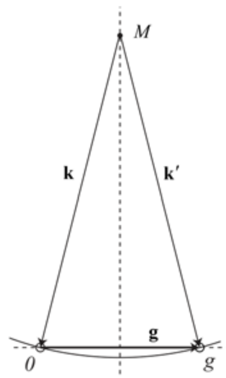
Crystallography & Structure of Nanomaterials

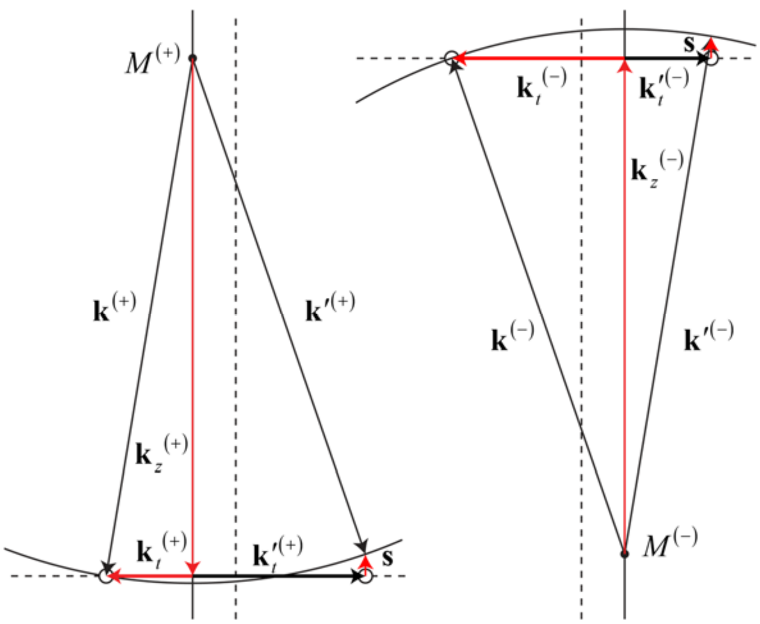
8. Electron Diffraction

Scattering geometry

Consider electron diffraction from a thin, crystalline foil. A reciprocal-space construction shows the Ewald sphere with radius *k* centered at the excitation point $M^{(+)}$. The incident-beam wave vector $\mathbf{k}$ extends from $M^{(+)}$ to the reciprocal space origin *0* on the surface of the sphere. A diffracted wave vector $\mathbf{k}'$ extends from $M^{(+)}$ towards the reciprocal lattice point $\mathbf{g}$ for the corresponding lattice planes. At the Bragg condition, $\mathbf{g}$ is on the sphere. Otherwise, the gap is a measured by the excitation error $\mathbf{s_g}$ (or $\mathbf{s}$, if we are only discussing one beam), which points *from* $\mathbf{g}$ *to* the Ewald sphere. By convention – and for practical reasons – the vector $\mathbf{s_g}$ is oriented from *g* to the sphere, in a direction normal to the plane of the thin foil, which is normally vertical. The scattered wave vector can then be written $\mathbf{k}' = \mathbf{k} + \mathbf{g} + \mathbf{s_g}$.



We will call the wave vector of the downward-oriented incident beam $\mathbf{k}^{(+)}$, and that of the scattered wave vector $\mathbf{k}'^{(+)}$. The incident wave vector can be decomposed into vertical and tangential components as $\mathbf{k}^{(+)} = \mathbf{k}_z^{(+)} + \mathbf{k}_t^{(+)}$, and the scattered wave vector as $\mathbf{k}'^{(+)} = \mathbf{k}'_z + \mathbf{k}_t'^{(+)}$. The components are related by $\mathbf{k}_z'^{(+)} = \mathbf{k}_z^{(+)} + \mathbf{s_g}$ and $\mathbf{k}_t'^{(+)} = \mathbf{k}_t^{(+)} + \mathbf{g}$.

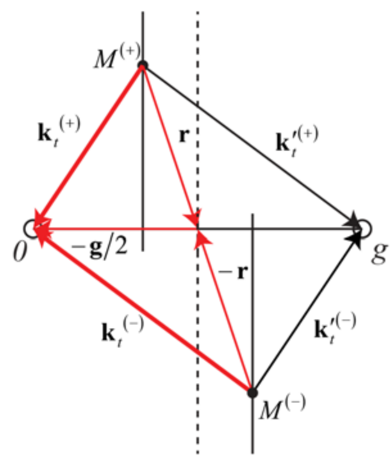


The theorem of reciprocity builds on the time-reversal symmetry in the equations for elastic scattering. That is, exchanging the orientations of the incident and diffracted beams with each other, and reversing their directions, should produce the the same diffracted amplitude. We should consider a different Ewald sphere in this case, which has its excitation point below *0*. We will call the upward pointing incident wave vector of the reciprocal experiment $\mathbf{k}^{(-)} = \mathbf{k}_z^{(-)} + \mathbf{k}_t^{(-)}$; the scattered wave vector in this case is $\mathbf{k}'^{(-)} = \mathbf{k}_z'^{(-)} + \mathbf{k}_t'^{(-)}$. The reciprocal experiment is performed when $\mathbf{k}^{(-)} = -\mathbf{k}'^{(+)}$ and $\mathbf{k}'^{(-)} = -\mathbf{k}^{(+)}$. Solving for $\mathbf{k}'^{(-)}$, we find

$$\begin{aligned}\mathbf{k}'^{(-)} &= -\mathbf{k}^{(+)} = -\left(\mathbf{k}'^{(+)} - \mathbf{g} - \mathbf{s_g}\right)\\ &= -\left(-\mathbf{k}^{(-)} - \mathbf{g} - \mathbf{s_g}\right)\\ \mathbf{k}'^{(-)} &= \mathbf{k}^{(-)} + \mathbf{g} + \mathbf{s_g}\end{aligned}$$

The scattered wave vector components for the reciprocal experiment are $\mathbf{k}_z'^{(-)} = \mathbf{k}_z^{(-)} + \mathbf{s_g}$ and $\mathbf{k}_t'^{(-)} = \mathbf{k}_t^{(-)} + \mathbf{g}$.

We are interested in the symmetry of diffraction from a zero-order Laue zone (ZOLZ) that we assume to be horizontal. Bragg diffraction from g can occur even when the diffraction plane containing $\mathbf{k}^{(+)}$ and $\mathbf{k}'^{(+)}$ is not perpendicular to the ZOLZ. A top view, with $M^{(+)}$ projected onto the ZOLZ, shows that $M^{(+)}$ lies on a line normal to $\mathbf{g}$ that bisects the line segment $0-g$. Defining a vector $\mathbf{r}$ that points from $M^{(+)}$ to the midpoint of $0-g$, we can write $\mathbf{k}_t^{(+)} = -\mathbf{g}/2 + \mathbf{r}$.



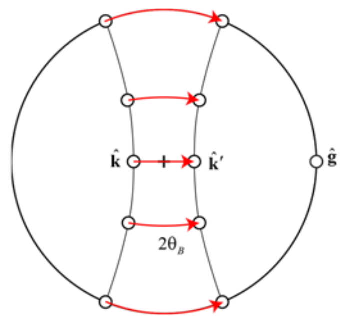
A projection onto a horizontal plane more clearly reveals the connection to 2-D electron diffraction patterns. The diffracted amplitude $\Psi_g^{(+)}$ in the actual experiment, with the beam directed downward from excitation point $M^{(+)}$, can be expressed as a function $\mathbf{k}_t^{(+)}$, i.e., $\Psi_g^{(+)}\left(\mathbf{k}_t^{(+)}\right)$ In the reciprocal experiment, with the beam directed upward from $M^{(-)}$, the diffracted amplitude $\Psi_g^{(-)}$ varies with $\mathbf{k}_t^{(-)}$. For a particular setting, with $\mathbf{k}_t^{(+)} = -\mathbf{g}/2 + \mathbf{r}$, and the reciprocal experiment, with, $\mathbf{k}_t^{(-)} = -\mathbf{g}/2 - \mathbf{r}$, would result in the same diffracted amplitude. Thus

$$\Psi_g^{(+)}(-\mathbf{g}/2 + \mathbf{r}) = \Psi_g^{(-)}(-\mathbf{g}/2 - \mathbf{r})$$

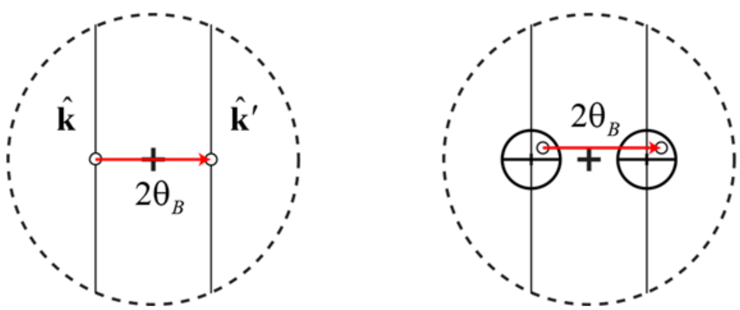
We may not actually perform the reciprocal experiment, but we can use this relationship to deduce features in diffraction patterns from samples with certain types of symmetry.

Diffraction groups

Consider a stereographic projection along the zone axis of a crystal. The direction $\hat{\mathbf{g}}$ of an in-plane lattice vector $\mathbf{g}$ is positioned along the equitorial great circle. The loci of points in the cones containing all incident $\hat{\mathbf{k}}$ and scattered $\hat{\mathbf{k}}'$ beam directions satisfying the Bragg condition for $\mathbf{g}$ appear on curves separated by $2\theta_B$.

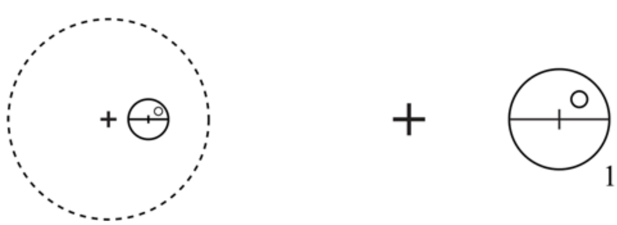


In high-energy electron diffraction, we are primarily interested in low-angle diffraction features for reflections near the Bragg condition. We now focus on a small angular portion of the stereographic projection near the zone center. For scattering at the Bragg condition, with the zone axis direction in the plane of diffraction, the incident and scattered directions are displaced by θ_B on opposite sides of the zone axis. These points are indicated below for reference. Scattering away from the Bragg condition will occur within a region of points around these points, indicated by larger disks.



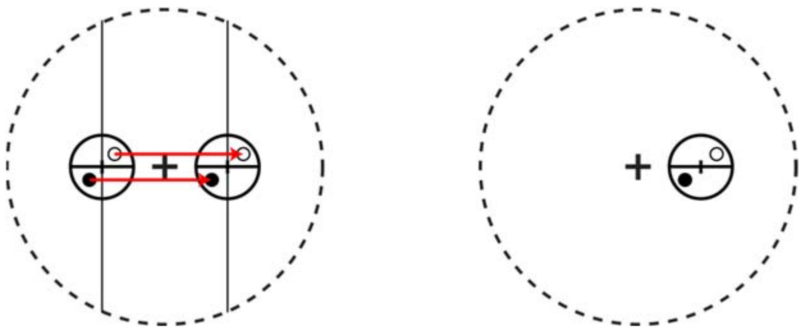
Diffraction group 1

Finally, we disregard the incident beam direction and only show that scattered-beam direction. The Bragg condition is indicated by a tick through the disk in the vertical direction, normal to $\mathbf{g}$. In the absence of any symmetry, the incident-beam disk and other annotations are omitted. The resulting diagram shows the symmetry of diffraction group 1.

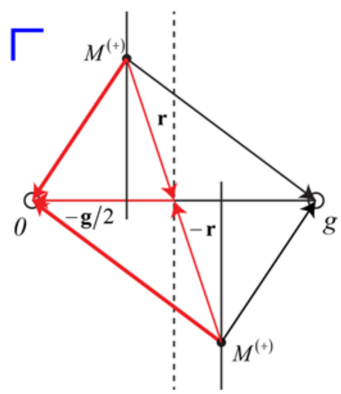


Diffraction group 1_R

In the reciprocal experiment, the direction of the incident beam from below projects onto a point opposite the intersection of the scattering vector and the tick mark indicated the exact Bragg position. Likewise, the corresponding scattering direction is opposite the exact Bragg position within the scattering disk. We indicate these points by filled circles, because they are upward pointing directions, rather than downward.



If the crystal point group has a horizontal mirror plane m_h through its center, we can infer that, for an RLV $\mathbf{g}$ parallel to the mirror plane, a beam incident from $M^{(-)}$ below the sample, with $\mathbf{k}_t^{(-)} = -\mathbf{g}/2 - \mathbf{r}$, should give rise the the same diffracted amplitude as would a beam incident from $M^{(+)}$ above the sample, with $\mathbf{k}_t^{(+)} = -\mathbf{g}/2 - \mathbf{r}$.



But, by reciprocity, the former will equal the amplitude from $M^{(+)}$ with $\mathbf{k}_t^{(+)} = -\mathbf{g}/2 + \mathbf{r}$. Thus, there is symmetry in the diffracted amplitude of the *g*-CBED disk, such that

$$\Psi_g^{(+)}(-\mathbf{g}/2 + \mathbf{r}) = \Psi_g^{(+)}(-\mathbf{g}/2 - \mathbf{r}) \quad \text{// with horizontal mirror}$$

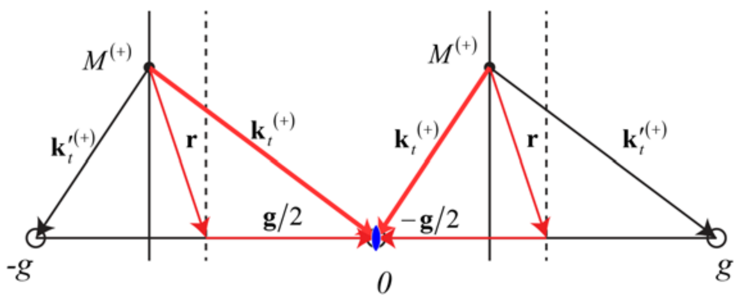
The symmetry related points, indicated by small circles within the CBED disk, are located opposite from each other about the symmetry center of the disk. The disk will therefore have twofold rotational symmetry about this point, which is indicated by the subscript *R*.

Diffraction group 2_R

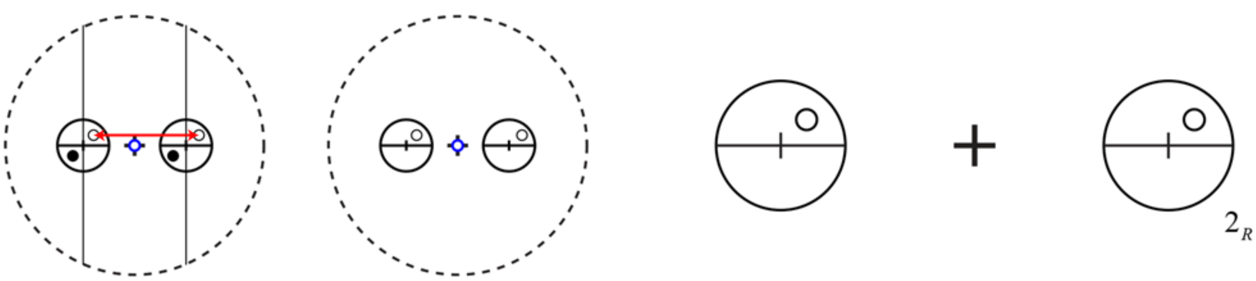
Similarly, if the foil has an inversion point at its center that preserves the symmetry of the crystal, then excitation from $M^{(+)}$ by g with $\mathbf{k}_t^{(+)} = \mathbf{g}/2 + \mathbf{r}$ should give rise to the same diffracted amplitude with $-g$ when $M^{(+)}$ satisfies $\mathbf{k}_t^{(+)} = -\mathbf{g}/2 + \mathbf{r}$. Thus

$$\Psi_g^{(+)}(-\mathbf{g}/2 + \mathbf{r}) = \Psi_{-g}^{(+)}(\mathbf{g}/2 + \mathbf{r}) \quad \text{//with inversion center}$$

The recirpocal-space construction is shown below

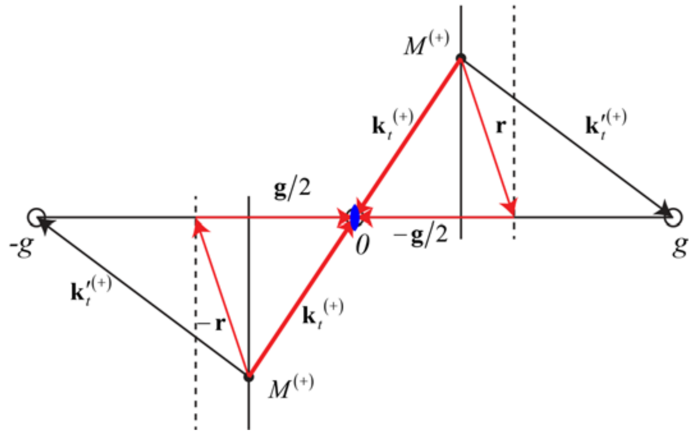


In the stereographic projection, we see that a symmetry equivalent excitation point has its reciprocal across the symmetry center of the g disk from the corresponding scattering direction. Scattering from the incident beam in the original scattering direction, then produces Bragg diffraction by $-\mathbf{g}$ into the direction of the initial incident beam. If this is the only symmetry present, the corresponding diffraction group is 2_R.The $\pm g$ disks are symmetric under a twofold rotation about the zone axis, combined with twofold rotations of each disk about the symmetry center of the disk.

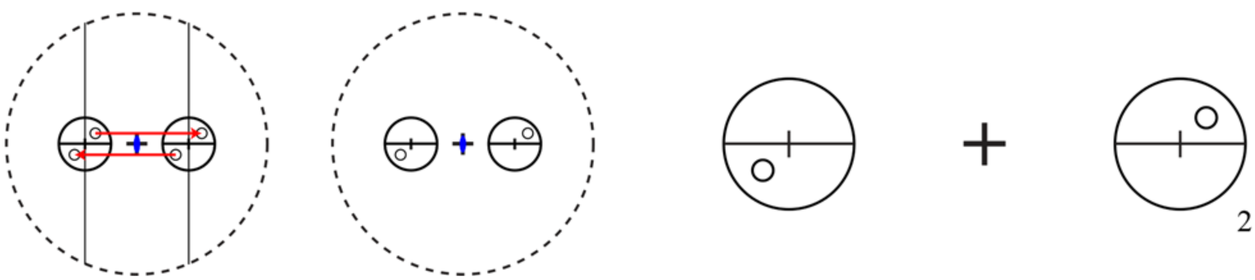


Diffraction group 2

Some of the diffraction symmetries can be identified without invoking reciprocity. For example, if the crystal has a 2 axis parallel to zone axis, the ZOLZ pattern will have the same symmetry.



This gives rise to a corresponding twofold rotational symmetry about the zone center between $\pm g$ disks. In this case, the dark-field disks do not have the *R* symmetry, because there are no symmetry features that arise from reciprocity.



We can continue to apply this reasoning to all 32 crystallographic point groups, classifying the symmetry of the ZOLZ pattern along every possible zone axis. It has been shown that this results in 31 distinct diffraction groups. Further, the collection of possible diffraction groups that can be identified for any of the point groups is unique. Thus, one can uniquely identify the point group, from which the space group is derived, based on convergent-beam electron diffraction (CBED) zone-axis pattern ZAP symmetries. We can determine the lattice type from other aspects of the diffraction patterns, such as systematic and periodic absences. Thus, the combined information allows determination of many (if not all) of the 230 crystallographic space groups. [B. F. Buxton, et al., *Philos. Trans. R. Soc. A,* **281**, 171 (1975).]