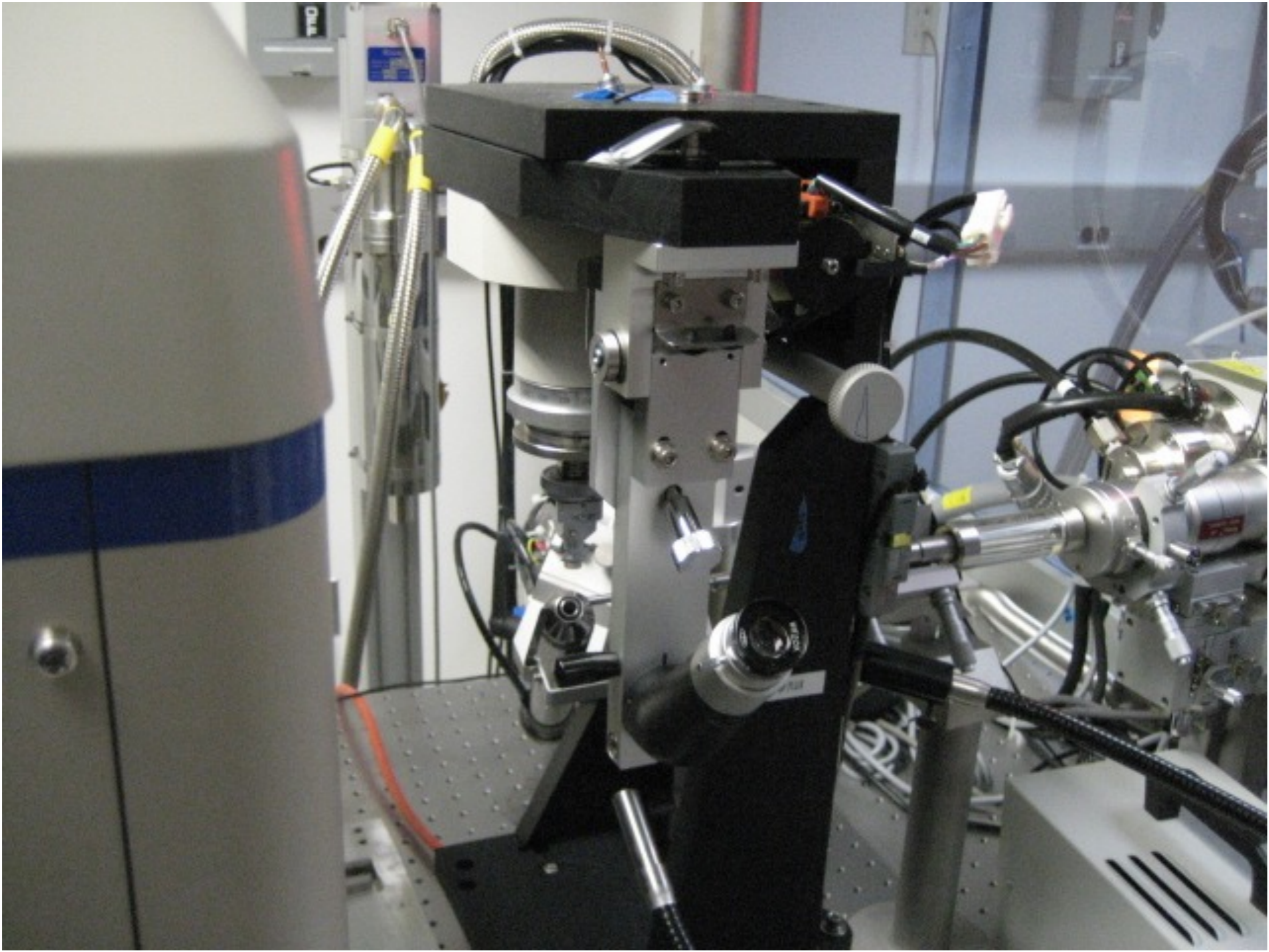




“Home” Source - Rotating Anode



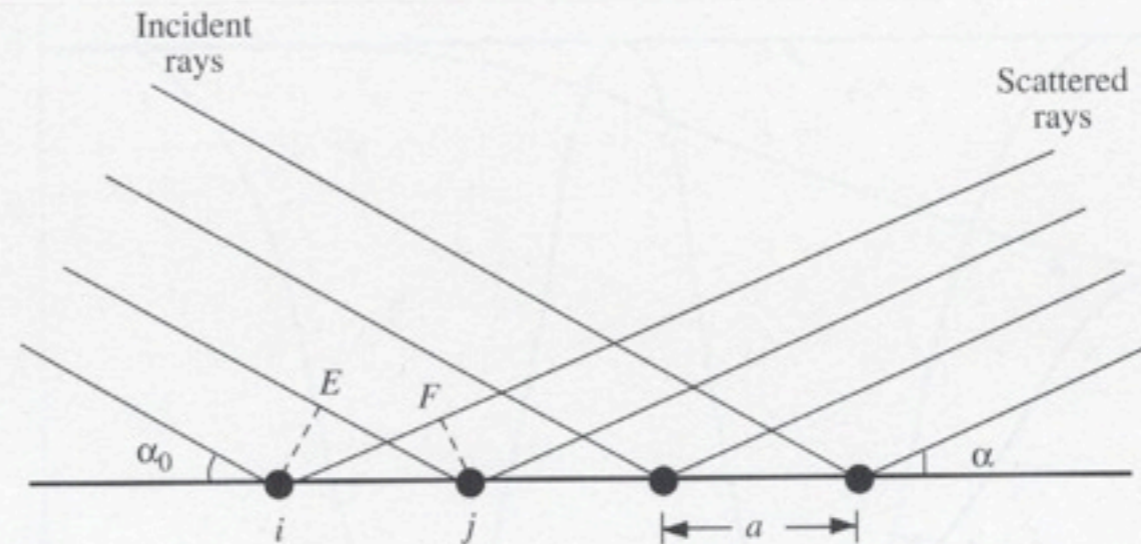




Diffraction One-Dimensional Lattice

► FIGURE 12.6

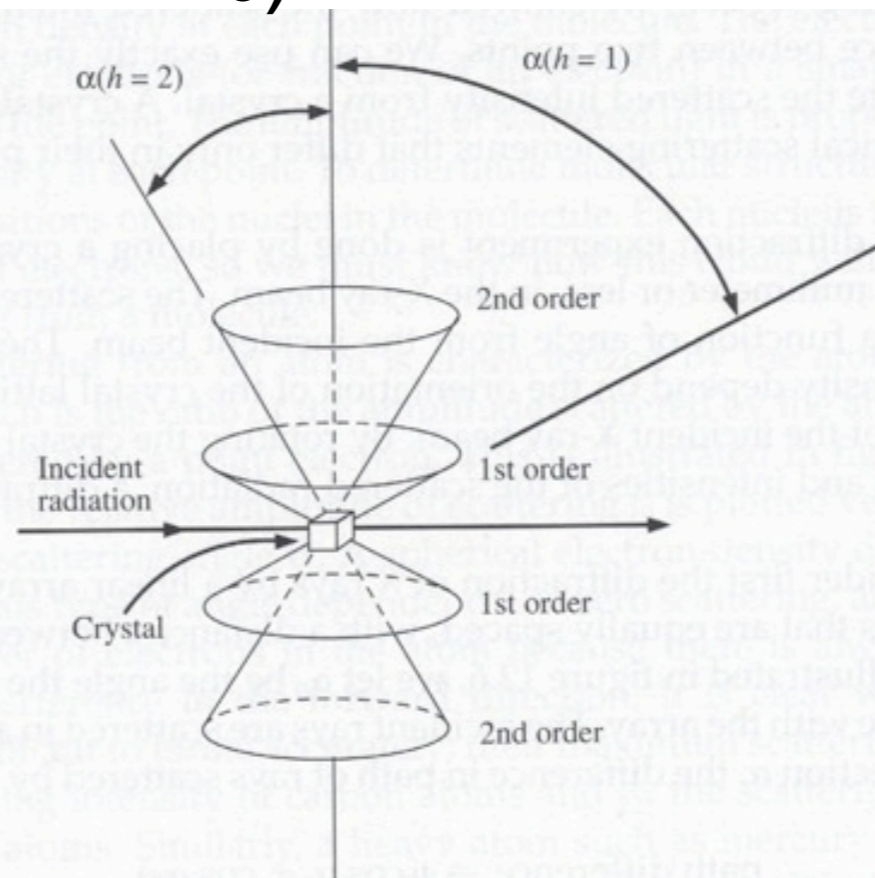
Scattering of incident rays by a row of point scatterers of spacing a . The dashed line iE is perpendicular to the incident beam; the dashed line jF is perpendicular to the scattered beam. The path difference of rays scattered by any two adjacent scatterers i and j is thus $(iF - jE)$, which is equal to $a \cos \alpha - a \cos \alpha_0$, or $a(\cos \alpha - \cos \alpha_0)$.



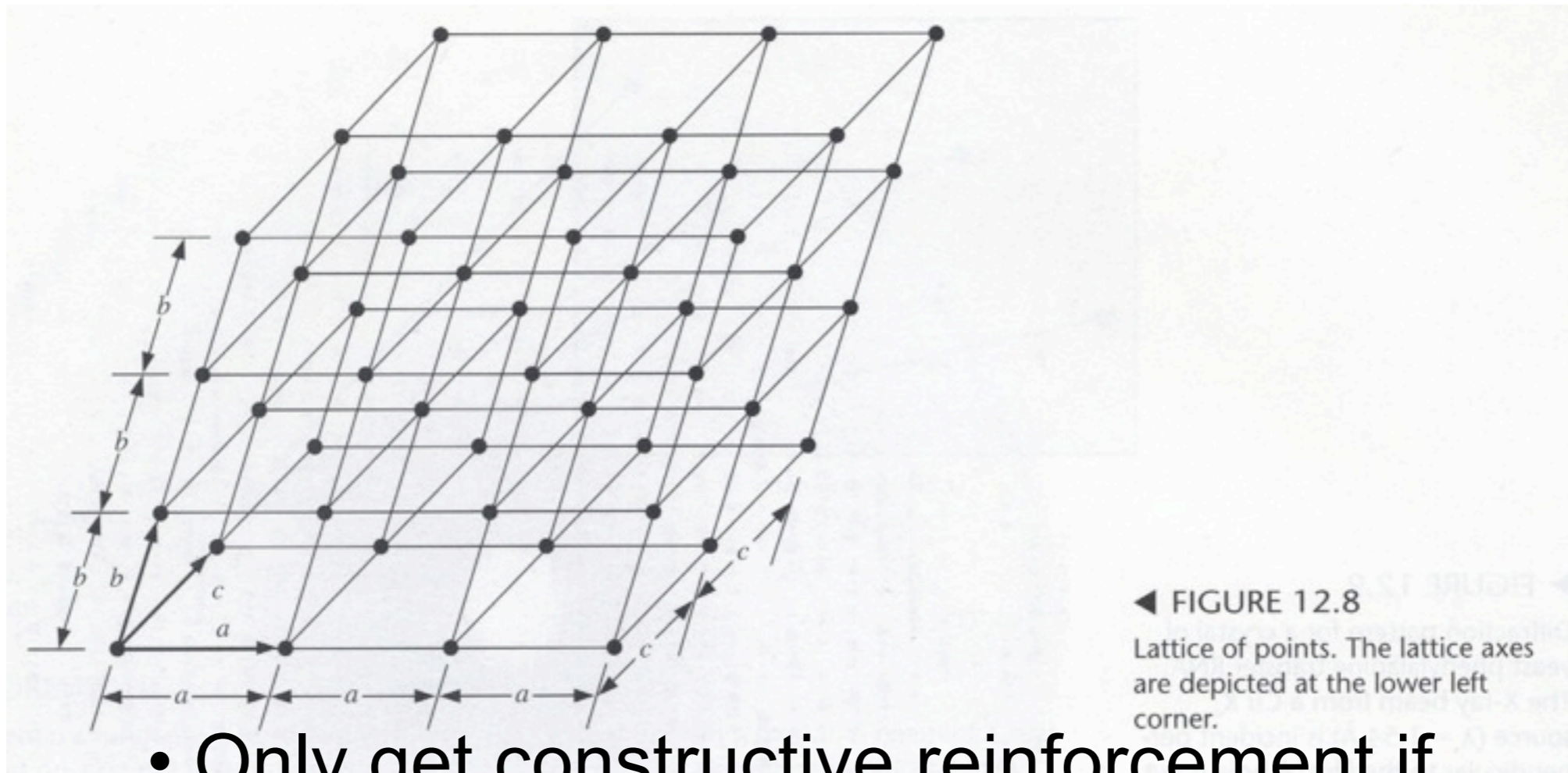
- Only get constructive reinforcement if $a(\cos \alpha - \cos \alpha_0) = h\lambda$

► FIGURE 12.7

Equidistant point scatterers arranged in the vertical direction at the apices of the cones. With an incident angle $\alpha_0 = 90^\circ$, Eq. (12.6) reduces to $a \cos \alpha = h\lambda$, or $\alpha = \cos^{-1}(h\lambda/a)$. Cones with $h = 1$ (first order) and $h = 2$ (second order) are shown. Note that $\cos \alpha = \cos(-\alpha)$; thus, in this particular case, for each order there are two cones 180° apart. The zero-order diffraction ($h = 0$) is not shown.



Diffraction Three-Dimensional Lattice



- Only get constructive reinforcement if

$$a(\cos\alpha - \cos\alpha_0) = h\lambda$$

$$b(\cos\alpha - \cos\alpha_0) = k\lambda$$

$$c(\cos\alpha - \cos\alpha_0) = l\lambda$$

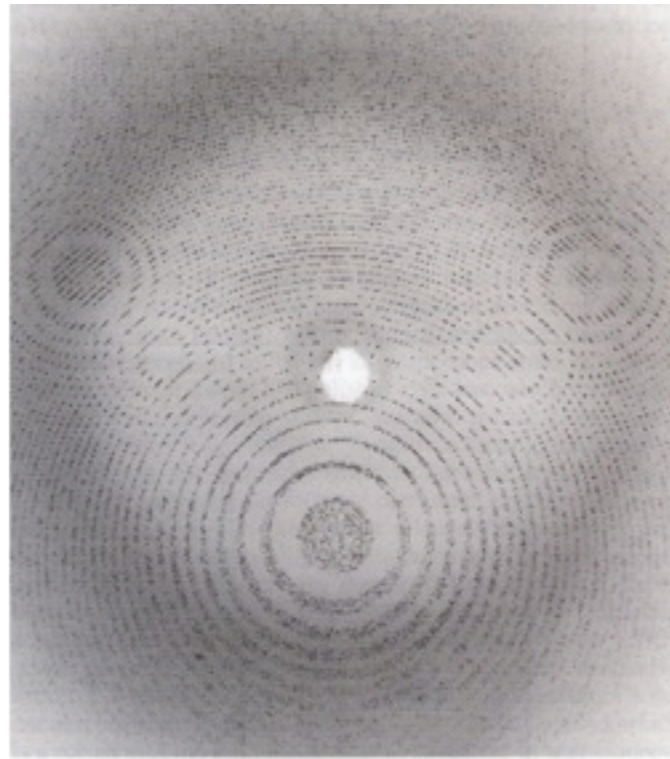
von Laue's equations

hkl are called Miller indices

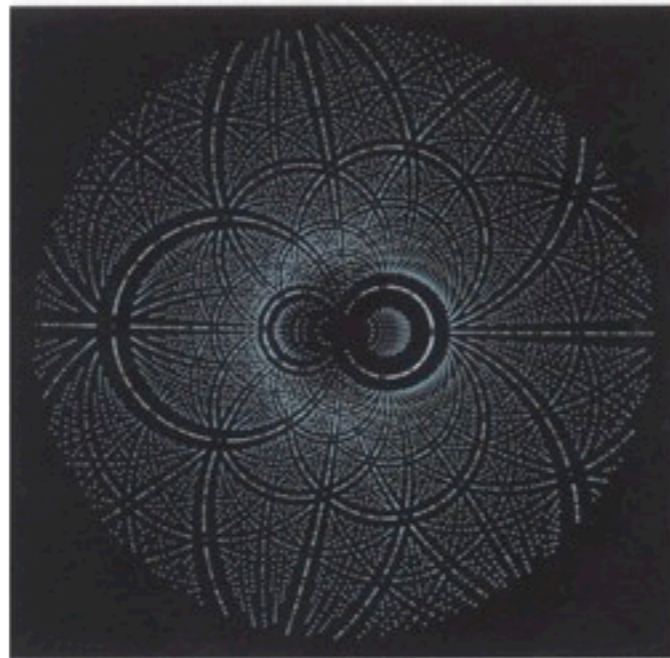
Each reflection is given a unique set of Miller indices

Reciprocal Lattice

Monochromatic vs Polychromatic X-rays



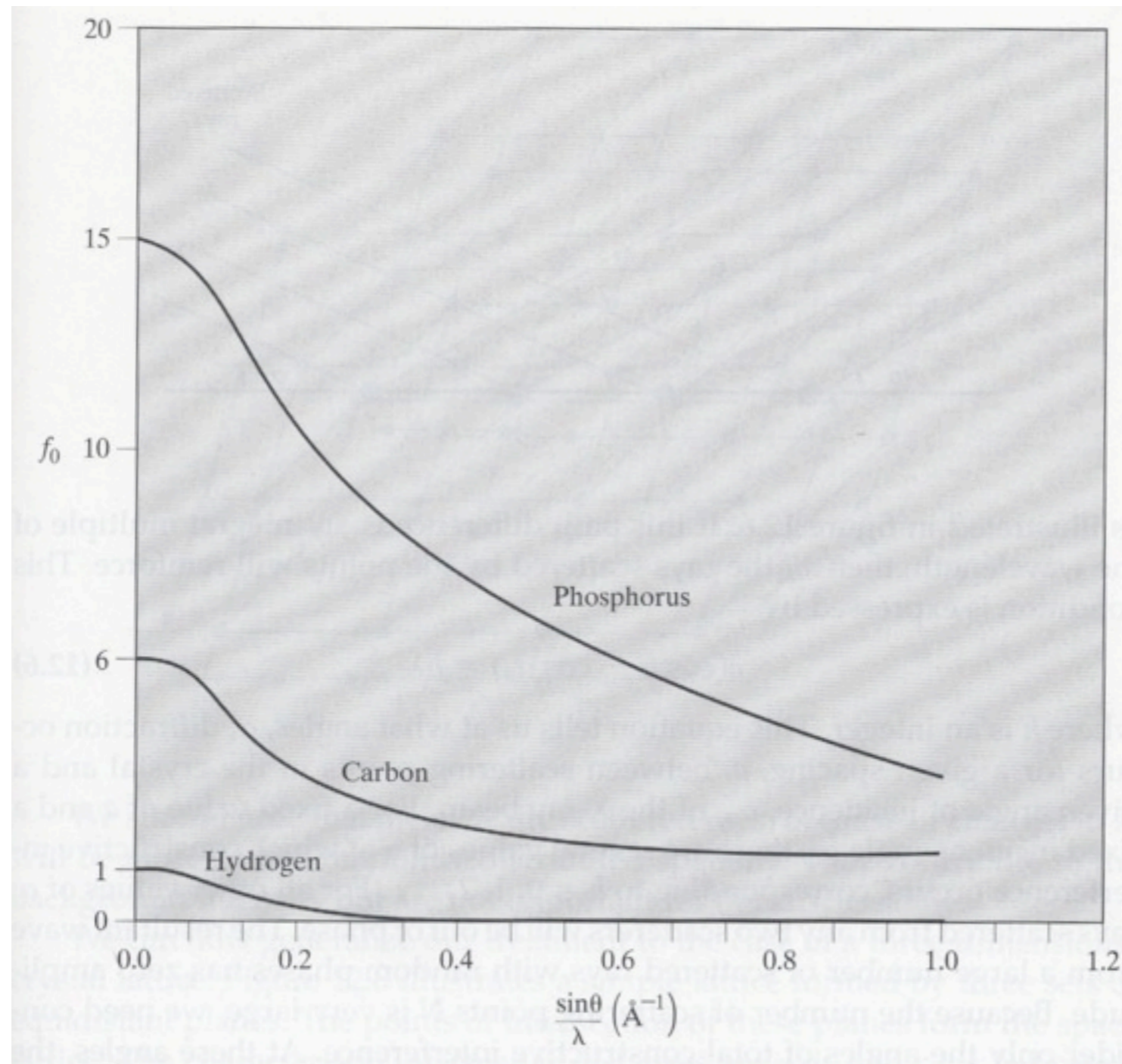
Monochromatic



Polychromatic

Fig. 8.1.4.2. Single-crystal SR diffraction patterns. (a) Rhinovirus monochromatic oscillation photograph recorded at CHESS (Arnold *et al.* 1987; see also Rossmann & Erickson, 1983). Copyright (1987) International Union of Crystallography. (b) Prediction of a protein crystal Laue diffraction pattern (for an illuminating bandpass, without monochromator, $\sim 0.4 < \lambda < 2.6 \text{ \AA}$). The colour coding is according to the multiplicity of each spot: turquoise for singlet reflections, yellow for doublets, orange for triplets and blue for quartet or higher-multiplicity Laue spots. Reproduced with permission from Cruickshank *et al.* (1991). Copyright (1991) International Union of Crystallography.

Scattering Factors



◀ FIGURE 12.5

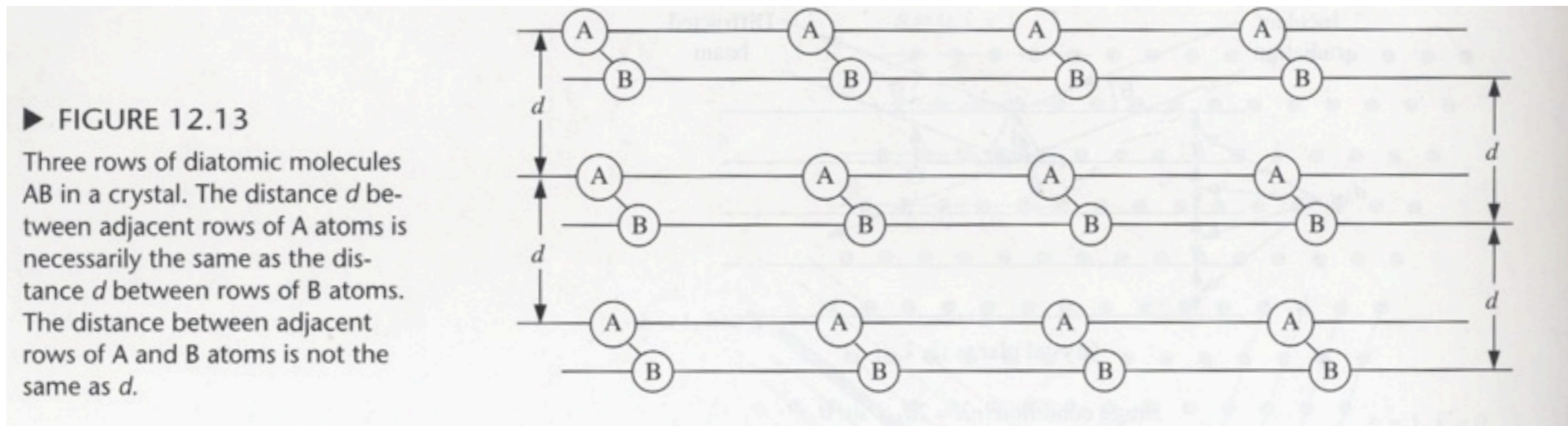
Dependence of atomic scattering f_0 on $(\sin \theta)/\lambda$. The angle between the incident and scattered rays is $\Theta = 2\theta$. The curves shown are for hydrogen (atomic number 1), carbon (atomic number 6), and phosphorus (atomic number 15). Note that when θ approaches zero, the value of f_0 approaches the number of electrons per atom.

- Scattering factor (f_0) ratio of the amplitude scattered by an atom to the amplitude scattered by a point electron

Intensity of Reflections

- For theoretical point scatter (a point that scatters X-rays in all directions) the intensity of the reflection is the same regardless of angle
- For real atoms the intensity of the reflection is a function of $(\sin\theta)/\lambda$
- Can predict the diffraction pattern if we know the lattice (space group), unit cell dimensions, distance from crystal to detector, orientation of lattice relative to X-ray beam
- BUT the intensity of the reflection depends on the composition and orientation of molecules in the asymmetric unit

Two Atoms in a Lattice



- Spacing between one row of A and another row of A is the same as a row of B and another row of B (distance d unit cell)
- Therefore the same angle θ will be will cause reinforcement
- The distance between A and B as well as the scattering factors for each atom will dictate intensity

Determination of Molecular Structure

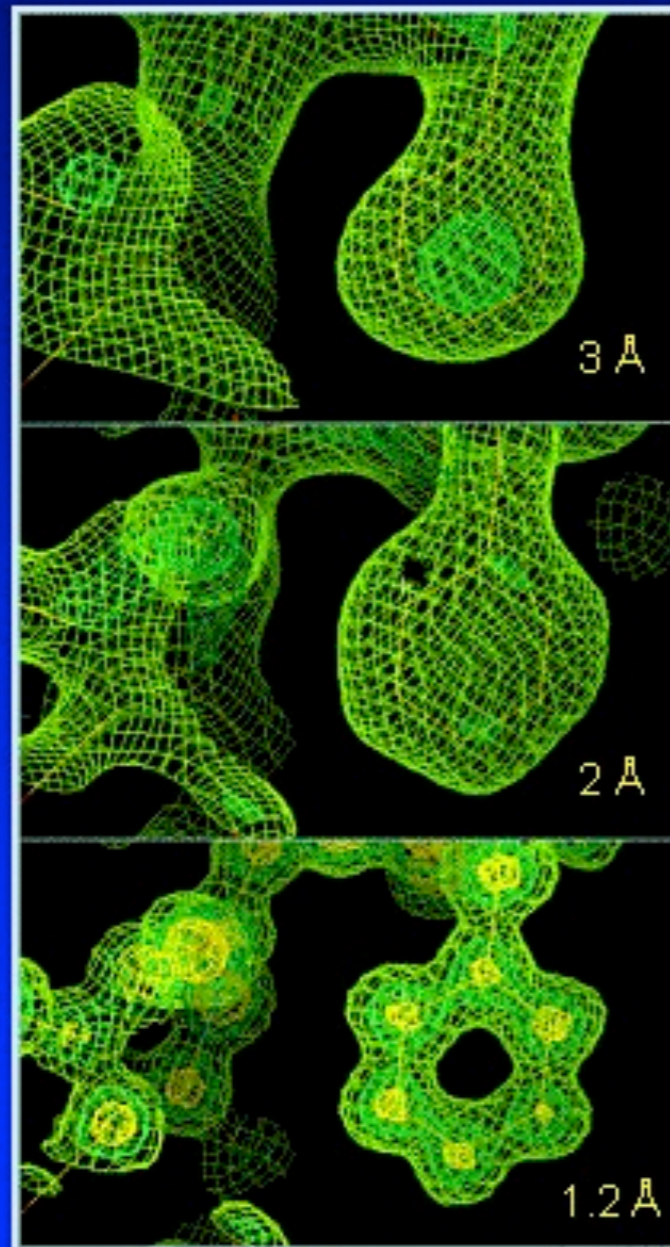
- Given the atomic coordinates of molecule in unit cell and the scattering factors for each atom we can calculate the phase difference for the scattered waves
- Each wave is characterized by an amplitude and a phase
- We need to add the scattered X-rays from all atoms in unit cell
- The amplitude depends on the atomic number (number of electrons) and the phase depends on the coordinates and scattering angle
- $F(hkl) = \sum f e^{i\alpha}$ for all atoms in the asymmetric unit
 - $F(hkl)$ structure factor for the entire molecule
 - f = scattering factor of an atom
 - α = phase factor for scattering from the atom
 - $i = \sqrt{-1}$
- Intensity (I) of the reflection can be measured but phases (α) need to be calculated
- $I(hkl) = F(hkl)^2$

Calculation of Electron Density

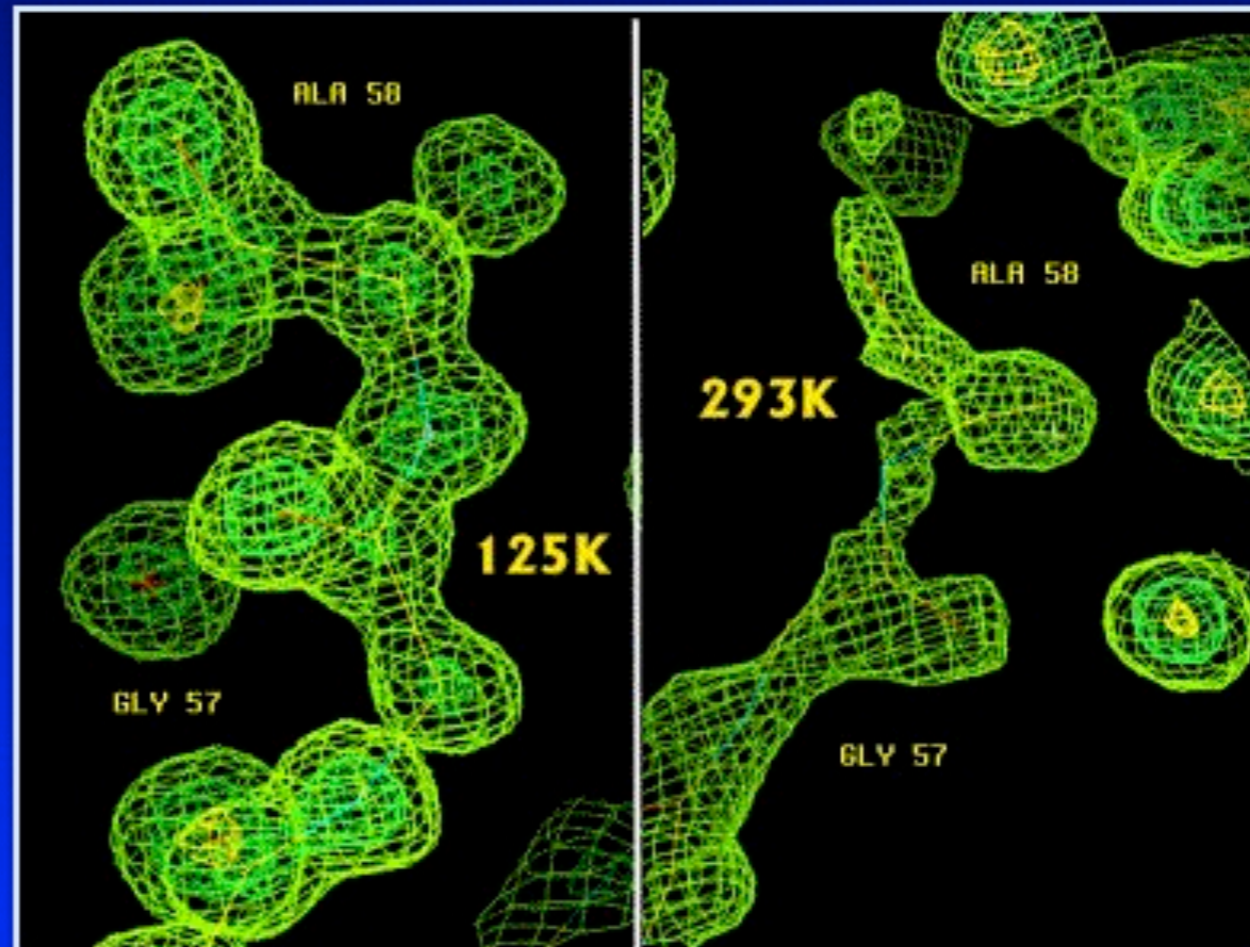
- Use Fourier transformation to calculate the electron density at position X, Y, Z
- electron density represented by $\rho(X, Y, Z)$
- can use this to calculate the density over the entire unit cell
- obtain a distribution of electron density



Importance of resolution



Reduced disorder at low temperature



Dramatic improvements in the overall structure are likely to result from better definition of disordered regions regardless of resolution