Miller planes, the Bragg law etc.

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Specifying directions

Consider any line from the origin O of the unit cell, where the edges of the cell has the vectors **a**, **b**, and **c**, to some point P. We write down the coordinates of P in terms of fractions of a, b, and c. We then express these fractions as whole numbers $[u, v, w]$, which specifies the direction of OP. If the line does not pass through the origin, it should be suitably shifted. In vector notation:

$$\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

Miller indices for planes

Consider a plane in a coordinate system that has the intercepts P, Q and R. In other words, this plane is passes through three points, (P,0,0), (0,Q,0) and (0,0,R). The equation of a plane is:

$$x/P + y/Q + z/R = 1$$

Multiply both sides of the equation by PQR. Then:

$$QRx + PRy + PQz = PQR$$

We define:

$$h = QR \quad k = PR \quad l = PQ$$

Then we can also write:

$$hx + ky + lz = PQR$$

The equation could (perhaps) be simplified if the LHS and RHS had a common factor. The plane is described simply by specifying (hkl) (within parentheses). The task then is to find the intercepts along the different axes. If the plane passes through the origin, consider a parallel plane that does not so that the intercepts can be determined.

For example, a plane with the intercepts $P = 1$, $Q = 2$ and $R = 3$ is described by the equation:

$$6x + 3y + 2z = 6$$

This equation cannot be simplified and the plane is described as (632).

Note that an (hkl) Miller plane is the *first* plane from the origin which makes intercepts with the axes at a/h, b/k and c/l. Alternately, (hkl) Miller planes will, within a single unit cell, intercept the x axis h times, the y axis k times and the z axis l times.

The Weiss zone law

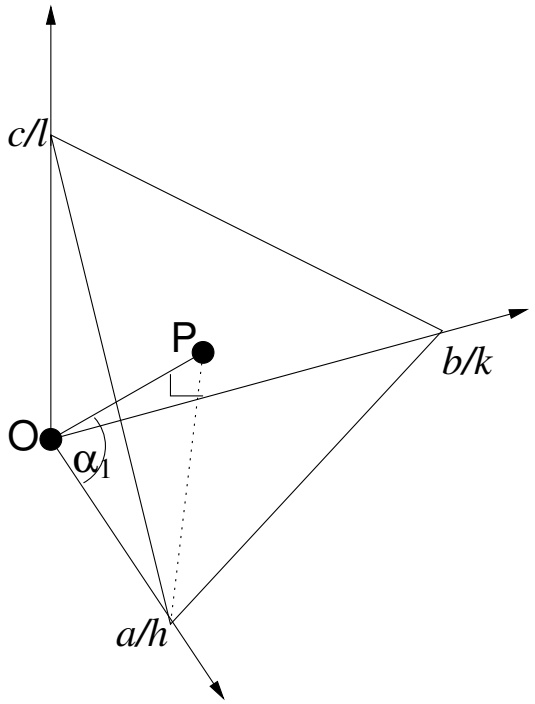
If a Miller plane (hkl) is contains (is parallel to) $[uvw]$, then:

$$hu + kl + lw = 0$$

This law permits planes and/or directions to be determined.

d_{hkl}: The perpendicular distance between (hkl) Miller planes.

The distance between neighboring Miller planes is the same as the nearest perpendicular distance between the origin and the closest Miller plane.



Considering the right triangle formed with the line OP, of length d_{hkl} and the intercept to the a axis. Let the angle of the right triangle between OP and the b axis be α_2 and with the c axis be α_3 (these are not indicated).

$$\cos\alpha_1 = \frac{d_{hkl}}{a/h} = (\frac{h}{a})d_{hkl}, \text{ and similarly } \cos\alpha_2 = (\frac{k}{b})d_{hkl}, \text{ and } \cos\alpha_3 = (\frac{l}{c})d_{hkl}$$

Now by the Pythagoras theorem, if the axes are orthogonal, $\cos^2\alpha_1 + \cos^2\alpha_2 + \cos^2\alpha_3 = 1$ which implies:

$$(\frac{h}{a})^2 d_{hkl}^2 + (\frac{k}{b})^2 d_{hkl}^2 + (\frac{l}{c})^2 d_{hkl}^2 = 1$$

or

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

X-ray diffraction

The generation of X-rays

Electrons from a glowing filament (usually tungsten or rhenium) are accelerated by applying a DC field (typically of about 30-40 kV). These accelerated electrons are then bombarded against a cooled metal target (Fe, Cu, Mo ...). The electrons slow down when they enter the metal, so they loose energy. This lost energy is emitted as a continuous radiation called *brehmsstrahlung* radiation, usually in the X-ray region of the electromagnetic spectrum (with energies of the order of kV). In addition to the broad *brehmsstrahlung* radiation, there are the so-called *characteristic* X-ray peaks associated with electronic transitions in the target material. These characteristic X-radiations have a much higher intensity than does the *brehmsstrahlung*. The energies of the characteristic radiation depends on which atomic shell of the target material is being excited by the incident

electrons (K, L *etc*), as well as the atomic number of the target. The energy of the characteristic radiation is proportional to the atomic number raised to the fourth power.

In lab X-ray diffraction experiments, characteristic radiation from the K shell of Cu (with a wavelength around 1.5 Å) or from the K shell of Mo (with a wavelength around 0.7 Å) is typically used.

Diffraction and the Bragg law

After Röntgen discovered X-rays, people started to shine them on crystals. Max von Laue made some important early contributions, and notes since the wavelengths of X-rays are comparable to the spacings between atoms in crystals, interesting interference effects can be anticipated.

W. L. Bragg looked at the results of Laue's experiments and thought that there is a simple way to understand the effects of the X-rays passing through the crystals. He suggested that the Miller planes act as mirrors that reflect the X-rays and that the condition for reflection is constructive interference, which depends on the wavelength of the X-rays (λ), the angle at which they fell upon the crystal (θ) and the distance d_{hkl} between nearest neighbor (hkl) planes. He performed experiments with his father, W. H. Bragg, and they suggested the law:

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

for which they were awarded (father and son) a Nobel Prize in 1915.

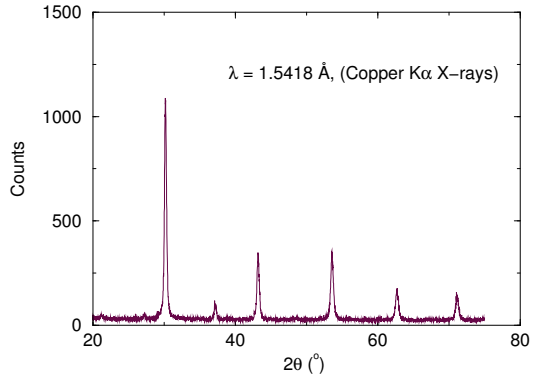
n is usually absorbed into the (hkl) Miller plane.

From simple geometrical considerations, d_{hkl} can be calculated for an orthorhombic cell ($a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$) to be

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

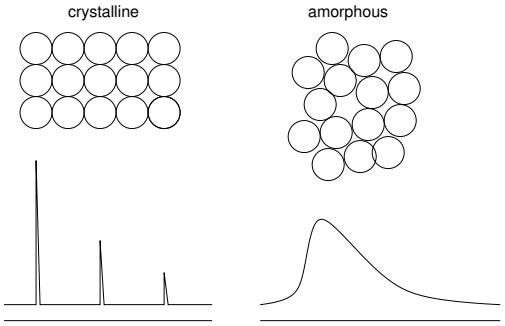
For the cubic cell ($a = b = c$ and $\alpha = \beta = \gamma = 90°$) and the tetragonal cell ($a = b \neq c$ and $\alpha = \beta = \gamma = 90°$) this formula becomes simpler.

So by acquiring X-ray diffraction data on a crystalline system, it is possible to measure the distances between planes of atoms in the unit cells, and this provides us information on the structure. The figure below is an X-ray diffraction pattern on the cubic perovskite $BaZrO_3$ (whose structure was described in the previous class).



Amorphous compounds and glass

Not all solids will *diffract* X-rays well. Some solids have X-ray diffraction patterns with only rather broad peaks. Typically, these are amorphous solids or glasses that do not have long range order. See the handout.



Quasicrystals

See the handout.