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5.4. Electron-diffraction methods

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5.4.1. Determination of cell parameters from single-crystal patterns (By A. W. S. Johnson)

5.4.1.1. *Introduction*

This article treats the recovery of cell axes and angles from (*a*) a single pattern with suitable Laue zones and (*b*) two patterns with different zone axes. It is assumed that instrument distortions, if significant, are corrected and that the patterns are free of artefacts such as twinning, double diffraction *etc*. (Edington, 1975). The treatment is valid for convergent-beam, micro and selected-area electron-diffraction patterns and accelerating voltages above approximately 30 kV. Relevant papers are by LePage (1992) and Zuo (1993), and background reading is contained in Edington (1975), Gard (1976), and Hirsch, Howie, Nicholson, Pashley & Whelan (1965).

The basic requirement in the determination of the unit cell of a crystal is to find, from one or more diffraction patterns, the basis vector set, $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, of a primitive reciprocal unit cell. The Cartesian components of these vectors form an orientation matrix

$$\boldsymbol{UB} = (\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*),$$

which, when inverted, gives the vector components of the corresponding real-space cell. The elements of $\boldsymbol{UB}$ can be measured directly from the diffraction pattern in millimetres. Define axes x and y to be in the recording plane and z in the beam direction. A point in the diffraction pattern x, y, z is then related to the indices h, k, l by

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \boldsymbol{UB} \begin{pmatrix} h \\ k \\ l \end{pmatrix}.$$

Note that points with non-zero z are observed on the plane $z = 0$, see Fig. 5.4.1.1.

The metric $\boldsymbol{M}$ of $\boldsymbol{UB}^{-1}$ is used to find the unit-cell edges and angles as

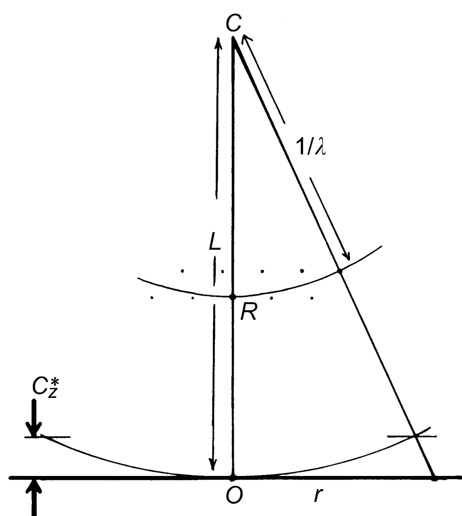

Fig. 5.4.1.1. Diffraction geometry. Crystal at C with the direct transmitted beam, CRO, intersecting the reciprocal-lattice origin at R and the recording plane at normal incidence at O. The camera length L is CO and the reciprocal of the wavelength λ is CR.

Table 5.4.1.1. *Unit-cell information available for photographic recording*

	Pattern type	Constants known	Information available
(1)	Zero zone	None or λ or L	d ratios and interplane angles
(2)		$L\lambda$ or L and λ	d values and interplane angles
(3)	Multiple zone	None or L	As for (1)
(4)		$L\lambda$	As for (2)
(5)		λ	Unit-cell axial ratios and angles
(6)		L and λ	Unit-cell axes and angles
(7)	Two or more zero-zone patterns*	None or L	As for (5)
(8)		$L\lambda$	As for (6)

* See text, Subsection 5.4.1.2.

$$\boldsymbol{M} = \boldsymbol{UB}^{-1} \cdot (\boldsymbol{UB}^{-1})^T,$$

where T means the transpose. Then,

$$\boldsymbol{M} = \begin{pmatrix} \mathbf{a}\cdot\mathbf{a} & \mathbf{a}\cdot\mathbf{b} & \mathbf{a}\cdot\mathbf{c} \\ \mathbf{a}\cdot\mathbf{b} & \mathbf{b}\cdot\mathbf{b} & \mathbf{b}\cdot\mathbf{c} \\ \mathbf{a}\cdot\mathbf{c} & \mathbf{b}\cdot\mathbf{c} & \mathbf{c}\cdot\mathbf{c} \end{pmatrix}$$

gives

$$a = L\lambda(\mathbf{a}\cdot\mathbf{a})^{1/2},$$
$$b = L\lambda(\mathbf{b}\cdot\mathbf{b})^{1/2},$$
$$c = L\lambda(\mathbf{c}\cdot\mathbf{c})^{1/2},$$
$$\cos\gamma = \mathbf{a}\cdot\mathbf{b}/(\mathbf{a}\cdot\mathbf{a}\;\mathbf{b}\cdot\mathbf{b})^{1/2},$$
$$\cos\beta = \mathbf{a}\cdot\mathbf{c}/(\mathbf{a}\cdot\mathbf{a}\;\mathbf{c}\cdot\mathbf{c})^{1/2},$$

and

$$\cos\alpha = \mathbf{b}\cdot\mathbf{c}/(\mathbf{b}\cdot\mathbf{b}\;\mathbf{c}\cdot\mathbf{c})^{1/2},$$

where L is the effective distance between the diffracting crystal and the recording plane and λ is the wavelength. These quantities are defined in Fig. 5.4.1.1 together with the nomenclature and geometrical relationships required in this article.

If necessary, the cell is reduced to the Bravais cell according to the procedures given in *IT* A (1983, Chapter 9.3), before calculating the metric.

In practice, there may be a difficulty in choosing a vector set that describes a *primitive* reciprocal cell. Although a record of any reasonably dense plane of reciprocal space immediately exposes two basis vectors of a cell, the third vector lies out of the plane of the diffraction pattern containing the first two vectors and may not be directly measurable. Hence, some care must be taken to ensure that the third vector chosen makes the cell

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primitive. This presents no difficulty in the non-zero-zone analysis given in Subsection 5.4.1.3 but needs consideration when two patterns are used as described in Subsection 5.4.1.2.

Unit-cell parameters may be partly or fully determined depending on the extent of knowledge of the effective camera length L and wavelength λ, and upon the type and number of patterns. The different situations are distinguished in Table 5.4.1.1 for photographic recording. Note that L is simply a magnification factor.

The accuracy of the non-zero-zone analysis described in Subsection 5.4.1.3 will depend on the influence of spiral, radial, and elliptical distortions. The camera length and wavelength need to be known to better than 1%.

For measurements made using microscope deflector systems, a knowledge of L may not be required depending on the location of the deflectors in the microscope column. Instead, the calibration factor of the deflectors, in suitable units, will replace L.

5.4.1.2. *Zero-zone analysis*

Two patterns are required that represent different sections through the reciprocal lattice. The angle of rotation p between these sections must be known, as well as the trace of the rotation axis in the plane of the pattern. Define the plane of the first pattern as the xy plane with the x axis, for convenience, coincident with the trace of the rotation axis. The coordinates x_0, y_0 of reflections in the first pattern are then measured. The coordinates x_1, y_1 of spots in the patterns rotated by p relative to the first pattern are then measured, care being taken to align the trace of the rotation axis with the x axis of the measuring equipment for each pattern. The coordinates of these reflections are then reduced to the coordinate system of the first pattern by the relations $x_0 = x_1$, $y_0 = y_1 \cos(p)$, $z_0 = y_1 \sin(p)$. The coordinates of all reflections measured are placed in a table that is scanned to extract the three shortest non-coplanar vectors. If the patterns come from dense, neighbouring zones, it is likely that these vectors define a primitive cell.

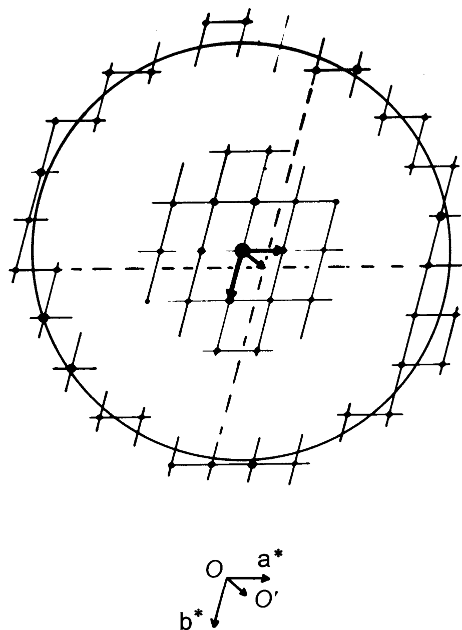

Fig. 5.4.1.2. A diffraction pattern with the crystal oriented at a zone axis. The lower diagram shows the zero-zone vectors $\mathbf{a}^*$ and $\mathbf{b}^*$, and OO', the projection on the xy plane of $\mathbf{c}^*$.

5.4.1.3. *Non-zero-zone analysis*

One pattern with well defined Laue zones taken at an arbitrary zone allows the recovery of a third vector not in the plane of the pattern. First find the components for the two shortest zero-zone vectors $\mathbf{a}^*$ and $\mathbf{b}^*$ (see Fig. 5.4.1.2). For the third vector, measure the x and y coordinates of a non-zero-zone vector. These are then transformed to components in the coordinate system defined by the two shortest vectors of the zero zone. Then the fractional part of each transformed component is taken. If the vector comes from a Laue zone of order n, these fractional parts must be divided by n. A transformation back to Cartesian coordinates gives the x and y components of the third vector $\mathbf{c}^*$, point O' in Fig. 5.4.1.2. In practice, it is best to measure a set of vectors at roughly equal angles around the zone so that an average can be taken to improve accuracy.

For certain space groups and special orientations, it is possible for half of the zero-zone reflections to be absent. If sufficient non-zero-zone vectors have been measured, two different vectors OO' should be found. New axes $(\mathbf{a}^* + \mathbf{b}^*)/2$ and $(\mathbf{a}^* - \mathbf{b}^*)/2$ must then be chosen and the x and y coordinates of $\mathbf{c}^*$ recalculated.

The z component of $\mathbf{c}^*$ is obtained (Fig. 5.4.1.1) from

$$c_z^* = L[1 - 1/(1 + r^2/L^2)^{1/2}]/n,$$

where r is the radius of the Laue circle of order n.

We now have the orientation matrix $\boldsymbol{UB}$ as

$$\boldsymbol{UB} = \begin{pmatrix} a_x^* & b_x^* & c_x^* \\ a_y^* & b_y^* & c_y^* \\ 0 & 0 & c_z^* \end{pmatrix},$$

and the measurement of the pattern is complete.

After transformation of the axes defined by $\boldsymbol{UB}$ to the Bravais axes, the inverse of the resulting $\boldsymbol{UB}_{\rm Bravais}$ will index the pattern using

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix} = \boldsymbol{UB}^{-1}_{\rm Bravais} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

5.4.2. Kikuchi and HOLZ techniques (By A. Olsen)

Lattice-parameter determination based on selected-area electron-diffraction patterns requires accurate calibration of the camera constant K. This constant depends on the electron wavelength λ and the camera length L and is given by $K = \lambda L$. Because the camera constant cannot be determined with sufficient accuracy in a transmission electron microscope, a number of methods for determination of lattice parameters (or electron wavelength)

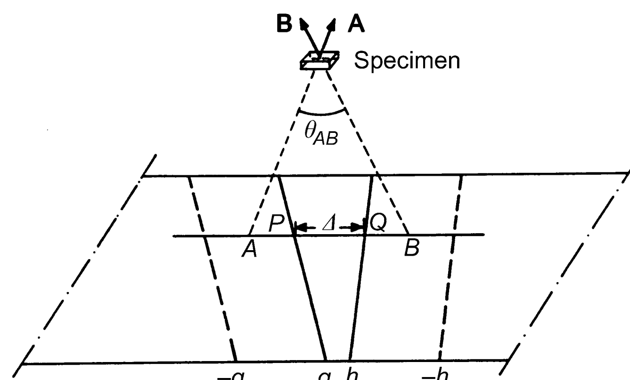

Fig. 5.4.2.1. Schematic diagram showing the geometry of a Kikuchi pattern.

references