Notes on Crystallography

Mark Steadman

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1 Basic Crystal Geometry and Terminology

We can define a crystal structure as the the infinite repetition of identical groups of atoms.

Def The set of mathematical points that determine a crystal is termed the lattice.

Def The atoms that are attached to the lattice are termed the basis.

Def In n dimensions we can expresss any point in the crystal $\mathbf{r'} = \mathbf{r} + u_1\mathbf{a_1} + \cdots + u_n\mathbf{a_n}$, with $u_1, \cdots, u_n$ integers and $\mathbf{a_1}, \cdots, \mathbf{a_n}$ vectors in $\Re^n$ termed the translation vectors. The lattice and translation vectors are termed primitive if the atoms look the same from any lattice point using integers $\mathbf{u_1}, \cdots, \mathbf{u_n}$. Def The primitive translation vectors define the primitive crystal axes.

Def The shape, e.g in $\Re^3$ a parallelepiped, defined by primitive axes is called a primitive cell. It has volume $V_c = |\mathbf{a_1} \bullet \mathbf{a_2} \times \mathbf{a_3}|$ Every crystal structure has a unit cell, not nescessarily the primitive cell, which has the full symmetry of the crystal. Thus, we can identify various symmetries to classify crystals by lattice type or point groups and space groups.

Def The planes of a crystal are defined by Miller Indices, notated (hkl). These are defined as points in the reciprocal lattice or as the inverse intercepts along lattice vectors. To find the Miller indices of a plane.

1) Find the intercepts of the plane with the crystal axes. If it is negative indicate this with a bar.

2) Take the reciprocal of the intercepts and scale so that all are integers with a greatest common divisor of 1.

3) If the plane fails to intercept an axis its index for that axis is 0.

Def A family of planes is a set of planes that are equivalnet by symmetry and is denoted by hkl.

Def The direction in the direct axes given by $h\mathbf{a_1} + k\mathbf{a_2} + l\mathbf{a_3}$ is denoted by [hkl]. And all directions equivalent are denoted by ¡hkl¿.

Prop The reciprocal primitive lattice vectors in three dimensions are given by: $\mathbf{b_1} = 2\pi\frac{\mathbf{a_2}\times\mathbf{a_3}}{\mathbf{a_1}\bullet(\mathbf{a_2}\times\mathbf{a_3})}$ $\mathbf{b_2} = 2\pi\frac{\mathbf{a_3}\times\mathbf{a_1}}{\mathbf{a_2}\bullet(\mathbf{a_3}\times\mathbf{a_1})}$ $\mathbf{b_3} = 2\pi\frac{\mathbf{a_1}\times\mathbf{a_2}}{\mathbf{a_3}\bullet(\mathbf{a_1}\times\mathbf{a_2})}$ These satisfy $exp(i\mathbf{K} \bullet \mathbf{R}) = 1$ for all vectors $\mathbf{K}$ in the reciprocal lattice and $\mathbf{R}$ are the the direct lattice positon vectors. These also satisfy $b_i b_j = \delta_{ij}$.

PropThe plane given by Miller Indices (hkl) in the reciprocal lattice is orthoganal to the direction in the reciprocal lattice given by $G = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3}$.

2 Bragg Defraction and the Structure Factor

Theorem Constructive interference occurs if the path difference between 2 adjacent Bragg Planes if they satisfy $n\lambda = 2dsin(\theta)$ where n is an integer, λ is the wavelength of the light, d is the distance between the two planes and θ is the angle of incidence.

Lemma When light hits a Bragg plane it is reflected back with the angle of incidence equal to the angle of reflection and in phase.

Lemma Constructive interference occurs when the path length of two waves differ by an integer number of wavelengths.

Theorem The phase of diffraction for an electron located at position r relative to the origin of the crystal is given by: $2\pi\mathbf{k}' - \mathbf{k} \bullet \mathbf{r}$

Def The resulting wave from a diffraction is termed the structure factor and is given by $F(s) = 1(e)exp(2\pi i\mathbf{s} \bullet \mathbf{r})$ for a single electron.

Prop For several electrons it is given by $F(s) = \Sigma_j exp(2\pi i\mathbf{s} \bullet \mathbf{r})$ and for a continuous electron distribution it is given by $F(s) = \int_{space} \rho(r)exp(2\pi\mathbf{s} \bullet \mathbf{r})dr$, where ρ is the charge density as a function of position.

3 Fourier Interpretation

Def For a 1 dimensional function n(x) of period T we can expand it as $f(x + T) = f(x) = a_0 + \Sigma_{n=1}^{\infty}[a_n cos(2\pi nx/T) + b_n sin(2\pi nx/T) = \Sigma_{n=-\infty}^{n=+\infty} c_n e^{2\pi i/Tx}$. a_n, b_n, c_n are termed the Fourier coefficents and are given by:

$a_n = \frac{2}{T}\int_{x_1}^{x_2} f(x)cos(2\pi nx/T)dx$

$b_n = \frac{2}{T}\int_{x_1}^{x_2} f(x)sin(2\pi nx/T)dx$

$c_n = \frac{1}{T}\int_{x_1}^{x_2} f(x)e^{-2\pi inx/T}dx.$

Theorem $F(s) = \int_{space} \rho(r)exp(2\pi\mathbf{s} \bullet \mathbf{r})dr = int_{cell}\rho(x)exp(2\pi i\mathbf{h} \bullet \mathbf{x})dx = F(h)$.

Proof

Def The structure factor in the above equation is a Fourier Transform which are of the general form. The inverse Fourier Transform is given

Theorem The Fourier Transform of a Fourier Transform recovers the original function. Thus, the electron density function $\rho(x) = \frac{1}{V}\Sigma_h exp(2\pi i\mathbf{h} \bullet \mathbf{x})$

Def The convultion of two functions is defined to be $C(\mathbf{u}) = f(\mathbf{x}) \otimes g(\mathbf{x}) = \int_{space} f(\mathbf{x})g(\mathbf{u} - \mathbf{x})d\mathbf{x})$

Prop. The convultion operation is commutative.

Theorem Covultion Theorem. For any Fourier Transform

$T(f(\mathbf{r})) = \int_{space} f(\mathbf{r})exp(2\pi\mathbf{s} \bullet \mathbf{r})dr$

$T(f \otimes g) = T(f)T(g), T(fg) = T(f) \otimes T(g)$ Proof 1)$T(f(x) \otimes g(x)) = T(\int_{-\infty}^{\infty} f(x)g(u-x)dx) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(x)g(u-x)dxe^{2\pi isu}du = int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(x)g(w)e^{2\pi is(x+w)}dxdw = \int_{-\infty} 6\infty f(x)e^{2\pi isx}dx\int_{-\infty} 6\infty g(w)e^{2\pi isw}dw = \int_{-\infty} 6\infty f(x)e^{2\pi isx}dx\int_{-\infty} 6\infty g(x)e^{2\pi isw}dx = T(f(x))T(g(x))$ $2)T(f \otimes g) = T(f)T(g)$ Define F=T(f), f=T^{-1}(F), G=T(g), g=R^{-1}(G). Then we have T[T^{-1}(F)⊗T^{-1}(G)]=FG and T^{-1}(F)⊗ T^{-1}(G)=T^{-1}(FG)
But we could have done the same thing with the regular functions as well.

Def The Patterson Function is defined to be

$P(u, v, w) = \Sigma_{hkl}|F_{hkl}|^2 e^{-2\pi i(hu+kv+lw)}$

Theorem $P(\mathbf{u}) = \rho(\mathbf{r}) \otimes \rho(-\mathbf{r})$