Outline

• The geometry of electron diffraction
• Crystallography
• Kinematics Theory of Electron diffraction
• Diffraction from crystals

Why use diffraction in the TEM

- the first event occurring between electrons and specimen
- measure the average spacing between layers or rows of atoms;
- determine the orientation of a single crystal or grain;
- find the crystal structure of an unknown material; identify unknown phase
- measure the size, shape and internal stress of small crystalline regions.
- relate the crystallography to the image, giving TEM its great advantage over SEM and visible-light microscope.

The geometry of electron diffraction
In analogy, for a 3-D crystal, a similar path difference arguments shows that the diffraction of monochromatic electron beam by the regularly spaced 3-D array gives an interference patterns of beams.

Kinematical theory of electrons diffraction and assumption

1. The e-beam is monochromatic, that is the electrons all have the same energy and wavelength.
2. The crystal is free from distortion.
3. Only a negligible fraction of the incident beam is scattered by the crystal, that is every atom in the crystal receives an incident wave of same the amplitude.
4. The incident and scattered waves may be treated as plane waves.
5. There is no interaction between the incident beam and scattered wavelets, that is the refractive index of crystal is unity.
6. There is no attenuation of e-beam with increasing depth in the crystal, that is no absorption.
7. There is no re-scattering of scattered waves.
8. The **kinematical approach** is satisfactory for general description of diffraction patterns.
9. Dynamic theory of electron diffraction is more realistic.
The path difference is

\[ \Delta = PO' + O'Q = d_{hkl} \sin \theta + d_{hkl} \sin \theta \]

\[ \Delta = 2d_{hkl} \sin \theta \]

For in-phase arrival at observation, or constructive interference, this path length difference must be equal to an integral number of wavelength, \( n\lambda \), or

- This is called Bragg Law. \( n \) labels the various diffraction orders for a given set of planes.
- high order of \( n \) in Bragg Law usually is for spectrometry
- \( n \) equal 1 is for diffraction
Now, you can operate through one unit cell.
Crystal Planes (Miller Indices)

Consider a Point in space whose coordinates are \([u \ v \ w]\) intercepting the coordinate system. From Analytical Geometry we have the following:

\[
\frac{x}{u} + \frac{y}{v} + \frac{z}{w} = 1
\]

\[
\frac{1}{u} \cdot x + \frac{1}{v} \cdot y + \frac{1}{w} \cdot z = 1
\]

\[
h \cdot x + yk + l \cdot z = 1
\]

As

\[
\left[ \frac{1}{h} \right] = u \\
\frac{1}{k} = v \\
\frac{1}{l} = w
\]
Crystal Planes (Miller Indices)

- Origin = o
- Take intercepts along x, y, and z. For example, if the plane is (111) ... 1 intercept in x dir., 1 intercept in y direction, and 1 intercept in z dir. [these terminate at the green (colored) dots]

In the case (110): Please note that in the z-direction the plane is parallel to the axis. So the plane never meets the z-axis.
Given the photo of the plane as above, you are asked to index the planes or you want to know \((hkl)\).

**Procedure:** Take intercepts along axes

1. \(x=1, y=1\) and \(z=1\). [these terminate at the green (colored) dots]
2. A common numerator is \(\frac{1}{1} \frac{1}{1} \frac{1}{1} = \frac{1}{1} \frac{1}{1} \frac{1}{1}\)
3. The plane = \((h k l) = (1 1 1)\)
4. \{111\} includes a set of planes (111), (11-1), (-111) and (1-11)

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Given the photo of the plane as above, you are asked to index the planes or you want to know \((hkl)\).

**Procedure:** Take intercepts along axes

1. \(x=1, y=1\) and \(z=\infty\). [these terminate at the green (colored) dots, except for z-axis]
2. Plane is: \(\frac{1}{1} \frac{1}{1} \frac{1}{\infty} = \frac{1}{1} \frac{1}{1} \frac{1}{\infty}\)
3. The plane = \((h k l) = (1 1 0)\)
Zone (Axis) Law

- The normals to \{hkl\} are normal to [uvw].
- \{hkl\} planes of a zone are all parallel to one line: the zone axis [uvw].

If a plane (hkl) lies in a zone [uvw], i.e. [uvw] is parallel to plane (hkl) and the normals to \{hkl\} are all normal to [uvw].
Lattice plane spacing and Miller indices

For a cubic crystal $a=b=c$

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

$$OC = d_{hkl}$$

For orthorhombic

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

(h k l) Plane
d-spacing of crystal planes, only a few of planes satisfy Bragg’s Law, i.e. diffraction occurs

Let’s go back to discuss how to find effective ways to describe the crystal diffraction: as shown before
• If we consider the lattice of a crystal, then we can see that many different planes with different spacings exist within that one lattice.
• It is difficult to imagine how a beam of waves entering a crystal might be diffracted with so many different planes set at different angles to the beam, all with different spacings.
• Which, if any of these planes will satisfy the Bragg law?
• To help us we use the idea of reciprocal lattices.
Equations connecting the Crystal Parameters \((h, k, l)\) and d-spacing with beam parameters \((\lambda)\)

**Bragg’s Law**

\[ n\lambda = 2d_{hkl}\sin\theta \]

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

- \(d\) = Interlayer spacing of Atoms
- \(n=1\). This is also Index
- \(\lambda\) = Wavelength in nm
- \(a\) = Lattice parameter (nm)
- \((h k l)\) = Crystal Plane or Miller Indices
The reciprocal lattice: thinking in reciprocal space

In order to make it easier to understand the information in a diffraction pattern, we use reciprocal lattices. A reciprocal lattice is a construction drawn in reciprocal space, where we use reciprocal space. A dimension of $1/d$, where $d$ is the spacing between crystal planes, is frequently used.

Consider a beam of waves to be incident on a crystal. The measurement, $r$, made from the diffraction pattern, tells us about $\theta$. From this we can deduce $1/d$, since we know that for diffraction of radiation of wavelength, $\lambda$, the Bragg angle, $\theta$, increases with $1/d$. 

$$\frac{1}{d_{hkl}} = \frac{2}{n\lambda} \sin \theta_B$$
The reciprocal lattice: thinking in reciprocal space

Why introduce another lattice: reciprocal lattice
• give a physical picture of diffraction geometries
• give a pictorial representation of diffraction
• visualize how diffraction patterns will vary as the orientation and physical characteristics of the specimen variation

What the reciprocal lattice is and what the reciprocal space is
• a lattice in reciprocal space
• the reciprocal space and real space are nothing but simply geometrical construction, different geometrical coordinate systems. Real space is linear scale relationship but reciprocal space is a reciprocal relationship.
• the reciprocal space to real space, it is like a new world in Gulliver’s Travels, but the relationship to “our “ world is not a linear scaling factor but a reciprocal one.
• Simply, if something (an object or length) is large in real space, then it’s small in reciprocal space
• Any crystal can be express in real space and reciprocal space, i.e. real lattice and reciprocal lattice.
Simply, if something (an object or length) is large in real space, then it’s small in reciprocal space.
Example ZrO2 micro-crystalline

Don’t take any TEM image of a crystal without a corresponding diffraction pattern!!

Real Space

Reciprocal Space
TEM dark field image of a thin annealed Ni-Fe layer with SAD pattern from the marked grain indexed with fcc structure in [111] zone axis
Diffraction (prior knowledge)
Diffraction is an interference effect which leads to the scattering of strong beams of radiation in specific directions. Diffraction from crystals is described by the Bragg Law
\[ n \lambda = 2d \sin \theta \]
where \( n \) is an integer (the order of scattering), \( \lambda \) is the wavelength of the radiation, \( d \) is the spacing between the scattering entities (e.g. planes of atoms in the crystal) and \( \theta \) is the angle of scattering. Electron and X-ray diffraction are both particularly powerful because their wavelengths are smaller than the typical spacings of atoms in crystals and strong, easily measurable, diffraction occurs.
How to define the reciprocal lattice

- simply in reciprocal lattice, sets of parallel (hkl) are represented by a single point located a distance $1/d_{hkl}$ from the lattice origin instead of Miller index (hkl)
- this definition is from Bragg’s Law, wherein the vector $\mathbf{K}$ is reciprocally related to diffraction($\theta, \lambda$) and crystal $d_{hkl}$

\[ 2d_{hkl} \sin \theta = n\lambda \]

\[
\frac{2 \sin \theta}{\lambda} = \frac{n}{d_{hkl}} = |\mathbf{K}| \]
How to geometrically define the reciprocal lattice to specify the crystal planes?

- A family of planes in crystal can be specified by two quantities: (1) their orientation in the crystal (hkl) and (2) their d-spacing ($d_{hkl}$).
- The orientation is defined by the direction of their normal.
- Specify the d-spacings ($d_1$ and $d_2$): set a moduli of a vector is inversely proportional to the d-spacing, i.e., equal to $c/d_{hkl}$, $c$ is a constant, and may be taken as unity. This is like defining the Miller Indices (inverse the intercepts), so it is not surprising.
- The new introduced vectors, $d^*1$ and $d^*2$, are called reciprocal (lattice) vectors. Their dimensions are 1/length, 1/Å.
- $d^*1$ and $d^*2$ specify the planes 1 and 2 (magnitude $|d^*1| > |d^*2|$).
- The end points of the vectors, reciprocal lattice points, represent the planes.
A monoclinic crystal ($a \neq b \neq c$ and $\alpha = \beta = 90^\circ \neq \gamma$) is used as an example (2-D, and $b$ is normal paper plane), $\{h0l\}$ section.

- Reciprocal lattice unit cell: $a^* = d^*100$, and $|a^*| = 1/d100$; $c^* = d001$, and $|c^*| = 1/d001$
- Extend to 3-D, obtain three components of reciprocal unit cell vectors: $a^*$, $b^*$, and $c^*$
- So $d^*_{hkl} = ha^* + kb^* + lc^*$, e.g. $d^*102 = 1a^* + 0b^* + 2c^*$
- In analogy, in direct space, direction symbols $r[uvw]$ are simply the components of unit cell direct lattice vector:
  $$r[uvw] = ua + vb + wc$$
- Miller indices $(hkl)$ are simply the components of unit cell reciprocal lattice vector.

(a) A monoclinic unit cell perpendicular to the $b$ axis. The traces of plane $\{h0l\}$ is parallel to $b$.

(b) The reciprocal vectors, $d^*_{hkl}$. Draw $d^*_{hkl}$, note that: $d^*_{hkl}$ is normal to $(hkl)$, and $d_{hkl} = 1/ |d^*_{hkl}|$, e.g. the length $d^*002 = 2d^*001$, and $d^*003 = 3d^*001$.

(c) The reciprocal lattice defined by these vectors. i.e. the end point of these vectors form a lattice: reciprocal lattice. Each reciprocal lattice represents a plane.
All reciprocal points form a reciprocal unit cell.

We use the notation (hkl) to designate planes in a real lattice. In a reciprocal lattice, the reciprocal lattice points (re: points) are labeled (or indexed) the same, since they represent the planes in the real lattice. The unit cell is for a monoclinic crystal.

Reciprocal points in the re-lattice satisfy the vector addition.

e.g. (110)=(010)+(100)

A reciprocal point represents a plane.
 Mathematical definition of the reciprocal lattice

In real space, we can define any lattice vector, \( \mathbf{r}_n \) by

\[
\mathbf{r}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}
\]

Where \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) are unit cell vector, \( n_1, n_2, n_3 \) are all integers

In reciprocal space, we can define any lattice vector, \( \mathbf{r}^* \) by

\[
\mathbf{r}^* = m_1 \mathbf{a}^* + m_2 \mathbf{b}^* + m_3 \mathbf{c}^*
\]

Where \( \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^* \) are unit cell vector, \( m_1, m_2, m_3 \) are all integers

Further define

\( \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{c} = \mathbf{c}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{a} = 0 \), i.e. \( \mathbf{a}^* \) is normal to both \( \mathbf{b} \) and \( \mathbf{c} \), etc

\( \mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 1 \), only for cubic \( \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^* \) are parallel to \( \mathbf{a}, \mathbf{b}, \mathbf{c} \)
Further define
\[ \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{c} = \mathbf{c}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{b} = 0 \], i.e. \( \mathbf{a}^* \) is normal to both \( \mathbf{b} \) and \( \mathbf{c} \), etc.

\[ \mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 1 \], only for cubic \( \mathbf{a}^* \), \( \mathbf{b}^* \), \( \mathbf{c}^* \) are parallel to \( \mathbf{a}, \mathbf{b}, \mathbf{c} \).

If \( V_c \) is the volume of unit cell, \( V_c = a \cdot b \cdot c \).

So \( \mathbf{a}^* = (\mathbf{b} \times \mathbf{c})/V_c \), also indicate \( \mathbf{a} \) is orthogonal to \( \mathbf{b} \) and \( \mathbf{c} \).

Just as \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \) need not be normal one another, \( \mathbf{a}^*, \mathbf{b}^*, \) and \( \mathbf{c}^* \) also not necessarily normal one another.

Next, we will find the reciprocal lattice vector \( \mathbf{g} \) (or \( \mathbf{d}_{hk1}^* \)) for plane \((hkl)\). If \((hkl)\) define a plane, what does the reciprocal lattice vector \( \mathbf{g}_{hk1} \) tell us? \( \mathbf{g}_{hk1} \) is defined as

\[ \mathbf{g}_{hk1} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \]

The definition of the plane \((hkl)\) is that it cuts the \( a, b, \) and \( c \) axes at \( 1/h, 1/k, \) and \( 1/l \) respectively.

\( OA = a/h \)
\( OB = b/k \)
\( OC = c/l \)
So, \( \mathbf{g}_{hkl} \) is normal to plane (hkl)

Next, we need find the magnitude of reciprocal lattice vector \( \mathbf{g}_{hkl} \)

\[
A \mathbf{B} \cdot \mathbf{g}_{hkl} = \left( \frac{\mathbf{b}}{k} - \frac{\mathbf{a}}{h} \right) \cdot \left( h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* \right) = 0
\]

\[
A \mathbf{C} \cdot \mathbf{g}_{hkl} = B \mathbf{C} \cdot \mathbf{g}_{hkl} = 0
\]

Vector \( \mathbf{AB}\mathbf{OB} - \mathbf{OA} = \frac{\mathbf{b}}{k} - \frac{\mathbf{a}}{h} \)

\( \mathbf{AC}\mathbf{OC} - \mathbf{OA} = \frac{\mathbf{c}}{l} - \frac{\mathbf{a}}{h} \)

\( \mathbf{BC}\mathbf{OC} - \mathbf{OB} = \frac{\mathbf{c}}{l} - \frac{\mathbf{b}}{k} \)
Consider a unit vector $\mathbf{n}$ parallel to $\mathbf{g}_{hkl}$, and hereby $\mathbf{n}$ is normal to plane $(hkl)$.

So $\mathbf{n} = \frac{\mathbf{g}_{hkl}}{|\mathbf{g}_{hkl}|}$

Therefore, the shortest distance from origin $O$ to the plane $(hkl)$ is dot product of $\mathbf{n}$ with vector $\mathbf{OA}$ or $\mathbf{OB}$ or $\mathbf{OC}$. This distance is d-spacings of plane $(hkl)$, $d_{hkl}$.

\[
\frac{d_{hkl}}{h} = \frac{\mathbf{n} \cdot \mathbf{a}}{h} = \frac{\mathbf{g}_{hkl} \cdot \mathbf{a}}{|\mathbf{g}_{hkl}| \cdot h} = \left( h\mathbf{\alpha}^* + k\mathbf{\beta}^* + l\mathbf{\gamma}^* \right) \frac{\mathbf{a}}{h} \\
\]

\[
d_{hkl} = \frac{1}{|\mathbf{g}_{hkl}|} 
\]
Therefore, we have proved vector $\mathbf{g}_{hkl}$ is normal to plane (hkl), and its magnitude is equal to $1/d_{hkl}$. This conclusion is equivalent to the results derived from geometrical construction, i.e. $\mathbf{g}_{hkl} = d^*_{hkl}$.

The vector $\mathbf{g}_{hkl}$ completely specifies the plane (hkl).

A plane in real space is equivalent to a vector or a lattice point in reciprocal space. In other words, we can use a point or a vector in reciprocal space to represent a crystal plane. This is physically similar to the diffraction patterns.