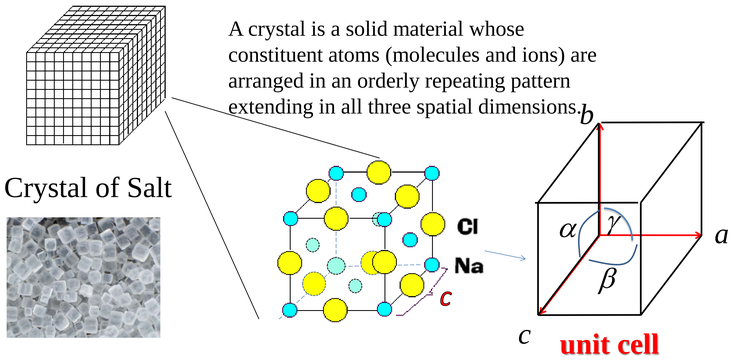
CHEMISTRY
TEXAS A&M UNIVERSITY

XRDLab TAMU
CUM VIDEBIMUS LUMEN

Crystallography How do you do?

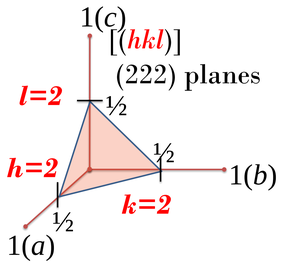
Structure from crystals
There are roughly 50 000 000 000 000 000 000 atoms of Na and Cl in a single crystal of salt. To describe the structure of salt at the atomic level we would need to describe roughly 5 x 10^{19} atomic positions!! BUT there is an easier way. A crystal has long range three-dimensional order. If we could describe a small portion of that order (unit cell) we could then use SYMMETRY to describe the whole crystal! AND that is what we do.

Describing Order in Space….



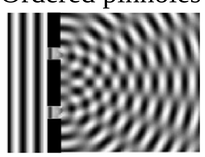
- The **unit cell** is a parallepiped that describes the smallest unique volume of the crystal (cell parameter **: *a, b, c, α, β, γ***)
- There are 230 ways (**space groups**) to **arrange objects in the unit cell** that brings a periodic arrangement of the objects back to their original positions.

The **Miller Indices *(h,k,l)*** (Grid) are the reciprocal of the intercepts of imaginary planes that dissect the unit cell with the crystallographic indices : ***h , k, l.***



Crystals and Photons…

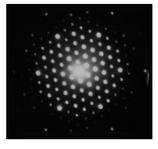
Ordered pinholes



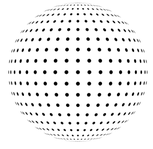
Orderly Scattering (diffraction)

- **Electrons in atoms scatter high energy photons (particles)**
- **Ordered electrons (atoms) scatter orderly**
- **Crystals have long-range 3D ordered atoms**

1D diffraction pattern



2D diffraction pattern



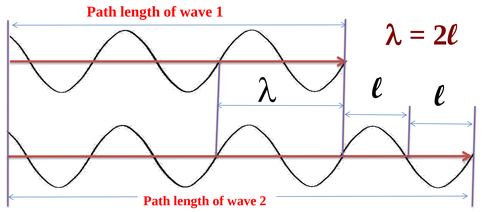
3D diffraction pattern

X-ray Diffraction is ..
X-rays scatter off of electrons, in a process of absorption and re-admission. Diffraction is the accumulative result of the X-ray scattering of a group of electrons. For an incident X-ray photon of monochromatic wavelength, coherent waves are produced at an angle of theta (2-θ with respect to the incident X-ray). if the electron groups interact with the X-ray and are spaced at a distance *d* then the interaction is described by Bragg's law :

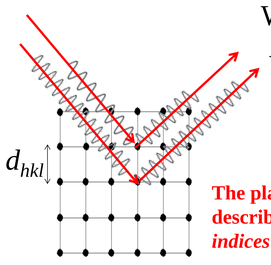
$$n\lambda = 2d\sin(\theta).$$

The intensity of the scattered X-ray is proportional to the number of electrons that the X-ray scatters from.

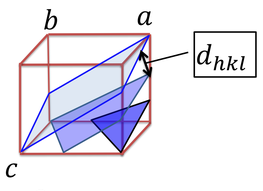
Two parallel waves show constructive interference when they are in **phase** i.e. when $\mathbf{n_1}\ell = \mathbf{n_2}\lambda$ (where $\mathbf{n_1}$ and $\mathbf{n_2}$ are integers)

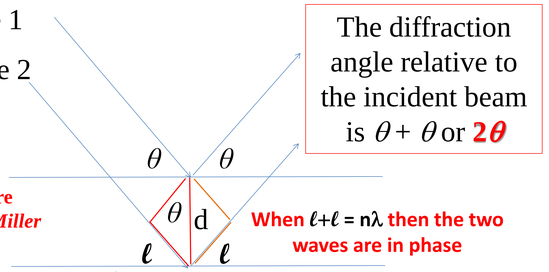


Waves diffract off of planes (of electrons)

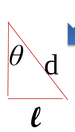


The distance between the planes is d_{hkl}





The diffraction angle relative to the incident beam is $\theta + \theta$ or 2θ



Bragg's Law
$\ell/d = \sin\theta$
$\ell = d\sin\theta$
(since $n\lambda = \ell+\ell$ then)
$n\lambda = 2\ell = 2d\sin\theta$
therefore..
$d^* = 1/d = 2\sin\theta/\ n\lambda$

$\boldsymbol{d^*}$ and $\boldsymbol{\theta}$ can be described by the Miller Indices and cell parameters

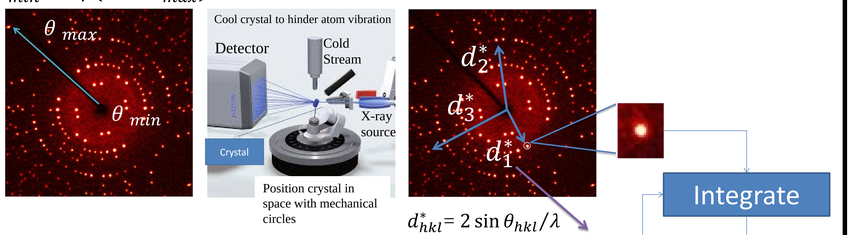
$$(2\sin\theta/\lambda)^2 = (1/d_{hkl})^2 = d^{*2}_{hkl} = a^{*2}h^2 + b^{*2}k^2 + c^{*2}l^2 + 2b^*c^*kl\cos\alpha^* + 2a^*c^*hl\cos\beta^* + 2a^*b^*hk\cos\gamma^*$$

Where $\boldsymbol{d}^*$ = reciprocal of $\boldsymbol{d}$ and $\boldsymbol{a}^*$ is the recip. of $\boldsymbol{a}$ and $\boldsymbol{b}^*$ is the recip. of $\boldsymbol{b}$ *etc*…

From Diffraction to structure….
Normally one would use a microscope to view small objects. If we use a light microscope we cannot look at objects smaller than the wavelength of light which is about 10 $^{-6}$ m. Since the atom has dimensions of about 10^{-10} m we cannot image an atom with a photon of light. X-rays, on the other hand, have a wavelength of about 10 $^{-10}$ m and are suitable for imaging objects at the atomic scale but cannot be lensed, so we must do what a lens would do only with X-rays, math and modeling ….

Collect Data and Integrate

Resolution limit
$d_{min} = \lambda/(2\sin\theta_{max})$ Diffractometer



$d^*_{hkl} = (1/d_{hkl})$ → ***where*** *the atoms are*
$I(hkl)$ → ***what*** *the atoms are*

Convert $I(hkl)$ to a Wave

$$|F_{hkl}|_{obs} = \sqrt{kI_{hkl}}$$

$$\rho(xyz) = \sum_h \sum_k \sum_l |F_{hkl}|_{obs} \cos 2\pi(hx + ky + lz - \alpha')$$

[electron density map with grid (*x, y, z*)]

[phase angle]

$$\tan^{-1}\left(\frac{\sum_i f_i \sin 2\pi(hx_i + ky_i + lz_i)}{\sum_i f_i \cos 2\pi(hx_i + ky_i + lz_i)}\right) = \alpha_{hkl}$$

[positions of the atoms (*i*) are (x_i, y_i, z_i) and $f_i = f_{calc,i}\exp(-2\pi^2 U d^{*2})$ where *U* are displacement parameters]

[start with random phase angles or atomic positions and deduce initial phase angles]

$\rho(xyz)$ = Electron Density Map (wave)