

Planes perpendicular to vectors

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Say you have a vector in real space, expressed say in direct lattice terms, for example $\vec{p} = p_a\vec{a} + p_b\vec{b} + p_c\vec{c}$ where \vec{a} is the a lattice parameter, which is a vector.

You may want the *reciprocal* plane(s) perpendicular to this vector.

Why?

Because correlations in a crystal collapse the scattering into features perpendicular to the direction of the correlation. In a normal, fully ordered three dimensions (3D) crystal, this collapsing happens in all three directions, so the scattered intensity coming off the atoms gets concentrated at points, the reciprocal lattice points, usually denoted hkl .

If you have only two dimensional ordering, the scattering is collapsed down in two directions but not the third, giving rise to rods or lines of scattering in reciprocal space (that is, in diffraction space). If there are only one dimensional correlations, the scattering collapses into sheets, that is, it is delocalised in two dimensions and only localised in one dimension (because there are only correlations in one dimension).

In diffuse scattering the crystal is typically long-range ordered in three dimensions, and the diffraction pattern shows nice Bragg peaks (hkl reflections). However, there can also be disorder, for example in the motions of the molecules or the chemical; substitution of one species of atom or molecule for another.

In a molecular crystal, one can sometimes identify a chain of molecules running through the crystal, and interactions within these chains are likely to be much stronger than those within. That tends to mean that the motions of the molecules along the direction of the chain (call that ‘longitudinal’ motion) is highly correlated, while it is not well correlated laterally.

In such a situation, the single crystal diffuse scattering will show ‘sheets’ of scattering perpendicular to the length of the chain.

Let’s say the chain of molecules extends along an arbitrary real-space direction, which we’ll define by the vector \vec{p} as above.

Now, a plane perpendicular to \vec{p} can be specified by giving two (nor more) non-collinear vectors that lie in it. Let’s look at two vectors and we’ll call them \vec{q} and \vec{r} , for no good reason.

Then we can say that

$$\vec{p} \cdot \vec{q} = \vec{p} \cdot \vec{r} = 0 \tag{1}$$

but note that we are *not* assuming $\vec{q} \cdot \vec{r} = 0$, since right angles within the plane are not that important — especially as for generality I am not assuming orthogonal axes.

Now, \vec{q} exists in reciprocal space, so it is a linear combination of the reciprocal lattice vectors, \vec{a}^* , \vec{b}^* and \vec{c}^* like this

$$\vec{q} = q_{a^*} \vec{a}^* + q_{b^*} \vec{b}^* + q_{c^*} \vec{c}^* \quad (2)$$

and these reciprocal vectors are defined in terms of the direct space vectors like this

$$\vec{a}^* = \frac{2\pi \vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \quad (3)$$

and similarly for the other reciprocal vectors. The important thing for us to note is that this means \vec{a}^* is perpendicular to \vec{b} and \vec{c} . This is important when we go to take dot products later on. The bottom line here is basically the volume of the unit cell, and 2π is just a scalar, so from the point of view of defining the plane that we want, these are not important.

Ignoring the scalar parts, substituting eq. 3 into eq. 2 gives

$$\vec{q} = q_{a^*} (\vec{b} \times \vec{c}) + q_{b^*} (\vec{c} \times \vec{a}) + q_{c^*} (\vec{a} \times \vec{b}) \quad (4)$$

and since we have more variables than we need if we are to satisfy eq. 1, we can arbitrarily set $q_{c^*} = 0$.

Now, considering the dot product of \vec{q} and \vec{p} , in full it is

$$\begin{aligned} \vec{p} \cdot \vec{q} = & p_a q_{a^*} \vec{a} \cdot (\vec{b} \times \vec{c}) + p_a q_{b^*} \vec{a} \cdot (\vec{c} \times \vec{a}) + \\ & p_b q_{a^*} \vec{b} \cdot (\vec{b} \times \vec{c}) + p_b q_{b^*} \vec{b} \cdot (\vec{c} \times \vec{a}) + \\ & p_c q_{a^*} \vec{c} \cdot (\vec{b} \times \vec{c}) + p_c q_{b^*} \vec{c} \cdot (\vec{c} \times \vec{a}) \end{aligned} \quad (5)$$

and this is useful because, to take the last term on the first line as an example, \vec{a} is perpendicular to $(\vec{c} \times \vec{a})$ by the very nature of the cross product. This means that any terms with a repeated vector go to zero. Further, in the remaining terms the vector part is just of the form $\vec{a} \cdot (\vec{b} \times \vec{c})$ which is the unit cell volume and a constant, which we can also factor out to be left with

$$\vec{p} \cdot \vec{q} = p_a q_{a^*} + p_b q_{b^*} \quad (6)$$

which is nice and simple. This is not a surprise but still...

The next step is to find another vector in that plane. This is just \vec{r} , and if we use the same logic but, to make \vec{r} non-collinear with \vec{p} , we choose r_{b^*} to be zero, we get an equation analogous to eq. 6. These can be summed up as

$$\vec{q} = \vec{a}^* - \frac{p_a}{p_b} \vec{b}^* \quad \text{and} \quad \vec{r} = \vec{a}^* - \frac{p_a}{p_c} \vec{c}^* \quad \text{and} \quad \vec{s} = \vec{b}^* - \frac{p_b}{p_c} \vec{c}^* \quad (7)$$

where \vec{s} is a fairly straightforward extension.

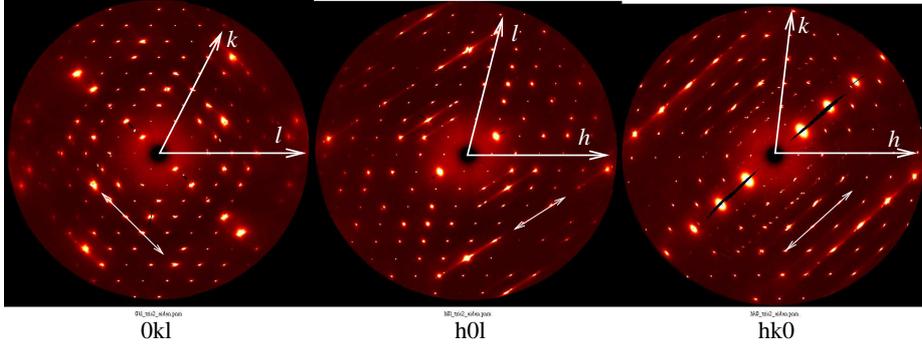


Figure 1: Observed data, measured at the Advanced Photon Source, showing what looks like multiple crystallites with similar orientations.

Now, in terephthalic acid (TPA), triclinic polymorph of form II, each molecule has a $-\text{COOH}$ group at each end. These H-bond strongly with the groups on neighbouring molecules and you get strongly correlated chains of molecules running along the $[-111]$ (direct space) direction. This then suggests that the planes of scattering perpendicular to these chains will extend in the directions

$$\vec{q} = \vec{a}^* + \vec{b}^* \quad \text{and} \quad \vec{r} = \vec{a}^* + \vec{c}^* \quad \text{and} \quad \vec{s} = \vec{b}^* - \vec{c}^* \quad (8)$$

or

$$\vec{q} = (110) \quad \text{and} \quad \vec{r} = (101) \quad \text{and} \quad \vec{s} = (01\bar{1}) \quad (9)$$

Now, does this work? Figure 1 is some data from TPA, diffuse scattering data measured on a synchrotron. It also shows the reciprocal axes and the white, two-ended arrows show the directions of the diffuse planes and by counting Bragg spots it can be seen that these agree with the calculation above.

This means that we can ascribe these features to correlations in the displacements of the TPA molecules linked by the $-\text{COOH}$ groups.