9. Electron diffraction and diffraction imaging analysis

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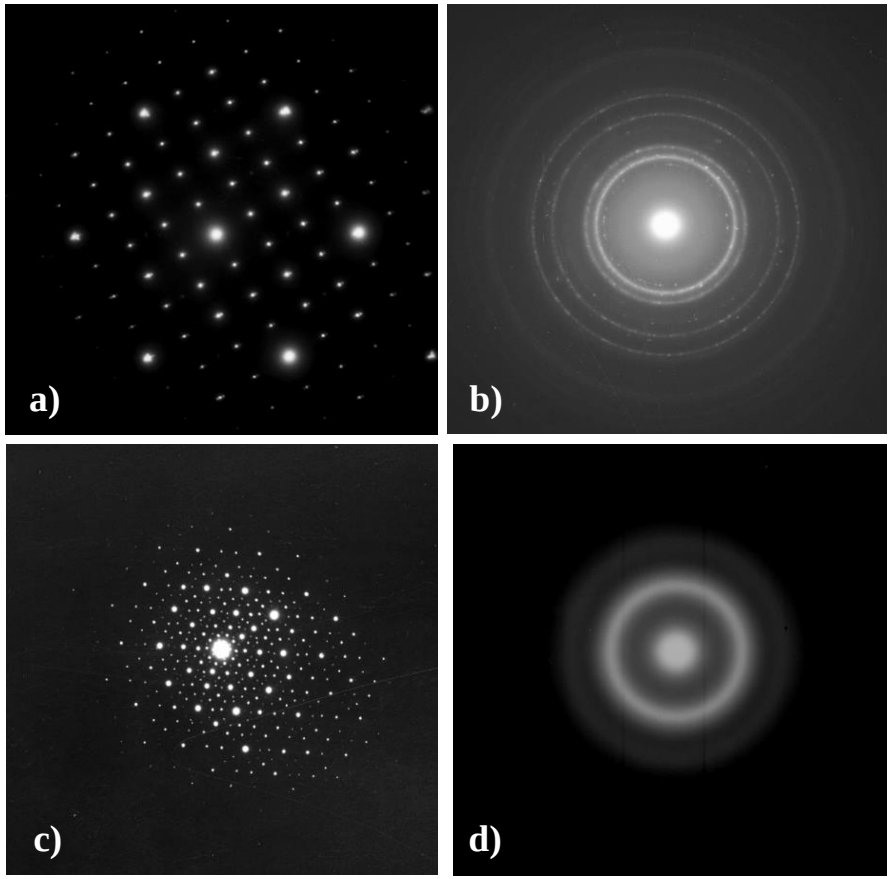
9.1 Overview

- Common electron diffraction patterns

The diffraction patterns of crystalline, quasi-crystalline and amorphous materials are shown in the figure.



a) Single crystal b) Polycrystal c) Quasicrystal d) Amorphous

9.1 Overview

- Characteristics of electron diffraction

Compared with X-ray diffraction, electron diffraction has the following characteristics:

- The wavelength of the electron wave λ is very small, so the diffraction angle 2θ is very small (about 10^{-2}rad), the radius of the reflection sphere ($1/\lambda$) is very large, and the reflection sphere near the reciprocal origin O* is close to a plane.

- The thickness ***t*** of the transmission electron microscope sample is very small, resulting in a large reciprocal lattice point extension (***1/t***), so that crystal planes slightly deviating from the Bragg condition can also produce diffraction.

- When the crystal belt axis [uvw] is parallel to the incident beam, on the zero-level reciprocal surface that is tangent to the reflecting sphere, the array points near the reciprocal origin O* can intercept the reflecting sphere, thus producing diffraction, so a single The crystal diffraction pattern is a projection of a two-dimensional reciprocal plane.

- The scattering factor of atoms to electrons is about 4 orders of magnitude greater than the scattering factor of X-ray.

9.2 Principles of electron diffraction

- Bragg's law

It is already known from the principle of X-ray diffraction that Bragg's law is a necessary condition for diffraction of crystal planes. It still applies to electron diffraction. The general form of Bragg's equation is:

$$2d\sin\theta = \lambda$$

The accelerating voltage is 100 ~ 200 kV, the wavelength of the electron beam is on the order of 10^{-3}nm, and the interplane spacing of common crystals is on the order of 10^{-1}nm, then there is:

$$\sin\theta = \lambda / 2d \approx 10^{-2}$$

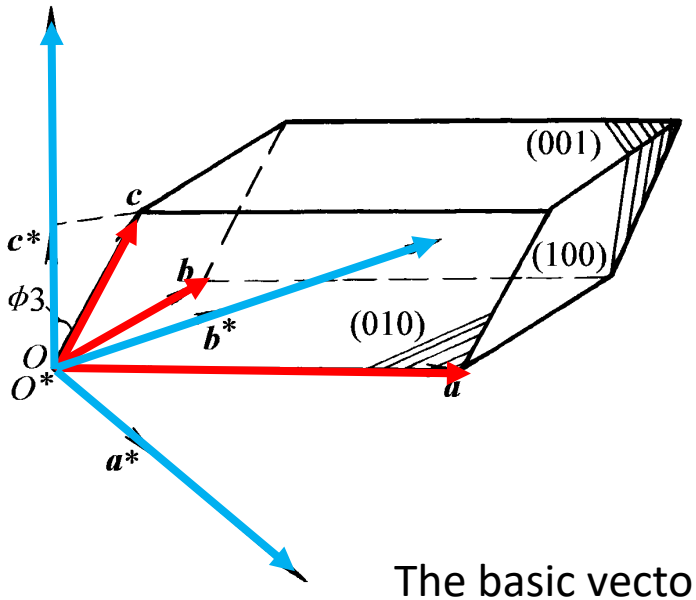
$$\theta = 10^{-2}\text{rad} < 1°$$

It shows that the diffraction angle of electron diffraction is very small, which is one of the main reasons why its diffraction pattern characteristics are different from X-ray diffraction.

9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram

1. Definition of reciprocal lattice basis vectors



Assume that the basic vectors of the positive lattice are a, b, and c, and define the corresponding basic vectors of the reciprocal lattice as a*, b*, c*, then we have:

$$\boldsymbol{a}^* = \frac{\boldsymbol{b}\times\boldsymbol{c}}{V}, \quad \boldsymbol{b}^* = \frac{\boldsymbol{c}\times\boldsymbol{a}}{V}, \quad \boldsymbol{c}^* = \frac{\boldsymbol{a}\times\boldsymbol{b}}{V}$$

In the formula, V is the volume of the positive lattice unit cell, and we have:

$$V = \boldsymbol{a}\cdot(\boldsymbol{b}\times\boldsymbol{c}) = \boldsymbol{b}\cdot(\boldsymbol{c}\times\boldsymbol{b}) = \boldsymbol{c}\cdot(\boldsymbol{a}\times\boldsymbol{b})$$

The basic vector of the reciprocal lattice is perpendicular to the plane determined by the two other basic vectors in the real lattice.

9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram

2. Properties of reciprocal lattice

Basic vector

$$\boldsymbol{a}^* \cdot \boldsymbol{b} = \boldsymbol{a}^* \cdot \boldsymbol{c} = \boldsymbol{b}^* \cdot \boldsymbol{a} = \boldsymbol{b}^* \cdot \boldsymbol{c} = \boldsymbol{c}^* \cdot \boldsymbol{a} = \boldsymbol{c}^* \cdot \boldsymbol{b} = 0$$

$$\boldsymbol{a}^* \cdot \boldsymbol{a} = \boldsymbol{b}^* \cdot \boldsymbol{b} = \boldsymbol{c}^* \cdot \boldsymbol{c} = 1$$

The point product of basic vectors with the synonym name is 0, from which the direction of the basis vector of the reciprocal lattice can be determined; the product of basic vector points with the same name is 1, from which the size of the basis vector of the reciprocal lattice can be determined.

9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram

2. Properties of reciprocal lattice

Reciprocal vector: In the reciprocal space, the array point vector pointing from the reciprocal origin O* to the coordinate ***h k l*** is called the reciprocal vector, denoted as $\boldsymbol{g}_{hkl}$.

$$\boldsymbol{g}_{hkl} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$$

The geometric relationship between the reciprocal vector $\boldsymbol{g}_{hkl}$ and the (***h k l***) crystal plane in the positive lattice is:

$$\boldsymbol{g}_{hkl} \perp (hkl), \quad g_{hkl} = \frac{1}{d_{hkl}}$$

The reciprocal vector $\boldsymbol{g}_{hkl}$ can be used to characterize the characteristics (orientation and interplanar spacing) of the corresponding (***h k l***) crystal plane in the positive lattice.

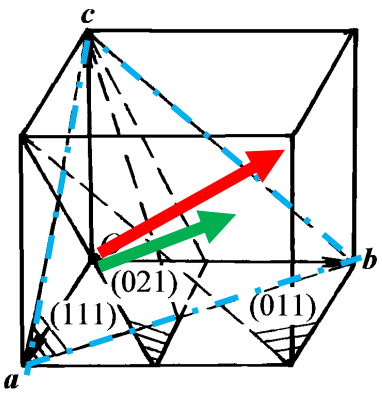
9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram

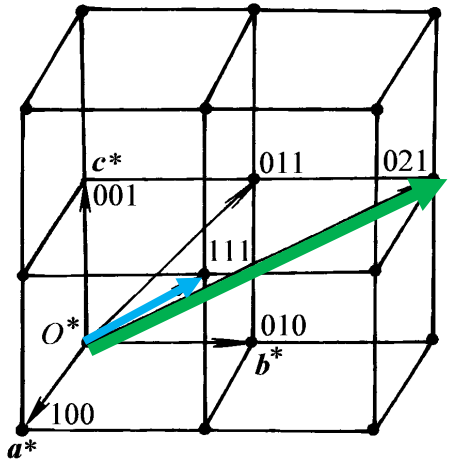
2. Properties of reciprocal lattice

For the cubic crystal system, we have

$$\boldsymbol{a}^* // \boldsymbol{a}, \boldsymbol{b}^* // \boldsymbol{b}, \boldsymbol{c}^* // \boldsymbol{c}, a^* = \frac{1}{a}, b^* = \frac{1}{b}, c^* = \frac{1}{c}$$



$\boldsymbol{a}=\boldsymbol{b}=\boldsymbol{c}=0.1\text{nm}$

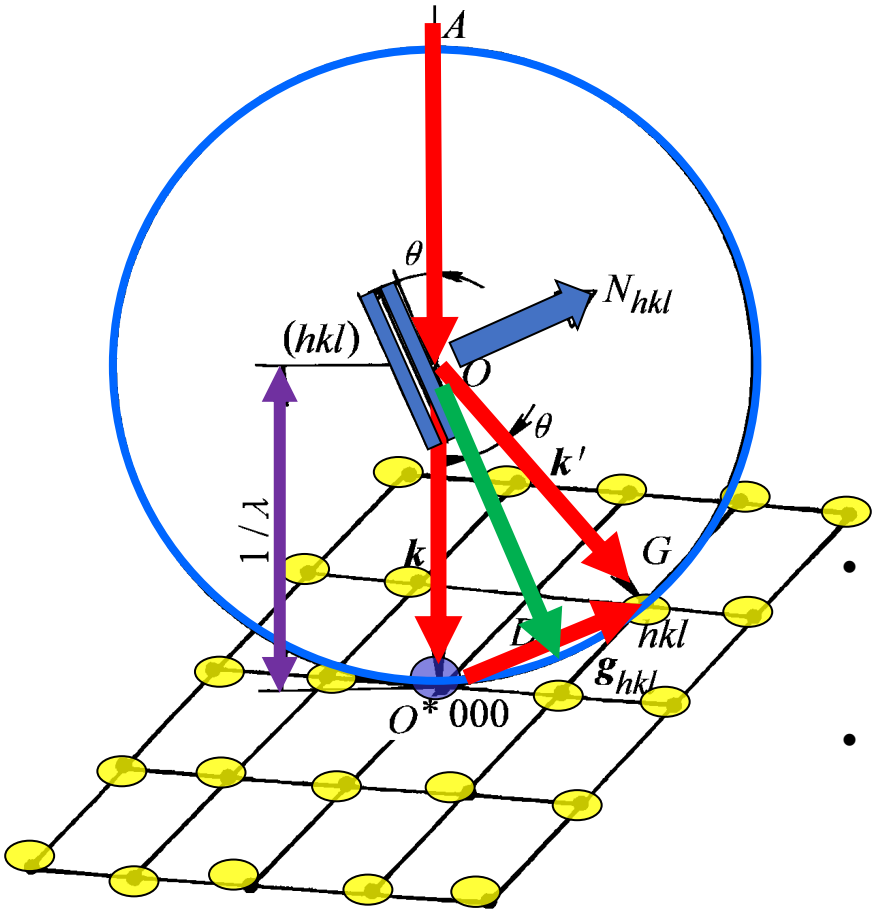


$\boldsymbol{a}^*=\boldsymbol{b}^*=\boldsymbol{c}^*=10\text{nm}^{-1}$

For the cubic crystal system, the same exponential crystal orientation and the crystal plane are perpendicular to each other, that is, the crystal orientation [***h k l***] is the normal line of the crystal plane (***h k l***), [***h k l***] // $\boldsymbol{g}_{hkl}$

9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram



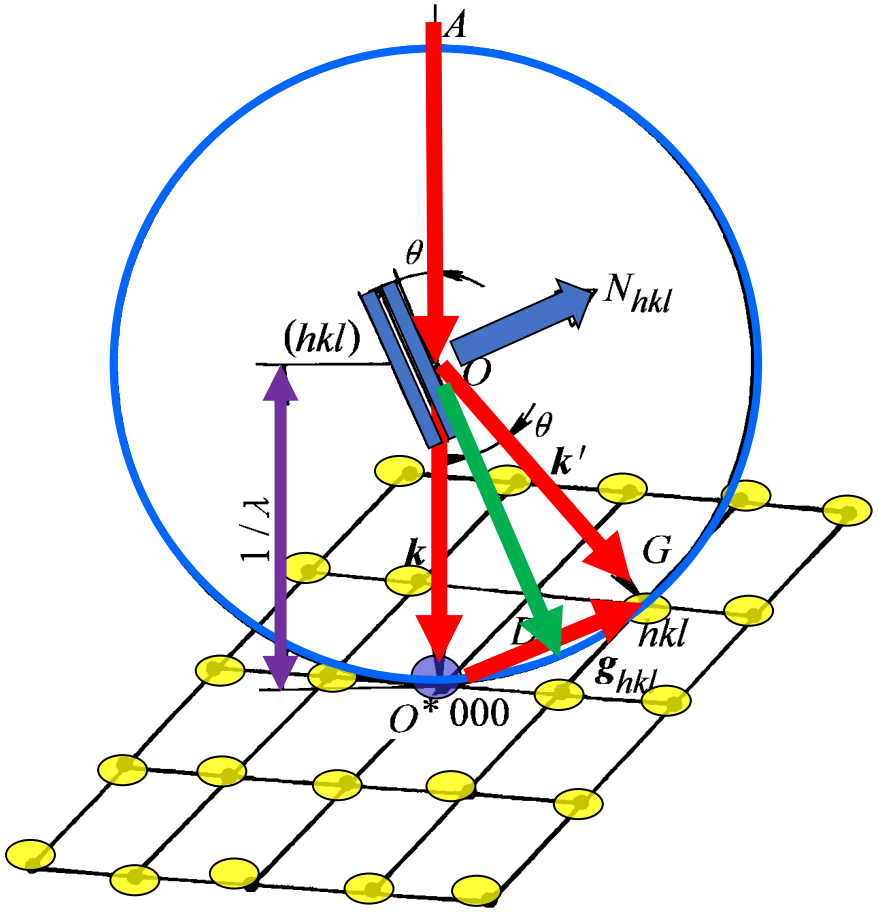
1. With O as the center of the sphere, the crystal is placed at the center of the sphere O.
2. Construct a sphere with radius 1/λ.
3. Construct a sphere with radius 1/λ.
4. OO* is the direction of the incident electron beam.
5. OG is the assumed direction of the diffracted beam, intersecting the sphere at point G.

- At this time, O*G is connected. OD is the extension line of the crystal plane (***h k l***) and O*G intersects at point D.
- O*G and OD are perpendicular, and O*G=1/d; satisfy the Bragg diffraction condition.

$$2*1/\lambda*\sin\theta = 1/d$$

9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram



Incident wave vector $\boldsymbol{k}$ ($k = 1/\lambda$)

$\boldsymbol{k'}$ is the diffraction wave vector, representing the (***h k l***) crystal plane diffraction beam direction.

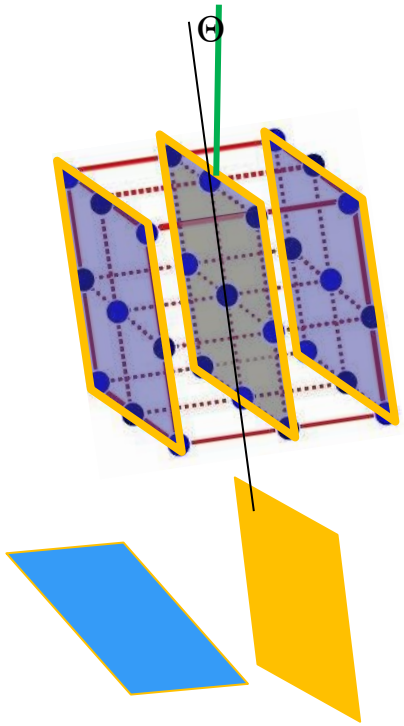
$$\boldsymbol{k' - k = g_{hkl}}$$

$\boldsymbol{g_{hkl}}$ is the reciprocal vector of (***h k l***), which is parallel to the normal direction of (***h k l***).

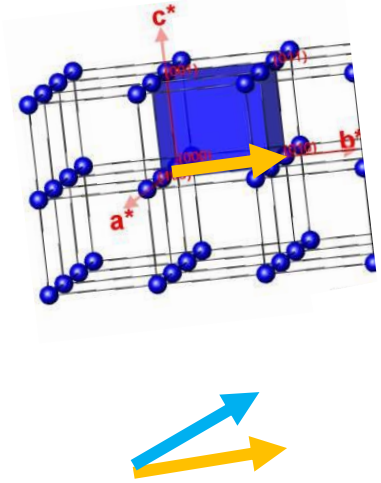
The reciprocal vector $\boldsymbol{g_{hkl}}$ represents the characteristics of the (***h k l***) crystal plane in real space, so it is also called $\boldsymbol{g_{hkl}}$ as the diffraction crystal plane vector.

9.2 Principles of electron diffraction

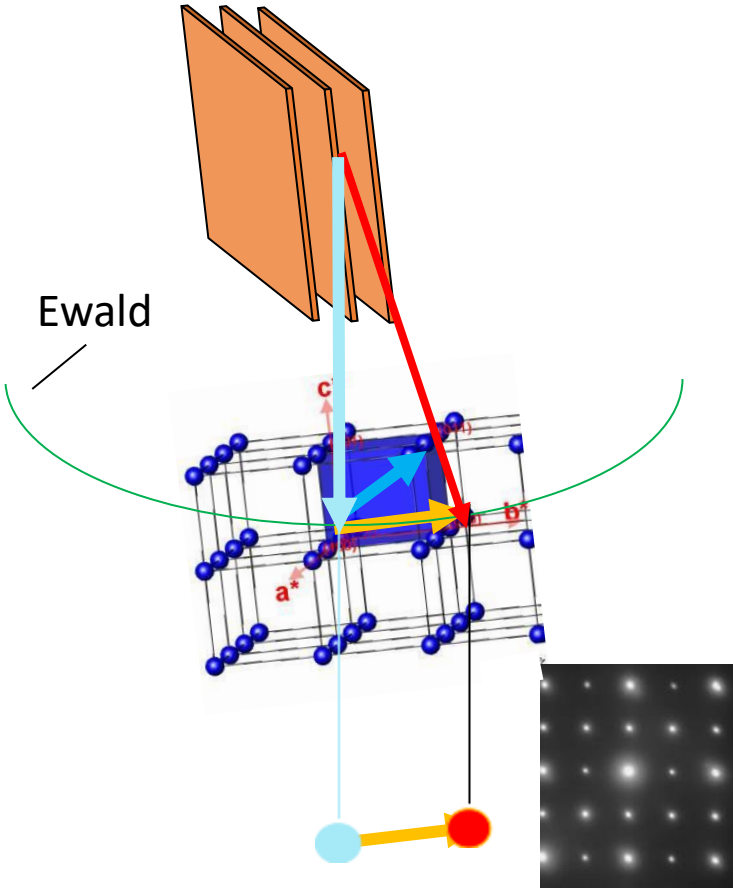
- Reciprocal lattice and Ewald diagram



3D crystal plane
(real space)



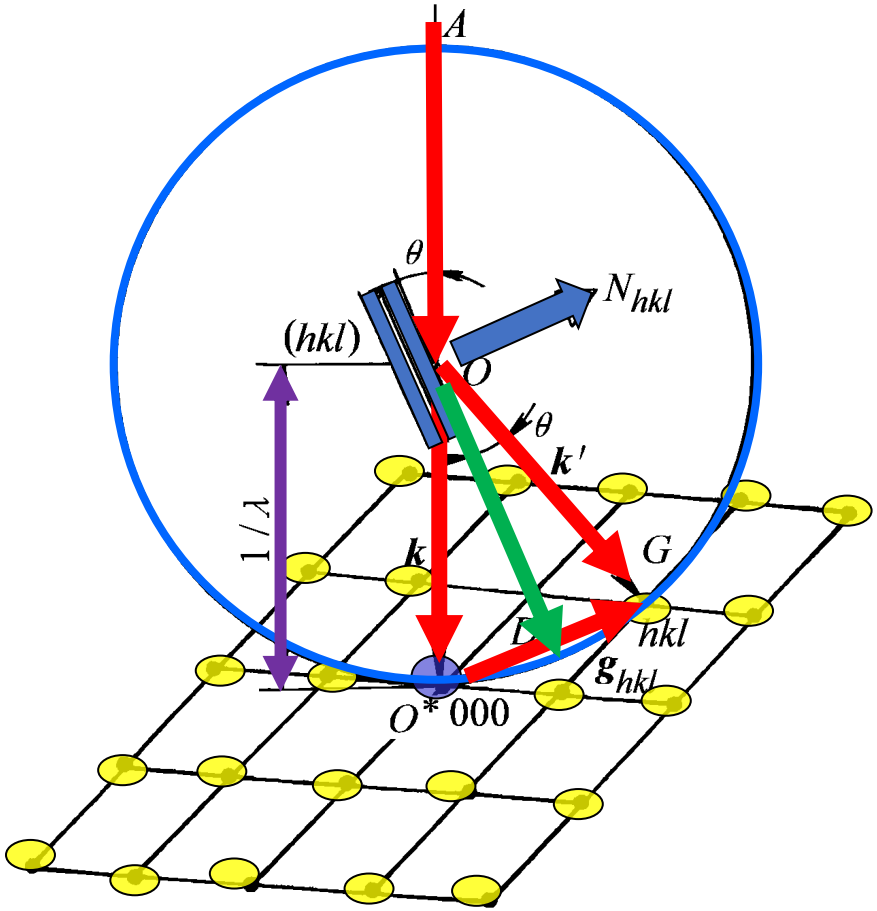
3D reciprocal space
(vector)



Reciprocal matrix point projection of two-dimensional reciprocal plane (point)

9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram

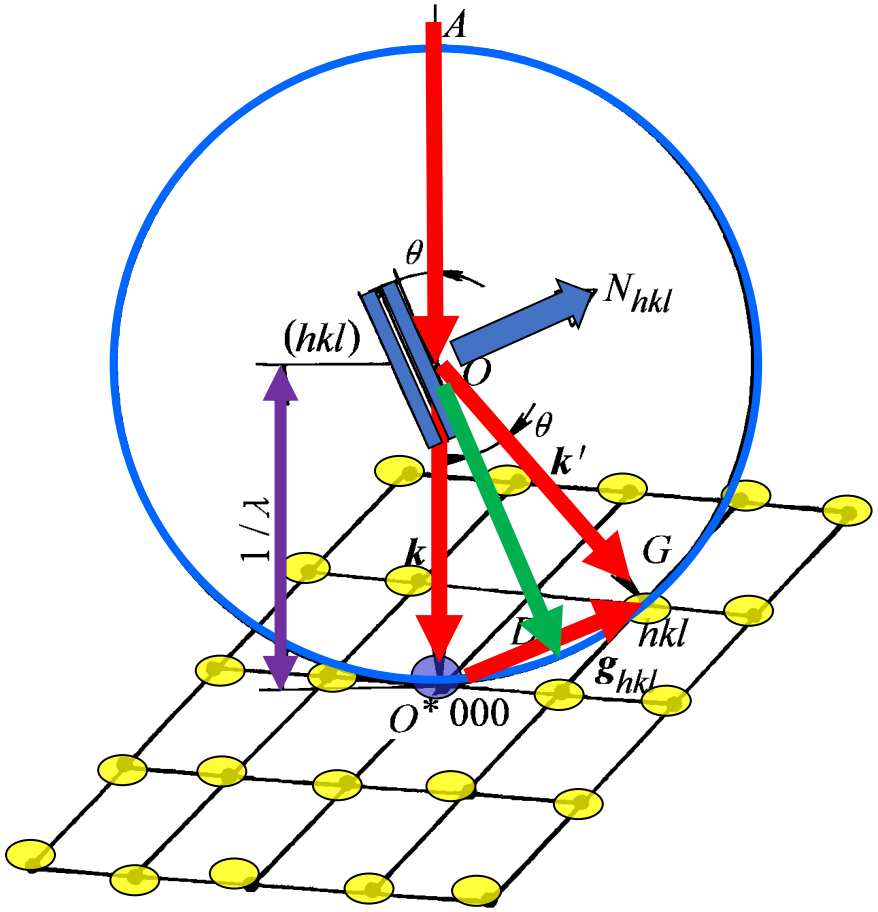


If the reciprocal lattice point G corresponding to the (***h k l***) crystal plane falls on the reflecting sphere, (***h k l***) satisfies the Bragg condition.

The Ewald sphere diagram is the geometric expression of Bragg's law, which can intuitively determine whether the (***h k l***) crystal plane satisfies the Bragg condition.

9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram

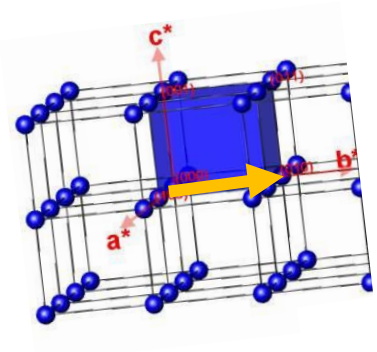


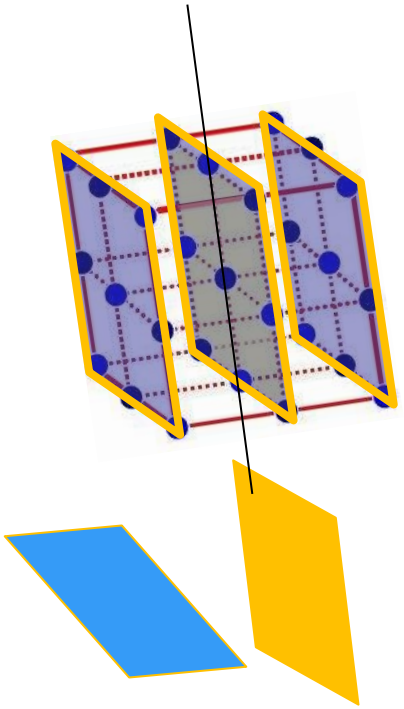
The three vectors ***k'***, ***k*** and $\boldsymbol{g_{hkl}}$ in the Ewald sphere clearly describe the relative geometric relationship between the incident beam direction, the diffracted beam direction and the reciprocal vector of the diffraction crystal plane. The reciprocal vector $\boldsymbol{g_{hkl}}$ represents the characteristics of the (***h k l***) crystal plane in positive space. Therefore, it is also called $\boldsymbol{g_{hkl}}$ as the diffraction crystal plane vector.

9.2 Principles of electron diffraction

- Reciprocal lattice and Ewald diagram

If the arrangement of each $\boldsymbol{g}_{hkl}$ vector in reciprocal space can be recorded, the relative orientation of each diffraction crystal plane in real space can be calculated. This is one of the main problems to be solved in electron diffraction analysis.





3D reciprocal space

Vector

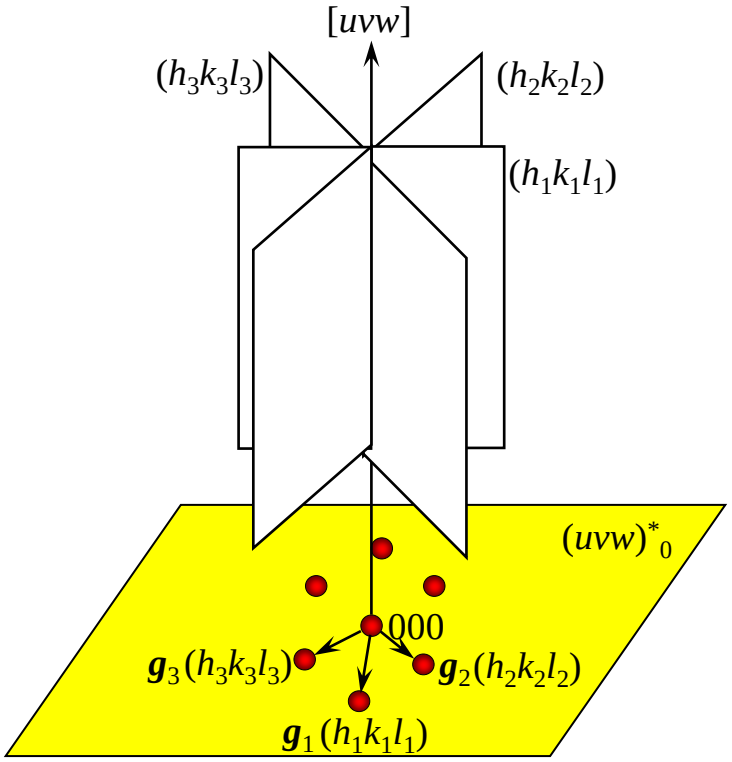
3D real space

Crystal plane

9.2 Principles of electron diffraction

- Zone law

All crystal planes parallel to a certain crystal direction [***u v w***] in the real lattice form a crystal band. This crystal direction is called the crystal band axis, as shown in the figure.



The reciprocal plane passing through the reciprocal origin O* (000) is called the zero-level reciprocal plane. Because ***r*** = [***u v w***] is perpendicular to the zero-level reciprocal plane (***u v w***)*0, so the reciprocal plane located on (***u v w***)*0 The vector $\boldsymbol{g_{hkl}}$ is also perpendicular to ***r***, so we have:

$$\boldsymbol{g}_{hkl} \cdot \boldsymbol{r} = 0$$

$$\boldsymbol{hu} + \boldsymbol{kv} + \boldsymbol{lw} = 0$$

The above equation is the zone law.

9.2 Principles of electron diffraction

- Zone law

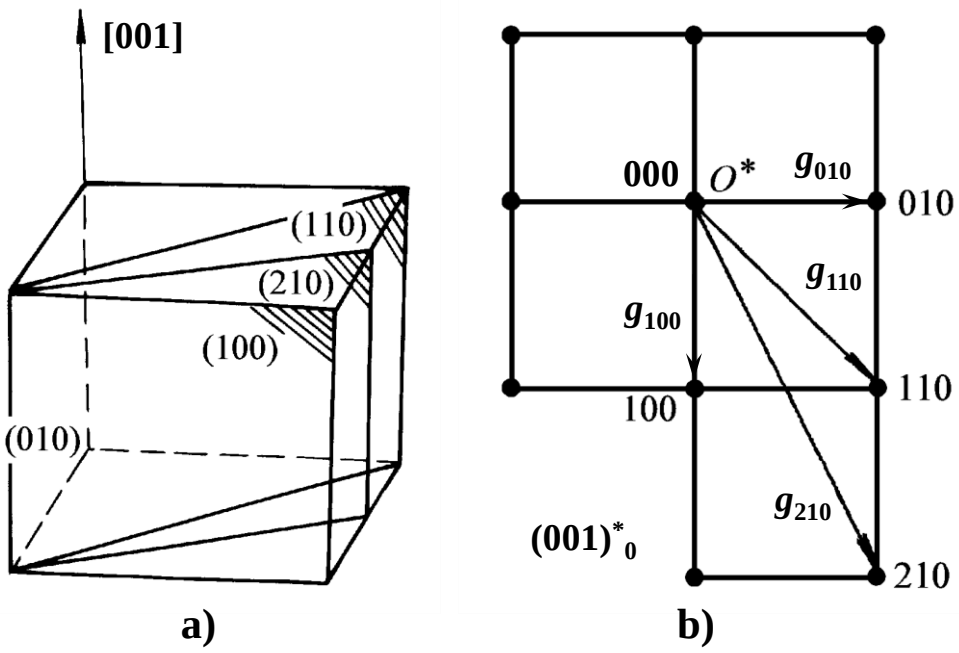
The Zone law gives the relationship between the crystal plane index (***h k l***) and the crystal band axis index [***u v w***]. The Zone law can solve the index of the intersection line (that is, the crystal band axis) of the two known crystal planes. For example, the index of the two known crystal planes is ($h_1\ k_1\ l_1$) and ($h_2\ k_2\ l_2$), the crystal band axis index [***u v w***] can be obtained, that is:

$$\begin{aligned} h_1u + k_1v + l_1w &= 0 \\ h_2u + k_2v + l_2w &= 0 \end{aligned} \quad \begin{cases} u = k_1 l_2 - k_2 l_1 \\ v = l_1 h_2 - l_2 h_1 \\ w = h_1 k_2 - h_2 k_1 \end{cases}$$

9.2 Principles of electron diffraction

- Zero-layer reciprocal plane

The single crystal electron diffraction pattern is the projection of the zero-layer reciprocal plane, and the index of the reciprocal lattice point is the index of the corresponding diffraction spot.



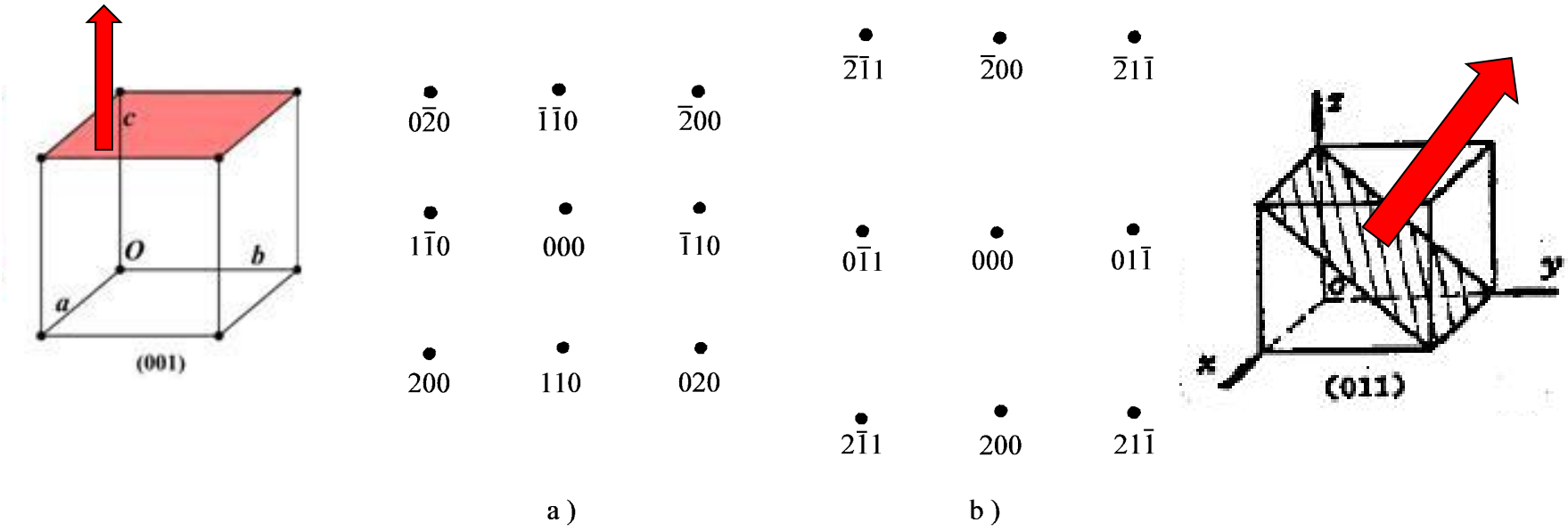
Cubic Crystal [001] Crystal axis and Reciprocal Surfaces $(001)^*_0$ **a**) real space, **b**) reciprocal space

For cubic crystals, if the crystal zone axis index [001] is taken, the corresponding zero-layer reciprocal plane is $(001)^*_0$. According to the crystal zone law, crystal planes such as (100) and (110) belong to the [001] crystal. band, and then according to the relationship between $\boldsymbol{g_{hkl}}$ and (***h k l***), $(001)^*_0$ can be drawn, as shown in the figure.

9.2 Principles of electron diffraction

- Zero-layer reciprocal plane

The picture shows the two zero-level reciprocal planes of a body-centered cubic crystal. The lattice points on the $(001)^*_0$ reciprocal surface are arranged in a square shape, while the lattice points on the $(011)^*_0$ surface are arranged in a rectangular shape, indicating that the orientation of the crystal can be determined by using the pattern of diffraction spots.



a) $(001)^*_0$, b) $(011)^*_0$

9.2 Principles of electron diffraction

- Structure factors

Satisfying the Bragg equation is only a necessary condition for diffraction, but whether diffraction can occur also depends on the structure factor $\boldsymbol{F_{hkl}}$ of the crystal plane. $\boldsymbol{F_{hkl}}$ is the combined amplitude of the scattered waves of all atoms in the unit cell in the diffraction direction of the (***h k l***) crystal plane, also known as structural amplitude.

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp[2\pi \mathrm{i}(hx_j + ky_j + lz_j)]$$

In the formula, $\boldsymbol{f_j}$ is the atomic scattering factor of the j-th atom located at ($\boldsymbol{x_j}$, $\boldsymbol{y_j}$, $\boldsymbol{z_j}$) in the unit cell, and ***n*** is the number of atoms in the unit cell.

Because the diffraction intensity $\boldsymbol{I_{hkl}}$ is proportional to $|\boldsymbol{F_{hkl}}|^2$, $\boldsymbol{F_{hkl}}$ reflects the diffraction ability of the crystal plane, that is, the larger the $\boldsymbol{F_{hkl}}$, the stronger the diffraction ability; when $\boldsymbol{F_{hkl}} = 0$, no diffraction will occur even if the Bragg condition is met, which is called this The phenomenon is extinction.

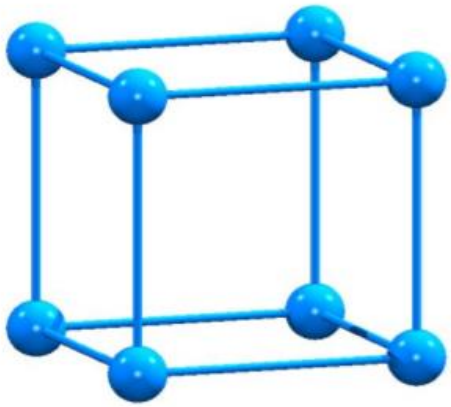
$\boldsymbol{F_{hkl}} \neq \boldsymbol{0}$ is called the sufficient condition for diffraction from the (***h k l***) crystal plane.

9.2 Principles of electron diffraction

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

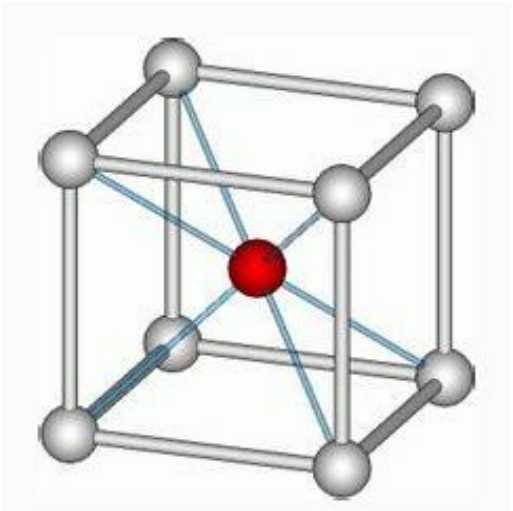
- Structure factors

The extinction rules of several common crystal structures are as follows:



Atomic coordinates (0,0,0)

Simple cubic: When h, k, l are any integers, $\boldsymbol{F_{hkl} \neq 0}$, and there is no system extinction phenomenon.



Atomic coordinates (0,0,0), (1/2, 1/2,1/2)

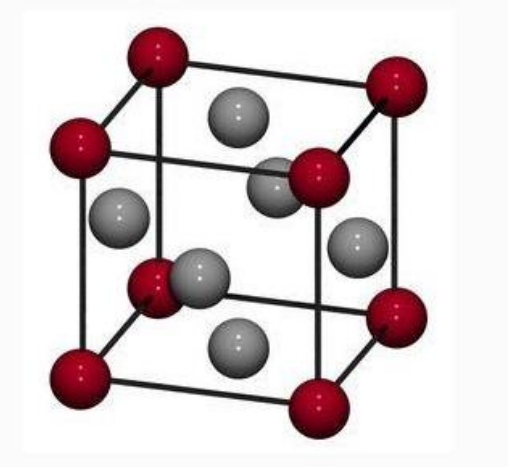
Body-centered cubic: When h + k + l = odd number, $\boldsymbol{F_{hkl} = 0}$, resulting in extinction, such as {100}, {111}, {210} and other crystal face families.

9.2 Principles of electron diffraction

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

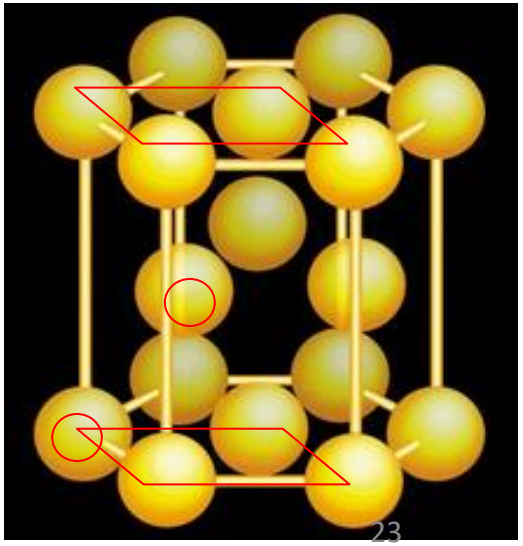
- Structure factors

The extinction rules of several common crystal structures are as follows:



Atomic coordinates (0,0,0), (0, 1/2,1/2), (1/2,0,1/2), (1/2, 1/2,0)

Face-centered cubic: When h, k, l are not all odd (even) numbers, $\boldsymbol{F_{hkl} = 0}$, resulting in extinction, such as {100}, {110}, {210} and other crystal face families.



Atomic coordinates (0,0,0), (1/3,2/3,1/2)

Hexagonal close-packed: h+2k = 3n, and when l = odd number, $\boldsymbol{F_{hkl} = 0}$, resulting in extinction, such as {001}, {111}, {221} and other crystal face families.

9.2 Principles of electron diffraction

- Discussion

1. In the crystal, the position of the atoms in the unit cell is represented by the fractional coordinates of the atom P in the unit cell and the origin O;

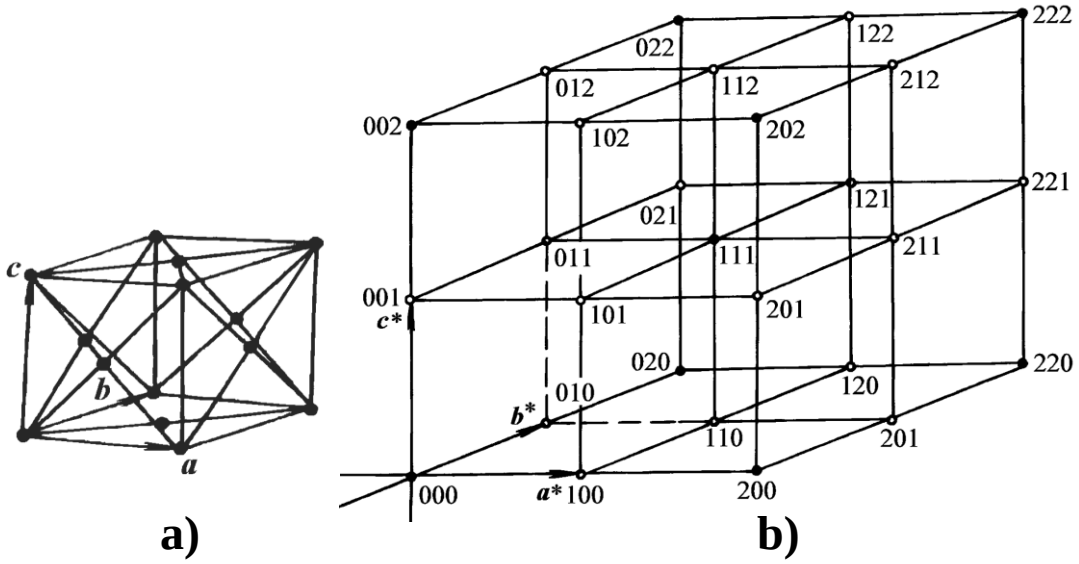
2. Vector OP = xa + yb + zc (a, b, c are unit vectors in the directions of the three crystal axes. In the crystal, the three crystal axes are specially specified according to the crystal system to which the crystal belongs. They are not rectangular coordinates, only cubic , tetragonal and orthorhombic crystal systems are similar to Cartesian coordinates);

3. Then x, y, z are the fractional coordinates of P. $0 \leq x,y,z < 1$. After the fractional coordinate reaches 1, it belongs to the next unit cell, so the 8 vertices are only labeled 0,0,0 (unit cell 8 vertices are exactly 1 atom).

9.2 Principles of electron diffraction

- Structure factors

If $|F_{hkl}|^2$ is used as the weight of the reciprocal lattice point, then the reciprocal lattice points are no longer equal to each other. Since the crystal plane with $F_{hkl} = 0$ cannot produce diffraction, those lattice points can be removed from the reciprocal lattice, leaving only the lattice points with $F_{hkl} \neq 0$. As shown in Figure, remove the lattice atoms ($F_{hkl} = 0$), and the reciprocal lattice of the face-centered cubic regular lattice is body-centered cubic.



Face-centered cubic crystal (**a**) real lattice and (**b**) corresponding reciprocal lattice

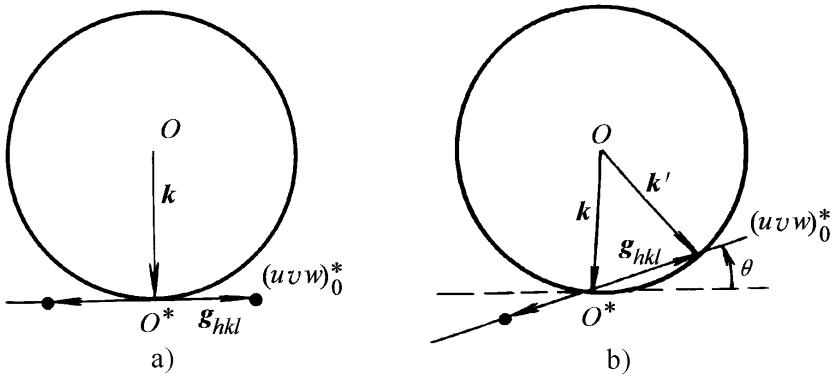
9.2 Principles of electron diffraction

- Deviation vector and reciprocal lattice point expansion

Figure is the commonly used diffraction conditions for diffraction analysis and diffraction contrast analysis. Under these two conditions, only 1~2 reciprocal array points on (uvw)*0 can accurately fall on the reflection sphere, because the Bragg condition is satisfied, and they can produce diffraction.

Why the diffraction pattern of single crystal is a projection of the zero-layer reciprocal plane lattice?

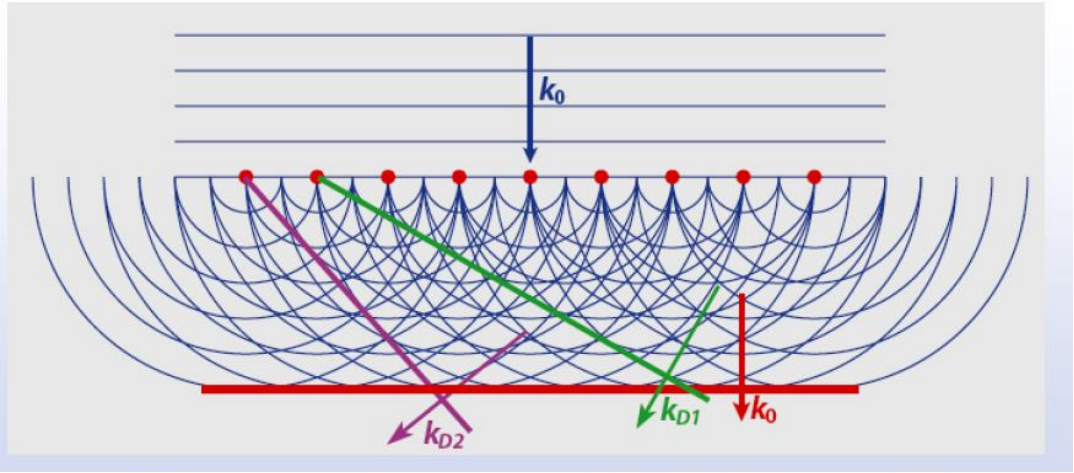
Because the size of the TEM sample is very small, the reciprocal lattice points expand and occupy a certain space. The amount of expansion is twice the reciprocal of the size of the crystal in that direction.

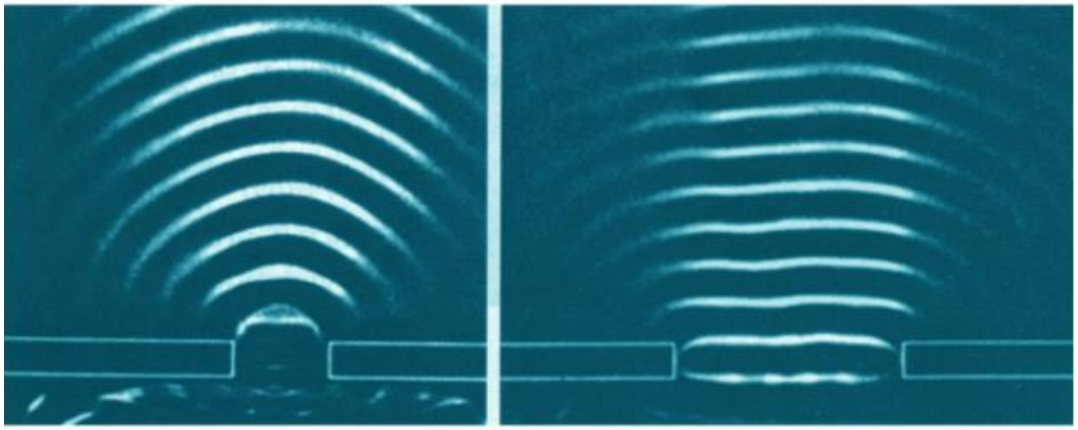


It is the expansion of the reciprocal array points that increases the chance of contact with the reflecting sphere, resulting in the array points near the reciprocal origin O* being able to intercept the reflecting sphere and diffract.

9.2 Principles of electron diffraction

- Deviation vector and reciprocal lattice point expansion





The diffraction of electrons by crystals is the result of the superposition of elastic scattered waves of each atom. Treating the atoms in the crystal as discrete scattering centers is helpful to discuss the superposition of scattered waves.

Diffraction direction?

A diffracted beam is a wave and has an intensity distribution, not a geometric straight line.

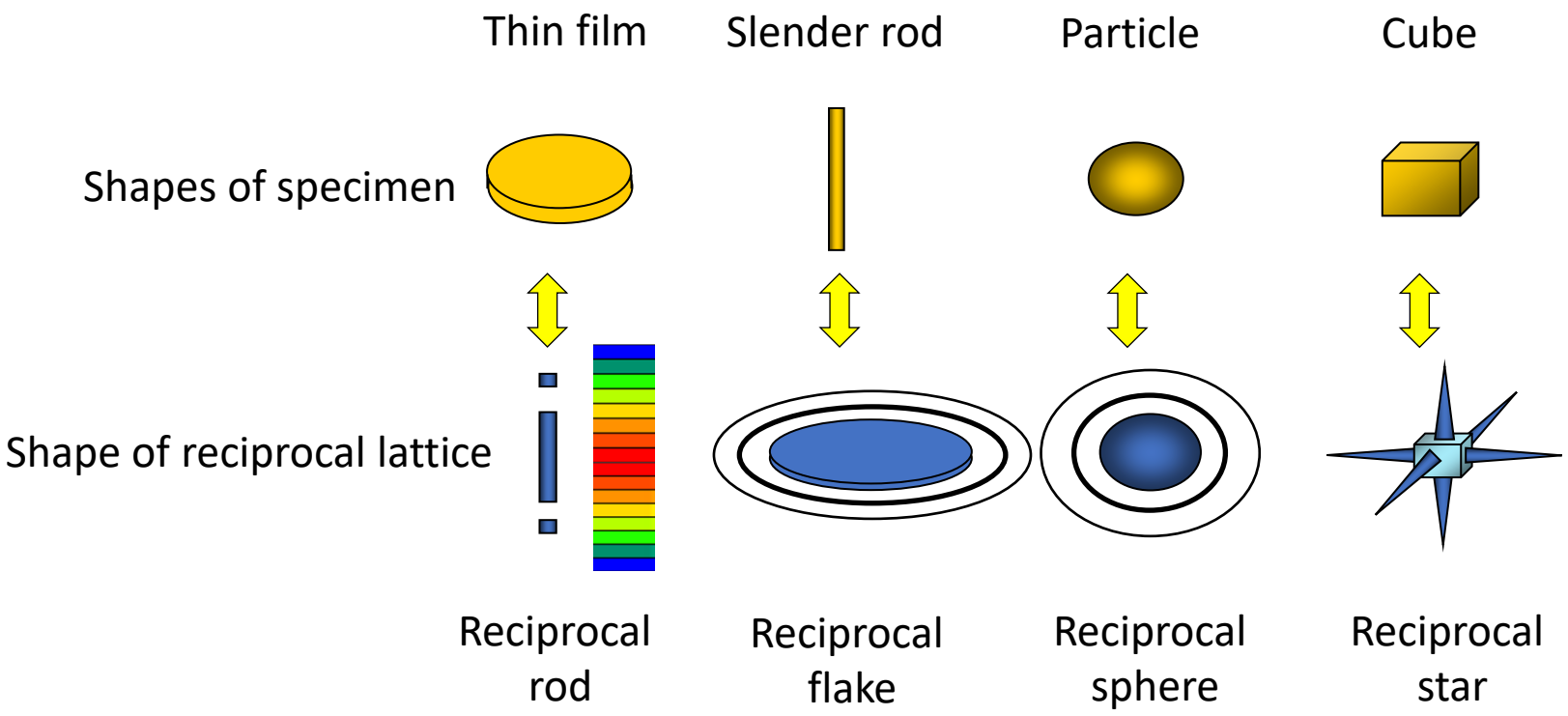
Diffraction intensity distribution?

The spatial distribution of diffracted beam intensity is related to the shapes involved in diffraction.

9.2 Principles of electron diffraction

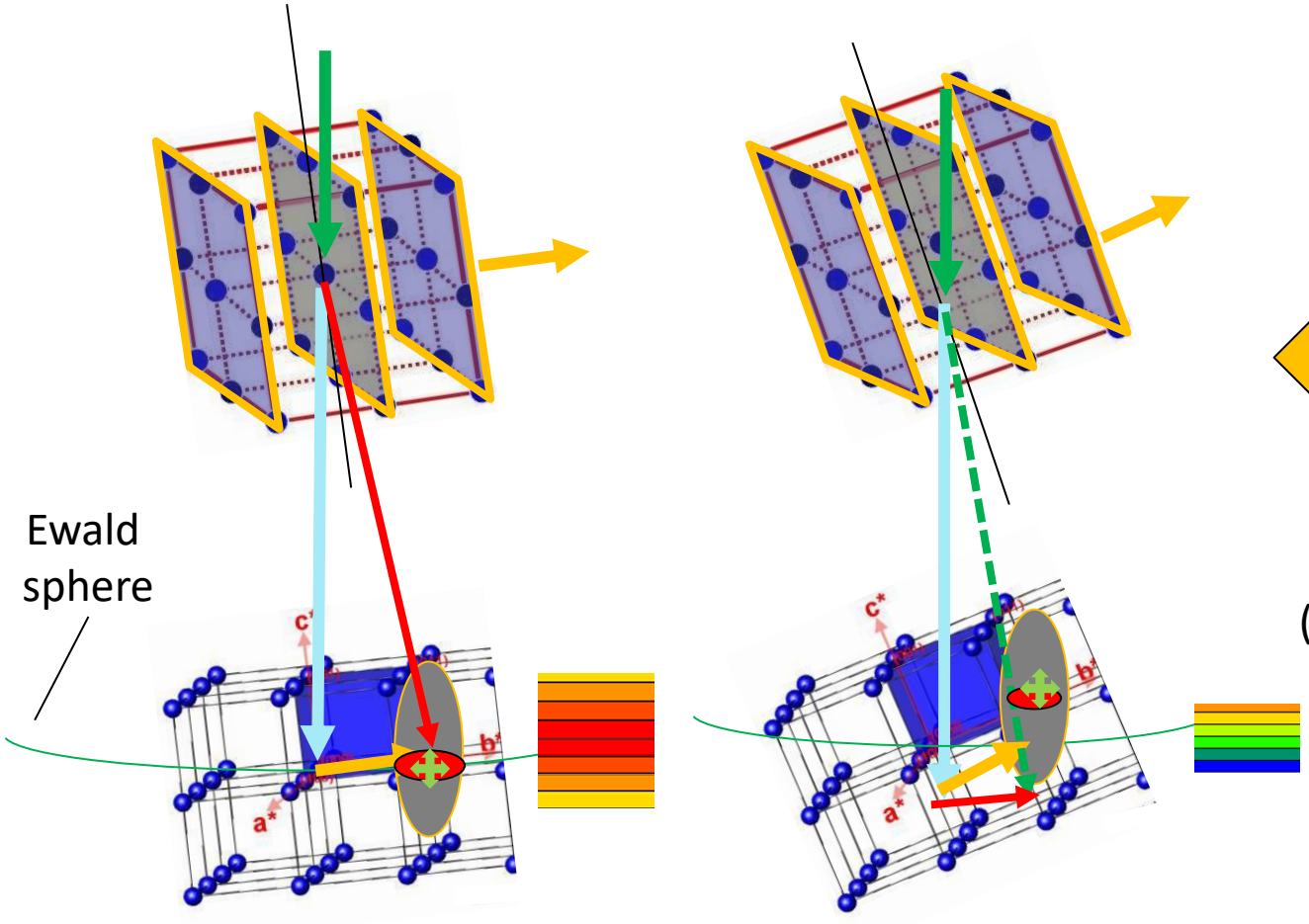
- Deviation vector and reciprocal lattice point expansion

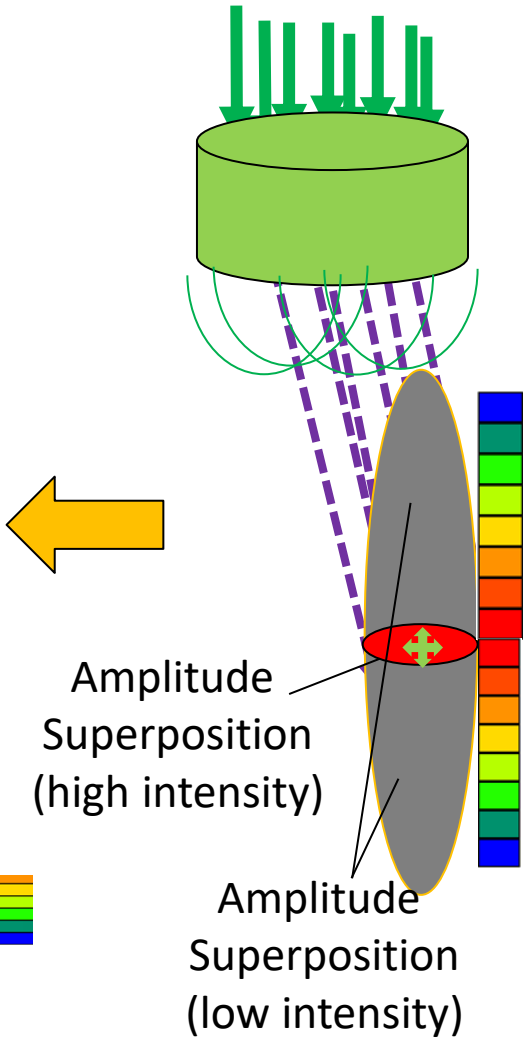
For standard samples under transmission electron microscopy, the corresponding reciprocal array (point or shape) is shown in Figure.



9.2 Principles of electron diffraction

- Deviation vector and reciprocal lattice point expansion





When does the superposition of high-intensity occur?

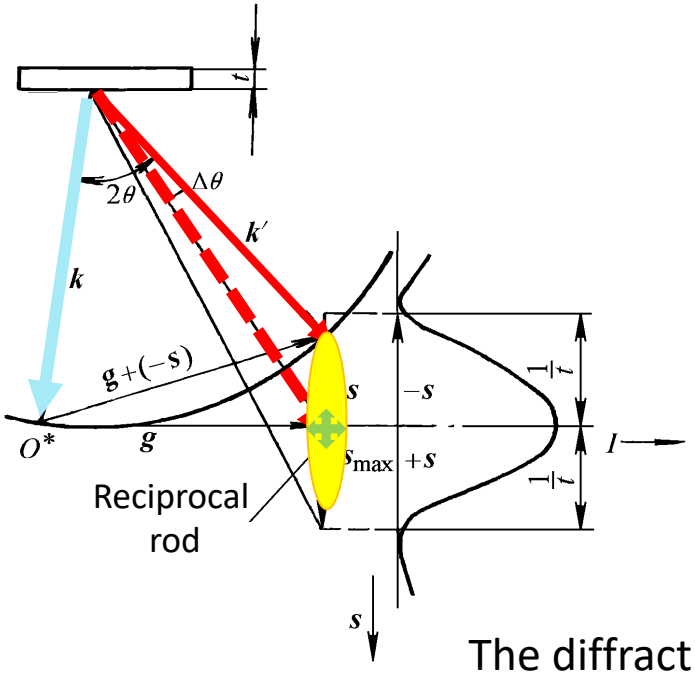
When does the superposition of low-intensity occur?

When is there no diffraction?

9.2 Principles of electron diffraction

- Deviation vector and reciprocal lattice point expansion

As shown in Figure, since the reciprocal array point expands into a reciprocal rod and intercepts the reflecting sphere, the distance from the center of the array point to the reflecting sphere is represented by ***s***, which is called the deviation vector.



- When the center of the reciprocal array point falls on the reflecting sphere, $\boldsymbol{s} = 0$;
- If the center of the array point falls within the reflecting sphere, $\boldsymbol{s} > 0$; conversely, if the center of the array point falls outside the reflecting sphere, $\boldsymbol{s} < 0$.
- When $\boldsymbol{s} = 0$, the diffraction intensity is the highest; as $|\boldsymbol{s}|$ increases, the diffraction intensity decreases; when $\boldsymbol{s} > 1/\boldsymbol{t}$, the reciprocal rod no longer intercepts the reflecting sphere.

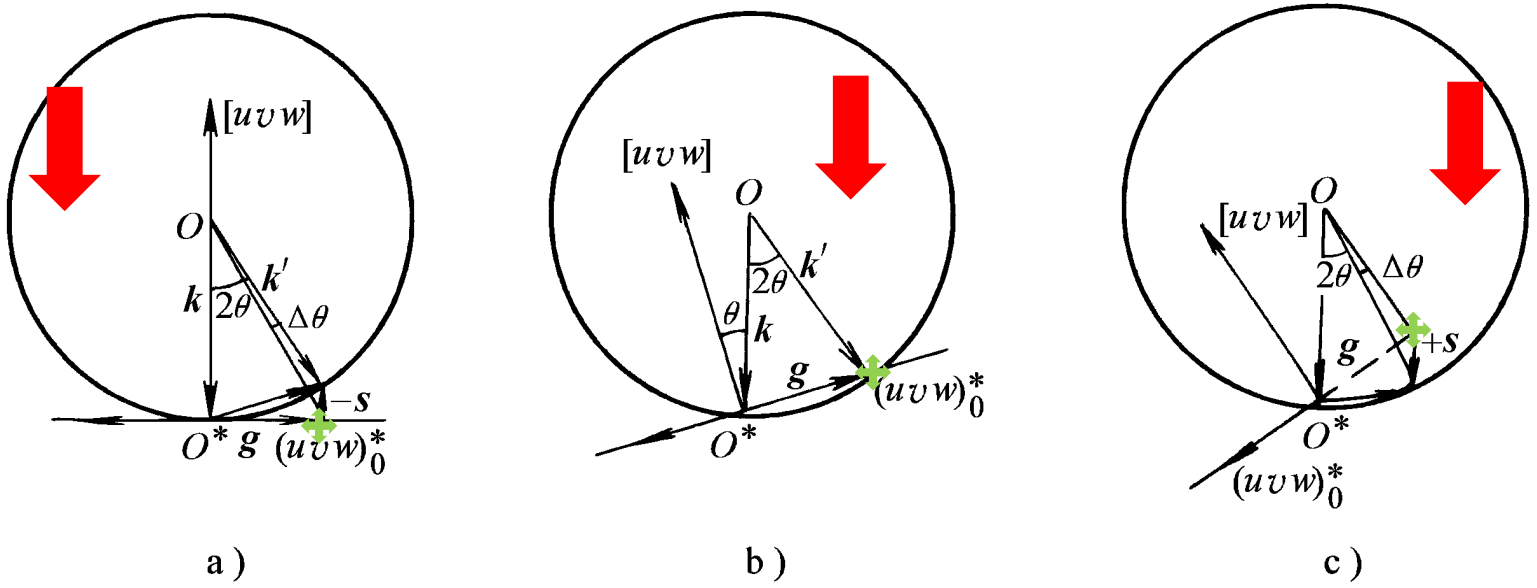
The diffraction equation deviating from the Bragg condition is:

$$\boldsymbol{k'} - \boldsymbol{k} = \boldsymbol{g} + \boldsymbol{s}$$

9.2 Principles of electron diffraction

- Deviation vector and reciprocal lattice point expansion

The figure shows the reflection sphere pattern under three typical diffraction conditions. When analyzing the crystal structure and crystal orientation, select the diffraction conditions shown in Figure **a**; when analyzing diffraction contrast, select the diffraction conditions shown in Figure **b** or **c**.

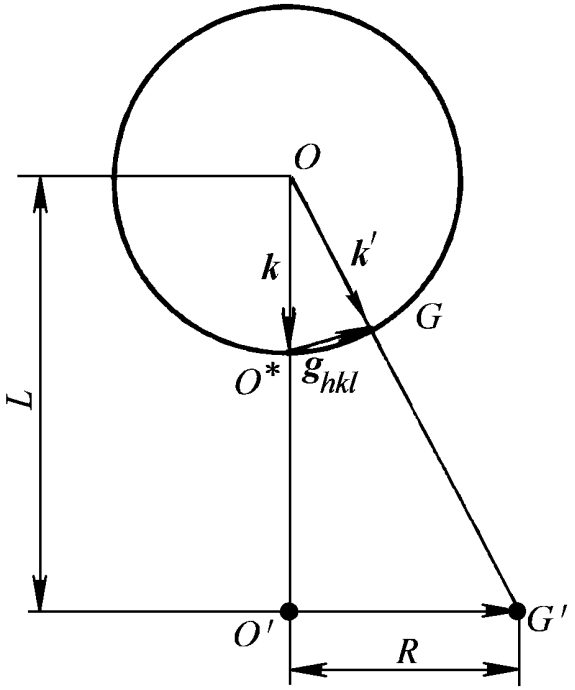


a) $s < 0$ **b)** $s = 0$ **c)** $s > 0$

9.2 Principles of electron diffraction

- Basic formula of electron diffraction

As shown in the figure, the sample is placed at the center ***O*** of the reflection sphere, and there is a fluorescent screen or film at a distance ***L*** below it. ***O′*** is the transmission spot, and ***G′*** is the diffraction spot. Since 2θ is very small, g_{hkl} and ***k*** are close to vertical, so we can get, $\triangle OO^*G \backsim \triangle OO'G'$.



Then we have: $R / L = g / k$

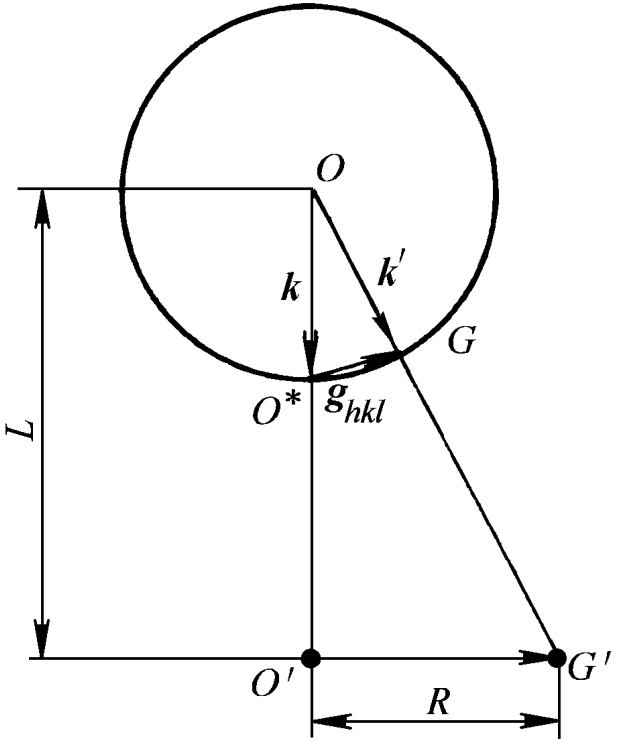
that is: $Rd = L\lambda$

Or: $R = L\lambda g$

In the formula, ***L*** is the camera length; λ is the wavelength of the electron beam; ***d*** is the diffraction crystal plane spacing $K=L\lambda$ is called the electron diffraction camera constant.

9.2 Principles of electron diffraction

- Basic formula of electron diffraction



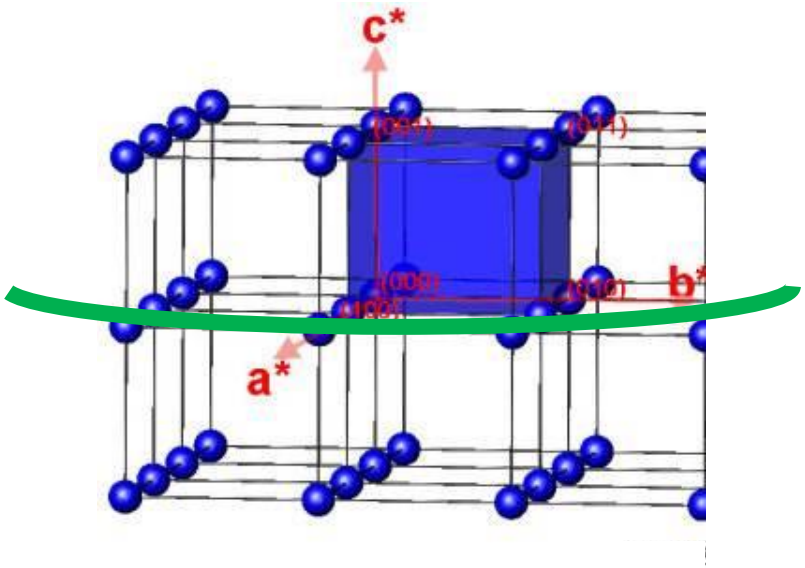
As shown in the figure, since $\boldsymbol{g_{hkl}}$ and $\boldsymbol{k}$ are close to perpendicular, it is considered that $\boldsymbol{R} \parallel \boldsymbol{g_{hkl}}$, and formula can be written as a vector form:

$$\boldsymbol{R = L\lambda\, g = K\, g}$$

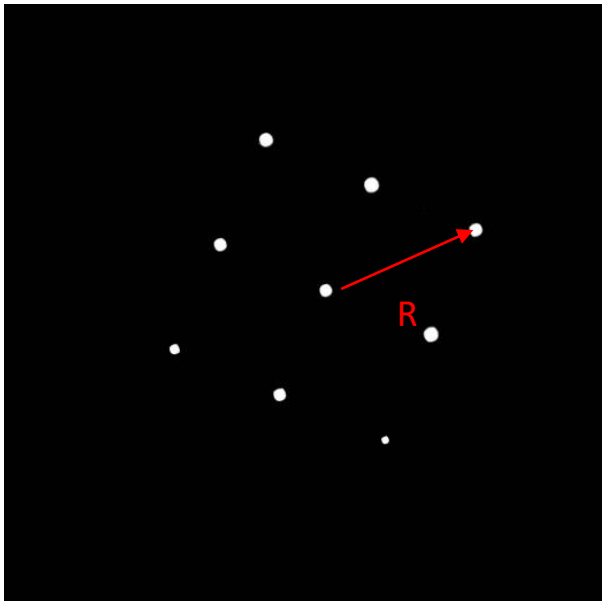
The formula shows that the diffraction spot vector ***R*** is the proportional amplification of the corresponding crystal plane reciprocal vector ***g***, so ***K*** is also called the magnification of electron diffraction.

9.2 Principles of electron diffraction

- Basic formula of electron diffraction



If the reciprocal lattice points near the reciprocal origin all fall on the reflecting sphere, the corresponding crystal planes can produce diffraction, and the obtained diffraction pattern is the projection of the lattice point arrangement on the zero-layer reciprocal plane.

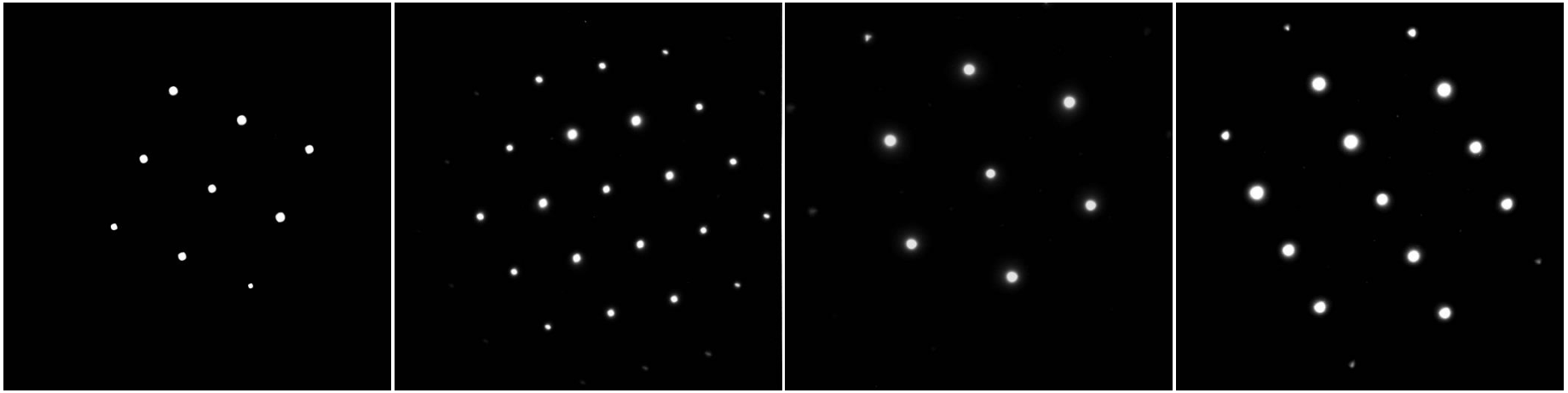


The diffraction spots can be directly regarded as the reciprocal lattice points of the corresponding diffraction crystal planes; the vector ***R*** of each spot is the corresponding reciprocal vector ***g***.

9.2 Principles of electron diffraction

- Basic formula of electron diffraction

When performing crystal structure determination or orientation analysis, it is often necessary to perform a series of tilts to obtain the electron diffraction patterns of several crystal bands in the same area of the sample. Figure shows several important low-index crystal band electron diffraction patterns of face-centered cubic crystals.

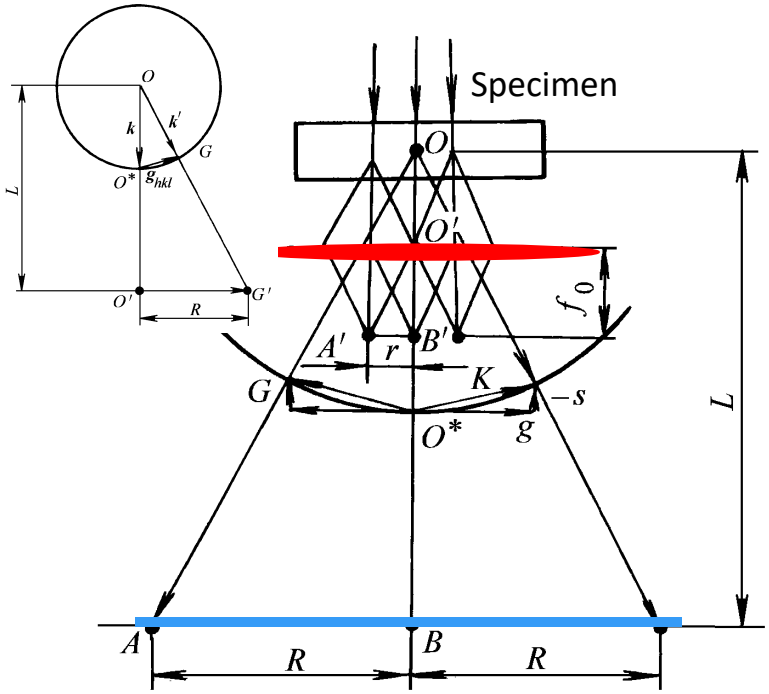


a) b) c) d)

Diffraction patterns of several low-index crystal bands in face-centered cubic crystals.
a) [001] b) [011] c) [111] d) [112]

9.3 Electron diffraction in electron microscopy

- Effective camera constants



Schematic of diffraction pattern formation

As shown in the figure, for electron diffraction in a transmission electron microscope, the focal length f_0 of the objective lens plays the role of the camera length L, and the diffraction spot spacing r on the back focal surface of the objective lens is equivalent to the diffraction spot spacing R on the film, so $r = f_0 \lambda g$.

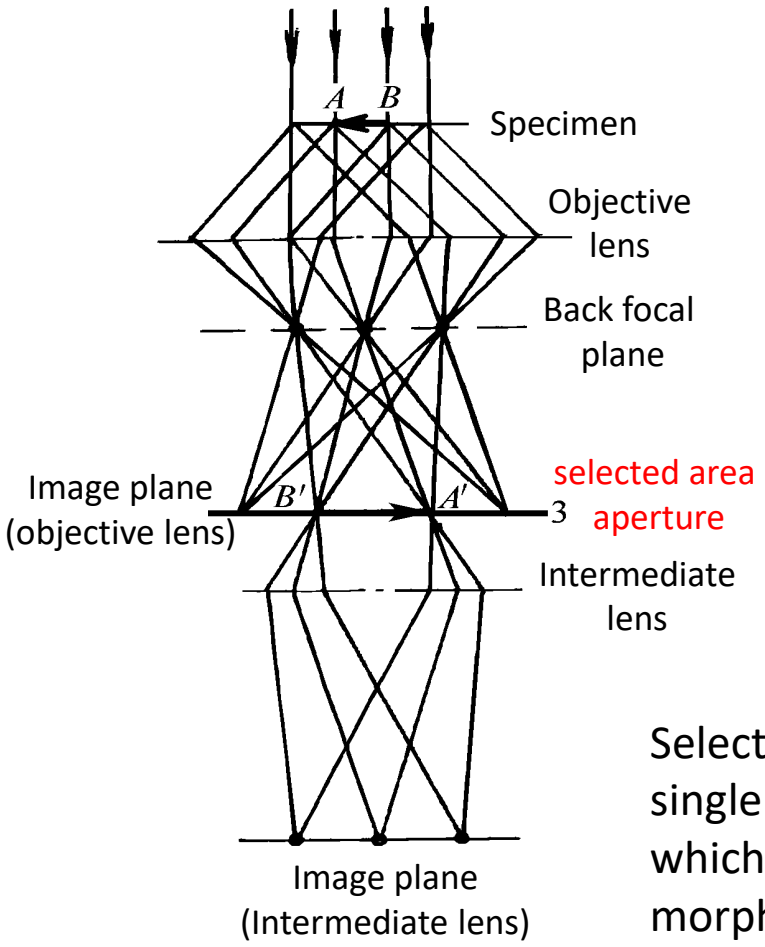
After the diffraction pattern on the back focal surface of the objective lens is amplified by the intermediate lens and the projection lens, $L' = f_0 M_i M_p$, $R' = r M_i M_p$, and L' is called the effective camera length, then we have:

$$R' = \lambda L' g$$

$K' = \lambda f_0 M_i M_p$, which is called the effective camera constant, and K will change as f_0, M_i and M_p change. Under normal circumstances, there is no need to distinguish between L and L'.

9.3 Electron diffraction in electron microscopy

- Selected Area of Electron Diffraction



After the incident electron beam passes through the sample, it forms a diffraction pattern on the back focal plane of the objective lens and forms an image on the image plane of the objective lens.

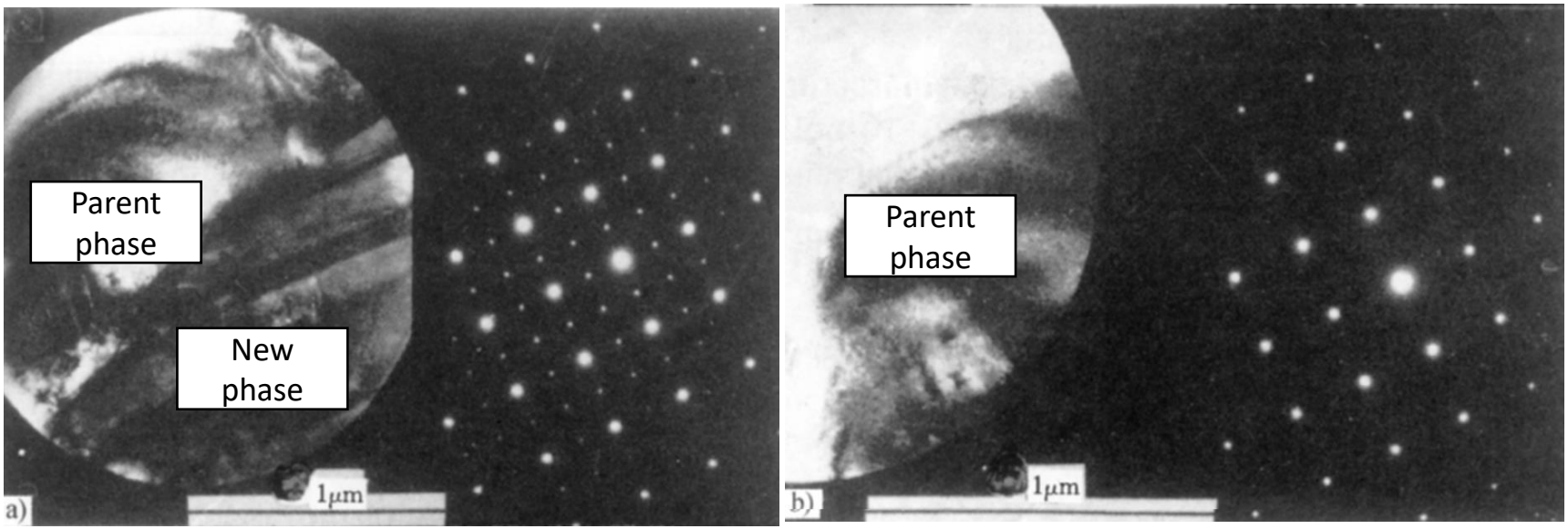
If an aperture is added to the image plane of the objective lens, it will only allow electrons within the range of $\boldsymbol{A'B'}$ to pass through, while blocking electrons outside the range of $\boldsymbol{A'B'}$. The electrons that eventually reach the fluorescent screen to form diffraction patterns only come from the ***AB*** area of the sample. This aperture limits and selects the area of the sample that forms the final diffraction pattern.

Selected area electron diffraction can be used to obtain single crystal diffraction patterns in polycrystalline samples, which can achieve micro-area correspondence between morphology observation and crystal structure analysis.

9.3 Electron diffraction in electron microscopy

- Selected Area of Electron Diffraction

The selected area of electron diffraction can be as small as 1 μm or less, as shown in Figure. When the ZrO_2-CeO_2 ceramic parent phase and the new phase coexist within the selected area, a composite diffraction pattern of the two phases can be obtained; If the selection range only has the parent phase, only the diffraction pattern of the parent phase can be obtained.



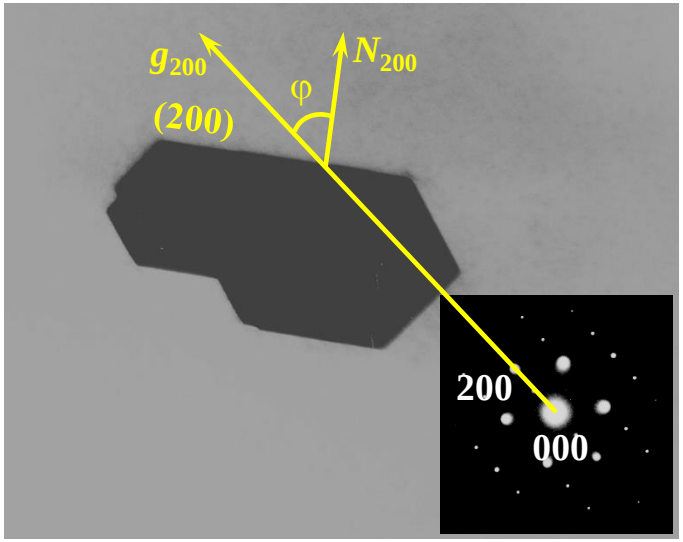
Electron Diffraction of ZrO_2-CeO_2 Ceramics

9.3 Electron diffraction in electron microscopy

- Magnetic rotating angle

When electrons pass through the electromagnetic lens, they make a spiral paraxial motion under the action of the magnetic field. When they reach the fluorescent screen, they will turn through a certain angle.

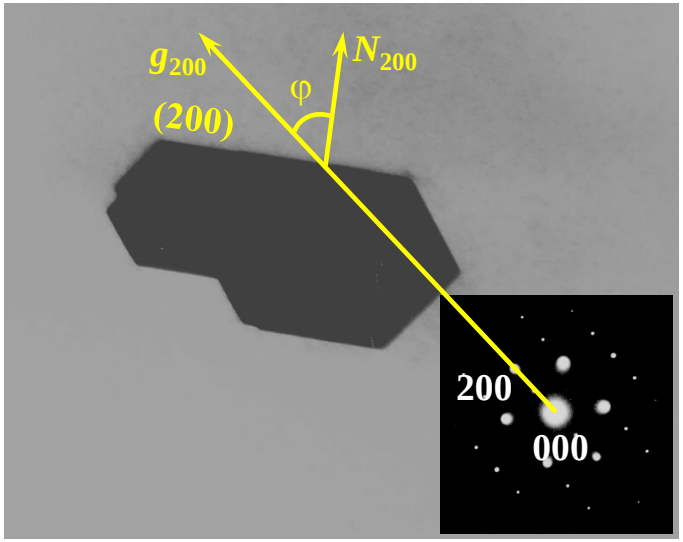
During the imaging operation, if the magnetic rotation angle of the image relative to the sample is φ_i. During the diffraction operation, the magnetic rotation angle of the diffraction pattern relative to the sample is φ_d, then the magnetic rotation angle of the diffraction pattern relative to the image is φ. $\varphi = \varphi_i - \varphi_d$



The method of calibrating the magnetic rotation angle uses known planar structural features, such as TiB crystal cylinders. The calibration method is shown in the figure.

9.3 Electron diffraction in electron microscopy

- Magnetic rotating angle



As shown in the figure, the spatial shape of the TiB crystal is a cylinder, the cross-section is fusiform, the (200) crystal plane is a cylinder, its normal direction in the image is $\boldsymbol{N_{200}}$, and the normal direction given by the diffraction pattern calibration result is $\boldsymbol{g_{200}}$, and the angle between $\boldsymbol{N_{200}}$ and $\boldsymbol{g_{200}}$ is the magnetic rotation angle φ.

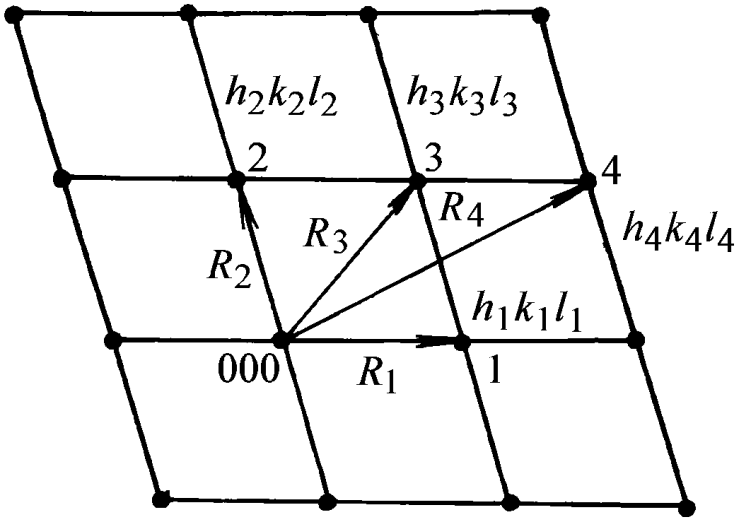
The magnetic rotation angle changes with changes in magnification and camera length. Table shows the magnetic rotation angle data of the CM12 transmission electron microscope at typical magnifications and camera lengths.

Magnification		10k	17k	22k	35k	45k	60k	100k	200k
Camera lens (mm)	530	16.0	14.5	12.7	7.5	-71.5	-72.5	-79.0	-74.5
	770	11.5	10.0	8.2	4.0	-76.0	-77.0	-74.5	-79.0
	1100	21.0	19.5	17.7	13.5	-66.5	-67.5	-69.5	-69.5

9.4 Calibration of single crystal electron diffraction patterns

- The purpose of calibrating electron diffraction patterns is to determine the lattice type, phase and orientation of the diffracted material by calibrating each diffraction spot index and crystal zone axis index.
- Geometric Characteristics of Single Crystal Electron Diffraction Patterns.

1. The single crystal electron diffraction pattern consists of regularly arranged spots, which are located on the grid points of a two-dimensional grid, as shown in the figure.



Geometric Characteristics of Single Crystal Electron Diffraction Patterns

2. The angle between any two diffraction spot vectors is equal to the angle between the corresponding two diffraction crystal planes

3. Take two diffraction spot vectors R_1 and R_2 in the pattern, and the remaining spot vectors R.

$$\boldsymbol{R = mR_1 + nR_2}$$

The relationship between the corresponding spot indices is: $\boldsymbol{(hkl) = (mh_1+nh_2\,,\, mk_1+nk_2\,,\, ml_1+nl_2)}$

9.4 Determinations of single crystal electron diffraction patterns

- Calibration of diffraction patterns of known crystal structures

1. Checking method

1) Measure the spot spacing $\boldsymbol{R_1}$, $\boldsymbol{R_2}$, $\boldsymbol{R_3}$ …., and measure the angle between $\boldsymbol{R_1}$ and $\boldsymbol{R_2}$ $\boldsymbol{\varphi}$.

2) Use the basic formula of electron diffraction to calculate the corresponding inter-plane spacing $\boldsymbol{d_1}$, $\boldsymbol{d_2}$, $\boldsymbol{d_3}$…. $\boldsymbol{Rd = L\lambda}$

3) Check substance cards, determined by $\boldsymbol{d}$ value $\{\boldsymbol{h_1k_1l_1}\}$, $\{\boldsymbol{h_2k_2l_2}\}$, $\{\boldsymbol{h_3k_3l_3}\}$…..

4) Select $(\boldsymbol{h_1k_1l_1})$ in the $\{\boldsymbol{h_1k_1l_1}\}$ crystal face family as the diffraction spot index corresponding to $\boldsymbol{R_1}$.

5) Select $(\boldsymbol{h_2k_2l_2})$ as the diffraction spot index corresponding to $\boldsymbol{R_2}$ in the $\{\boldsymbol{h_2k_2l_2}\}$ crystal plane family, and use the angle formula between crystal planes to calculate the angle $\boldsymbol{\varphi}$ between $(\boldsymbol{h_1k_1l_1})$ and $(\boldsymbol{h_2k_2l_2})$. If it matches the measured value, it means that $(\boldsymbol{h_2k_2l_2})$ was selected correctly; otherwise, reselect and check until it matches.

6) According to the two calibrated spot indexes $(\boldsymbol{h_1k_1l_1})$ and $(\boldsymbol{h_2k_2l_2})$, use vector operations to calibrate the remaining diffraction spot indexes $(\boldsymbol{hkl})$.

7) Use the Zone law to calculate the crystal band axis index $[\boldsymbol{uvw}]$.

9.4 Determinations of single crystal electron diffraction patterns

- Calibration of diffraction patterns of known crystal structures

Diffraction pattern of martensite in steel as shown in calibration diagram

1) Measurements of R_1, R_2, R_3, and φ.

$R_1=R_2=10.2\text{mm}$, $R_3=14.4\text{mm}$, $\varphi = 90^o$

2) Calculate d ($L\lambda = 2.05\ \text{mm}\cdot\text{nm}$).

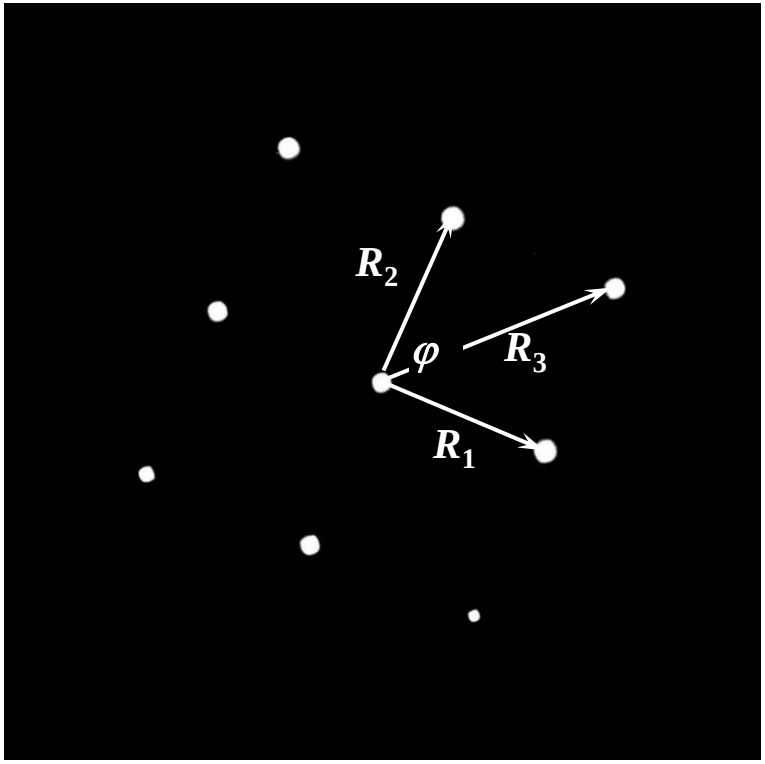
$d_1 = d_2 = L\lambda / R_1 = 0.201\ \text{nm}$

$d_3 = L\lambda / R_3 = 0.142\ \text{nm}$

3) Determine the corresponding crystal plane family index {hkl} based on the d value.

$d_1 = d_2 = 0.201\ \text{nm}$, which belongs to the {110} crystal plane family.

$d_3 = 0.142\ \text{nm}$, which belongs to the {200} crystal plane family.



9.4 Determinations of single crystal electron diffraction patterns

- Calibration of diffraction patterns of known crystal structures

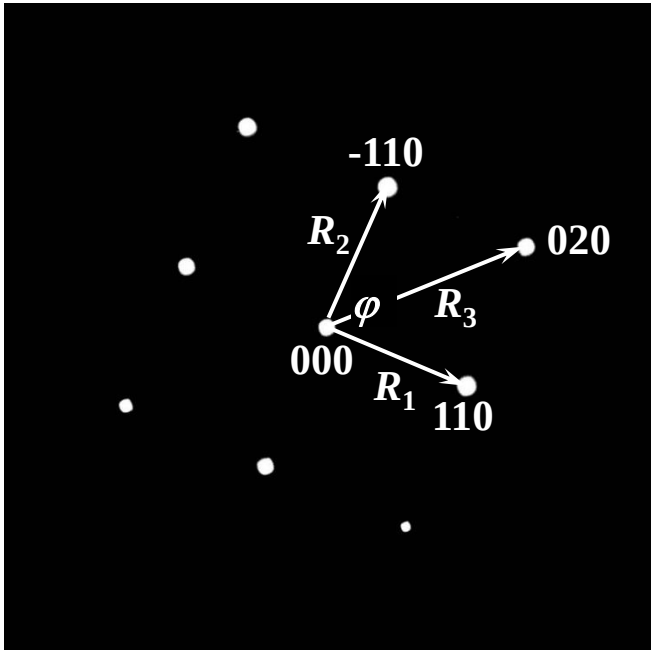
4) The crystal plane corresponding to the R_1 spot belongs to the {110} crystal plane family, and (110) is selected as its index.

5) In the {110} crystal plane family, (-110) is selected as the index of the corresponding spot of R_2. The calculated angle between (110) and (-110) is consistent with the measured value of 90º.

6) Calibrate other spot indexes: such as $R_3 = R_1+R_2$, then $(h_3k_3l_3)=(h_1+h_2\ k_1+k_2\ l_1+l_2)=(020)$; other diffraction spot indexes can be calibrated according to this.

7) Use the Zone law to calculate the crystal band axis index [***uvw***] = [001]

$$u = k_1l_2 - k_2l_1 = 0,\ v = l_1h_2 - l_2h_1 = 0,\ w = h_1k_2 - h_2k_1 = 1$$



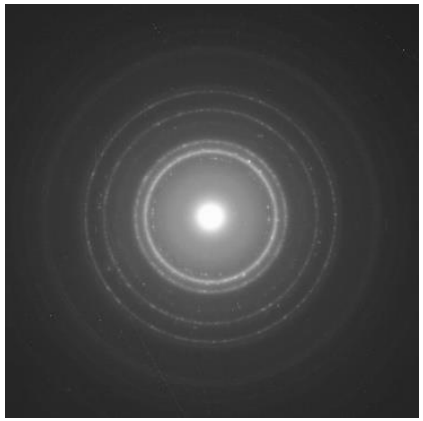
[001]

9.4 Determinations of single crystal electron diffraction patterns

- Calibration of diffraction patterns of known crystal structures

2. R^2 ratio method

The R^2 ratio method is more suitable for cubic polycrystalline diffraction pattern calibration.



1) Measure the diffraction spot spacing R_1, R_2, R_3, R_4 …., and arrange the R values in increasing order.

2) Calculate R^2 Determine the lattice structure and crystal plane family index {hkl} according to the R^2 ratio law.
For cubic crystals system:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{N}}, d^2 = \frac{a^2}{N}$$

The spot spacing R is inversely proportional to d, so R^2 is directly proportional to $N = h^2 + k^2 + l^2$, that is:

$$R_1^2 : R_2^2 : R_3^2 : \cdots = N_1 : N_2 : N_3 : \cdots$$

9.4 Determinations of single crystal electron diffraction patterns

- Calibration of diffraction patterns of known crystal structures

2. R^2 ratio method

- Body centered cubic crystal

$h + k + l$ = even-numbered crystal faces can produce diffraction. The values of $N = h^2 + k^2 + l^2$ are: 2, 4, 6, 8, 10…., that is

$$N_1:N_2:N_3:N_4:N_5: \ldots = 2:4:6:8:10: \ldots$$

- Face centered cubic crystal

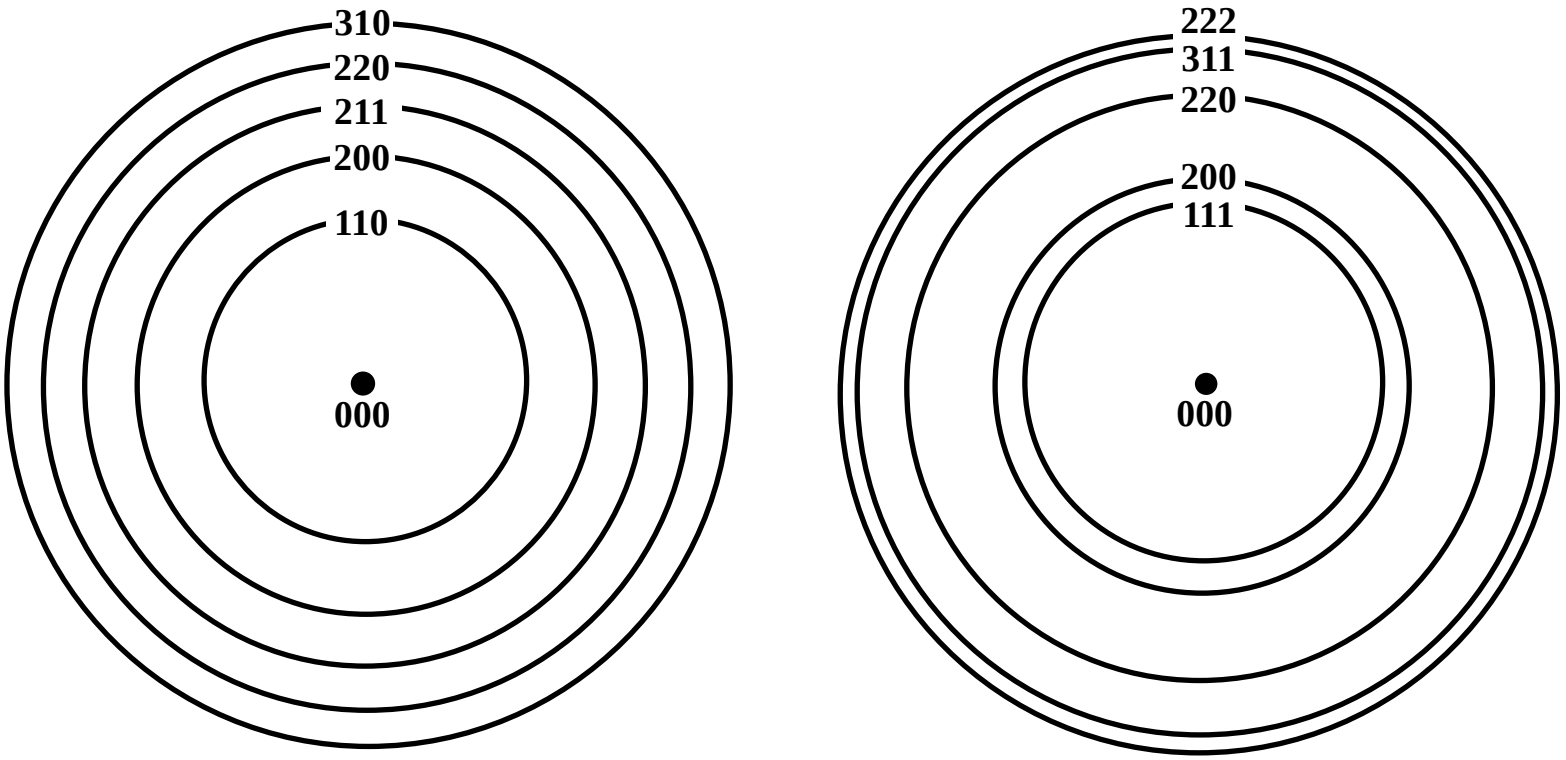
Diffraction can only occur when h, k, and l are all odd or all even. The values of $N = h^2 + k^2 + l^2$ are: 3, 4, 8, 11, 12….., that is

$$N_1:N_2:N_3:N_4:N_5: \ldots = 3:4:8:11:12: \ldots$$

9.4 Determinations of single crystal electron diffraction patterns

- Calibration of diffraction patterns of known crystal structures

2. R^2 ratio method



Calibration diagram of body-centered cubic (**a**) and face-centered cubic (**b**) polycrystal electron diffraction patterns

9.4 Determinations of single crystal electron diffraction patterns

- Calibration of diffraction patterns of unknown crystal structures

1) Measure the spot spacing R_1, R_2, R_3 …., and measure the angle between R_1 and R_2 φ.

2) Use the basic formula of electron diffraction to calculate the corresponding inter-plane spacing d_1, d_2, d_3…. $Rd = L\lambda$

3) According to the comparison between the ***d*** value series and the ***d*** series in the possible phase card, the physical phase is first determined; after the physical phase is determined, it can be carried out after step 3 of the trial calibration method of diffraction pattern calibration of known crystal structures. In order to make the calibration results reliable, the distance between the measured spots should be as large as possible. Generally, at least 4 spots should be selected for measurement.

In order to accurately identify the physical phase, other information such as the chemical composition and formation conditions of the diffracted material should be used to rule out impossible physical phases.

9.4 Determinations of single crystal electron diffraction patterns

- Calibration of diffraction patterns of unknown crystal structures

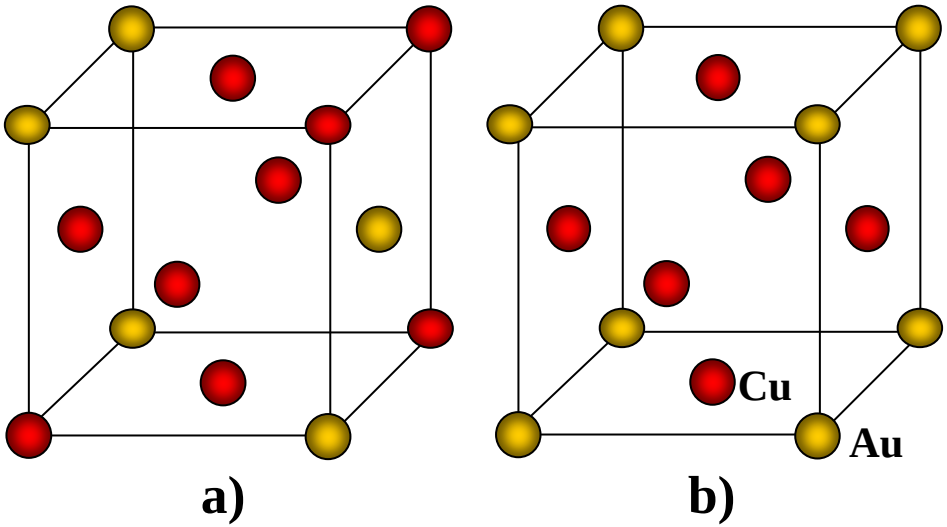
3. Standard pattern comparison method

- For cubic crystals, the ratio of the interplanar spacing and the angle between the two crystal planes have nothing to do with the lattice constant. Therefore, for substances with different lattice constants, the arrangement patterns of spots in the diffraction patterns of the same crystal band are similar. Therefore, we can draw the standard diffraction patterns of some commonly used low-index crystal bands, and compare the diffraction patterns to be calibrated with the standard patterns for calibration.
- According to the characteristics of the diffraction pattern (such as the ratio of two sides R_2 / R_1 and the angle between the two sides φ), a characteristic quadrilateral table is made, and the look-up table method can also be used for calibration.
- In addition, a computer program can also be used to calibrate the diffraction pattern, which requires inputting the lattice type and lattice parameters of the object phase, the camera constants of the electron microscope, and the measurement data of the diffraction pattern R_1, R_2, φ.

9.5 Complex electron diffraction patterns

- Super lattice spots

Taking the Cu_3Au face-centered cubic solid solution as an example, when it is disordered, Au and Cu atoms randomly occupy positions in the unit cell; when ordered, Au occupies the vertex corners and Cu occupies the face-centered position, forming a superlattice structure, as shown in the figure.



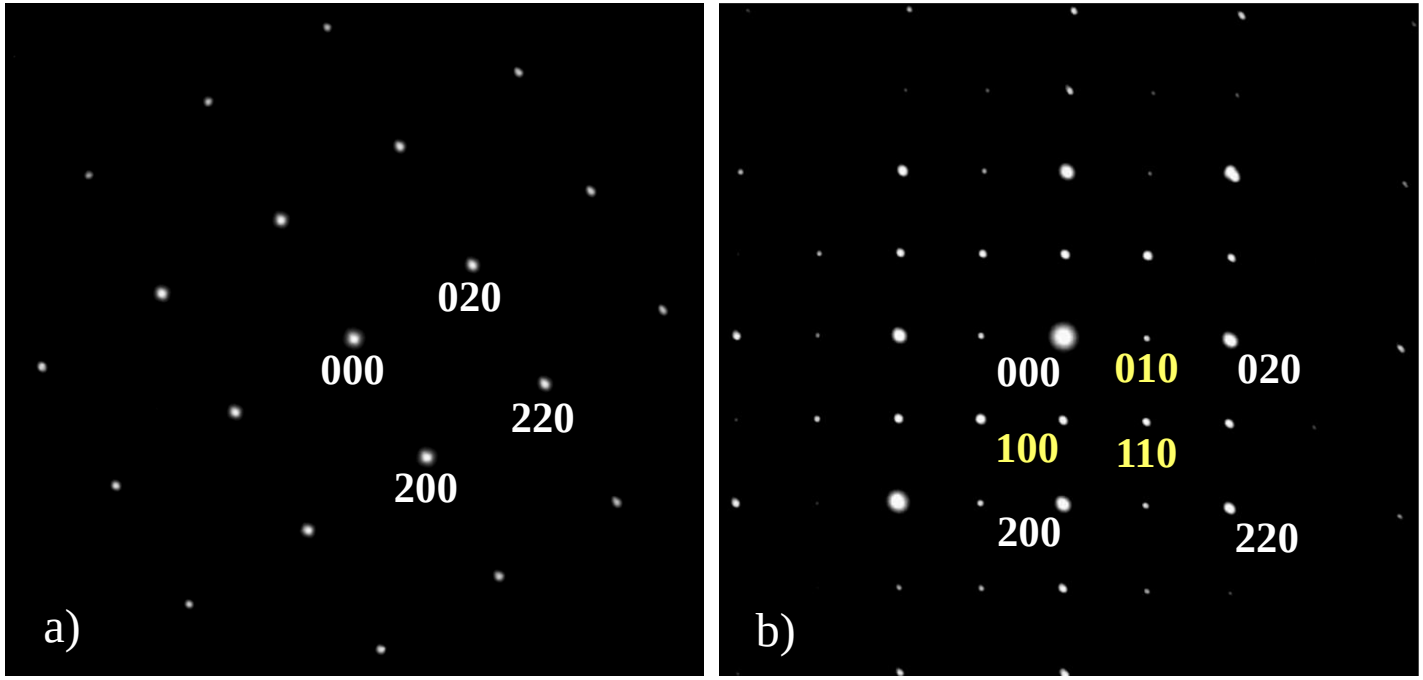
The positions of various atoms in Cu_3Au solid solution
a) Disordered solid solution b) Ordered solid solution

In the disordered state, when ***h***, ***k***, ***l*** are mixed with odds and evens, $F_{hkl} = 0$; while in the ordered state, when ***h***, ***k***, ***l*** are mixed oddly and evenly, $F_{hkl} = f_{Au} - f_{Cu} \neq 0$, super lattice spots will appear. Superlattice spots appear at locations where reflection is prohibited in disordered solid solutions, and the intensity of superlattice spots is low.

9.5 Complex electron diffraction patterns

- Super lattice spots

The diffraction spots of the body-centered cubic and face-centered cubic [001] crystal bands are all squarely distributed, but the locations of the superlattice spots are different, as shown in the figure below.

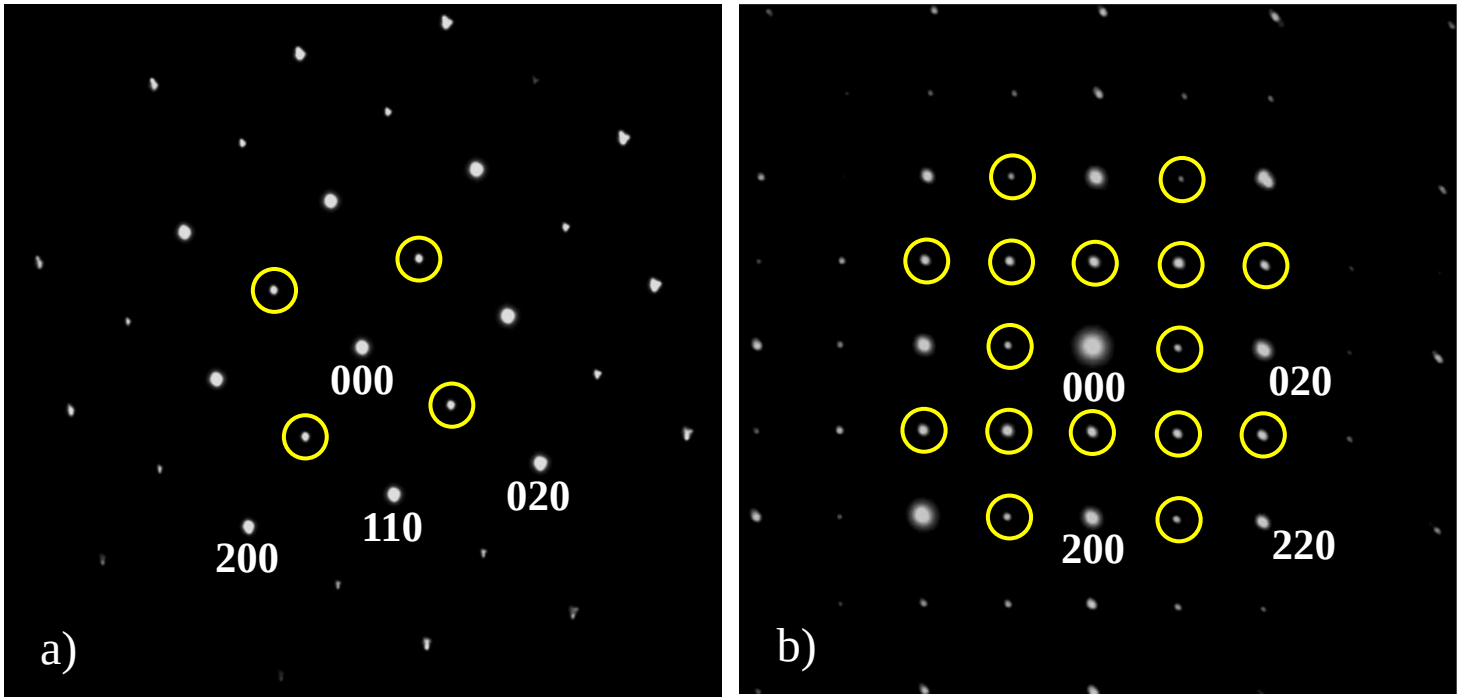


Electron diffraction pattern of Cu3Au solid solution [001] crystal band
a) Disordered solid solution b) Ordered solid solution

9.5 Complex electron diffraction patterns

- Super lattice spots

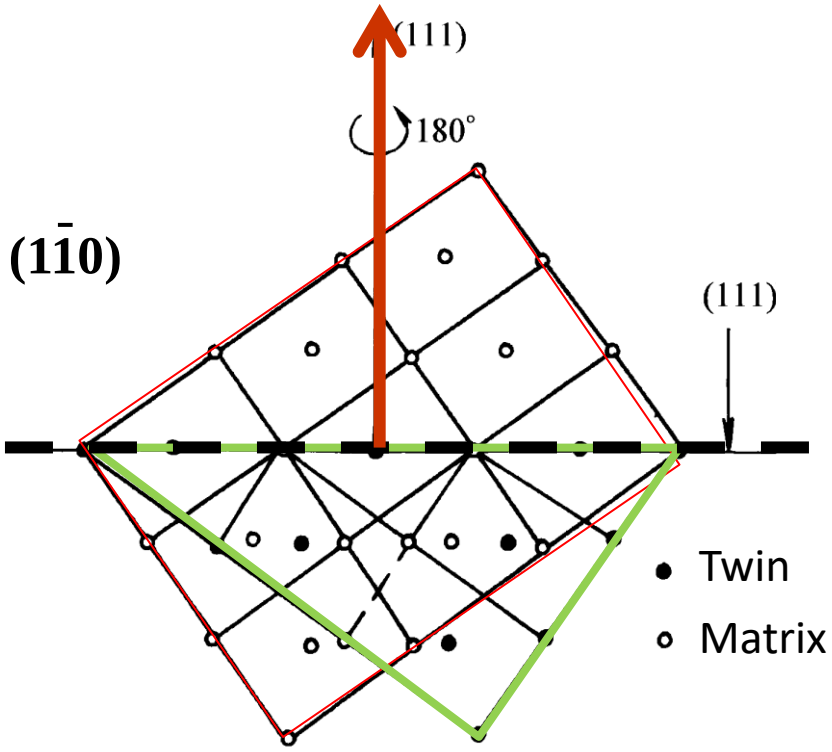
Comparing Figures a and b, it can be seen that the superlattice spots of the Cu_3Au ordered solid solution appear at the reflection position of the disordered solid solution extinction (***h k l*** is the mixed odd and even number).



Electron diffraction pattern of cubic ordered solid solution [001] crystal bands
a) Body-centered cubic b) Face-centered cubic

9.5 Complex electron diffraction patterns

- Twinning spots



The atomic arrangement of the $(1\bar{1}0)$ plane of the face-centered cubic (111) twin is shown in the figure.

If the twin plane (111) is used as a mirror for the reflection operation, the lattice of the matrix and the twins will overlap each other, which is called a reflection twin.

If the twin plane normal line [111] is used as the axis to perform a 180° rotation, the lattice of the matrix and the twins will also coincide with each other, which is called a rotational twin.

9.5 Complex electron diffraction patterns

- Twinning spots

The transformation formulas of body-centered and face-centered cubic twins are described into equations (1) and (2):

$$\begin{cases} h^t = -h + \frac{1}{3} p(ph+qk+rl) \\ k^t = -k + \frac{1}{3} q(ph+qk+rl) \\ l^t = -l + \frac{1}{3} r(ph+qk+rl) \end{cases} \quad \textbf{(1)}$$

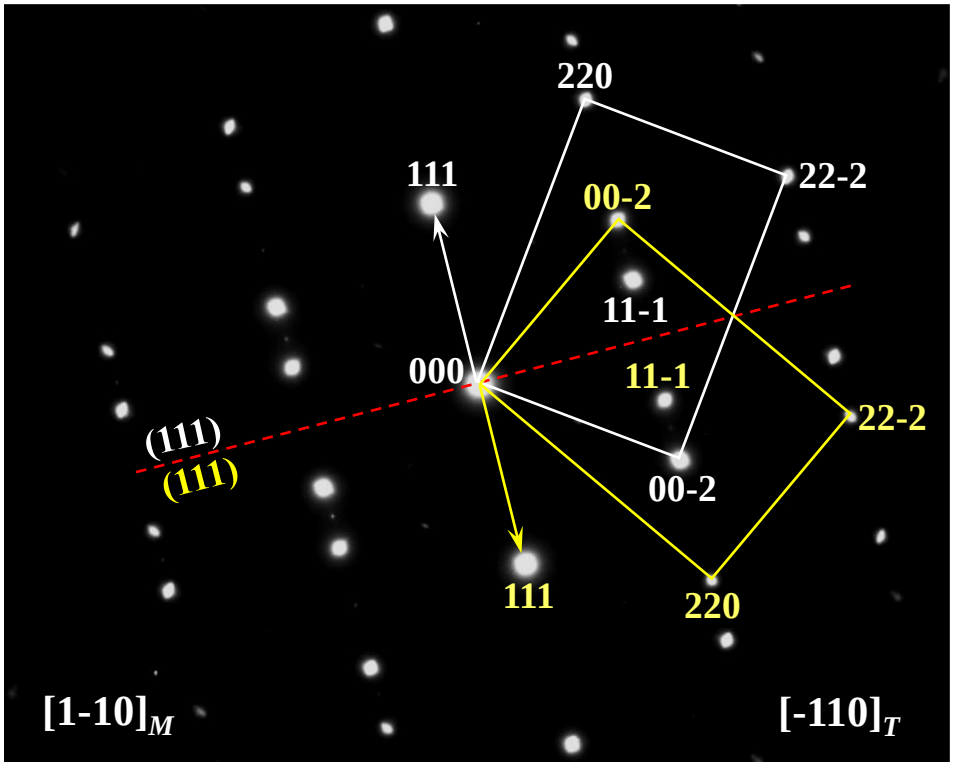
$$\begin{cases} h^t = -h + \frac{2}{3} p(ph+qk+rl) \\ k^t = -k + \frac{2}{3} q(ph+qk+rl) \\ l^t = -l + \frac{2}{3} r(ph+qk+rl) \end{cases} \quad \textbf{(2)}$$

In the formula (***h*^{t}*k*^{t}*l*^{t}**) is the index of the twin reciprocal lattice point (***hkl***) in the matrix lattice; ***pqr*** is the twin plane index, body-centered cubic {***pqr***}={112}, face-centered cubic {***pqr***}={111}

9.5 Complex electron diffraction patterns

- Twinning spots

As shown in the figure, according to the twin diffraction pattern and its calibration results, the reflection symmetry relationship between the matrix and the twin channel reciprocal lattice can be explained.



Face-centered cubic crystal (111) twin diffraction patterns and calibration results

9.6 Thin film sample preparation method

- Fundamental requirements

Due to the limitation of electron penetration ability, a certain method needs to be used to prepare thin crystal samples suitable for transmission electron microscopy, usually called thin film samples. Film samples should meet the following basic requirements:

1) The thin film sample must maintain the same organizational structure as the bulk sample. That is, the microstructure of the sample cannot change during the preparation process.

2) The film sample should be “transparent” to the electron beam.

3) The film sample must have a certain strength and stiffness to prevent the sample from being deformed or damaged during the process of clamping and loading the sample stage.

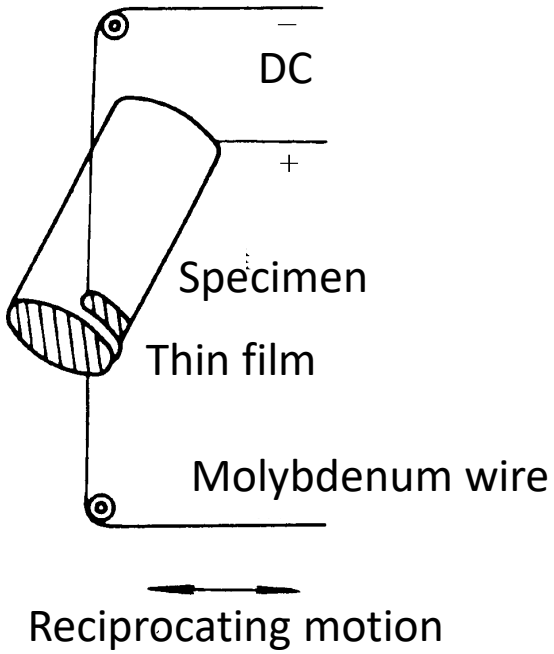
4) There should be no corrosion or severe oxidation on the surface of the film sample. Otherwise, it will cause a decrease in image clarity or artifacts.

9.6 Thin film sample preparation method

- Preparation process

1) Slicing: Cut thin slices with a thickness of about 0.2 ~ 0.3 mm from a large piece of material, and choose an appropriate cutting method according to the material, such as wire EDM (see picture), diamond disc saw, etc.; pay attention to the cutting parts and direction to make the analysis results of the sample representative.

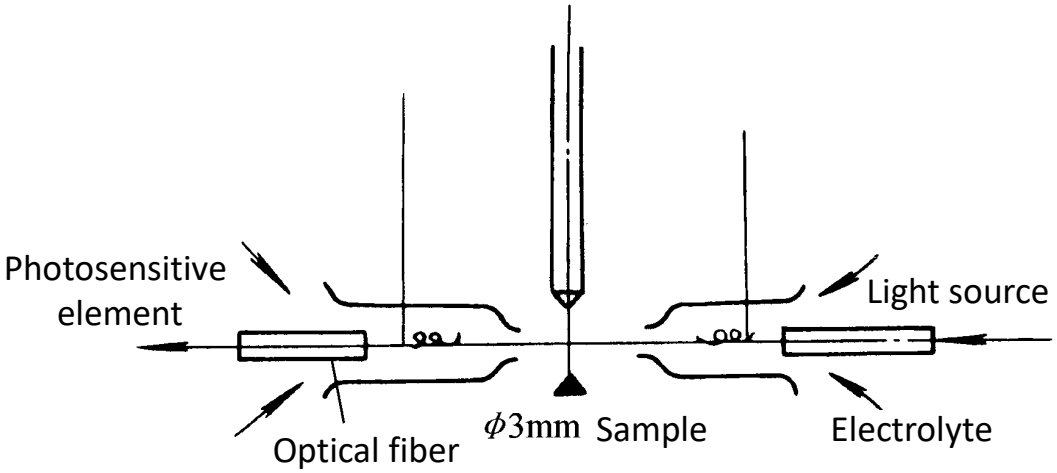
2) Pre-thinning: The pre-thinning thickness is controlled at 0.1 ~ 0.2 mm. It is mainly used to remove the surface damage layer caused by slicing. The methods include mechanical and chemical methods; the mechanical method is manual grinding without excessive force and sufficient cooling. Avoid changes in the tissue structure of the sample.

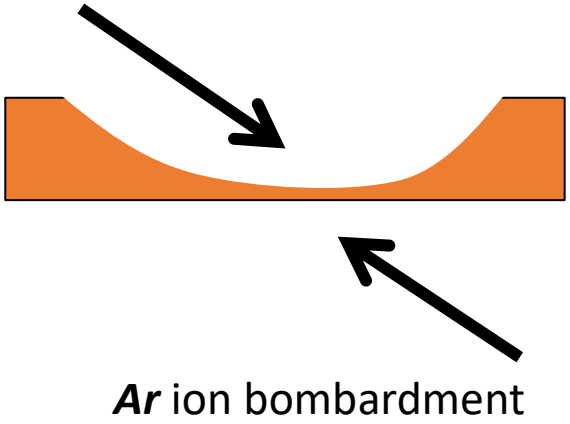


9.6 Thin film sample preparation method

- Preparation process

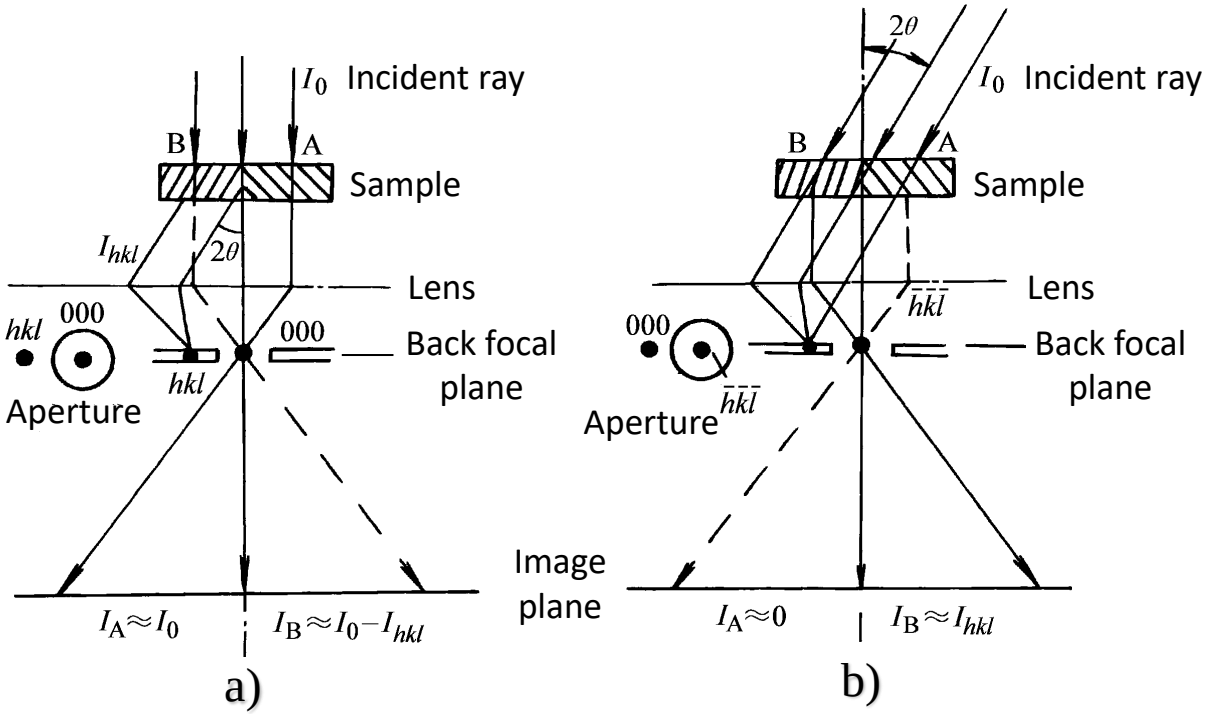
3) Final thinning: A sample with no corrosion and oxidation on the surface and transparent to the electron beam is obtained after final thinning. The methods are double-jet electrolytic polishing and ion thinning. For metal materials, efficient and simple double-jet electrolytic polishing is usually used. Ion thinning can be used for non-conductive materials, but this method is more time-consuming.





9.7 Principle of thin crystal diffraction contrast imaging

As shown in the figure, there are two adjacent crystal grains in the single-phase polycrystalline film sample. Assume that the orientations of all crystal faces of the A crystal grain are far away from the Bragg condition; while only the (***hkl***) crystal face of the B crystal grain satisfies the Bragg condition. The diffraction intensity is I_{hkl}.



Diffraction contrast imaging principle
a) Bright-field imaging **b**) Center dark-field imaging

9.7 Principle of thin crystal diffraction contrast imaging

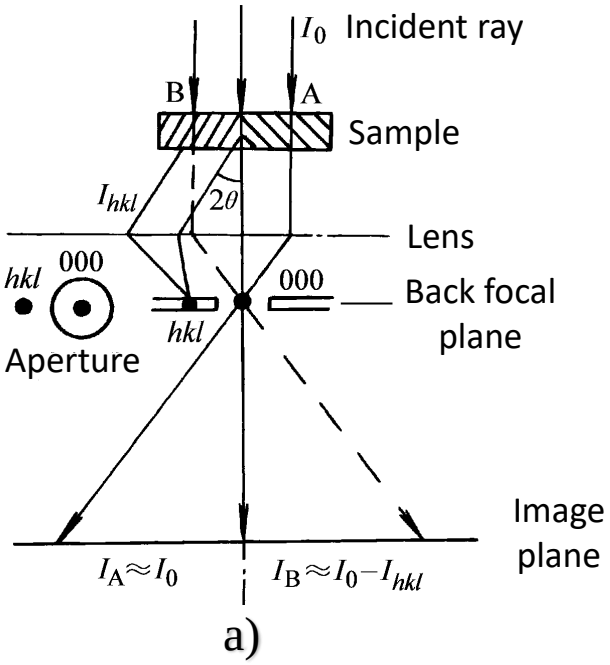
- Bright-field imaging

If the intensity of the incident electron beam is I_0, the intensity of the transmitted beam on the lower surface of the A crystal grain is approximately equal to the incident beam intensity I_0; while the intensity of the transmitted beam of the B crystal grain is (I_0 - I_{hkl}). The transmitted beam and the diffracted beam are focused by the objective lens, respectively. Transmission spots (000) and diffraction spots (***hkl***) are formed on the back focal plane.

If the objective aperture is used to block the diffracted beam of the B grain, and only the transmitted beam is allowed to pass through the aperture for imaging, and the intensities of the imaging electron beams for the A and B grains on the image plane are I_A and I_B, then we have:

$$I_A \approx I_0 \qquad I_B \approx I_0 - I_{hkl}$$

The intensity of the imaging electron beam is the brightness of the image, so grain A is bright and grain B is darker.



Bright-field imaging

9.7 Principle of thin crystal diffraction contrast imaging

- Bright-field imaging

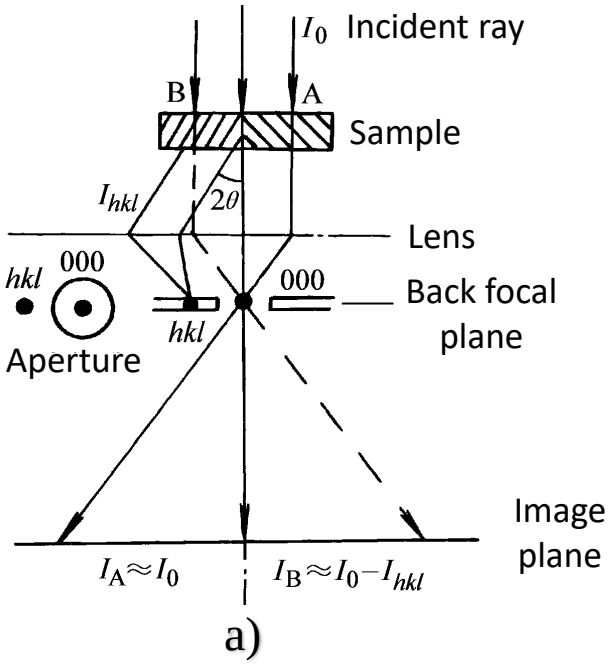
If the objective aperture is used to block the diffracted beam of the B grain, and only the transmitted beam is allowed to pass through the aperture for imaging, and the intensities of the imaging electron beams for the A and B grains on the image plane are I_A and I_B, then we have:

$$I_A \approx I_0 \qquad I_B \approx I_0 - I_{hkl}$$

The intensity of the imaging electron beam is the brightness of the image, so grain A is bright and grain B is darker. If the brightness of A grain is used as the background intensity and the contrast of B grain is:

$$\left(\frac{\Delta I}{I}\right)_B = \frac{I_A - I_B}{I_A} \approx \frac{I_{hkl}}{I_0}$$

Image contrast is related to the diffraction intensity in different areas, so it is called diffraction contrast.

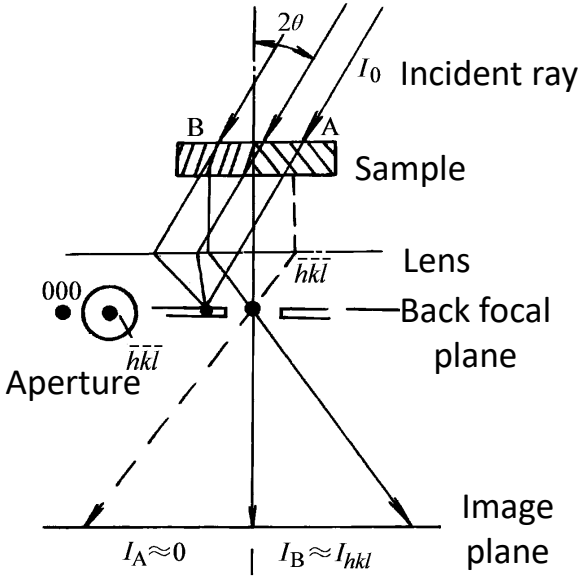


Bright-field imaging

9.7 Principle of thin crystal diffraction contrast imaging

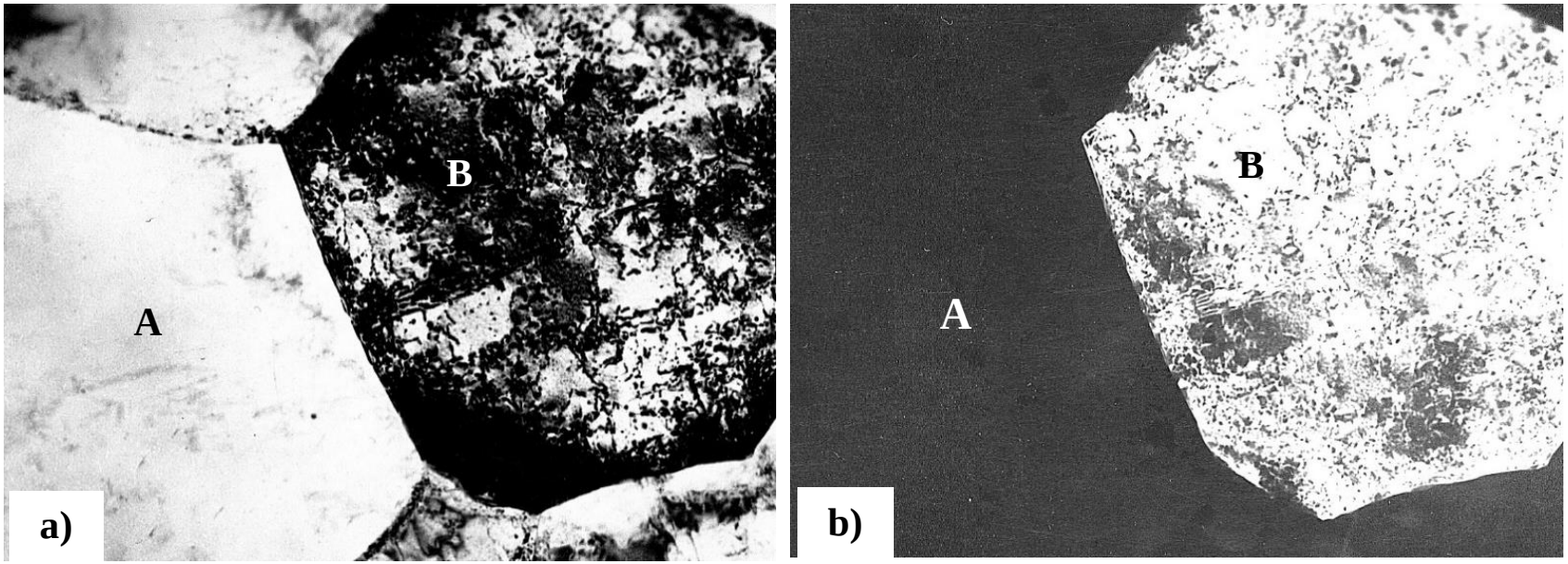
- Center dark-field imaging

The method that only allows the transmitted beam to pass through the objective aperture for imaging is called bright field imaging; if only the diffracted beam is allowed to pass through the objective aperture for imaging, it is called dark field imaging. During dark field imaging, the intensities of the electron beams imaging the A and B grains are respectively $I_A \approx 0$, $I_B \approx I_{hkl}$, so the B grain is bright, while the brightness of the A grain is approximately zero. The diffraction images of A and B grain morphology are shown in Figure. It can be seen that the contrast of the dark field image is significantly higher than that of the bright field image, which is one of the characteristics of dark field imaging.



9.7 Principle of thin crystal diffraction contrast imaging

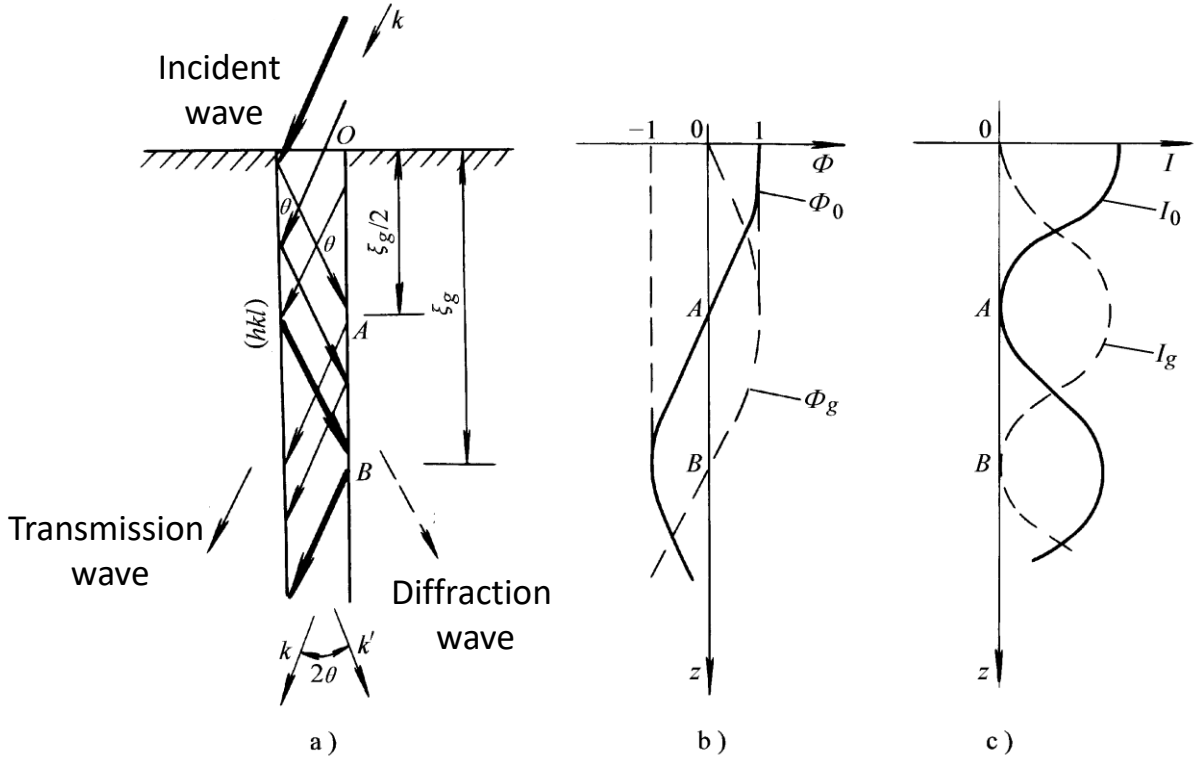
- Bright-field imaging and Center dark-field imaging



Contrast image of aluminum alloy grain morphology
a) bright field image b) central dark field image

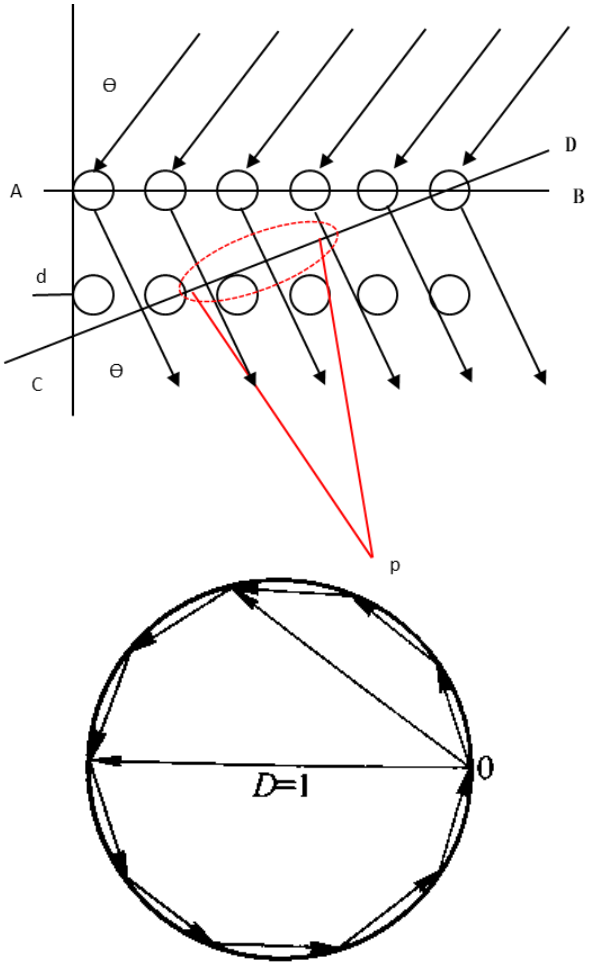
9.8 The theory of diffraction kinematics

Since atoms strongly scatter electrons, when the electron wave propagates in the sample, the amplitude and intensity will change periodically due to the interaction between the transmitted wave and the diffracted wave, as shown in Figure.



When the deviation parameter ***s*** = 0, the electron waves propagate in the depth direction within the crystal. **a**) Interaction of transmitted waves and diffracted waves **b**) Amplitude changes **c**) Intensity changes.

9.8 The theory of diffraction kinematics



Atomic Plane Scattering Amplitudes

Unit area of AB plane, diffraction wave amplitude nF_g, converted to CD plane, $nF_g / \cos\Theta$. Fresnel wave division banding method, the scattering amplitude of each layer of lattice $q = \lambda nF_g / \cos\Theta$

Suppose the scattering amplitudes of each layer of lattice planes are superimposed. In that case, we can find out how many layers of atoms the electron beam has been scattered by in the depth direction of the crystal before the diffraction amplitude reaches the maximum, which is exactly half of the extinction distance.

Returning to the origin after m layers, the diameter is $D = 1$ and the circumference is π. On the other hand: $mq=\pi$, $md=\zeta$; $\lambda nFg/\cos\Theta/d= \pi/\zeta$.

$$\xi_g = \frac{\pi d \cos\theta}{\lambda n F_g}$$

9.8 The theory of diffraction kinematics

When the deviation parameter s = 0, the periodic distance in which the diffraction wave intensity changes in the depth direction of the sample is called the extinction distance ξ_g.

$$\xi_g = \frac{\pi d \cos\theta}{\lambda n F_g}$$

In the formula, ***d*** is the interplanar spacing; ***n*** is the number of unit cells in the unit area on the atomic plane. ***1/n*** is the area of a unit cell, so the volume of the unit cell $V_c = d\,(1/n)$, substitute formula gives:

$$\xi_g = \frac{\pi V_c \cos\theta}{\lambda F_g}$$

In the formula, V_c is the unit cell volume; ϑ is the Bragg angle; F_g is the structure factor. The equation shows that the ξ_g value changes with the electron wavelength λ and Bragg angle ϑ.

9.8 The theory of diffraction kinematics

The extinction distance ξ_g values of several crystals are shown in the table.

Extinction distance values of several crystals under different accelerating voltages

Crystal	*hkl*	50kV	100kV	200kV	1000kV
Al	111	41	56	70	95
Fe	110	20	28	41	46
Zr		45	60	90	102

The extinction distance value of several crystals under 100kV

Crystal	*Z*	Lattice	*hkl*			
			110	111	200	211
Al	13	*fcc*		56	68	
Ag	47	*fcc*		24	27	
Au	79	*fcc*		18	20	
Fe	26	*bcc*	28		40	50

9.8 The theory of diffraction kinematics

- Contrast refers to the difference in intensity of each image point on the image plane, or the difference in brightness of each image point.

- In fact, the diffraction contrast is the difference in the intensity of the imaging electron beam at each image point on the image plane, which depends on the difference in the Bragg orientation of each point of the crystal film.

- The theory of diffraction kinematics is used to calculate the intensity of the diffracted beam and the transmitted beam at each point on the lower surface of the sample, that is, the intensity of the imaging electron beam at each image point on the image plane.

- The physical model of kinematics theory is relatively straightforward, and the derivation process of theoretical formulas is simple. Compared with the dynamic theory, kinetic theory is an approximate theory, and its application has certain limitations.

9.8 The theory of diffraction kinematics

- Basic assumptions and approximation methods

1) Basic assumptions

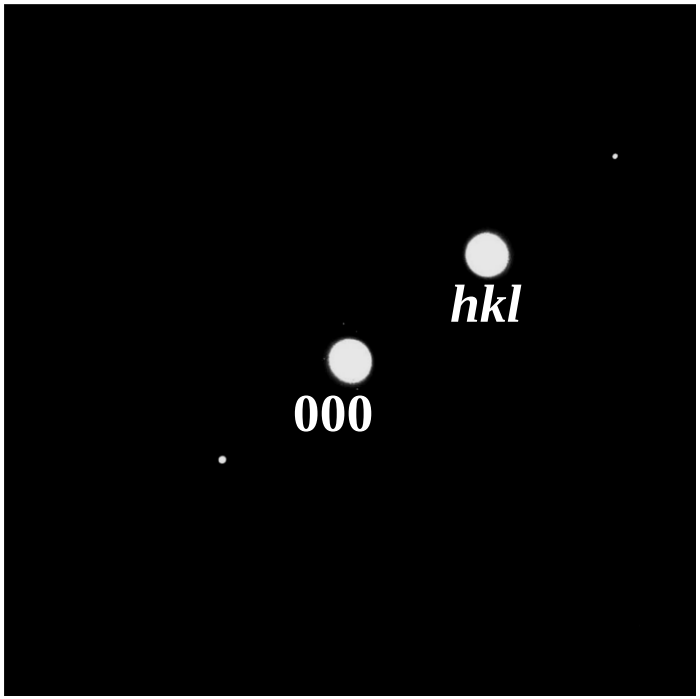
- The interaction between the transmitted and diffracted beams is not considered. This means that the intensity of the diffracted beam is always very small compared to the intensity of the transmitted beam. To satisfy this assumption, a larger deviation parameter ***s*** needs to be used during imaging.

- The absorption and multiple reflections of electron waves by crystal samples are not considered. This means that the electron wave is scattered no more than once during its passage through the sample. To meet this assumption, extremely thin samples must be used in the experiment.

9.8 The theory of diffraction kinematics

- Basic assumptions and approximation methods

2) Approximation methods



Double beam diffraction pattern

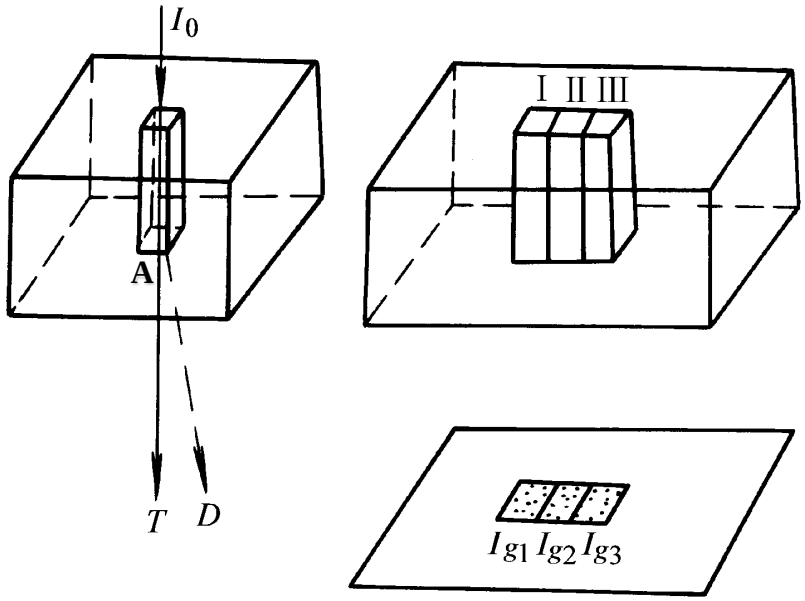
Although the intensity of the diffraction beam used for imaging is very small, it is still high enough compared with the intensity of the diffraction beam of other crystal planes. It can be seen that the diffraction intensity of other crystal planes is zero. In the diffraction pattern, there are only transmission spots and one diffraction spot, as shown in the Figure.

In this case, the transmitted beam intensity I_T and the diffracted beam intensity I_g approximately satisfy $I_0 = I_T + I_g = 1$. In the formula, $I_0 = 1$ is the incident beam intensity, which is the two-beam approximation.

9.8 The theory of diffraction kinematics

- Basic assumptions and approximation methods

2) Approximation methods

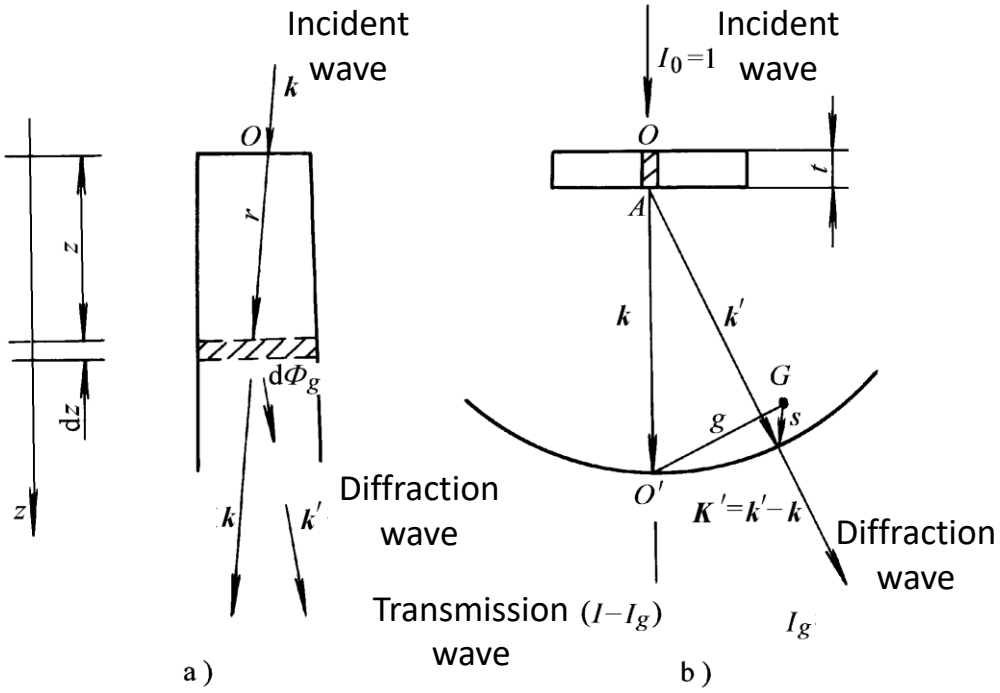


The diffracted beam intensity at a certain point A on the sample's lower surface is believed to come from the crystals' contribution in a cylinder. The method of selecting the cylinder is shown in the figure.

When calculating the diffraction intensity at point A, point A is taken as the center of the bottom surface of the cylinder. The cross-sectional size is equivalent to the size of the unit cell. When the cylinder penetrates the sample along the direction of the incident beam, a cylinder is taken with this point as the center when calculating the diffraction intensity at another point. And the diffraction waves between adjacent cylinders do not interfere with each other. This processing method is the cylinder approximation.

9.8 The theory of diffraction kinematics

- The diffraction intensity of an ideal crystal



Diffraction intensity of crystal column OA under kinematic conditions.

To calculate the diffraction intensity produced by cylinder OA in a crystal with thickness ***t***, first calculate the diffraction wave amplitude Φ_g at the lower surface of the cylinder.

Take a thickness element ***dz*** at the depth ***z*** in the cylinder, and the amplitude change of the diffraction wave caused by it is $d\Phi_g$, as shown in the figure.

$$d\Phi_g = \frac{\pi i}{\xi_g} e^{-2\pi i \boldsymbol{K}'\cdot\boldsymbol{r}} dz$$

Waves have amplitude and phase

9.8 The theory of diffraction kinematics

- The diffraction intensity of an ideal crystal

The diffraction amplitude $\boldsymbol{\Phi_g}$ at the lower surface of the crystal is equal to the superposition of the diffraction wave amplitudes of all thickness elements from the upper surface to the lower surface, that is:

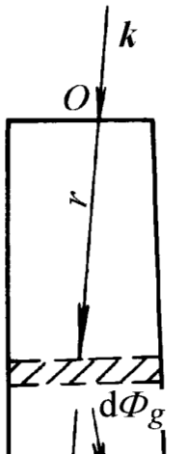
$$\Phi_g = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-2\pi \mathrm{i} \boldsymbol{K'} \cdot \boldsymbol{r}} \, \mathrm{d}\, z = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-\mathrm{i}\varphi} \, \mathrm{d}\, z$$

In the formula, $\boldsymbol{\varphi = 2\pi K' \cdot r}$ is the phase angle of the scattered wave at $\boldsymbol{r}$ relative to the scattered wave on the upper surface of the crystal. When deviating from the Bragg condition, the diffraction vector

$$\boldsymbol{K' = k' - k = g + s}$$

Since $\boldsymbol{g \cdot r}$ = integer, $\boldsymbol{s // r // z}$, and $\boldsymbol{r = z}$, the phase angle is expressed as:

$$\boldsymbol{\varphi = 2\pi K' \cdot r = 2\pi \, s \cdot r = 2\pi s z}$$



9.8 The theory of diffraction kinematics

- The diffraction intensity of an ideal crystal

Therefore, the diffracted wave amplitude at point A on the lower surface of the sample is:

$$\Phi_g = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-2\pi \mathrm{i} \boldsymbol{K}' \cdot \boldsymbol{r}} \, \mathrm{d}z = \frac{\pi \mathrm{i}}{\xi_g} \int_0^t \mathrm{e}^{-\mathrm{i}\varphi} \, \mathrm{d}z$$

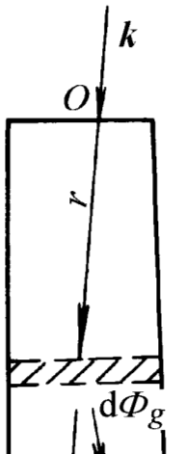
That is, the diffraction intensity is the square of the amplitude, from which the ideal crystal diffraction intensity formula is obtained.

$$\Phi_g = \frac{\pi \mathrm{i}}{\xi_g} \frac{\sin^2(\pi s t)}{\pi s} \mathrm{e}^{-\pi \mathrm{i} s t}$$

$$I_g = \Phi_g \cdot \Phi_g^* = \left(\frac{\pi}{\xi_g} \right)^2 \frac{\sin^2(\pi t s)}{(\pi s)^2}$$

The intensity of the transmitted wave can be approximately known:

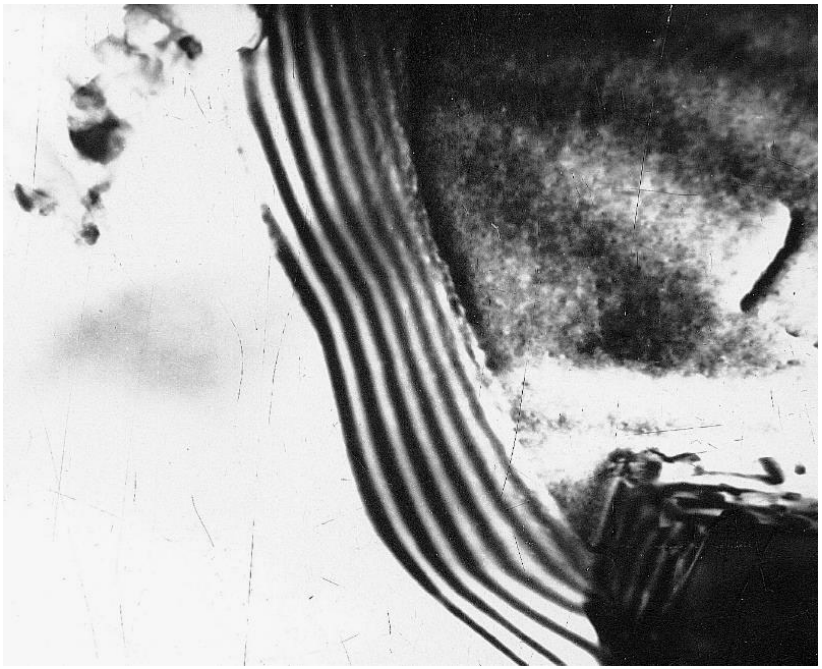
$$I_T = 1 - \left(\frac{\pi}{\xi_g} \right)^2 \frac{\sin^2(\pi t s)}{(\pi s)^2}$$



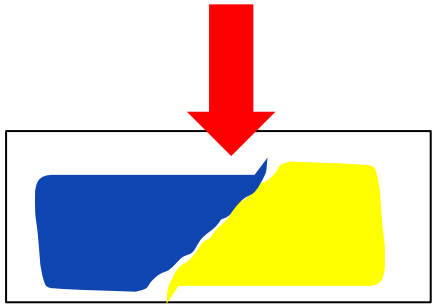
9.8 The theory of diffraction kinematics

- Application of basic equations of diffraction kinematics of ideal crystals

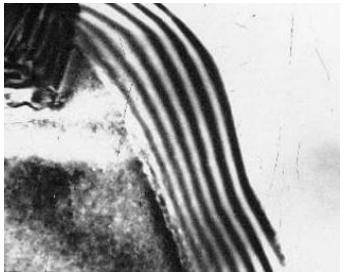
1. Equal-thickness fringes



Equal-thickness stripes at inclined grain boundaries.



Equal-thickness extinction fringes are a common contrast phenomenon. They often appear in wedge-shaped areas with continuously changing thicknesses at the **edge of holes** or **inclined grain boundaries**. They are characterized by alternating light and dark stripe contrast.



9.8 The theory of diffraction kinematics

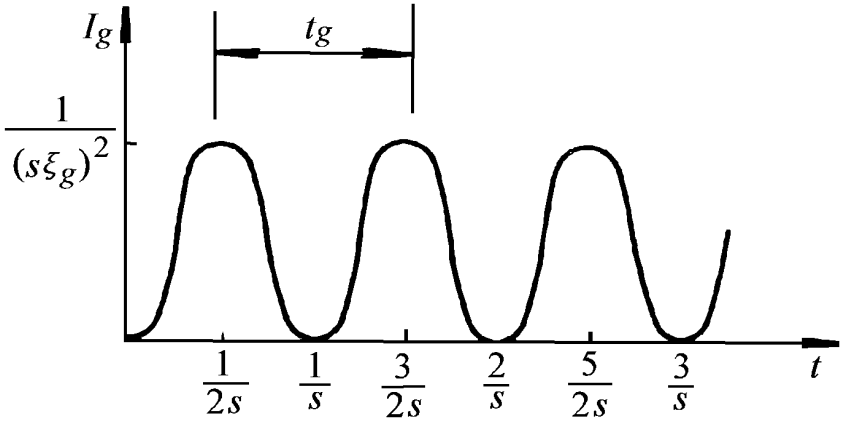
- Application of basic equations of diffraction kinematics of ideal crystals

1. Equal-thickness fringes

When the deviation parameter ***s*** is a constant, equation is rewritten as:

$$I_g = \Phi_g \cdot \Phi_g^* = \left(\frac{\pi}{\xi_g}\right)^2 \frac{\sin^2(\pi t s)}{(\pi s)^2} \quad \Rightarrow \quad I_g = \frac{1}{(s\xi_g)^2}\sin^2(\pi s t)$$

I_g changes periodically with the sample thickness ***t***. See Figure. The change period t_g is:

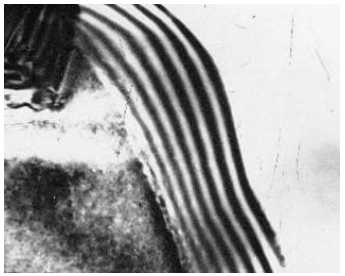


$t_g = 1/s$

When $t = n/s$, $I_g = 0$;

When $t = (2n+1)/2s$, I_g has a maximum value.

$$I_{g\max} = \frac{1}{(s\xi_g)^2}$$

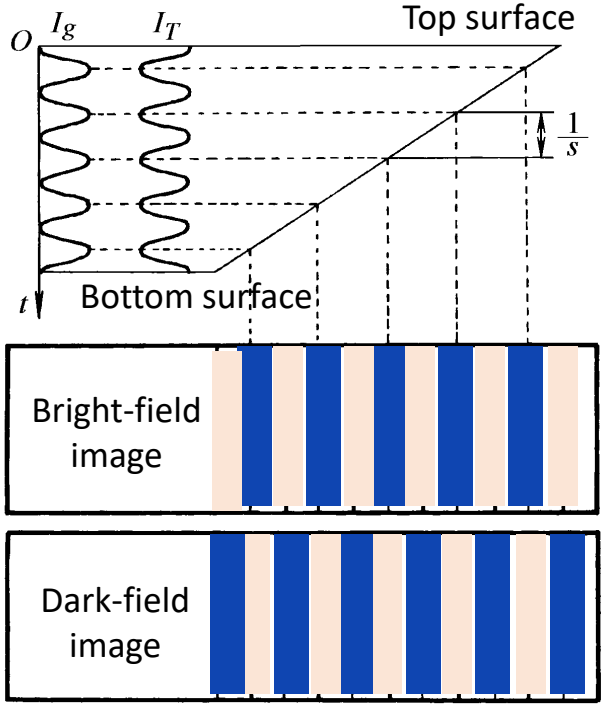


9.8 The theory of diffraction kinematics

- Application of basic equations of diffraction kinematics of ideal crystals

1. Equal-thickness fringes

Using the results of the periodic change of I_g with t, the equal-thickness fringes appearing at the wedge-shaped edge of the sample can be qualitatively explained. As shown in Figure, the thickness t of the wedge edge changes continuously, and I_g on the lower surface of the sample changes periodically with t.



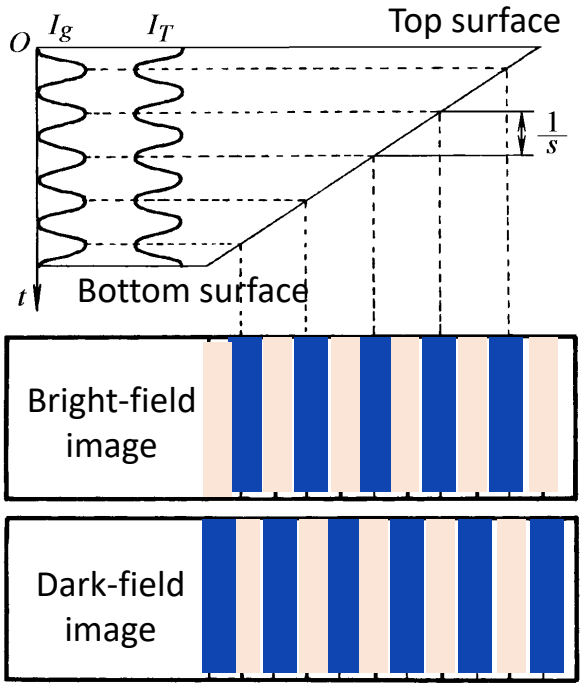
- At the edge, $t = 0$, $I_g = 0$, the corresponding position in the dark field image is dark stripes, and the bright field image is bright stripes.
- The diffraction intensity I_g at $t = (2n+1)/2s$ is the maximum value. The corresponding position in the dark field image is bright stripes, and the bright field image is dark stripes. This cycle creates a contrast of light and dark stripes.

9.8 The theory of diffraction kinematics

- Application of basic equations of diffraction kinematics of ideal crystals

1. Equal thickness fringes

As shown in Figure, it can be seen that in the bright-field image or dark-field image, the thickness ***t*** of the same bright stripe (or dark stripe) corresponding to the sample position is the same, so it is called an equal-thickness stripe. The spacing of stripes is proportional to the change period of ***1/s***, so the thickness ***t*** of the sample can be estimated by using the number ***n*** of equally thick stripes, that is, ***t = n /s***.

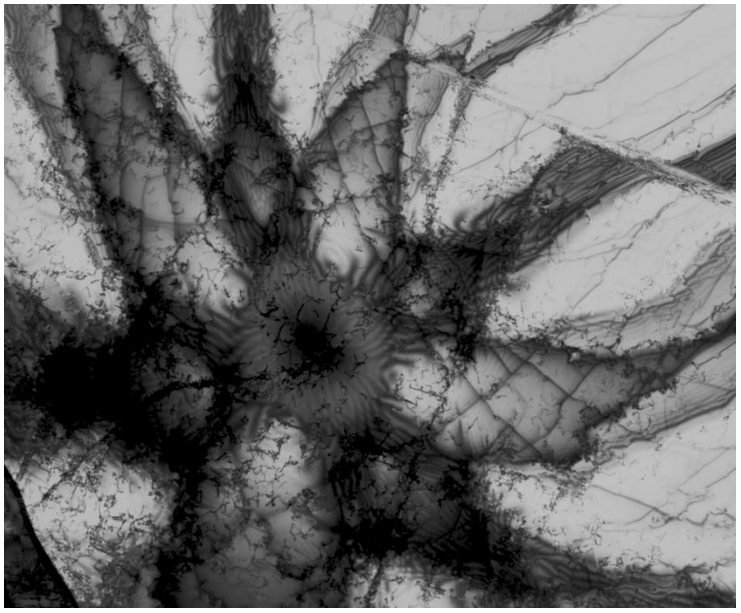


9.8 The theory of diffraction kinematics

- Application of basic equations of diffraction kinematics of ideal crystals

2. Equal-inclination fringes

Equal-inclination fringes are also a common contrast phenomenon. Since the **elastic bending** of the sample causes the appearance of such fringes, it is also called bending extinction fringes. Its contrast characteristics are shown in the figure below.



Contrast characteristics of equal-inclination fringes.

The following uses the theory of contrast kinematics to qualitatively explain the generation mechanism of equal-inclination fringes. Rewrite equation as

$$I_g = \Phi_g \cdot \Phi_g^* = \left(\frac{\pi}{\xi_g}\right)^2 \frac{\sin^2(\pi ts)}{(\pi s)^2}$$

$$I_g = \frac{(\pi t)^2}{\xi_g^2} \frac{\sin^2(\pi ts)}{(\pi ts)^2}$$

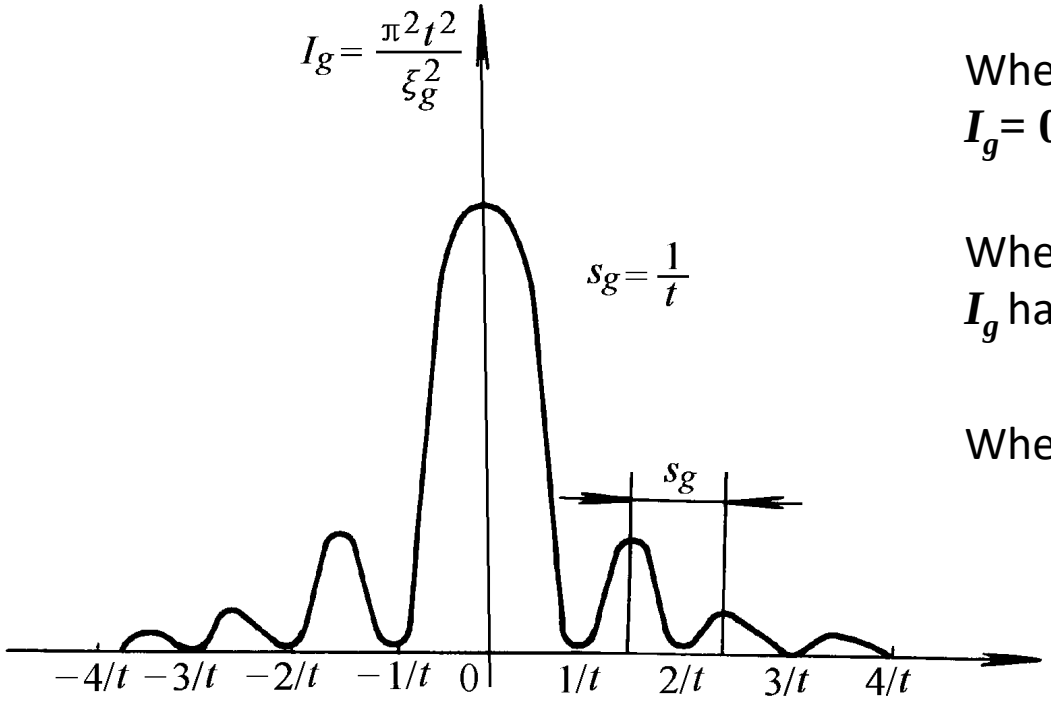
9.8 The theory of diffraction kinematics

$$I_g = \frac{(\pi t)^2}{\xi_g^2}\frac{\sin^2(\pi t s)}{(\pi t s)^2}$$

- Application of basic equations of diffraction kinematics of ideal crystals

2. Equal-inclination fringes

The equation shows that when ***t*** is a constant, I_g also changes with ***s***, and the change is shown in Figure below.



When $s = \pm 1/t, \pm 2/t, \pm 3/t, \ldots$
$I_g = 0$.

When $s = \pm 3/2t, \pm 5/2t, \pm 7/2t, \ldots$
I_g has extreme value.

When $s = 0$, I_g has the maximum value.

$$I_{g\max} = \frac{(\pi t)^2}{\xi_g^2}$$

Change of diffraction intensity I_g with deviation parameter ***s***.

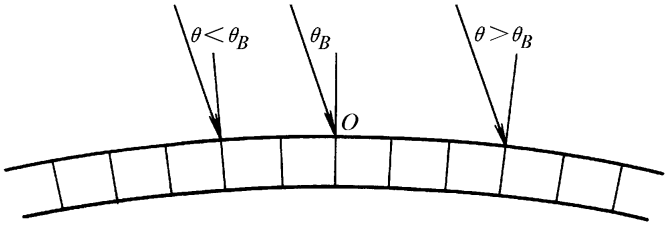
9.8 The theory of diffraction kinematics

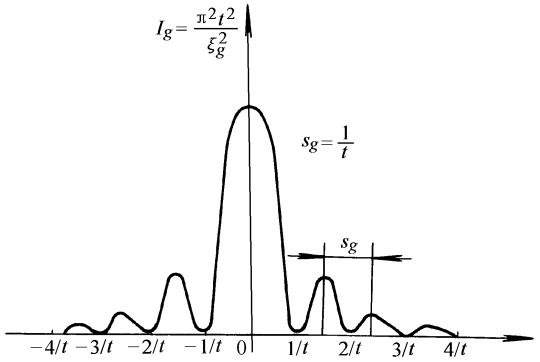
$$I_g = \frac{(\pi t)^2}{\xi_g^2}\frac{\sin^2(\pi t s)}{(\pi t s)^2}$$

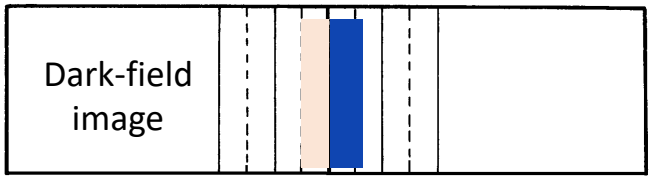
- Application of basic equations of diffraction kinematics of ideal crystals

2. Equal-inclination fringes

As shown in Figure, the diffraction crystal plane is deflected to both sides due to the elastic bending of the sample. Assume that the diffraction crystal plane at ***O*** is exactly in the Bragg orientation, $\theta = \theta_B$ $(s = 0)$; the signs of ***s*** on both sides of the ***O*** point are opposite, and $|s|$ continues to increase as the distance from the ***O*** point increases.







According to Figure, the change of I_g with ***s*** can be seen that at the sample position of $s = 0$, the diffraction intensity is maximum, and bright stripes appear here in the dark field image; on both sides, $I_g = 0$ and I_g takes an extreme value at different positions, dark and light stripes will appear one after another.

9.8 The theory of diffraction kinematics

- Application of basic equations of diffraction kinematics of ideal crystals

2. Equal-inclination fringes

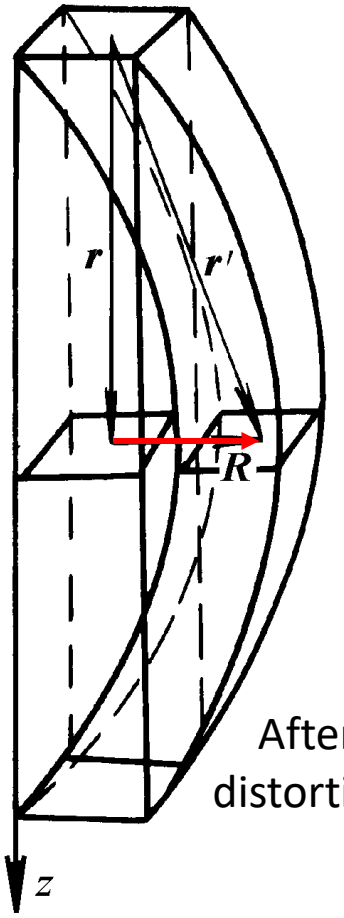
- From the above analysis, it can be seen that the same bright stripe (or dark stripe) corresponds to the position of the sample. Since the inclination angle of the diffraction crystal plane relative to the incident beam is the same (the s is the same), such stripes are called equal-inclination stripes.

- If the sample is elastically bent into a spherical surface, intersecting equal-inclination stripes will appear. When the sample is tilted, the position of the sample corresponding to $\boldsymbol{s = 0}$ will change. The position of equal-inclination fringes will also change accordingly, which is one of the characteristics.

- Because the degree of elastic bending of the sample in the observed area is very small, the degree of deviation $|\boldsymbol{s}|$ of the diffraction crystal plane is small, and the peak value of $\boldsymbol{I_g}$ decreases rapidly as $|\boldsymbol{s}|$ increases, so generally, only $\boldsymbol{s = 0}$ can be observed.

9.8 The theory of diffraction kinematics

- Diffraction intensity of non-ideal crystals



Before distortion

After distortion

The existence of crystal defects in non-ideal crystals will distort the crystal column, which can be expressed by the displacement vector ***R***.

The displacement vector of the undistorted crystal column is ***r***, and the displacement vector of the distorted crystal column is ***r'***.

$$\boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{R}$$

$$\varphi' = 2\pi \boldsymbol{K}' \cdot \boldsymbol{r}' = 2\pi(\boldsymbol{g} + \boldsymbol{s}) \cdot (\boldsymbol{r} + \boldsymbol{R})$$

Because $\boldsymbol{s} \cdot \boldsymbol{R} = 0$, then we have:

$$\varphi' = 2\pi sz + 2\pi \boldsymbol{g} \cdot \boldsymbol{R} = \varphi + \alpha$$

$\alpha = 2\pi \boldsymbol{g} \cdot \boldsymbol{R}$ called additional phase angle

$$\Phi_g = \frac{\pi \mathrm{i}}{\xi_g} \sum_{\cdot} \mathrm{e}^{-\mathrm{i}(\varphi+\alpha)} \, \mathrm{d}z$$

9.8 The theory of diffraction kinematics

- Diffraction intensity of non-ideal crystals

$$\Phi_g = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-\mathrm{i}(\varphi+\alpha)} \mathrm{d}z \qquad \Phi_g = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-2\pi \mathrm{i} \boldsymbol{K}' \cdot \boldsymbol{r}} \mathrm{d}z = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-\mathrm{i}\varphi} \mathrm{d}z$$

In the equation, $\mathbf{e}^{-\mathrm{i}\alpha} = \mathbf{e}^{-2\pi \mathrm{i}\, \boldsymbol{g}\cdot\boldsymbol{R}}$ is called the additional phase factor. An additional phase factor is introduced in the expression of the diffraction wave amplitude of a non-ideal crystal, which may cause the amplitude of the diffraction wave at the defect location to be different from that of the crystal at the non-defect location. Defects lead to display contrast.

- If the additional phase angle α caused by the defect is an integer multiple of 2π, the additional phase factor is 1 and does not affect the diffraction intensity. At this time, the defect does not show diffraction contrast.

- If the additional phase angle α caused by the defect is not an integer multiple of 2π, the additional phase factor is not equal to 1, and the existence of the defect contributes to the diffraction intensity. At this time, the defect will contrast differently from that without the defect.

9.9 Introduction to diffraction dynamics

- The kinematics theory is established on the premise of two basic assumptions. There are still some shortcomings, and it cannot explain some contrast phenomena perfectly.

- According to the kinematic theory, the variation period of the diffraction beam intensity of the sample is (**1/s**), and the spacing of equal-thickness extinction fringes is proportional to ***1/s***. When ***s→0***, the stripe spacing will tend to infinity.

- This is not the actual situation. Even when ***s*** = 0, the fringe spacing is still a finite value. At this time, it is proportional to the extinction distance ξ_g.

- The above situation shows that the kinematic theory is not applicable in some cases, or the experimental conditions do not meet the requirements of the basic assumptions of the kinematic theory.

- The fundamental difference between dynamics and kinematics theory is that **dynamics theory considers the interaction of transmission beams and diffracted beams**; it still uses two processing methods: double-beam approximation and cylinder approximation.

9.9 Introduction to diffraction dynamics

$$I_g = \frac{(\pi t)^2}{\xi_g^2}\frac{\sin^2(\pi t s)}{(\pi t s)^2}$$

- The shortcomings and scope of application of kinematics theory

The diffraction intensity formula derived from the kinematic theory is:

When $s = 0$, I_g has the maximum value. $I_{g\max} = \left(\frac{\pi t}{\xi_g}\right)^2$

When $t > \xi_g/\pi$, the $I_{g\max} > 1$, I_g will exceed the incident beam intensity (I_0=1).
It's wrong. To satisfy the kinematic assumptions, the thickness of the sample should:

$$t << \xi_g/\pi$$

That is, kinematic theory is applicable to extremely thin samples.

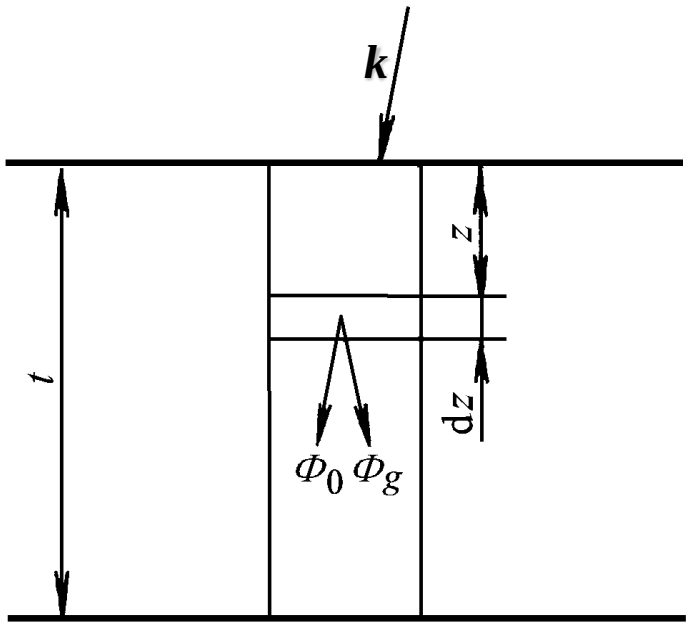
When s = constant, $t = (2n+1)/2s$, I_g have a maximum values: $I_{g\max} = \frac{1}{(s\xi_g)^2}$

If $|s\xi_g| < 1$, $I_{g\max} > 1$, false results for exceeding the incident beam intensity can also occur. Therefore, kinematic theory requires $|s\xi_g| >> 1$, so $|s| >> 1/\xi_g$. That is, the kinematic theory is suitable for larger deviation parameters.

9.9 Introduction to diffraction dynamics

- The kinetic equations of crystals

As shown in the figure, ***k*** is the incident wave vector. Assume that the **transmitted wave** and the **diffracted wave** pass through the thickness element ***dz*** in the cylinder, and the amplitude changes $\mathbf{d}\Phi_0$ and $\mathbf{d}\Phi_g$ caused are:



$$\left.\begin{aligned}\frac{\mathrm{d}\Phi_0}{\mathrm{d}z} &= \frac{\pi i}{\xi_0}\Phi_0 + \frac{\pi i}{\xi_g}\Phi_g\,\mathrm{e}^{2\pi i s z}\\ \frac{\mathrm{d}\Phi_g}{\mathrm{d}z} &= \frac{\pi i}{\xi_0}\Phi_g + \frac{\pi i}{\xi_g}\Phi_0\,\mathrm{e}^{-2\pi i s z}\end{aligned}\right\}$$

In the formula, ξ_0 is a parameter similar to ξ_g.

The formula shows that the diffracted wave contributes to the change in the amplitude of the transmitted wave and the change in the amplitude of the diffracted wave is also contributed by the transmitted wave, which is the result of the interaction of the two waves, the transmitted wave and the diffracted wave.

9.9 Introduction to diffraction dynamics

- The kinetic equations of crystals

By substituting the equations and using boundary conditions, the amplitudes of the transmitted and diffracted waves at the lower surface of the sample can be obtained.

$$\left.\begin{aligned}\Phi_0 &= \cos\left(\frac{\pi t\sqrt{1+\omega^2}}{\xi_g}\right) - \frac{i\omega}{\sqrt{1+\omega^2}}\sin\left(\frac{\pi t\sqrt{1+\omega^2}}{\xi_g}\right)\\ \Phi_g &= \frac{i}{\sqrt{1+\omega^2}}\sin\left(\frac{\pi t\sqrt{1+\omega^2}}{\xi_g}\right)\end{aligned}\right\}$$

The formula $\omega = s\xi_g$ indicates the degree to which the diffraction crystal plane deviates from the Bragg condition, and the effective deviation parameter s_{eff} is introduced.

$$s_{eff} = \frac{\sqrt{1+\omega^2}}{\xi_g} = \sqrt{s^2 + \xi_g^{-2}}$$

9.9 Introduction to diffraction dynamics

- The kinetic equations of crystals

The complete crystal diffraction intensity formula under dynamic conditions can be obtained.

$$I_g = \left(\frac{\pi}{\xi_g}\right)^2 \frac{\sin^2(\pi t s_{eff})}{(\pi s_{eff})^2} \qquad s_{eff} = \frac{\sqrt{1+\omega^2}}{\xi_g} = \sqrt{s^2 + \xi_g^{-2}}$$

The formula has the same form as the diffraction intensity formula derived from kinematic theory.

$$I_g = \Phi_g \cdot \Phi_g^* = \left(\frac{\pi}{\xi_g}\right)^2 \frac{\sin^2(\pi t s)}{(\pi s)^2}$$

1) When $s = 0$, $I_g = \sin^2(\pi t / \xi_g) \leq 1$, which will not exceed the incident beam intensity.

2) When $s = 0$, the change period of I_g in the depth direction of the sample is ξ_g, and the spacing between equal-thickness stripes is a finite value.

3) When $s >> 1/\xi_g$, $s_{eff} \approx s$, the kinematic results can be obtained from the dynamic diffraction intensity formula. The kinematic theory is an approximation of the dynamic theory under specific conditions.

9.8 The theory of diffraction kinematics

- Diffraction intensity of non-ideal crystals

$$\Phi_g = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-\mathrm{i}(\varphi+\alpha)} \mathrm{d}z \qquad \Phi_g = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-2\pi \mathrm{i} \boldsymbol{K}' \cdot \boldsymbol{r}} \mathrm{d}z = \frac{\pi \mathrm{i}}{\xi_g} \sum \mathrm{e}^{-\mathrm{i}\varphi} \mathrm{d}z$$

In the equation, $\mathbf{e}^{-\mathrm{i}\alpha} = \mathbf{e}^{-2\pi \mathrm{i}\, \boldsymbol{g}\cdot\boldsymbol{R}}$ is called the additional phase factor. An additional phase factor is introduced in the expression of the diffraction wave amplitude of a non-ideal crystal, which may cause the amplitude of the diffraction wave at the defect location to be different from that of the crystal at the non-defect location. Defects lead to display contrast.

- If the additional phase angle α caused by the defect is an integer multiple of 2π, the additional phase factor is 1 and does not affect the diffraction intensity. At this time, the defect does not show diffraction contrast.

- If the additional phase angle α caused by the defect is not an integer multiple of 2π, the additional phase factor is not equal to 1, and the existence of the defect contributes to the diffraction intensity. At this time, the defect will contrast differently from that without the defect.

9.10 Crystal defect analysis

As mentioned before, when the additional phase angle ($\boldsymbol{\alpha = 2\pi\, g\cdot R}$) caused by defects is an integer multiple of $\boldsymbol{2\pi}$, the additional phase factor $\boldsymbol{e^{-i\alpha} = e^{-2\pi i\, g\cdot R}}$ equals 1 and does not affect the diffraction intensity. , at this time, the defect does not show diffraction contrast and is called invisible.

$$\boldsymbol{g\cdot R = N} \text{ (Integrator)}$$

When the defect type is certain (***R*** is certain), the defects may show different contrasts due to the selection of different operating reflection ***g*** for imaging; when the operating reflection ***g*** used for imaging is selected, different types of defects (different R) may also appear.

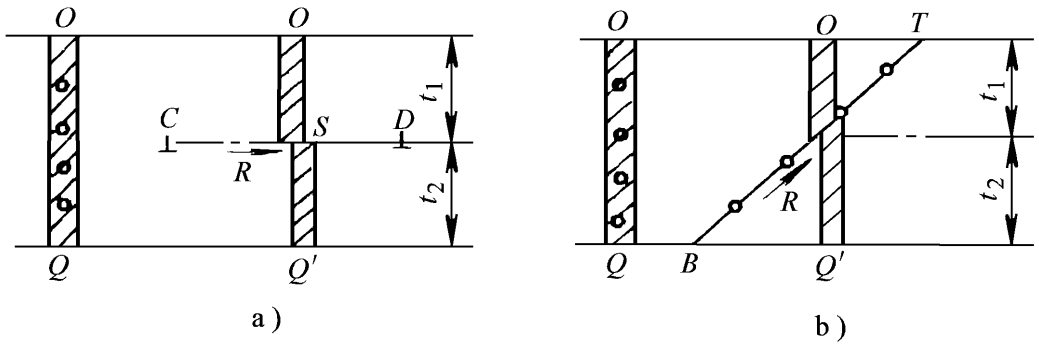
In particular, when $\boldsymbol{g\cdot R = 0}$, $\boldsymbol{R \perp g}$, the displacement vector ***R*** is within the diffraction crystal plane (***hkl***) corresponding to ***g***, and the existence of defects does not affect the orientation and spacing of the crystal plane, nor does it affect its diffraction intensity. The defect does not show contrast.

9.10 Crystal defect analysis

- Stacking fault

Stacking faults often exist in face-centered cubic or close-packed hexagonal crystals with low stacking fault energy. The stacking order of the close-packed faces has a problem, called stacking faults.

The orientation of the crystals on the upper and lower parts of the stacking fault is the same, but there is a relative constant displacement $\boldsymbol{R}$, see Figure. In a face-centered cubic crystal, the stacking fault plane is {111}, and the displacement vector is $\boldsymbol{R}_1 = \pm\frac{1}{3}\langle 111\rangle$ or $\boldsymbol{R}_2 = \pm\frac{2}{6}\langle 112\rangle$. The additional phase angle $\alpha = 2\pi\, \boldsymbol{g}\cdot\boldsymbol{R}$ they cause can only be 0 or $\pm 2\pi/3$ within the main value range.



When $\alpha = 0$, stacking faults do not show contrast.

When $\alpha = \pm 2\pi/3$, the contrast between stacking faults and the area without stacking faults is different.

9.10 Crystal defect analysis

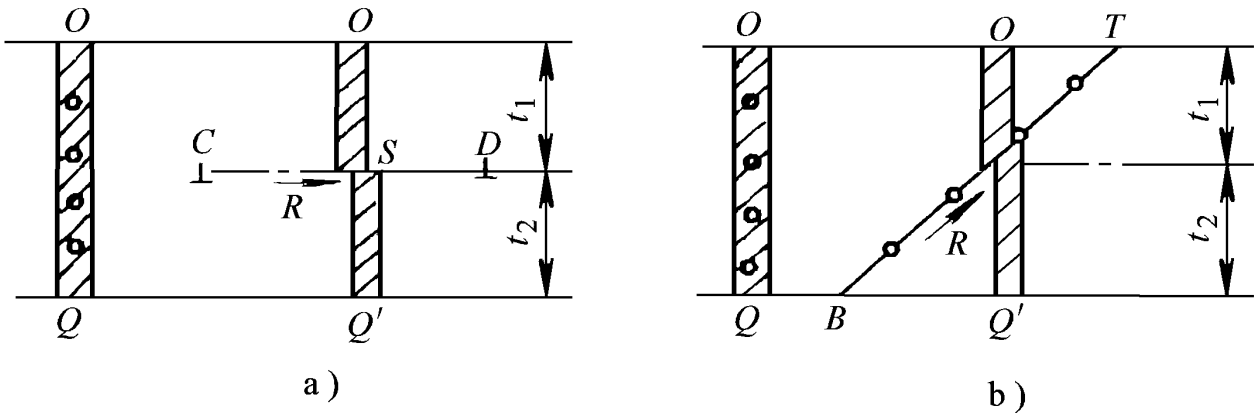
- Stacking fault

1. Stacking faults parallel to the film surface

As shown in Figure **a**, the stacking fault plane CD is parallel to the film surface. If the additional phase angle α caused by it is $2\pi/3$ or $-2\pi/3$, the stacking fault will show contrast.

2. Stacking faults inclined to the film surface

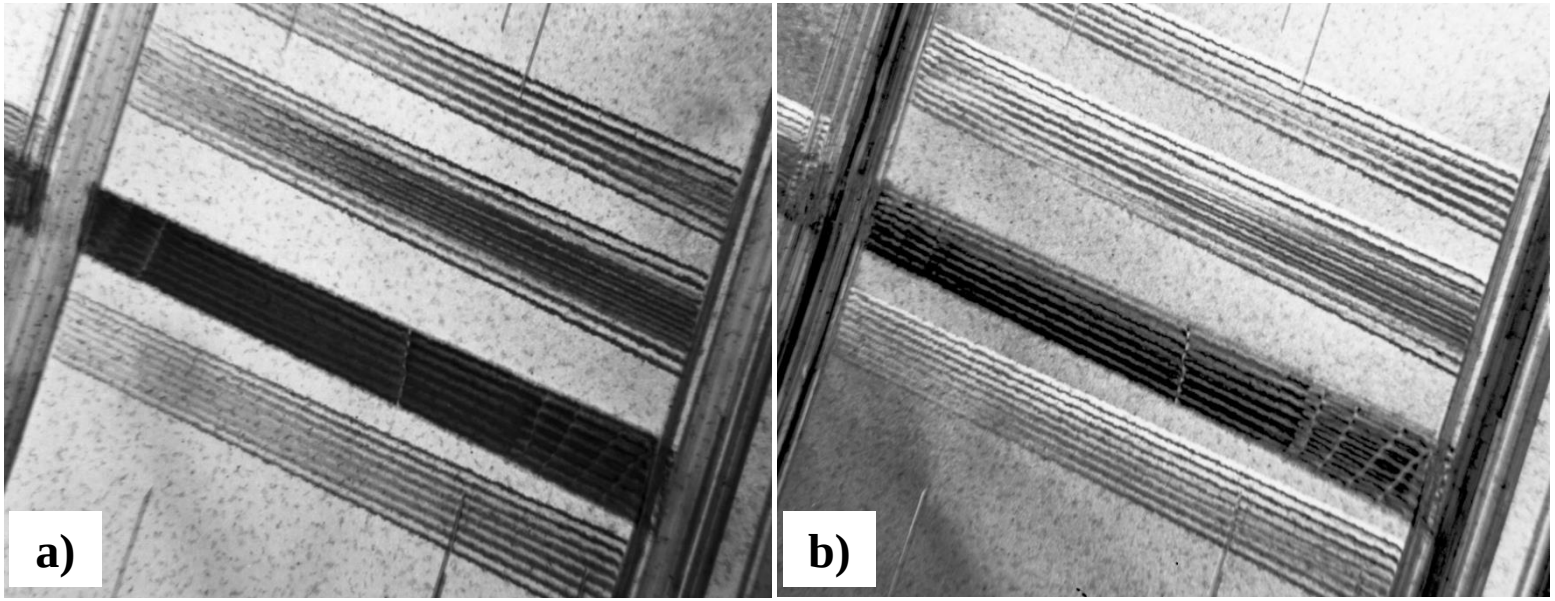
As shown in Figure **b**, the stacking fault plane TB is inclined to the film surface. When the additional phase angle α caused by it is $2\pi/3$ or $-2\pi/3$, the stacking fault will show contrast, and its contrast characteristics are: Alternating light and dark stripes.



9.10 Crystal defect analysis

- Stacking fault

For stacking faults that are inclined to the film surface, the contrast characteristics of the bright and dark field images are the contrast of bright and dark stripes parallel to the intersection of the stacking fault plane and the film surface. The contrast of the outer stripes in the bright field image is the same, while the contrast of the outer stripes in the dark field image is opposite, as shown in the figure below.

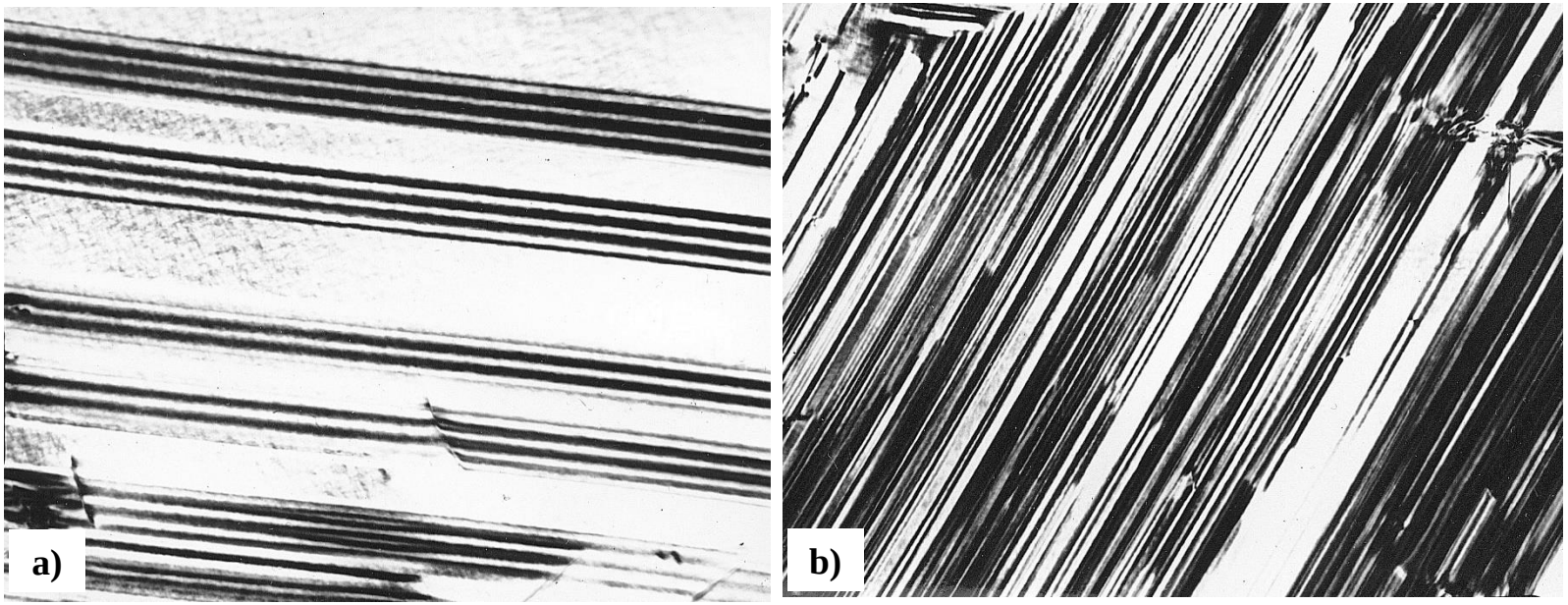


Bright-field Dark-field

9.10 Crystal defect analysis

- Stacking fault

When the stacking fault density in the crystal is high, the electron beam will pass through multiple stacking fault planes when propagating in the sample. At this time, its contrast depends on the sum of the additional phase angles caused by these stacking faults. The morphological characteristics are shown in the figure.



Morphology of high-density stacking faults in alloys

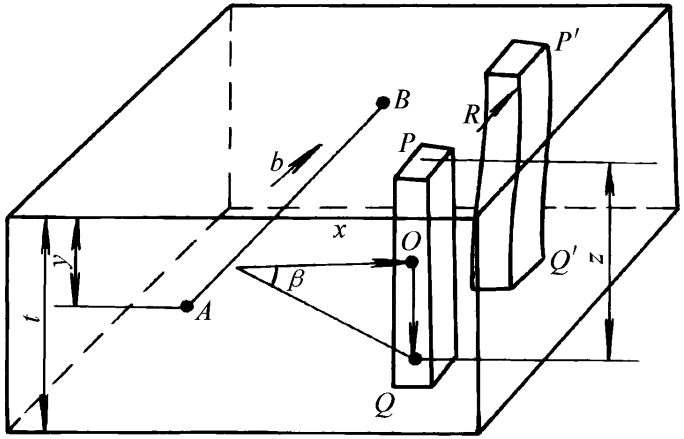
9.10 Crystal defect analysis

- Dislocation

The displacement vector ***R*** of the screw dislocation is parallel to the Brinell vector ***b***, that is,

$$\boldsymbol{R} = (\beta/2\pi)\,\boldsymbol{b}$$

In the formula, β is the helix angle. For screw dislocation, $\boldsymbol{g}\cdot\boldsymbol{R} = (\beta/2\pi)\boldsymbol{g}\cdot\boldsymbol{b}$. It can be seen that $\boldsymbol{g}\cdot\boldsymbol{R}$ generally cannot be a non-zero integer, so when $\boldsymbol{g}\cdot\boldsymbol{b} = \boldsymbol{0}$, the dislocation is not visible.



For edge or mixed dislocations, only residual contrast exists. When $\boldsymbol{g}\cdot\boldsymbol{b} = \boldsymbol{0}$ is satisfied and can be regarded as invisible.

9.10 Crystal defect analysis

- Dislocation

The Brinell vector $\boldsymbol{b}$ of the dislocation can be determined using the invisibility criterion. The principle of the method is as follows:

When the dislocation line is invisible, it meets the invisible criterion of $\boldsymbol{g} \cdot \boldsymbol{b} = \boldsymbol{0}$. At this time, $\boldsymbol{b} \perp \boldsymbol{g}$, $\boldsymbol{b}$ is located in the diffraction crystal plane ($\boldsymbol{hkl}$) corresponding to $\boldsymbol{g}$.

If two operations of reflection imaging are selected respectively to make the dislocation lines invisible, then it satisfies:

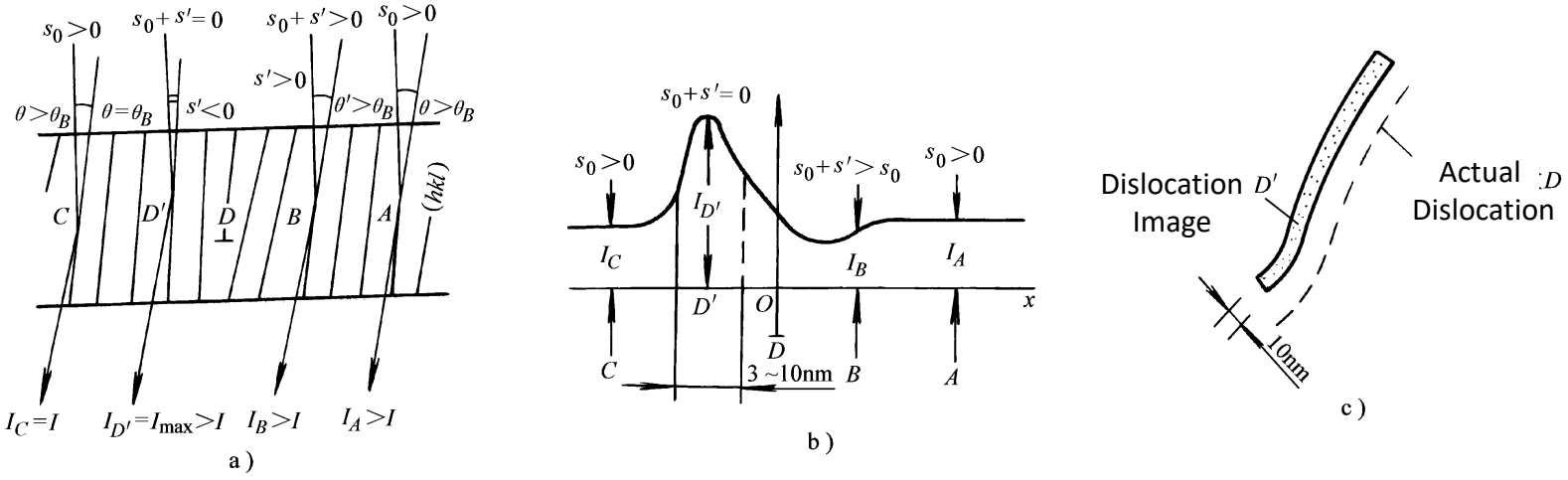
$$\begin{cases} \boldsymbol{g_1} \cdot \boldsymbol{b} = \boldsymbol{0} \\ \boldsymbol{g_2} \cdot \boldsymbol{b} = \boldsymbol{0} \end{cases}$$

It shows that $\boldsymbol{b}$ is parallel to the intersection line of the crystal planes ($\boldsymbol{h_1k_1l_1}$) and ($\boldsymbol{h_2k_2l_2}$) corresponding to $\boldsymbol{g_1}$ and $\boldsymbol{g_2}$. The simultaneous equation can calculate the direction of the dislocation Brinell vector $\boldsymbol{b}$.

9.10 Crystal defect analysis

- Dislocation

When $\boldsymbol{g \cdot b \neq 0}$, the dislocation line shows contrast. The following takes ductile dislocation as an example to illustrate the generation and characteristics of contrast, see Figure. The half-atom plane inserted at the dislocation line D is (***hkl***). Due to local distortion, the (***hkl***) orientations on both sides are deflected in the opposite direction, and an additional deviation parameter $\boldsymbol{s'}$ is introduced. On the left side of the dislocation line $\boldsymbol{s' < 0}$, on the right side of the dislocation line $\boldsymbol{s' > 0}$, as shown in Figure a.

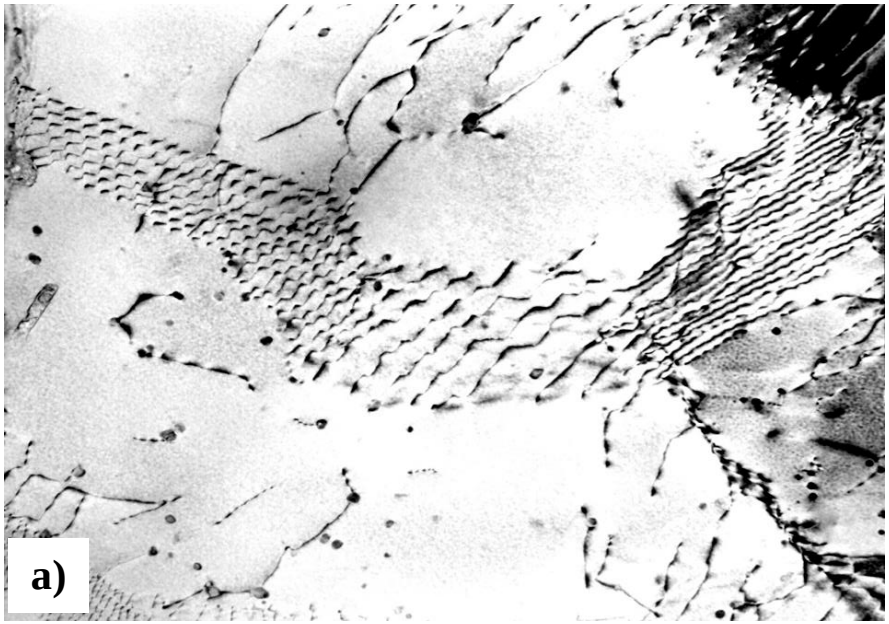


The generation and characteristics of edge dislocation contrast

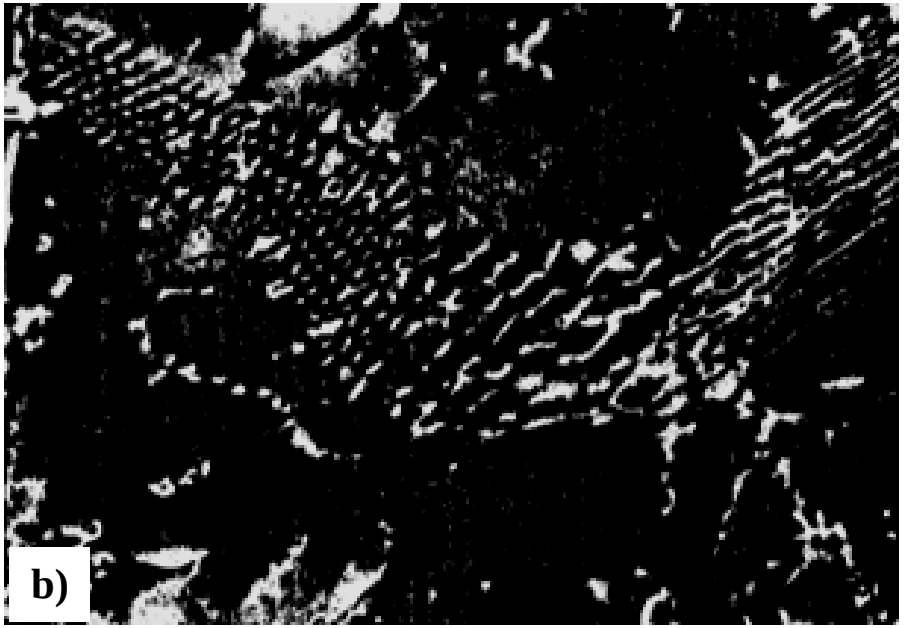
9.10 Crystal defect analysis

- Dislocation

Because a certain position near the dislocation line satisfies the Bragg condition and obtains the highest diffraction intensity, the dislocation image appears as dark lines in the bright field image, and the dislocation image appears as bright lines in the dark field image, as shown in the figure.



Bright-field

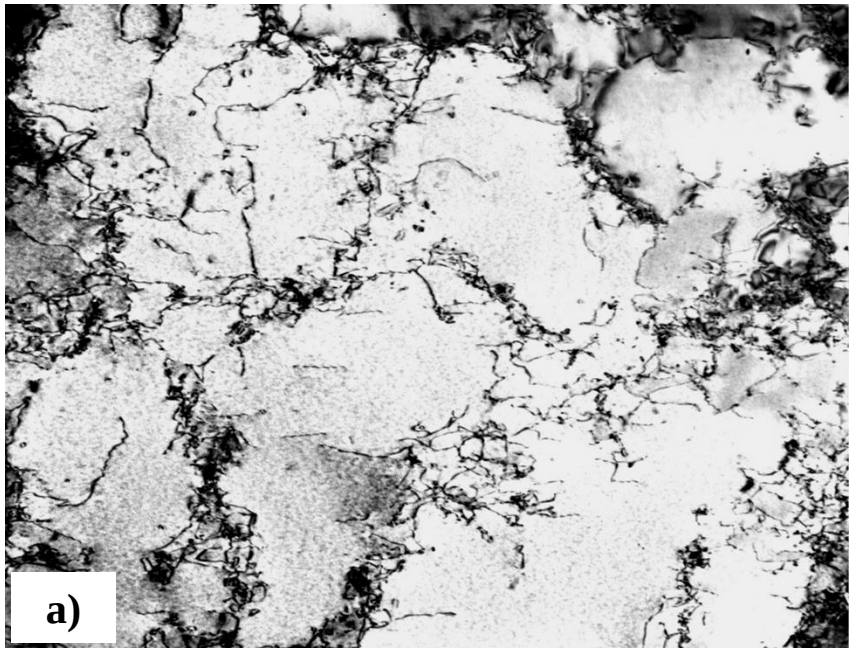


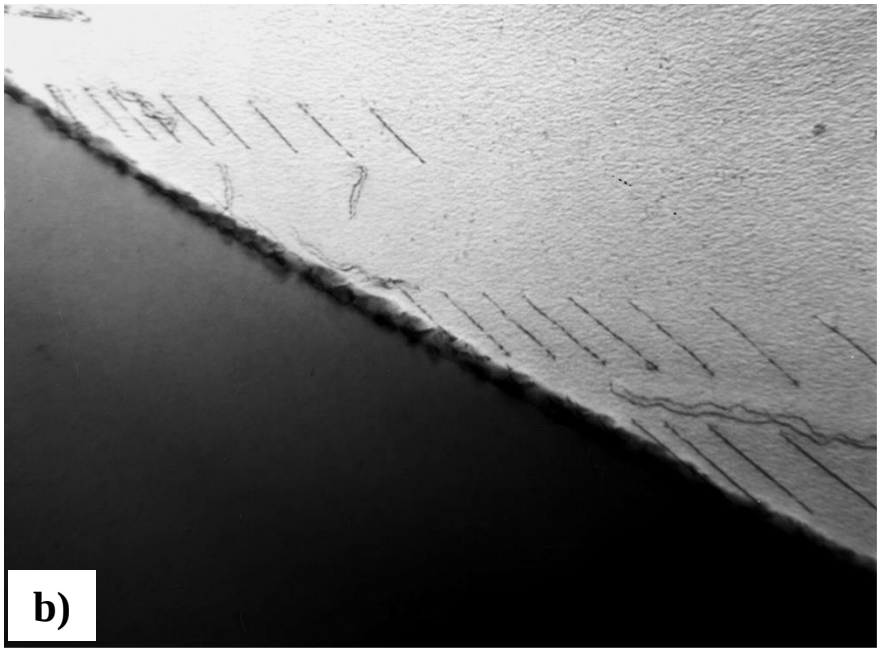
Dark-field

9.10 Crystal defect analysis

- Dislocation

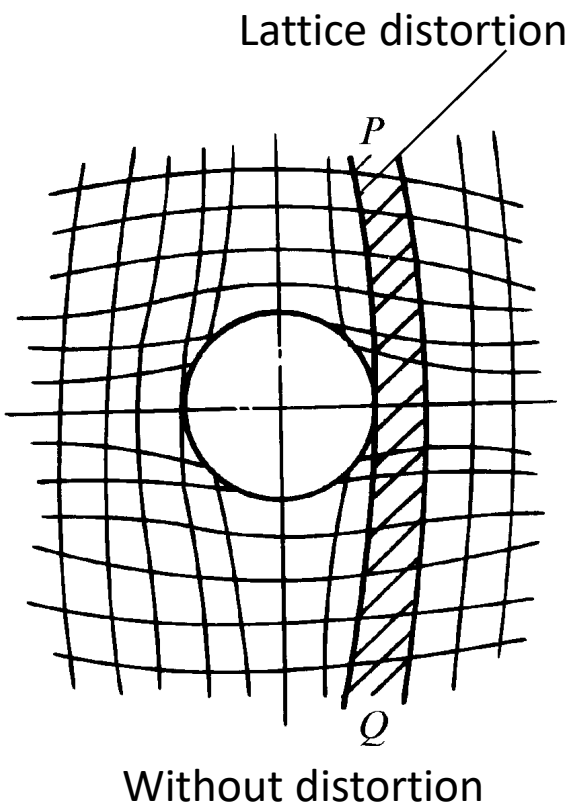
Figure **a** shows the dislocation cells formed due to dislocation entanglement during the metal deformation process.
Figure **b** shows dislocation plugging caused by dislocation glide hindered by grain boundaries.





9.10 Crystal defect analysis

- Second-phase particles



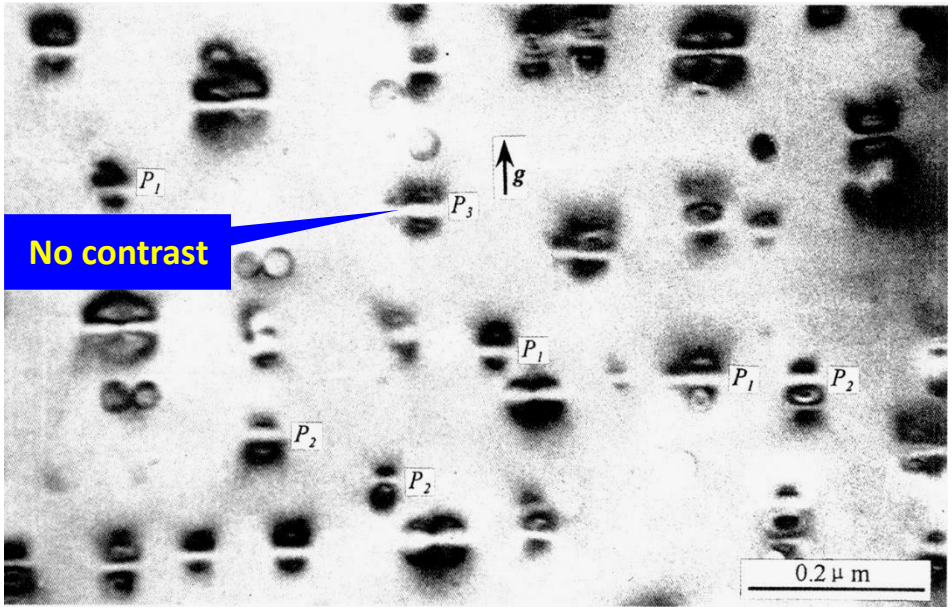
When the second phase particles and the matrix remain coherent or semi-coherent and have a degree of mismatch, the matrix near the phase interface will produce lattice distortion, see Figure.

This distortion can also be described by the displacement vector ***R*** of the defect, which will produce a contrast similar to crystal defects.

Strain contrast is relatively complex, and its characteristics depend on the shape of the second-phase particles and the intensity distribution of the strain field.

9.10 Crystal defect analysis

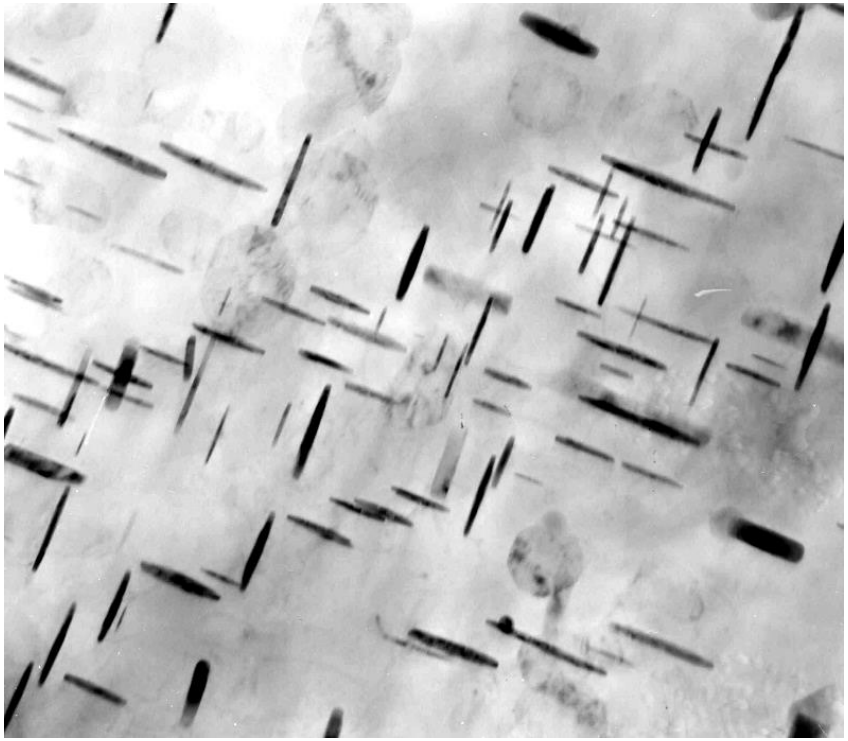
- Second-phase particles



As shown in the figure, the strain contrast of spherical particles is butterfly-shaped, and there is always a non-contrast line in the middle. The direction of the non-contrast line is perpendicular to the operating reflection ***g***, which means that the displacement vector ***R*** at the corresponding position is perpendicular to the operating reflection ***g***, so Satisfies $\boldsymbol{g}\cdot\boldsymbol{R}=\boldsymbol{0}$ without showing contrast. If the direction of the operating reflection ***g*** is changed, the direction of the no-contrast line will also change and always remain perpendicular to the operating reflection ***g***. This is the main feature of the strain contrast of spherical particles.

9.10 Crystal defect analysis

- Second-phase particles



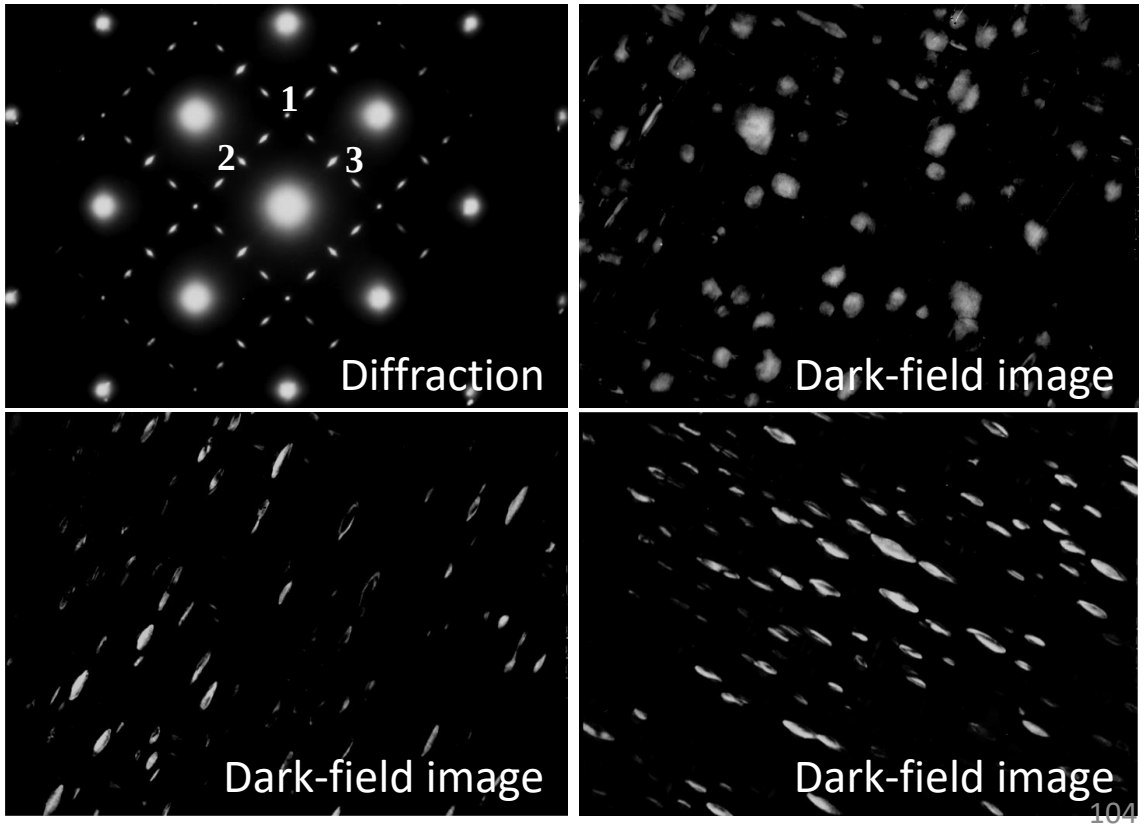
1) Orientation contrast: The contrast caused by the difference in the degree of Bragg conditions between the second phase and the matrix, resulting in the difference in diffraction beam intensity, is called orientation contrast. Orientation contrast is characterized by a second phase that appears uniformly bright or dark. The crystal structure of this second phase is usually quite different from the matrix, and its diffraction spots will appear. The diffraction beam of the second phase forms a dark field image to show the morphology of the second phase. This is a commonly used analysis technique.

9.10 Crystal defect analysis

- Second-phase particles

1) Orientation contrast

As shown in Figure, the dark field image obtained using three diffraction beams of γ″ phases with different orientations shows the shape, size, and distribution of γ″ phases with different orientations.

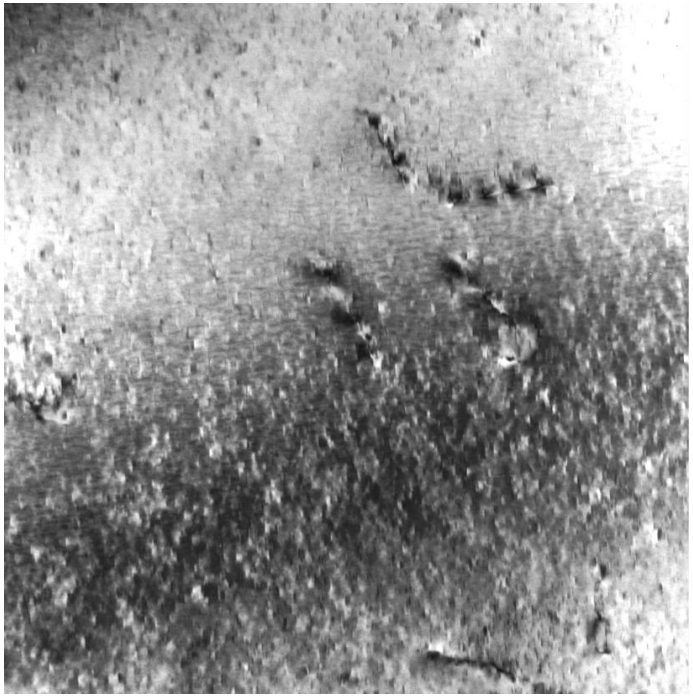


9.10 Crystal defect analysis

- Second-phase particles

2) structure factor contrast

When there is a difference in the structure factors of the second phase and the matrix, it will also lead to a difference in the intensity of the diffraction beam. The second phase shows a contrast different from the matrix, called structure factor contrast. The second phase shows the contrast of the structure factor—the same crystal structure as the matrix, such as G.P. regions and fine-ordered domains.



The picture is the diffraction contrast image of the G.P. zone in aluminum alloy. The fine particles dispersed in the photo are the G.P. zone, and the source of contrast is the structure factor contrast.