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Scattering - brief notes

1 The basics

As discussed in the tutorial, scattering from multiple point scatterers produces an observed amplitude given by

$$\Psi \sim \sum_i f_i \exp(\mathbf{K}.\mathbf{r}_i) \tag{1}$$

where $\mathbf{K}$ is the change in wavevector upon scattering, and f_i gives the relative strength of each type of scatterer. This can be written as the Fourier transform of the density of each individual scatterer type [1]:

$$\Psi \sim \int \mathrm{d}^3\mathbf{r}(f_1\rho_1(\mathbf{r}) + f_2\rho_2(\mathbf{r})...) \exp(\mathbf{K}.\mathbf{r}_i). \tag{2}$$

The nice thing about a crystal is that the same density of scatterers is reproduced in each unit cell. As such we can write the density as:

$$f_1\rho_1(\mathbf{r}) + f_2\rho_2(\mathbf{r})... = L(\mathbf{r}) * (f_1\rho_1^{\text{basis}}(\mathbf{r}) + f_2\rho_2^{\text{basis}}(\mathbf{r})...), \tag{3}$$

where $*$ represents a convolution, $L(\mathbf{r})$ is a sum of delta functions (one at each lattice point) and $\rho_i^{\text{basis}}(\mathbf{r})$ is the density of species i within the basis. Using the nice result of the convolution theorem, we find:

$$\Psi \sim \mathrm{FT}(L(\mathbf{r}))\ \ \mathrm{FT}(f_1\rho_1^{\text{basis}}(\mathbf{r}) + f_2\rho_2^{\text{basis}}(\mathbf{r})...) \tag{4}$$

The Fourier transform of the lattice is the reciprocal lattice - a sum of delta functions, one at each reciprocal lattice point. *Thus we expect peaks when the change in wavevector corresponds to a reciprocal lattice vector.*[2] The second term is called the Structure Factor, and it modifies the size of these peaks.

$$\mathrm{FT}(f_1\rho_1^{\text{basis}}(\mathbf{r}) + f_2\rho_2^{\text{basis}}(\mathbf{r})...) = S_{\mathbf{K}} = \sum_i f_i \exp(\mathbf{K}.\mathbf{r}_i), \tag{5}$$

where the sum runs over atoms in the basis, not over the whole crystal as in Eqn. 1. We can simplify this by writing $\mathbf{K}$ in terms of the primitive reciprocal lattice vectors $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, and $\mathbf{r}$ in terms of the primitive vectors of the direct lattice, $\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$, giving:

$$S_{h,k,l} = \sum_i f_i \exp\left(2\pi i(x_i h + y_i k + z_i l)\right). \tag{6}$$

2 Use of the Structure Factor

When the basis consists of more than one atom, the different contributions from within a unit cell can cause the peaks to be larger or smaller - this effect is encapsulated in the structure factor. The relative size of peaks can be used to distinguish between structures - for instance, see the final question in the tute work. These questions are usually easy to do: just substitute in the form factors, (h,k,l) vaues and atom coordinates of interest and evaluate $|S_{h,k,l}|^2$.

[1] For instance, if the unit cell contains Cs+ and Cl-, f_1 and ρ_1 would correspond to the scattering strength and density of Cs+ and f_2 and ρ_2 to Cl-. If you want to get *really* involved, for x-rays you can treat electrons themselves as the sole point scatterers. In this case, the separate factors f_1 and f_2 for Cs+ and Cl- arise naturally as Fourier transforms of the electron density around Cs+ and Cl-.

[2] Note - You can either associate each peak with the reciprocal lattice vector h, k, l or the (h, k, l) family of planes. I find the clearest way is to talk in terms of reciprocal lattice vectors.

3 Distinguishing different cubic structures

It is convenient to analyze cubic crystals using conventional cells. In the case of BCC and FCC, this entails pretending that you have a primitive cubic lattice with a basis of two and four atoms respectively, even though in fact all atoms are associated with a lattice point. If you substitute the coordinates of the BCC and FCC 'effective' bases into the equation for the structure factor, you should find that many of the primitive cubic peaks vanish. In fact, BCC peaks only survive if $h+k+l$ is even, and FCC peaks if h,k,l are all either odd or even. This allows you to work out the relative sizes of $|\mathbf{K}|^2$ that you would expect to see in the 3 cases (you should do this for yourself and remember it).

Of course, to be of any use we must actually compare to experiment. Generally, experimental results give us the wavelength used and the angles at which peaks are observed. We can use Bragg's law to calculate the separation of planes ($d_{h,k,l}$) corresponding to each peak, and then the result from question 2 to infer the size of the reciprocal lattice vector for each peak.

$$|\tau_{h,k,l}| = \frac{2\pi}{d_{h,k,l}} \tag{7}$$

Comparing the relative sizes of observed peaks to those predicted by the structure factor for each lattice type allows the lattice to be identified (see question 7).

4 Slightly complicated structures

Consider NaCl - this has an FCC structure with a basis of Na+ (0,0,0), Cl-(1/2,0,0). Working in the conventional cell, our 'effective' basis therefore has 8 atoms, which would give a messy structure factor if you tried to do it all at once. Alternatively, we can be a bit clever - let us return to Eqn. 3. Now instead of bunging all 8 atoms in our 'effective' basis into the second bracket, we can instead remember that our real basis has only two atoms, and keep the lattice explicitly as FCC for now. If you think carefully, you should be able to see that the lattice can be written as:

$$L_{\mathrm{FCC}}(\mathbf{r}) = L_{\mathrm{primitive}}(\mathbf{r}) * B_{\mathrm{FCC}}(\mathbf{r}), \tag{8}$$

in which B_{FCC} is simply a delta function at each of the lattice sites that we want to include in our 'effective' basis. Using the convolution theorem again, we find:

$$\Psi \sim \mathrm{FT}(L_{\mathrm{primitive}}(\mathbf{r}))\ \ \mathrm{FT}(B_{\mathrm{FCC}}(\mathbf{r}))\ \ \mathrm{FT}(\mathrm{Actual\ \ basis}). \tag{9}$$

The nice thing here is the pretend and actual parts of the basis are kept separate, making it easier to analyze and understand scattering results. Another way of saying this is that the structure factor $S_{h,k,l} = \mathrm{FT}(B_{\mathrm{FCC}}(\mathbf{r}))\ \ \mathrm{FT}(\mathrm{Actual\ \ basis})$ factorizes into a term due to the 'pretend' lattice basis and the actual basis which is repeated at each FCC lattice point.

$$S_{h,k,l} = \Big(\sum_j \exp\left(2\pi i(x_j h + y_j k + z_j l)\right)\Big)\Big(\sum_i f_i \exp\left(2\pi i(x_i h + y_i k + z_i l)\right)\Big). \tag{10}$$

In the above equation, the sum over j runs over the lattice points in the 'pretend' basis and the sum over i the atoms in the real basis.