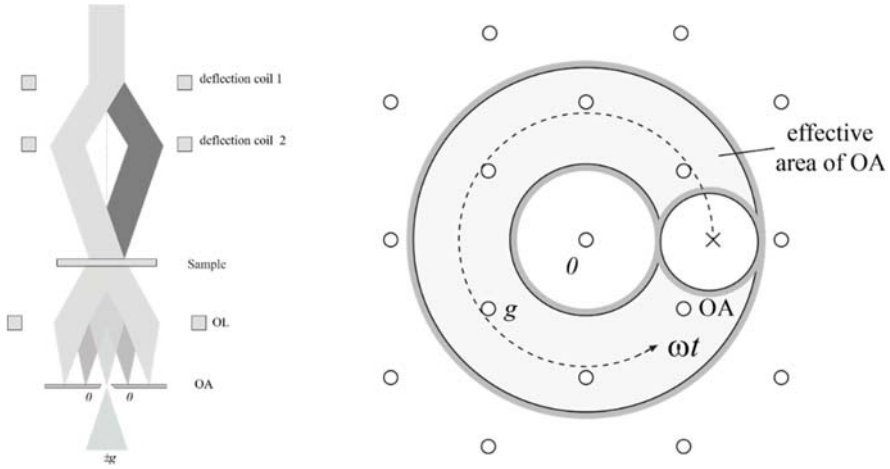
NANO 703-Notes

Chapter 12-Reciprocal space

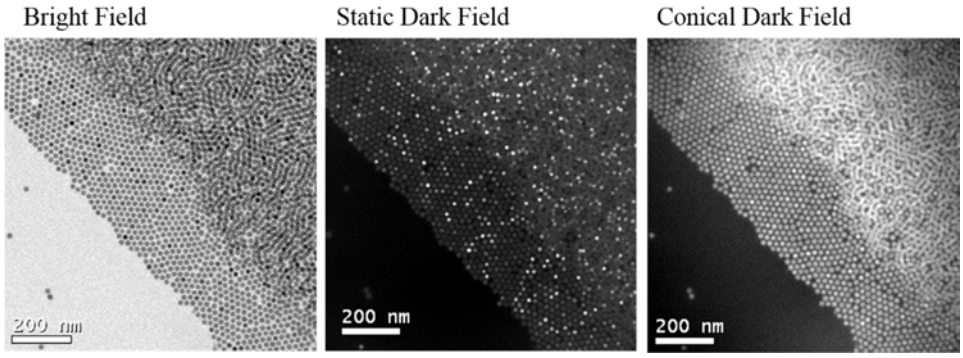
Conical dark-field imaging

We primarily use DF imaging to control image contrast, though STEM-DF can also give very high resolution, in some cases. If we have single crystal, a *g*-DF image can formed by tilting the beam in one particular direction. But for polycrystalline solids, powders, or nanomaterials, there may be many crystallographic orientations within the field of view. One trick to highlight a large fraction of these in dark-field mode is to rapidly precess the beam around the optic axis, with a small OA in the BFP of the OL. Sinusoidal signals can be sent to the CL deflection coils to drive the beam tilt in a circular path. We don't want any shifting of the beam, only tilt, so alignment is important. A particular reflection *g*, which appears as a ring in the diffraction pattern, can be brought onto the optic axis to form the dark-field image. We have achieved centered dark-field conditions for an entire diffraction ring, not just a spot.



Conical dark-field imaging of nanoparticles

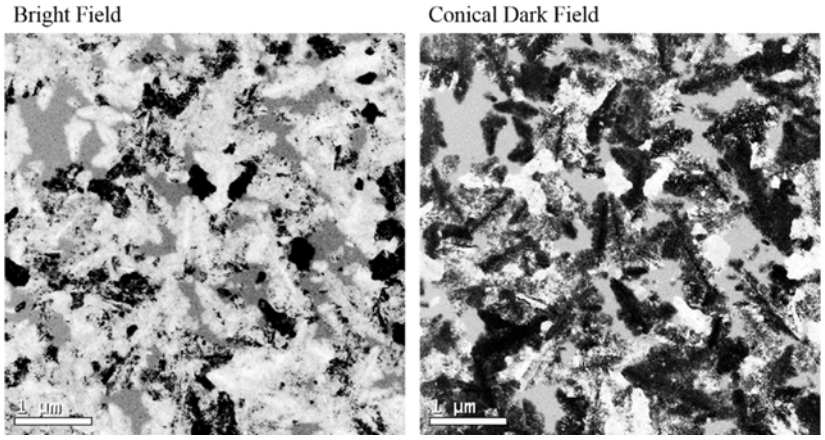
If the precession rate is several Hz or higher, the beam motion is not even noticeable. Switching the tilt angle to zero restores the BF image. With the beam tilted, stopping the precession gives a static DF image that highlights just a subset of the crystallites.



Partially crystallized material

One nice thing about DF imaging is it can highlight only features of interest, while masking others. Conical DF images of partially crystallized, hydrogenated amorphous silicon (a-Si:H) show very clear contrast between amorphous and crystallized areas. In the DF image, the crystals generally appear either white or black, depending on whether they are at or away from the Bragg condition of the reflection used

(111, in this case). The amorphous regions are essentially featureless in the DF image, making them easy to distinguish. In the BF image, these can show contamination or topography on the surface.



Direct and reciprocal lattice parameters

We know how to find the reciprocal-lattice basis vectors, given a particular set of direct-lattice basis vectors. We can identify lattice parameters and angles for these reciprocal-space vectors in an analogous fashion.

$$b_1 = |\mathbf{b}_1|,\ b_2 = |\mathbf{b}_2|,\ b_3 = |\mathbf{b}_3|$$

and

$$\mathbf{b}_2 \cdot \mathbf{b}_3 = b_2 \cdot b_3 \cdot \cos\beta_1,\ \mathbf{b}_3 \cdot \mathbf{b}_1 = b_3 \cdot b_1 \cdot \cos\beta_2, \text{ and } \mathbf{b}_1 \cdot \mathbf{b}_2 = b_1 \cdot b_2 \cdot \cos\beta_3$$

Say we have an orthorhombic crystal.

$$a_1 = a,\ a_2 = b,\ a_3 = c,\ \alpha_1 = \alpha_2 = \alpha_3 = 90°$$

We saw that the reciprocal lattice is also orthorhombic, i.e.,:

$$b_1 = \frac{1}{a},\ b_2 = \frac{1}{b},\ b_3 = \frac{1}{c},\ \beta_1 = \beta_2 = \beta_3 = 90°$$

Determining interplanar spacing

The interplanar (d) spacing used in Bragg's law is given by $d_{hk\ell} = 1/|\mathbf{g}_{hk\ell}|$, where

$$\mathbf{g}_{hk\ell} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3.$$

The general method to find the length of a vector is to dot it with itself and take the square root, so:

$$\begin{aligned}|\mathbf{g}_{hk\ell}| &= (\mathbf{g}_{hk\ell} \cdot \mathbf{g}_{hk\ell})^{0.5} \\ &= \left(h^2 b_1^{\,2} + k^2 b_2^{\,2} + l^2 b_3^{\,2} + 2kl\mathbf{b}_2 \cdot \mathbf{b}_3 + 2lh\mathbf{b}_3 \cdot \mathbf{b}_1 + 2hk\mathbf{b}_1 \cdot \mathbf{b}_2\right)^{0.5} \\ |\mathbf{g}_{hk\ell}| &= \left(h^2 b_1^{\,2} + k^2 b_2^{\,2} + l^2 b_3^{\,2} + 2klb_2 b_3 \cos\beta_1 + 2lhb_3 b_1 \cos\beta_2 + 2hkb_1 b_2 \cos\beta_3\right)^{0.5}\end{aligned}$$

This is fairly complicated for a low-symmetry crystal, but simplifies greatly with higher symmetry. Cubic, for example, reduces to:

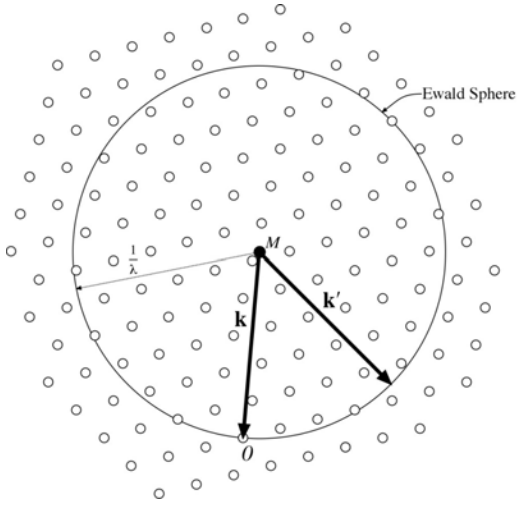
$$|\mathbf{g}_{hkl}| = \frac{\sqrt{h^2+k^2+l^2}}{a},\ d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

The *d*-spacing for orthorhombic is not what you might guess off the top of your head:

$$|\mathbf{g}_{hkl}| = \sqrt{\left(\frac{h}{a}\right)^2+\left(\frac{k}{b}\right)^2+\left(\frac{l}{c}\right)^2},\ d_{hkl} = 1\Big/\sqrt{\left(\frac{h}{a}\right)^2+\left(\frac{k}{b}\right)^2+\left(\frac{l}{c}\right)^2}$$

Ewald sphere

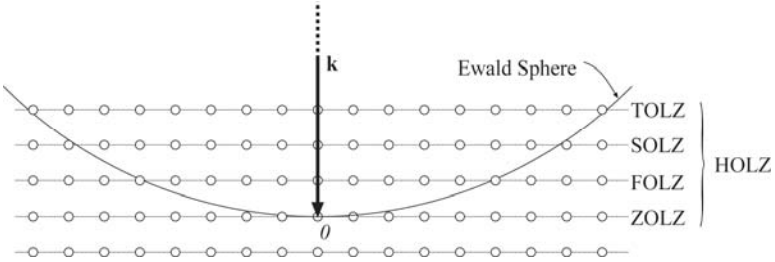
An important concept in diffraction is the Ewald sphere. It is a reciprocal-space construction used to examine the diffraction geometry. The Ewald sphere has radius $1/\lambda$. Its center is called the "excitation point", which we will label *M*. The reciprocal-space origin *0* is not at the center of the sphere, but rather on the surface of the sphere. The incident wave vector $\mathbf{k}$ (which has length $1/\lambda$) points from *M* to *0*.



We are mainly interested in elastic scattering for now, so we know any scattered wave vector $\mathbf{k}'$ will also have length $1/\lambda$. Thus, $\mathbf{k}'$ can also be drawn from *M* to the surface of the Ewald sphere. So the sphere tells us all possible diffracted wave vectors. If we superpose the sphere on a crystal's reciprocal lattice, we see the relationship between $\mathbf{k}$, $\mathbf{k}'$, and any RLV $\mathbf{g}$ for this crystal. The Bragg condition requires $\mathbf{k}'-\mathbf{k}=\mathbf{g}$. So the reciprocal-space distance from the reciprocal-lattice point *g* to the sphere is a measure of how far the corresponding lattice planes are from the Bragg condition.

Higher-order Laue zones

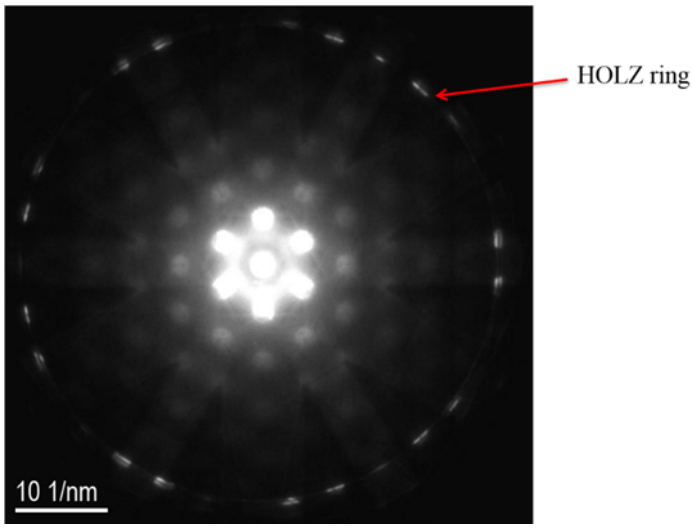
A plane of reciprocal lattice points is called a "Laue zone". When the plane contains *0*, and extends nearly perpendicular to the beam, it is called the zero-order Laue zone, or ZOLZ. But this is just one in a series of parallel planes. Each of the others is called a higher-order Laue zone, or HOLZ. The HOLZs only get close to the Ewald sphere at high angles, so we may have to look more carefully to see evidence of them in diffraction patterns. As the beam energy gets higher, the Ewald sphere curvature gets smaller, so the intersection with each HOLZ moves out to a larger radius in reciprocal space. (Surprisingly, though, the scattering angle for a HOLZ ring gets smaller as the beam energy increases.)



The HOLZ rings contain useful information. The reflections contributing to the ring arise from reciprocal-lattice points with RLVs that are not perpendicular to the beam direction. So the HOLZ ring radius can be used to determine the lattice parameter along the beam direction. Also, notice that as we tilt away from the axis of the Laue zone, even the intersection of the ZOLZ with the Ewald sphere becomes a circle.

Si <111>

One of the most interesting examples of a HOLZ diffraction ring arises from the silicon crystals oriented in the <111> orientation. This shows up best in convergent-beam diffraction, which we will discuss later.

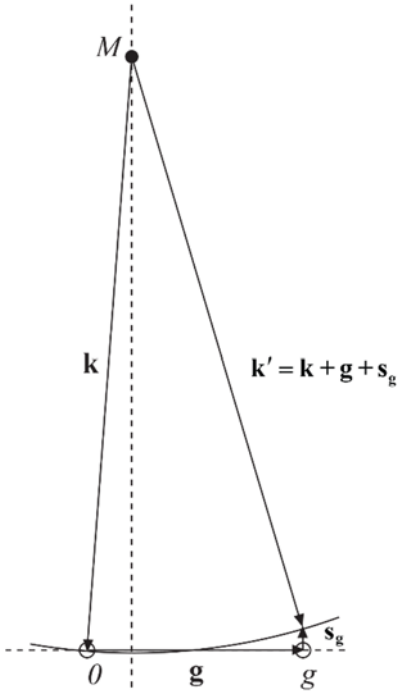


Excitation error (deviation parameter)

A measure of how far a particular set of lattice planes is from the Bragg condition is the distance of the corresponding reciprocal-lattice point from the Ewald sphere. The vector, which we call the excitation error $\mathbf{s_g}$, connecting a point *g* to the sphere, satisfies

$$\mathbf{k}' = \mathbf{k} + \mathbf{g} + \mathbf{s_g}$$

But this does not uniquely define. In different contexts, we may choose to measure it either: 1) perpendicular to $\mathbf{g}$; 2) parallel to $\mathbf{k}$; 3) normal to the surface of the thin TEM foil; or 4) along the direction of shortest distance to the sphere. Regardless, when we are at the Bragg condition, its length is zero (i.e., $s_g = 0$). Notice that the length of $\mathbf{s}_g$ is unchanged if either the sample or the beam is rotated about *g*.



Evaluating excitation error

We can pick a suitable orientation for sg and find an expression for its length. Say the foil normal is vertical ($\hat{\mathbf{n}} = -\hat{\mathbf{z}}$), The beam is directed downward with a tilt angle ϕ.

$$\mathbf{k} = k \cdot (-\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{z}})$$

In TEM, we are almost always interested in reflections arising from RLVs nearly perpendicular to $\hat{\mathbf{n}}$. Let's assume $\mathbf{g} = g\hat{\mathbf{x}}$. For reasons we will explore later, a good assumption is $\mathbf{s_g} = s_g\hat{\mathbf{z}}$. By convention, we have assumed $s_g < 0$ if g is outside the sphere.

The lengths of the incident and scattered wave vectors must be equal:

$$k = |\mathbf{k}| = |\mathbf{k} + \mathbf{g} + \mathbf{s_g}|$$

Square the lengths

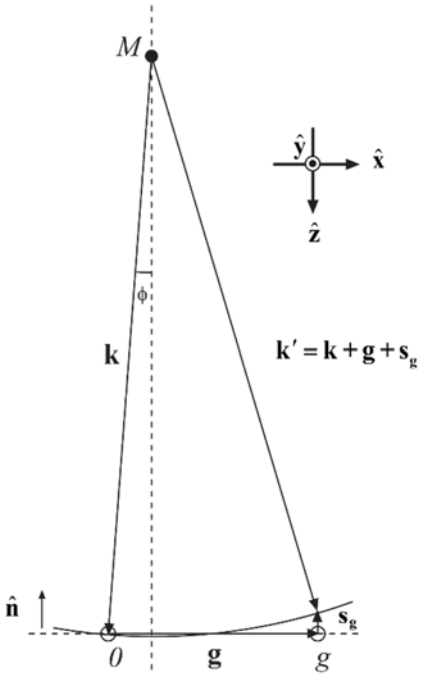
$$\cancel{k^2} = \cancel{k^2} + 2\mathbf{k} \cdot (\mathbf{g} + \mathbf{s_g}) + (\mathbf{g} + \mathbf{s_g})^2$$

This gives

$$s_g = -k \cdot \cos\phi \left[1 \pm \sqrt{1 + 2\left(\frac{g}{k}\right)\frac{\tan\phi}{\cos\phi} - \left(\frac{g}{k\cos\phi}\right)^2} \right]$$

There are two solutions: $+$ and $-$. The $+$ solution represents the intersection with the top of the sphere, which is not a good indication of the excitation. It is the $-$ solution we need. We are mainly interested in high-energy diffraction, with $g \ll k$. In this case,

$$s_g \approx g \cdot \tan\phi - \frac{g^2}{2k\cos\phi}$$



Sphere volume and ZOLZ intersection

The Ewald sphere has radius $1/\lambda$, so its reciprocal-space volume is $\Omega = 4\pi k^3/3$. We expect the intersection with the ZOLZ to be a circle. All points on the circle have $s_g = 0$, so the diameter g can be found by:

$$0 = g \cdot \tan\phi - \frac{g^2}{2k\cos\phi} \Rightarrow g = 2k \cdot \sin\phi$$

If the tilt angle is small, the diameter of the circle becomes

$$g \approx 2k\phi = \frac{2\phi}{\lambda}$$