Class Notes: Appendix 1
Reciprocal Lattice

We have noted that there is an inverse relationship between the angle of diffraction and the d-spacing which this pertains to through Bragg's Law,

$$d = \frac{\lambda}{2\sin\theta_B}$$

We have also noted that the Miller indicies are effectively written in normalized inverse size dimensions.

Further, we noted that there is a minimum size which can be measured $\lambda/2$ and no theoretical maximum size for diffraction experiments (the maximum size measurable having to do with experimental limitations such as the coherence length of the radiation and the condition of collimation).

The reciprocal lattice was derived by von Laue to describe the diffraction experiment in the space where the measurement was made, inverse space. ***This means that the XRD pattern you see on a piece of film is in inverse-space already!*** von Laue related this diffraction space to the crystalline space in a fairly simple manner which involves vectors.

We construct the reciprocal lattice by a system of three inverse lattice parameters, $\mathbf{b}_i$, which are related to the real space coordinates, $\mathbf{a}_i$, by cross products as shown on pp. 482, equations 1 to 3. *Remember a cross product results in a* ***vector*** *pointing perpendicular to the two vectors following the right hand rule and whose magnitude is the product of the two vector magnitudes times sin of the angle.* The direction of $\mathbf{b}_1$, for instance, is normal to $\mathbf{a}_2$ and $\mathbf{a}_3$, and has a magnitude of $1/d_{100}$. Points in inverse space correspond to sets of planes in real space with the d-spacing reflected as 1/vector length, $\mathbf{H}_{hkl} = h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3$. The zone axis rule can be easily derived in reciprocal space as shown on pp. 486.
A zone axis is described as a vector in real space:
$\mathbf{ZA} = u\mathbf{a}_1 + v\mathbf{a}_2+w\mathbf{a}_3$
And a plane spacing (plane normal with magnitude of the spacing) is described in inverse-space by a vector
$\mathbf{H}_{hkl} = h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3$
If these two vectors, the normal, (i.e. the plane normal, $\mathbf{H}_{hkl}$ is perpendicular to the zone axis, **ZA**), **H**, and the zone axis, **ZA**, are perpendicular then the plane is in the zone! For two perpendicular vectors the dot product is zero, *Remember dot product results in a scalar and is the product of the two magnitudes times the cos of the angle, here the angle is 90°.* $\mathbf{a}_1$ is normal to $\mathbf{b}_2$ and $\mathbf{b}_3$ by definition so the dot products between mixed indicies is zero. Only the products of the type $\mathbf{a}_i \cdot \mathbf{b}_i$ will have a value and the value will be 1. A plane in a zone follows the rule set in chapter 2:
uh+vk+wl = 0
(Calculation of the zone axis for two planes can also be determined using this and substituting for v and w from the definition using the two planes. Equation 2-4 pp. 45)

Reciprocal Lattice and XRD experiment

The diffraction experiment can be described in reciprocal space as discovered by von Laue. Consider the real space diffraction event as shown on pp. 487 as composed of an incident beam $\mathbf{S}_0$ and a diffracted beam $\mathbf{S}$. S is related to the momentum of the incident beam in a particle view of x-rays, $\mathbf{p} = h\nu/\mathbf{c} = h/\lambda\ (c/\mathbf{c})$. An atom is located at the origin, O and an atom on a set of planes at **OA**. The phase difference, φ, involves the vector difference between $\mathbf{S}_0$ and $\mathbf{S}$.

$\varphi = (2\pi/\lambda)\,(\mathbf{S}_0 - \mathbf{S})\cdot\mathbf{OA}$

von Laue determined that in order for diffraction to occur, $(\mathbf{S}_0 - \mathbf{S})/\lambda$ must have the value, $h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3$. We can write the von Laue;

$$\frac{S - S_0}{\lambda} = h b_1 + k b_2 + l b_3$$

Another way to define Bragg's law is in terms of the dot products of the unit real space vectors:

$$a_1 \cdot \left(S - S_0\right) = h\lambda$$

And so on. (Remember the dot product of two vectors is a scalar.)

From a geometric consideration it can be seen that $(\mathbf{S} - \mathbf{S}_0) = 2\sin\theta$, Figure A1-7 pp. 487, yielding the more familiar form of Bragg's law.

$\mathbf{S}_0/\lambda$ has units of inverse distance so it is a vector in inverse space. This vector is in a 3-d reciprocal lattice and the point of the vector hits the crystal lattice (000) plane spacing which is the origin, O, of reciprocal space for the problem of interest, Figure A1-8 pp. 498. The starting point for the vector, $\mathbf{S}_0/\lambda$, is at the center, C, of a sphere in this construction. The diffracted beam, $\mathbf{S}/\lambda$, emanates from (000) or O. This vector can be translated to start at C so the difference $(\mathbf{S}_0 - \mathbf{S})/\lambda$ can be graphically constructed. Remember that $\mathbf{S}$ and $\mathbf{S}_0$ are of the same length if the scattering is elastic. For elastic scattering variation of the diffraction angle, 2θ, the angle between $\mathbf{S}_0$ and $\mathbf{S}$, makes S trace a circle about C. If $\mathbf{S}$ is allowed to deviate from the plane of the paper, Figure A1-8, the circle becomes a sphere. The surface of this sphere is called "***The Sphere of Reflection***". Diffraction occurs when the vector $(\mathbf{S} - \mathbf{S}_0)/\lambda$ is equal to the vector $\mathbf{H}_{hkl}$ for the set of planes (hkl) whose normal is represented by a point in reciprocal space.

In this way we can make a reciprocal lattice construction for each diffraction experiment. Figure A1-9 pp. 490, shows a reciprocal lattice centered at O in inverse space with the sphere of reflection superimposed. If the perfect crystal is stationary it can be seen that it is highly unlikely that a normal to a set of planes will fall on the sphere of reflection, this means that there will be limited diffraction for a monochromatic x-ray and a perfect crystal fixed in position. Several things can be done to alleviate this situation.

1) We could vary the wavelength thereby scanning through a number of spheres of reflection of variable radius, $1/\lambda$. This is the Laue method. We consider that the sphere surface is the x-ray film and that the film can be made to intersect the crystal normal positions by inflation or deflation (smaller or larger λ). A **zone axis** will be a **plane** in reciprocal space passing through a set of hkl points which starts at (000). As the sphere inflates it will trace a **circle** on the surface of the sphere of reflection which when projected on a flat sheet of Polaroid or film will form an arc as observed in the Laue experiment. (pp. 93, figure 3.6)

2) For a fixed sphere of reflection, fixed wavelength, the crystal could be rotated about (000) or O so more planes could come into coincidence with the sphere of reflection. If this is done on a single axis this results in the spots of the rotating crystal method (Figure 3-10 pp. 96). For Figure 3-10 a Debye-Scherrer camera was used which is a strip of film on the circumference of the sphere of reflection.

3) If the crystal is rotated in two angles simultaneously this is identical to a powder sample or a polycrystalline (grainy) sample. A single plane normal in coincidence with the sphere of reflection will be rotated about the incident beam axis at some point leading to a circle on the surface of the sphere of reflection which, when projected on a flat film leads to the Debye-Scherrer rings commonly observed. Figure 3-13, pp. 99 shows this for a Debye-Scherrer camera.

Variants to this occur when there are few grains so that all of these rotations are not present. This leads to spotty Debye-Scherrer rings, figure 9-1 pp. 283, the spottier the rings the larger the grains. (Grain sizes larger than 0.1µm)

A second variant occurs when the crystals display preferred orientation in the incident beam such as in a fiber pattern, figure 9-11 pp. 302. For these cases the reciprocal lattice points are preferentially rotated about a direction of preferred orientation. Since the reciprocal lattice points are normal to the planes, the arcs show up 90° to the direction of plane orientation as was observed in the first lab with a hair in a laser beam. The reciprocal lattice construction shows this orthogonal relationship between plane orientation and diffraction pattern orientation immediately.

For the powder method, the inverse crystal lattice can be rotated about the sphere of reflection or equivalently, the sphere of reflection can be rotated about the crystalline origin O or (000). The latter leads to a second sphere of twice the diameter of the sphere of reflection, $2/\lambda$. This second, larger sphere reflects the smallest size plane spacing which can be observed under any geometric condition, $\lambda/2$, and is called the "***Limiting Sphere***" for the diffraction experiment, figure A1-11 pp. 492.

MORE APPLICATIONS

All diffraction effects (anything we have discussed) can be described in terms of real space or reciprocal space. Often there are distinct advantages to dealing with these problems in reciprocal space. One example is given at the end of appendix 1, thermal asterism in a Laue pattern. Thermal vibrations leads to a probability function for the position of plane spacings as shown in figure A1-14. A Laue photograph is a direct image of this probability function as described in Cullity.