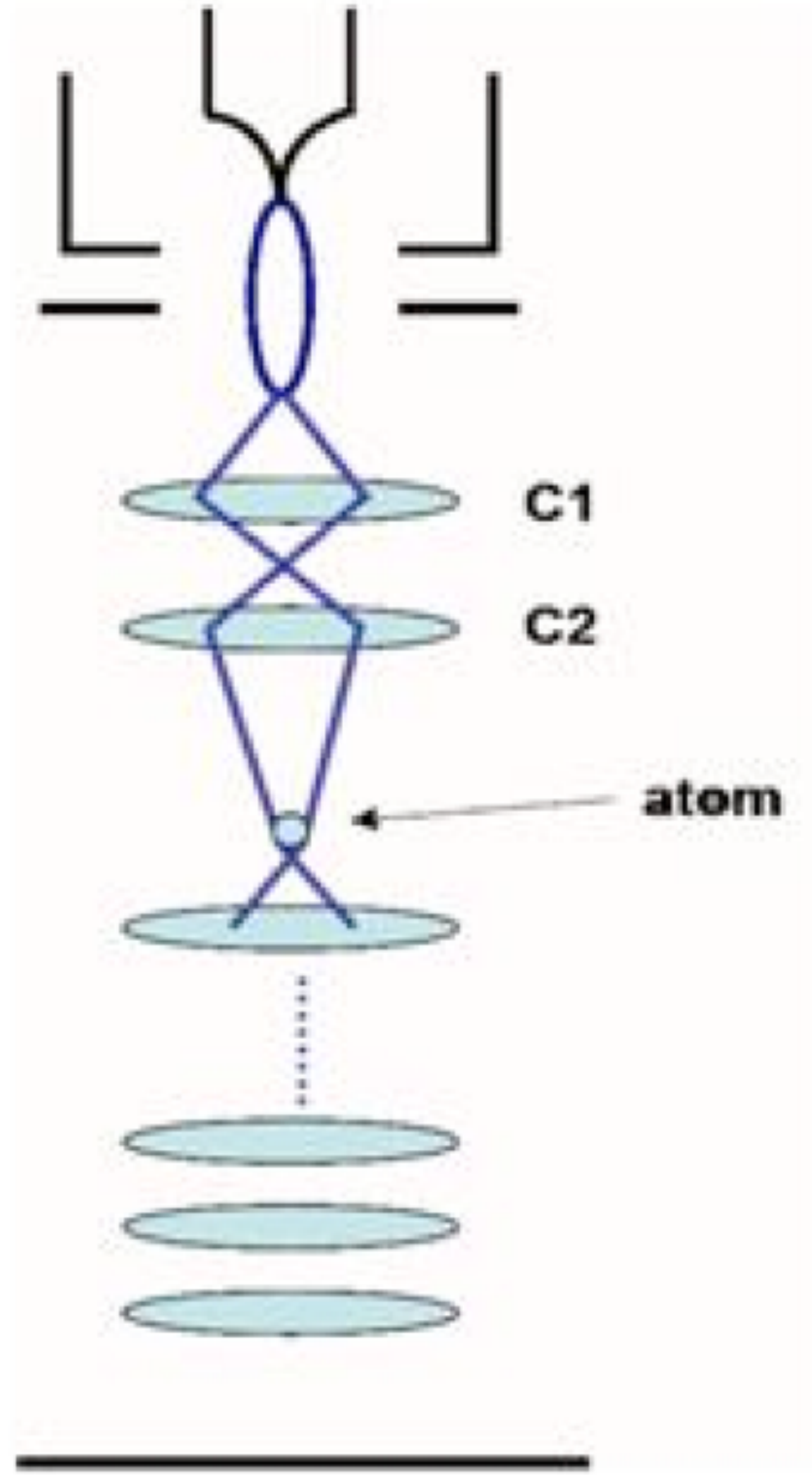
Chapter 3 Diffraction Theory

Elastic scattering

- interaction of e^- beam / atom (chapter 3)
- interaction of e^- beam / unit cell (chapter 16)
- interaction of e^- beam / crystalline sample (chapter 16)
- reciprocal lattice(chapter 12)
- Diffraction Pattern
- Shape Effect of Nano-object (Chapter 17)

3.1 interaction of e$^-$ beam / atom



電子與原子作用

- 電子與原子的作用基本上可分成兩大類

(a)彈性散射(elastic scattering)

入射電子不損失能量,因此我們稱之為“彈性散射”

(b)非彈性散射(inelastic scattering)

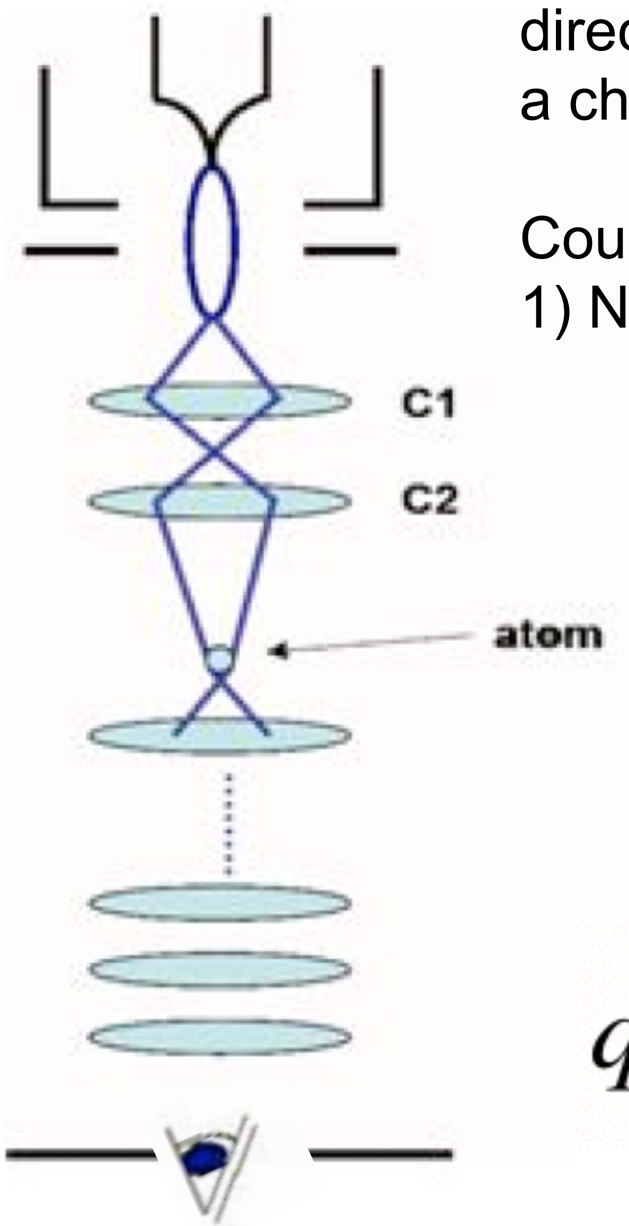
入射電子損失能量,因此我們稱之為“非彈性散射”

3.1.1 Elastic Scattering (particle picture)

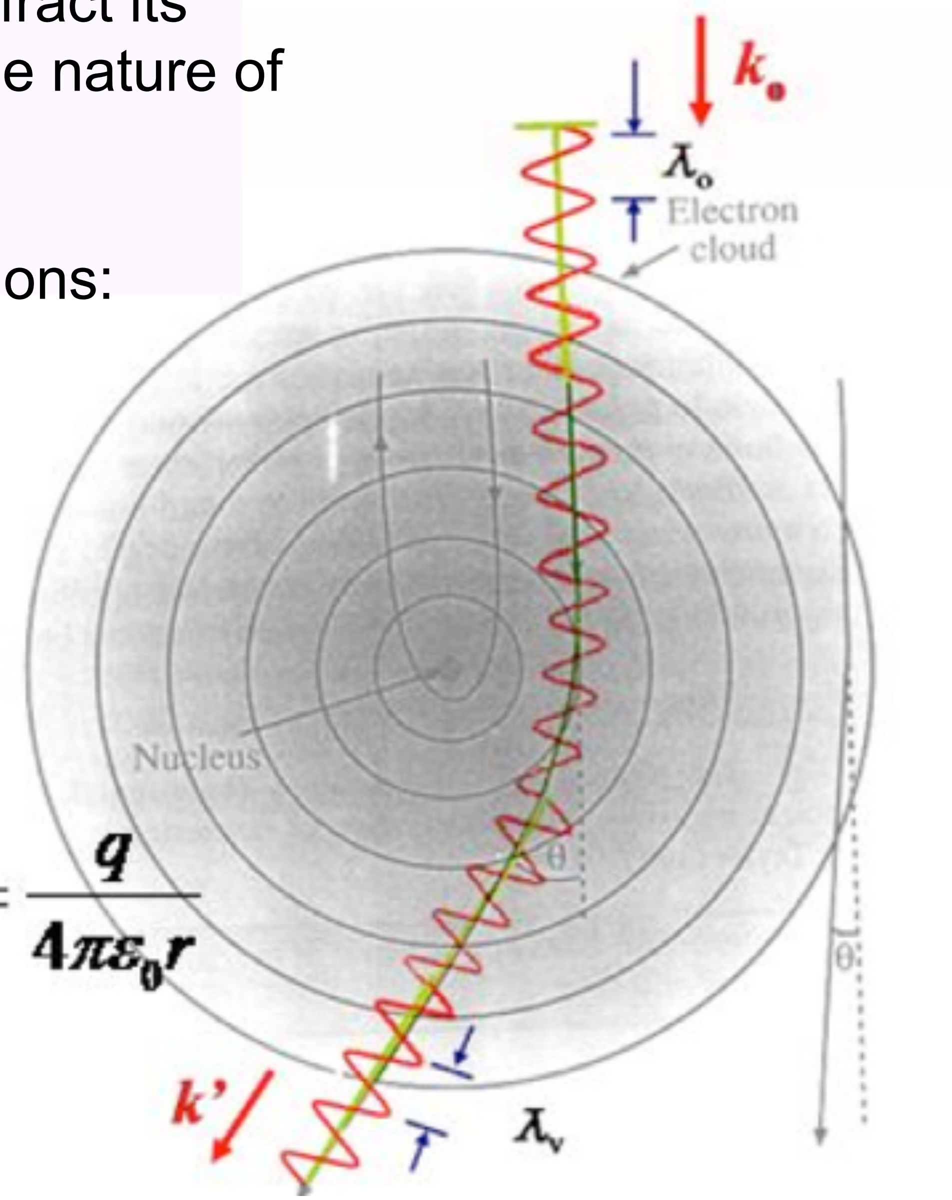
NTHU

As an electron approaches an "isolated" atom, it feels Coulomb potential of atom, it will diffract its direction due to Coulomb force. This is the nature of a charge particle.

Coulomb potential includes two contributions:
1) Nucleus 2) Electron Cloud



$$F_{coul} = -\frac{eq}{4\pi\varepsilon_o r^2}$$



$$V(r) = \frac{q}{4\pi\varepsilon_0 r}$$

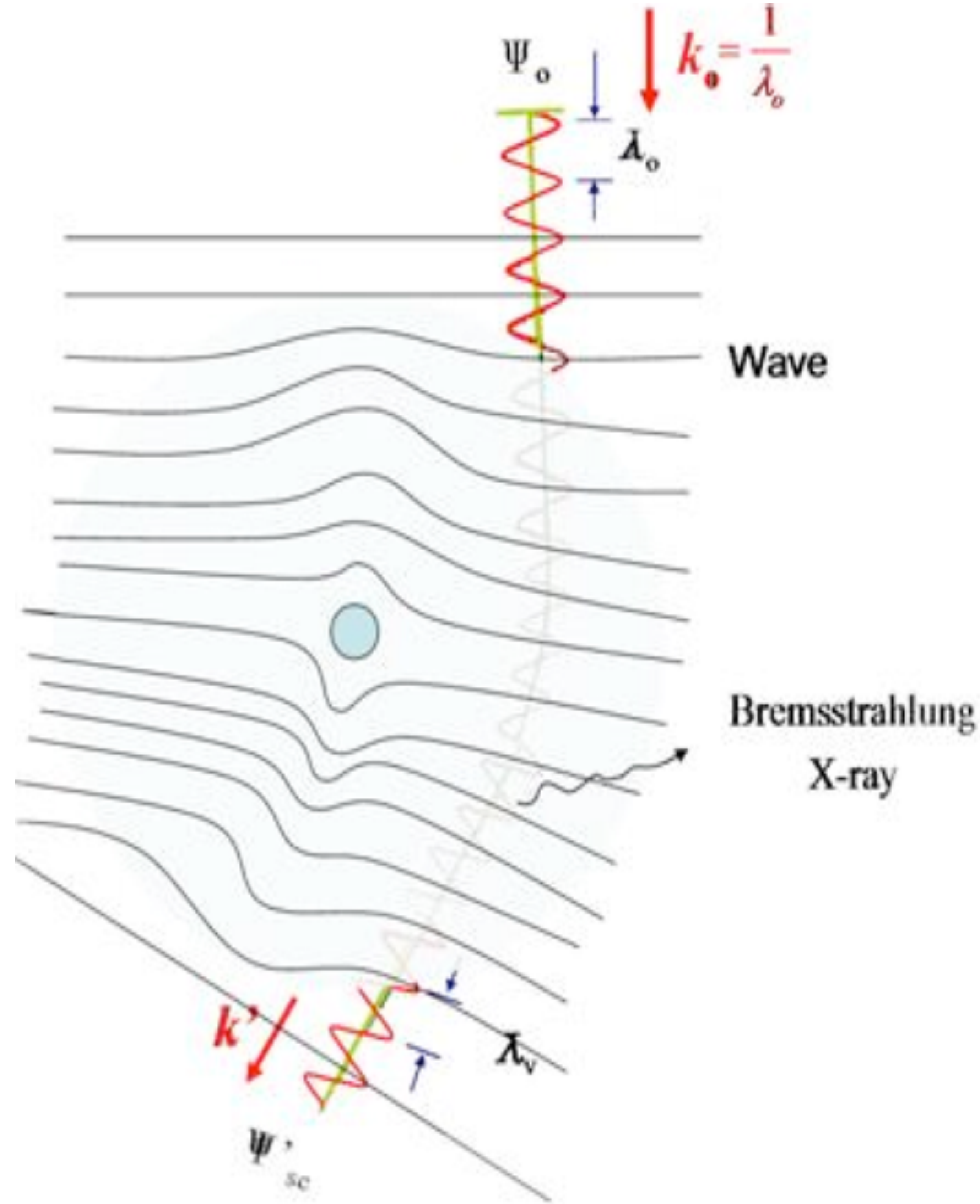
$$q = e[z\delta(r) - \rho(r)]$$

Nucleus Electron Cloud

Noting that x-ray is electro-magnetic wave only interacts with electron could but not nucleus.

3.1.2 Wave Model of Electron Scattering

- 入射電子可近似為平面波,因為波長比起觀察者距離短得太多
- 當入射電子波接近原子核時,就會感受到原子庫侖位能的作用,因而改變波長及方向
  - 這就如同光波進入不同的介質(如由空氣進入水中),引起折射。
- 連續加速和減速的帶電粒子亦伴隨(連續)產生x-ray成為Bremsstrahlung X-ray
- 折射率與原子庫侖位能有關



$$n = \frac{\lambda_0}{\lambda_v} = \left(1 + \frac{V}{E_0}\right)^{1/2}$$

$$\lambda_0 \cong \frac{12.2}{E_0^{\ 1/2}} \qquad \lambda_v \cong \frac{12.2}{(E_0 + V)^{1/2}}$$

$$n \cong 1 + 10^{-4}, E_0 = 100kV, V \cong 10volts$$

3.1.3 Imaging of Single Atom

NTHU

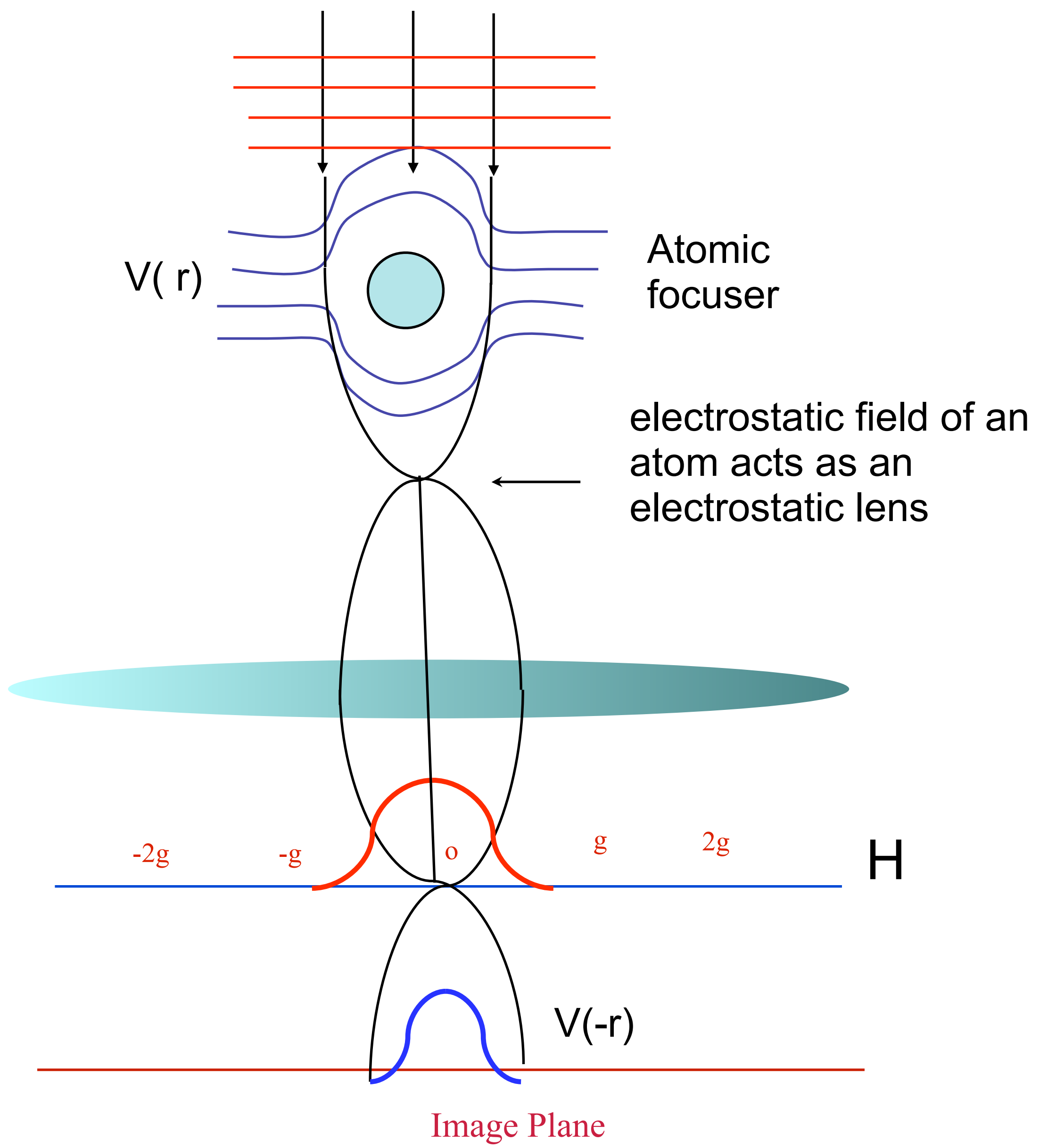
Incoming electron interacts with electrostatic potential contributing from both nucleus and electron cloud (X-ray only interacts with electron cloud)

$$V = \frac{e[z\delta(r) - \rho(r)]}{4\pi\varepsilon_o r}$$

Lens does two focus action
(two Fourier transforms in Math)

$$f^{el}(\theta) = f^{el}(H) = \pi\Im(U(r)) = \frac{2\pi me}{h^2}\Im(V_{at}(r))$$

$\mathcal{F}^{-1}(f^{el}) = \mathcal{F}^{-1}(\mathcal{F}(V(r)))$:



Further on atomic scattering factor

NTHU

$$V = \frac{e[z\delta(r) - \rho(r)]}{4\pi\varepsilon_o r}$$

$$f^{el}(\theta) = f^{el}(H) = \pi\Im(U(r)) = \frac{2\pi me}{h^2}\Im(V_{at}(r))$$

$$f^{el}(H) = \frac{1}{H^2}\frac{me^2}{2\pi h^2\varepsilon_o}\{Z - f^x(H)\}$$

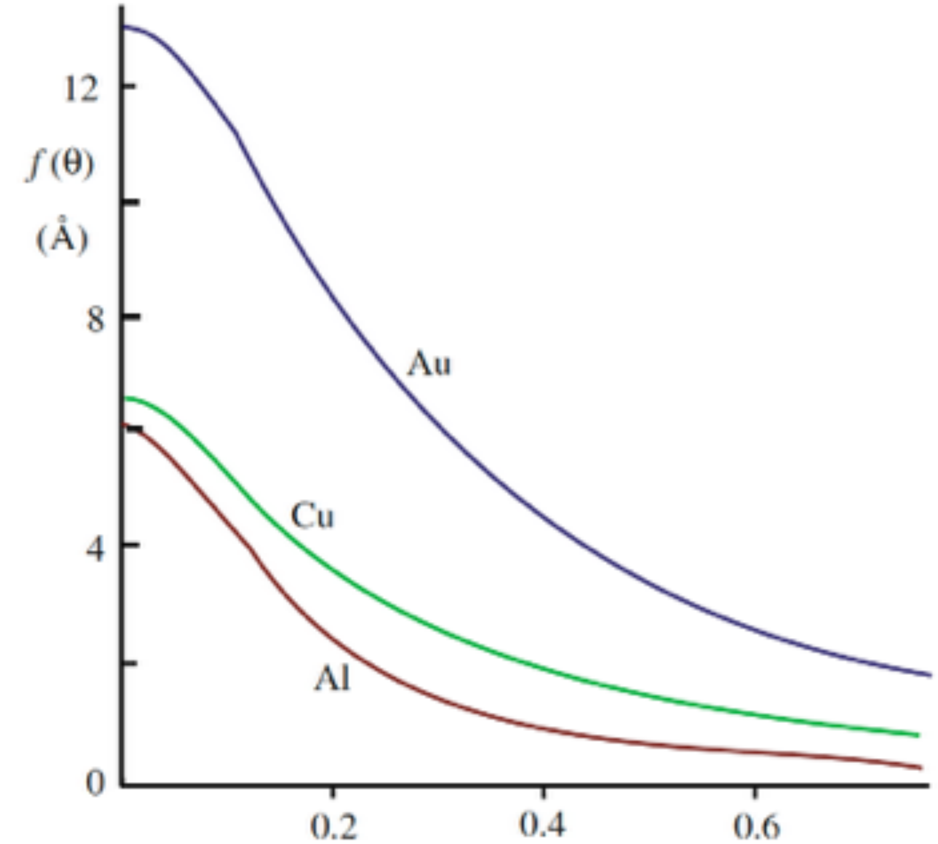
$$\boxed{|\vec{H}| = \frac{2\sin(\frac{\theta}{2})}{\lambda}}$$

$$f^{el}(\theta) = \frac{\lambda}{\sin(\frac{\theta}{2})}\frac{me^2}{8\pi h^2\varepsilon_o}\{Z - f^x(H)\}$$

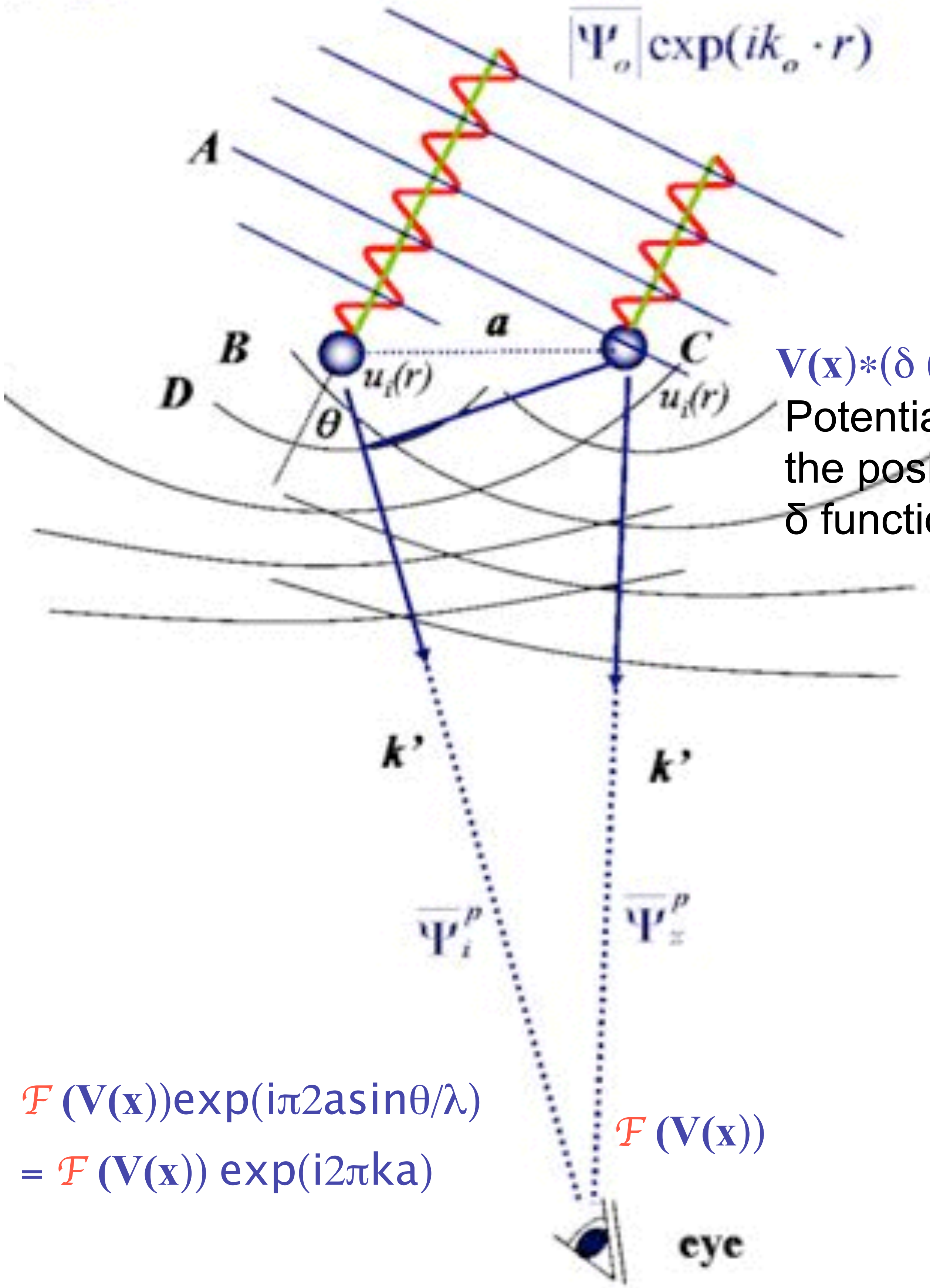
$f^x(H)$ or $f^x(\Theta)$ is called x-ray scattering factor and is the Fourier transform of electron cloud, since the x-ray only interacts with the electron cloud.

The unit of $f^{el}(\Theta)$ is the length (nm)

- $\boldsymbol{f}^{el}$ decreases as increasing of θ
- $\boldsymbol{f}^{el}$decreases as decreasing of λ
- $\boldsymbol{f}^{el}$increases as increasing of Z
- refer to "P.A. Doyle Hartree-Folk X-Ray and Electron Scattering Factors".Acta Cryst.(1968)A24, 390



雙原子繞射—— coherent length > “a”



V(x)∗(δ (x)+ δ (x+a))

Potential is placed at the positions given by δ functions

$\mathcal{F}$ (V(x))exp(iπ2asinθ/λ)

= $\mathcal{F}$ (V(x)) exp(i2πka)

$\mathcal{F}$ (V(x))

- 對遠方的觀察者P而言,所看到的總繞射波為

$$\Psi_1^p + \Psi_2^p$$

  - Ψ_1^P與Ψ_2^P相差一個相位

相位=波程差/λ

=(AB+BD)/λ

- 事實上,對觀察者而言r_p>>a, 所偵測到的總繞射波為

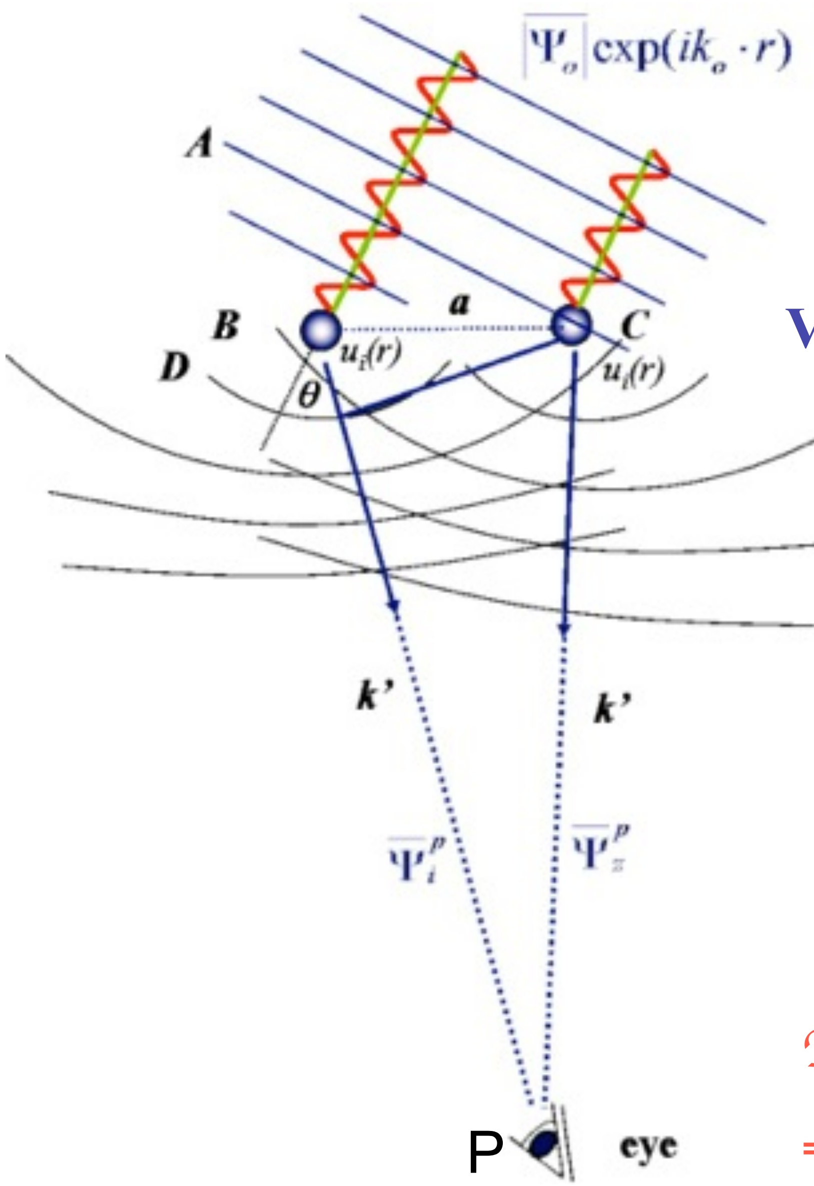
*入射波被雙原子（位能和）繞射

3.1.4 Scattering (Diffraction) from two atoms

—— coherent length > “a”

NTHU

TEM CENTER



•For observer at far distance P, he saw the incoming wave was diffracted by the sum of electrostatic potential of bi-atoms (Fraunhofer Diffraction)

$$V(x)*(\delta(x)+\delta(x+a))$$

Potential is placed at the positions given by δ functions

$$\mathcal{F}(V(x)*(\delta(x)+\delta(x+a)))$$

$$=\mathcal{F}(V(x)).(1+\exp(2\pi iHa))$$

$$=f^{el}\exp(\exp(2\pi i\,0))+f^{el}(\exp(2\pi iHa))$$

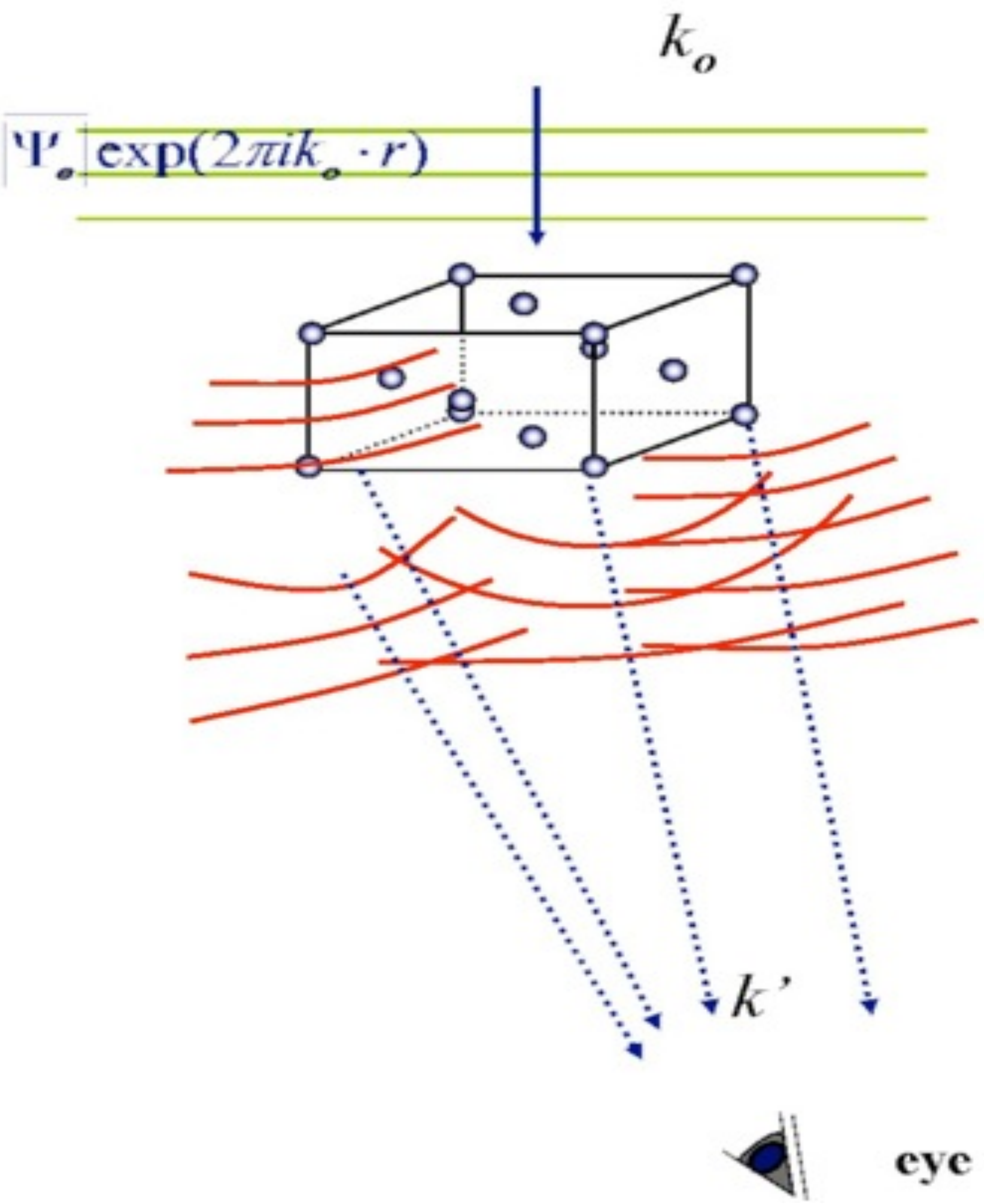
amplitude of wave depends on the atomic potential (kinds of atom)

interference of two diffracted waves

phase of wave gives the relative position of atoms

second atom produces phase shift

3.2 Scattering (Diffraction) from unit cell



- 入射波通過晶胞時,“屬於”晶胞的原子依其相對位置不同,而產生不同相位差的繞射波
- 在遠方的觀察者（透鏡的聚焦面,很遠平行光被聚焦到此）,觀察到這些波的總和
- 在遠方觀察者偵測到的強度與入射波振幅晶胞內原子位能,晶胞內原子相對為置有關

結構因子

- 晶胞對入射電子的散射基本上與單一原子相同,所不同的只是多了一個結構因子(structure factor)
- 在晶胞內原子間距離不同相對位置,及數目不同,繞射波亦不同

$$F(\theta) = \sum_i f_i(\theta) e^{2\pi i \underline{H} \cdot r_i}$$

3.2.1 結構因子

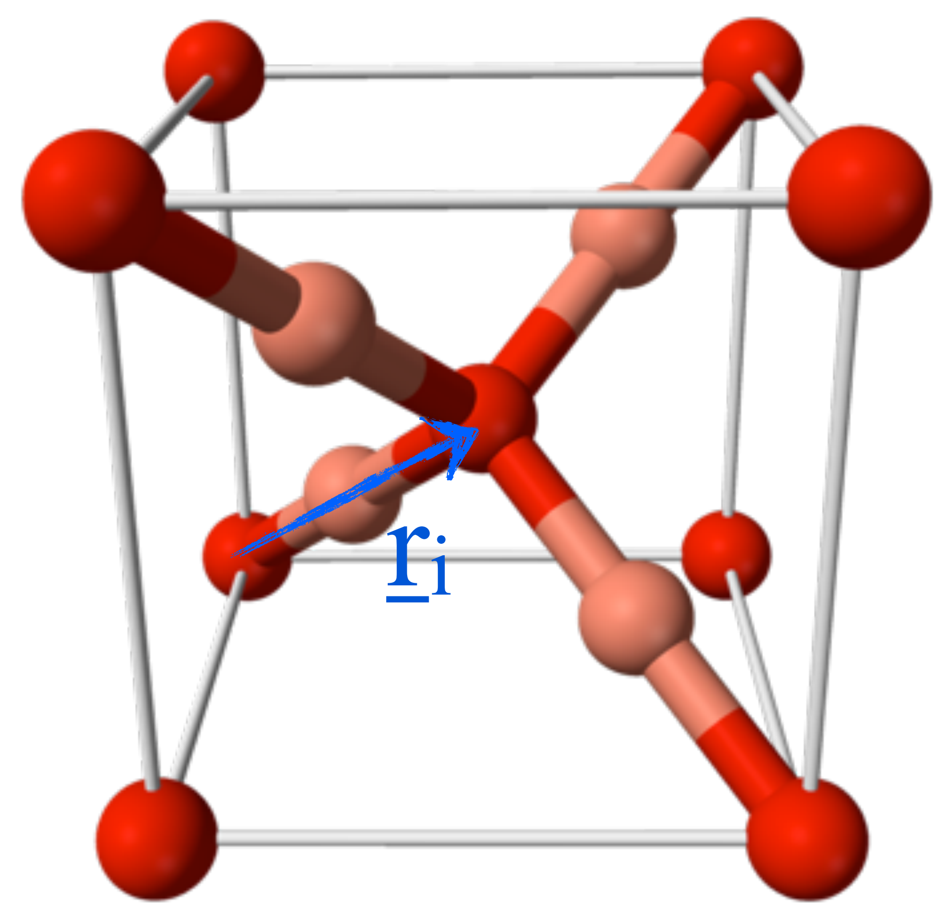
$$F(\theta) = \sum_i f_i(\theta) e^{2\pi i \underline{\mathrm{H}}\, \underline{\mathrm{r}}_i}$$

1. f_i是在第i個原子位能U_i的傅立葉轉換

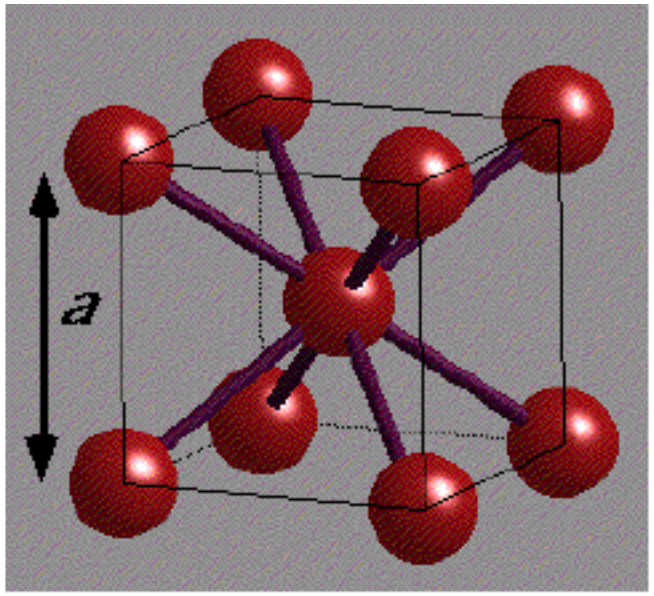
2. r_i為第i個原子的座標(x_i, y_i, z_i)-實空間向量

3. $\underline{\mathrm{H}}$為倒空間向量

$$F(\theta) = \sum_i^{\infty} f_i e^{2\pi \mathrm{i}(hx_i + ky_i + lz_i)}$$



3.2.2 幾個重要的結構因子



(a)體心立方(body-center cubic,bcc)

晶胞內有兩個原子(0,0,0)及(1/2,1/2,1/2)

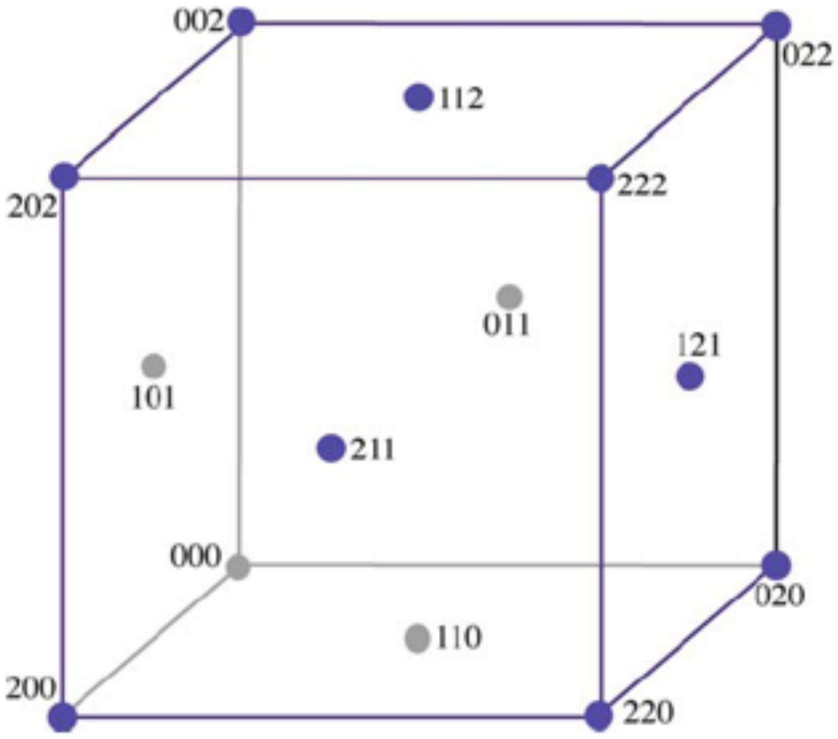
$F=f\{\exp(2\pi i(h\cdot 0+k\cdot 0+l\cdot 0)+\exp(2\pi i(h\cdot 1/2+k\cdot 1/2+l\cdot 1/2)\}$

$=f\{1+\exp(\pi i(h+k+l)\}$ h,k,l 為平面指數

選擇法擇(selection rule)

F=2f 要是 h+k+l=偶數

=0 要是 h+k+l=奇數



體心立方的晶體結構的倒空間是面心立方

(b)面心立方(face-center cubic,bcc)

晶胞內有四個原子(0,0,0), (1/2,1/2,0), (0,1/2,1/2)及(1/2,0,1/2)

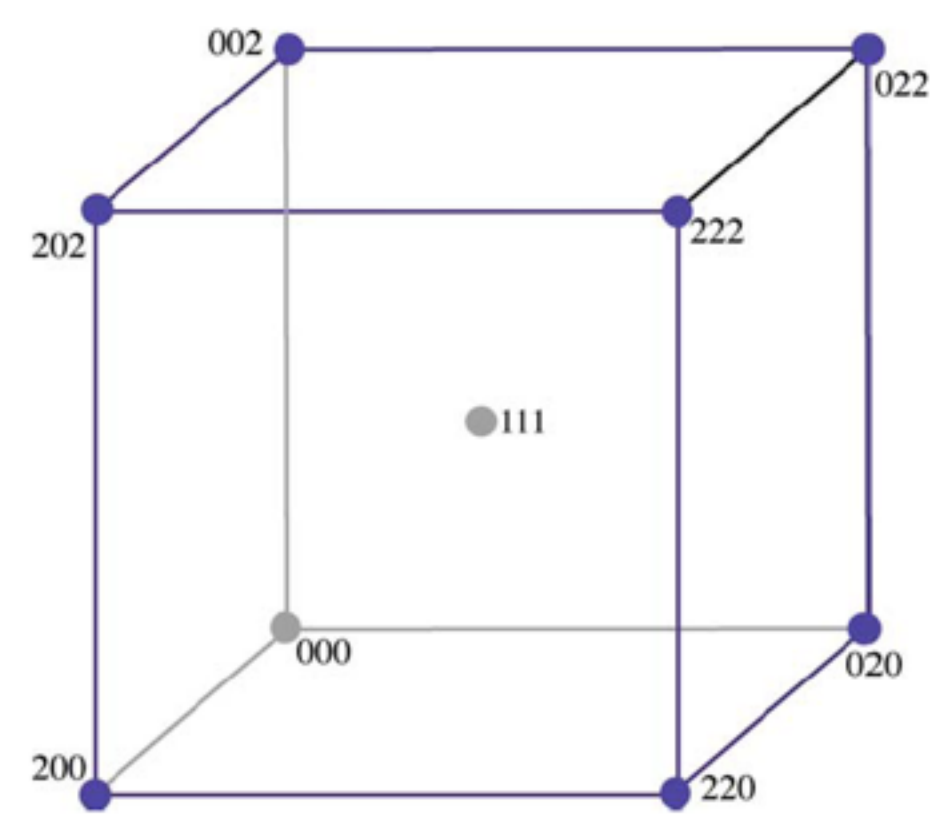
$F=f\{\exp(2\pi i(h\cdot 0+k\cdot 0+l\cdot 0)+\exp(2\pi i(h\cdot 1/2+k\cdot 1/2+l\cdot 0)+\exp(2\pi i(h\cdot 0+k\cdot 1/2+l\cdot 1/2)+\exp(2\pi i(h\cdot 1/2+k\cdot 0+l\cdot 1/2)\}$

$=f\{1+\exp(\pi i(h+k))+\exp(\pi i(k+l))+\exp(\pi i(h+l))\}$ h,k,l 為平面指數

選擇法擇(selection rule)

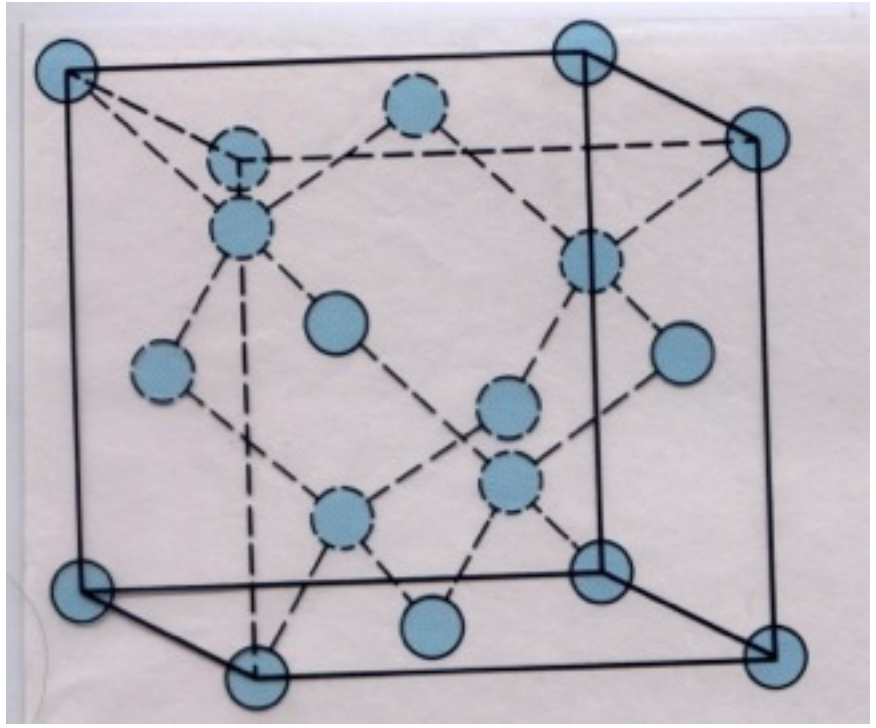
F=4f 要是 h, k, l=un-mixed

=0 要是 h, k, l=mixed



面心立方的晶體結構的倒空間是體心立方

(c) 面心立方結構與鑽石結構



Diamond: $+\left(\frac{1}{4}\frac{1}{4}\frac{1}{4}\right)$

a	b	c	d
$(0\,0\,0)$	$(\frac{1}{2}\,\frac{1}{2}\,0)$	$(\frac{1}{2}\,0\,\frac{1}{2})$	$(0\,\frac{1}{2}\,\frac{1}{2})$
$(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$	$(\frac{3}{4}\,\frac{3}{4}\,\frac{1}{4})$	$(\frac{3}{4}\,\frac{1}{4}\,\frac{3}{4})$	$(\frac{1}{4}\,\frac{3}{4}\,\frac{3}{4})$

Basis: super lattice diffraction

$F=f\{\exp(2\pi i(h\cdot 0+k\cdot 0+l\cdot 0)+\exp(2\pi i(h\cdot 1/4+k\cdot 1/4+l\cdot 1/4)\}$

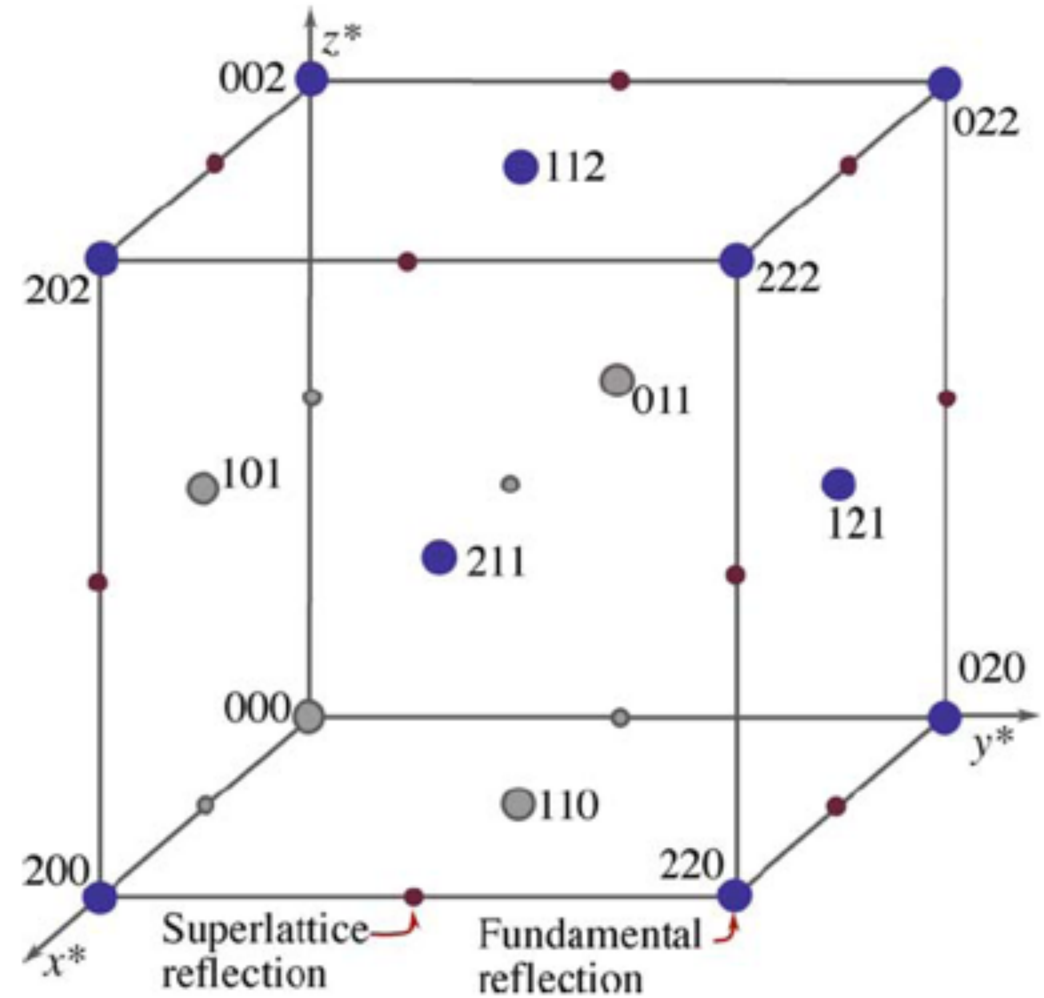
$\{1+\exp(\pi i(h+k)+\exp(\pi i(k+l)+\exp(\pi i(h+l)\}$

Lattice fundamental diffraction

(d) NiAl (L10)

$$Ni(000), Al(\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2})$$

$$F = \left\{ f_{Ni} + f_{Al} \exp(2\pi i \frac{1}{2}(h+k+l) \right\}$$



選擇法則

$F = f_{Ni} + f_{Al}$ h+k+l=偶（基本晶格, fundamental lattice）

$= f_{Ni} - f_{Al}$ h+k+l=奇 （對bcc而言這項是0,超晶格 superlattice）

(e) Ni_3Al, $Cu_3Au(LI_2)$ 結構(有序結構)

Al(0 0 0),Ni(1/2 1/2 0),(1/2 0 1/2),(0 1/2 1/2)

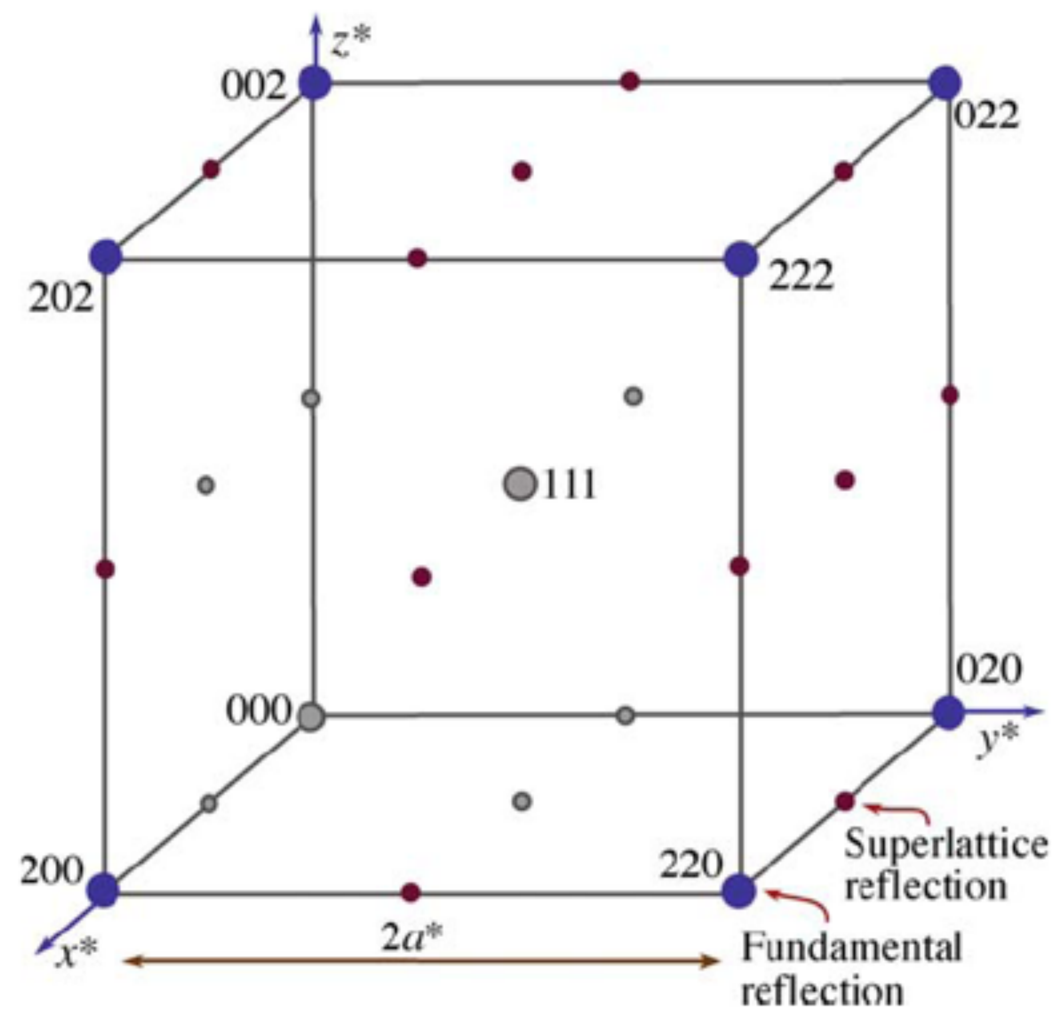
$$F = f_{Al} + f_{Ni}\left\{e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right\}$$

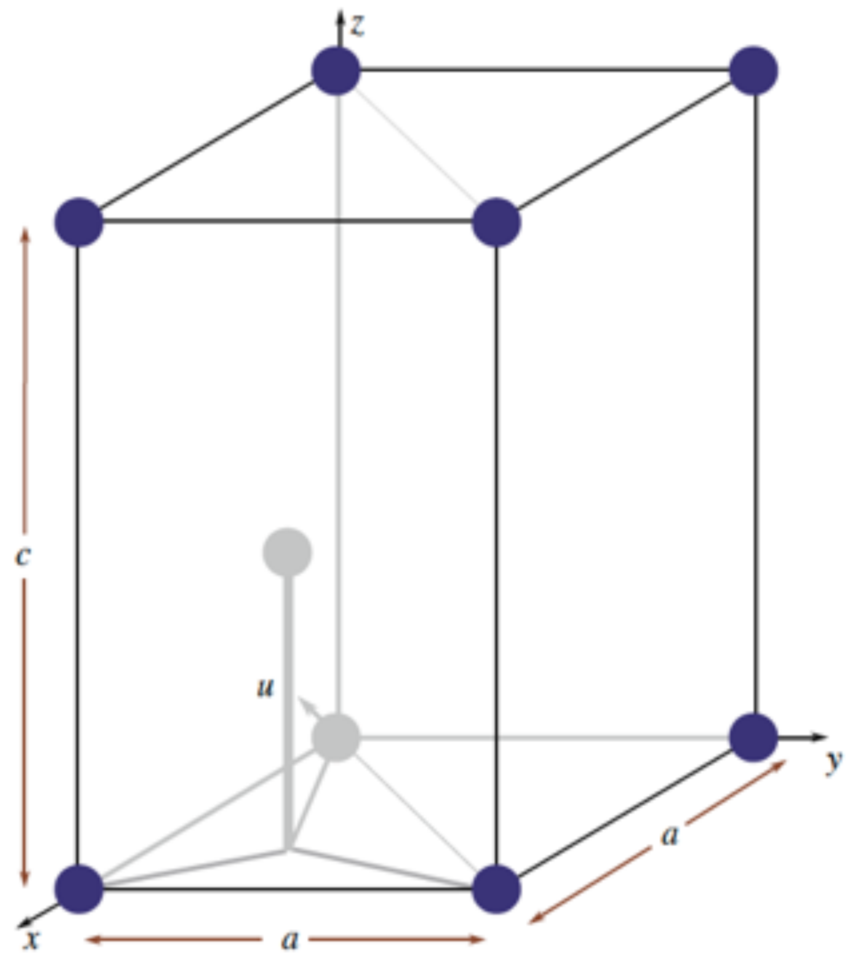
$$F = (f_{Al} + 3f_{Ni})$$

h,k,l 全偶或全奇 基本晶格(fundamental lattice)

$=2(f_{Al}-f_{Ni})$ h,k,l 是混合奇數或偶數 超晶格(super lattice)

若Ni_3Al及Cu_3Au為無序結構則超晶格點陣消失





Crystal type	Reflection present for	F	No. of lattice points per cell
Primitive	Any h, k, l	f	1
Body centered	$(h + k + l) = 2n$	$2f$	2
Face centered including GaAs and NaCl	h, k and l all odd or all even	$4f$	4
Diamond	As fcc but if all even and $h + k + l \neq 4n$ then absent, anyway		
Base centered	h, k and l all odd or all even	$2f$	2
			Example reflection
Hexagonal close-packed	$h + 2k = 3n$ with l odd	0	0001
	$h + 2k = 3n$ with l even	$2f$	0002
	$h + 2k = 3n \pm 1$ with l odd	$f3$	$01\bar{1}1$
	$h + 2k = 3n \pm 1$ with l even	f	$01\bar{1}0$

3.3 interaction of e⁻ beam / crystalline sample

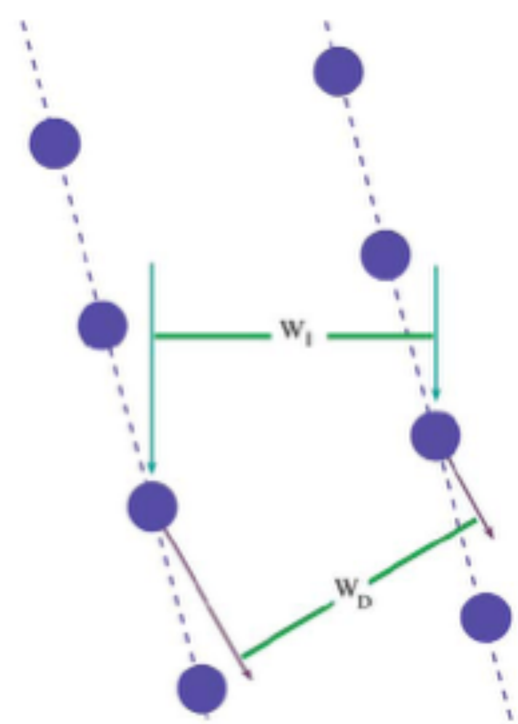
相位差=(AB+BC)/λ= n 時,有建設性干涉

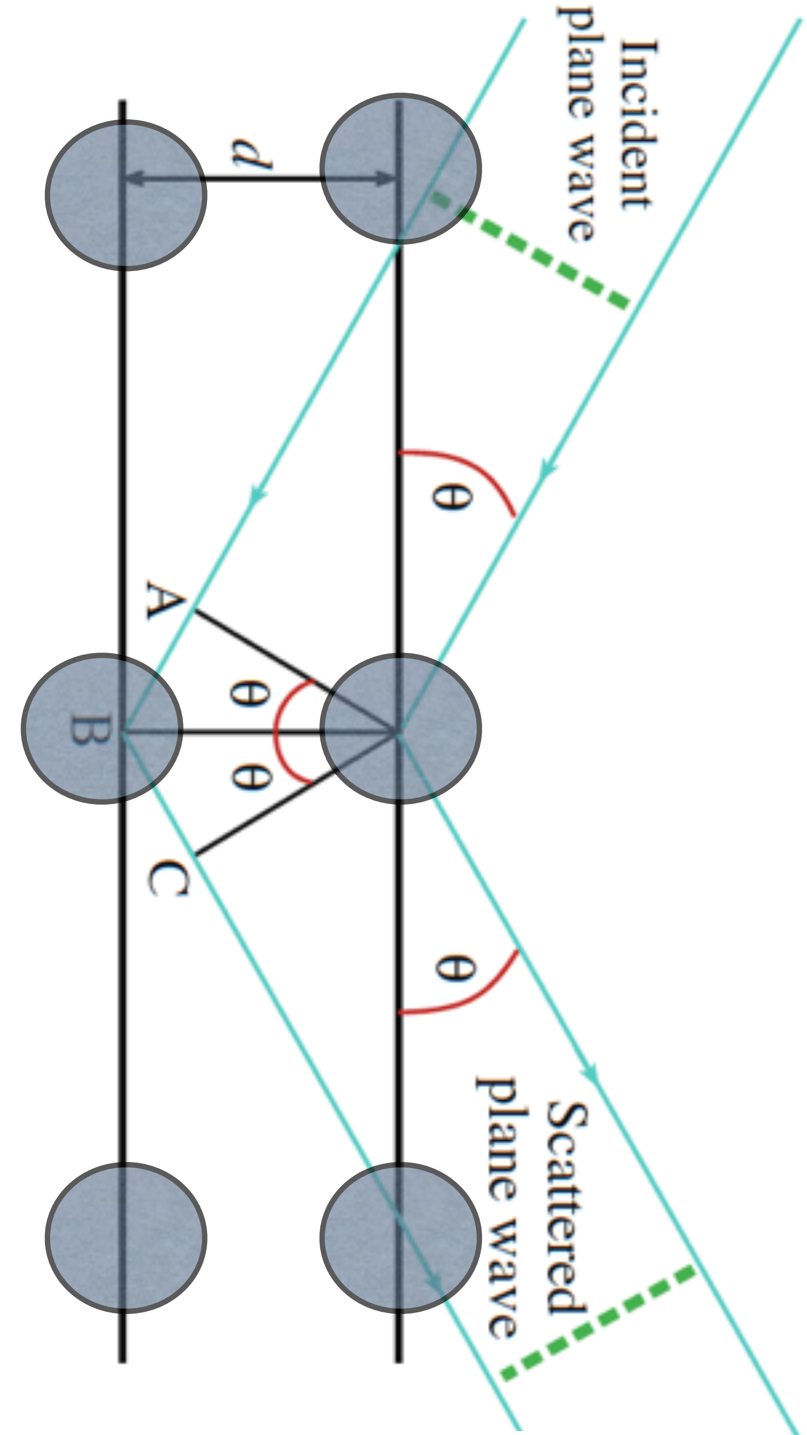
若平面間距為d,反射角θ_B 　　$AB+BC=2d \sin \theta_B = n \lambda$

此公式稱為Bragg's Law

Bragg 因此公式而得到諾貝爾獎.

- 從Bragg's公式我們可以清楚地看到平面間距愈小者繞射角愈大,因此若我們知道入射波的波長λ(=$12.2/E^{1/2}$),我們可藉由散射角度的量測來決定平面的間距.
- 這是電鏡繞射術在結晶訊息的重要工作.





$$n\lambda = 2d \sin \theta_B$$

Bragg's law

以“波”的觀念來看：

$\underline{H}$=k’-k_0 (Bragg’s condition)

$\underline{H}$ ⊥ 原子平面跡 (plane trace)

原子平面跡是k_0及k’的分角線

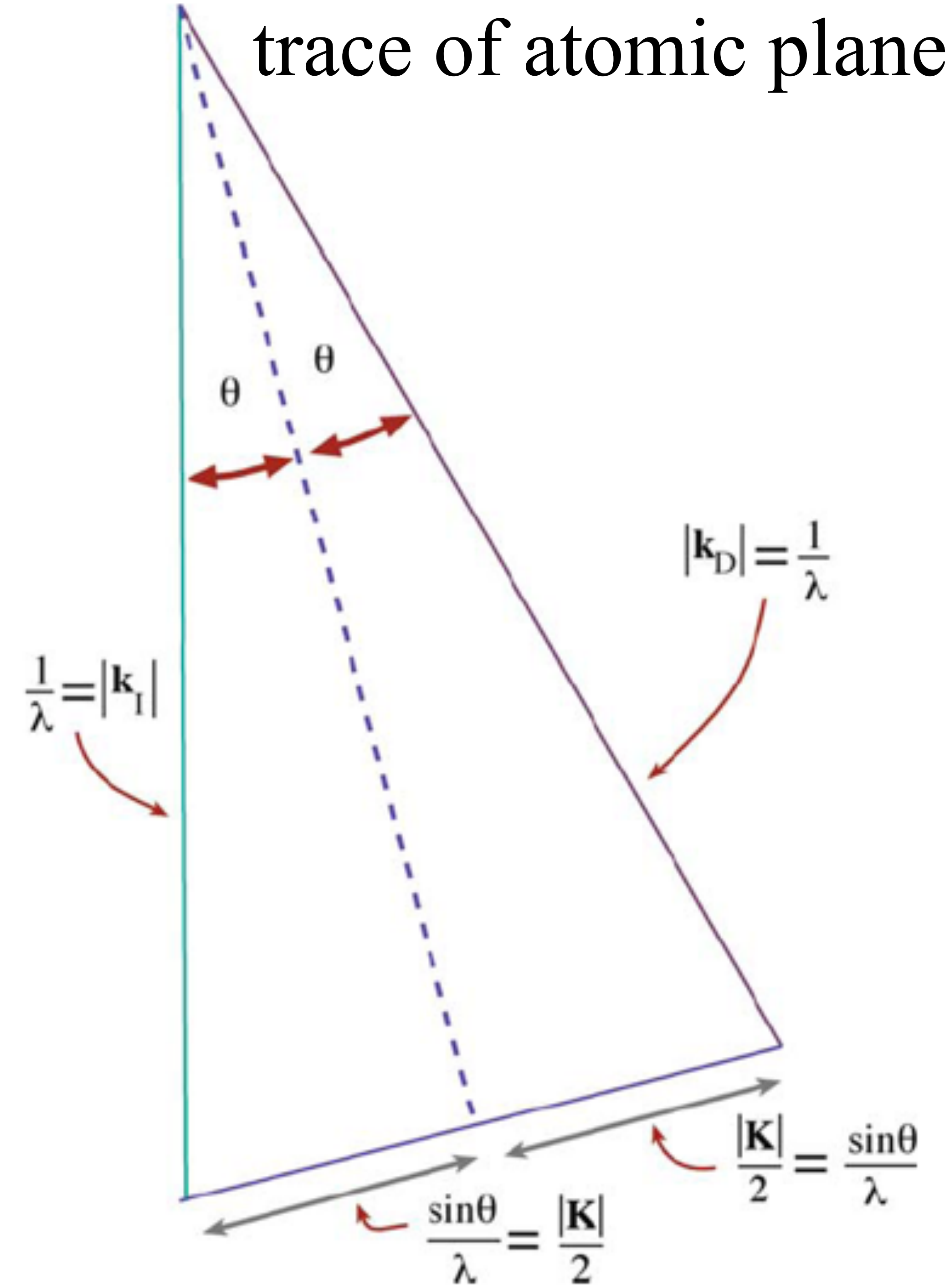
$1/2\,|H|=|k_0|\sin\theta_B$, $|k_0|=1/\lambda$

$\lambda=2/|H|\ \sin\theta_B$, 與 $\lambda=2d\sin\theta_B$ 比較

$|H|=1/d$, 且$\underline{H}$ //原子平面之法向量

（有建設性干涉的原子平面）

⊥原子平面跡



{$\underline{H}$}代表晶體可產生“建設性”干涉的平面組,其方向為平行平面之法向量且長度為對應的平面間距之倒數—倒晶格空間

3. 3.1 實空間與倒空間

(晶體結構與繞射花樣)

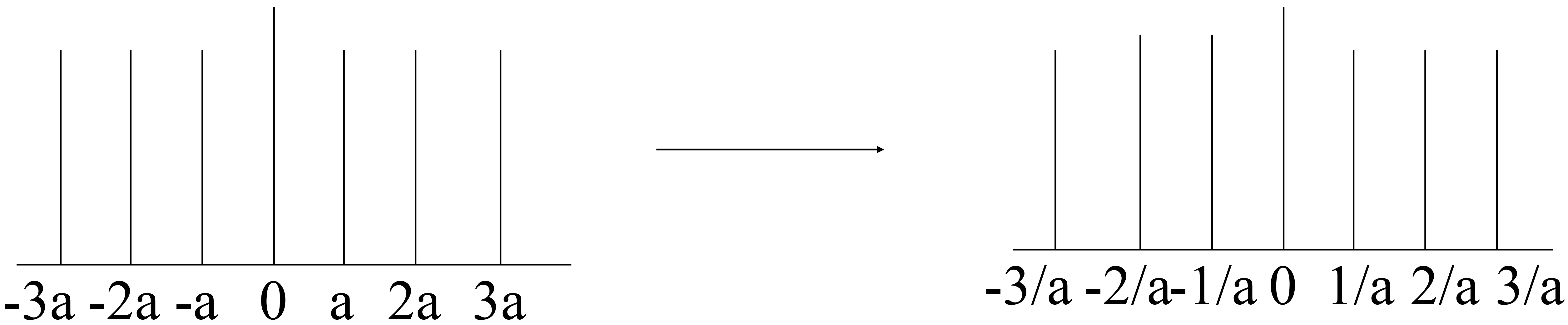
為何需要另一個空間?

•倒空間能使我們方便描述及處理晶體繞射的問題
•事實上,“倒”晶格空間和“實”晶格空間一樣的“真實”
•我們可以把晶體想成有兩個“晶格”一個“實”晶格,
一個“倒”晶格
實晶格是晶體本身,倒晶格則是繞射空間的點陣

Fourier Transform of periodic function

$$f(x)=\sum_{-\infty}^{\infty}\delta(x-na)$$

$$\tilde{f}(H)$$



晶體原子結構

（實空間）

倒空間

繞射花樣

$$\tilde{f}(H)=\int_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\delta(x-na)\exp(-2\pi ikx)dx$$

$$=\int_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\delta(x-na)\exp\{-2\pi ik(x-na)\}\exp(-2\pi ikna)dx$$

$$=\sum_{-\infty}^{\infty}\exp(-2\pi ikna)=\frac{1}{1-\exp(-2\pi ika)}$$

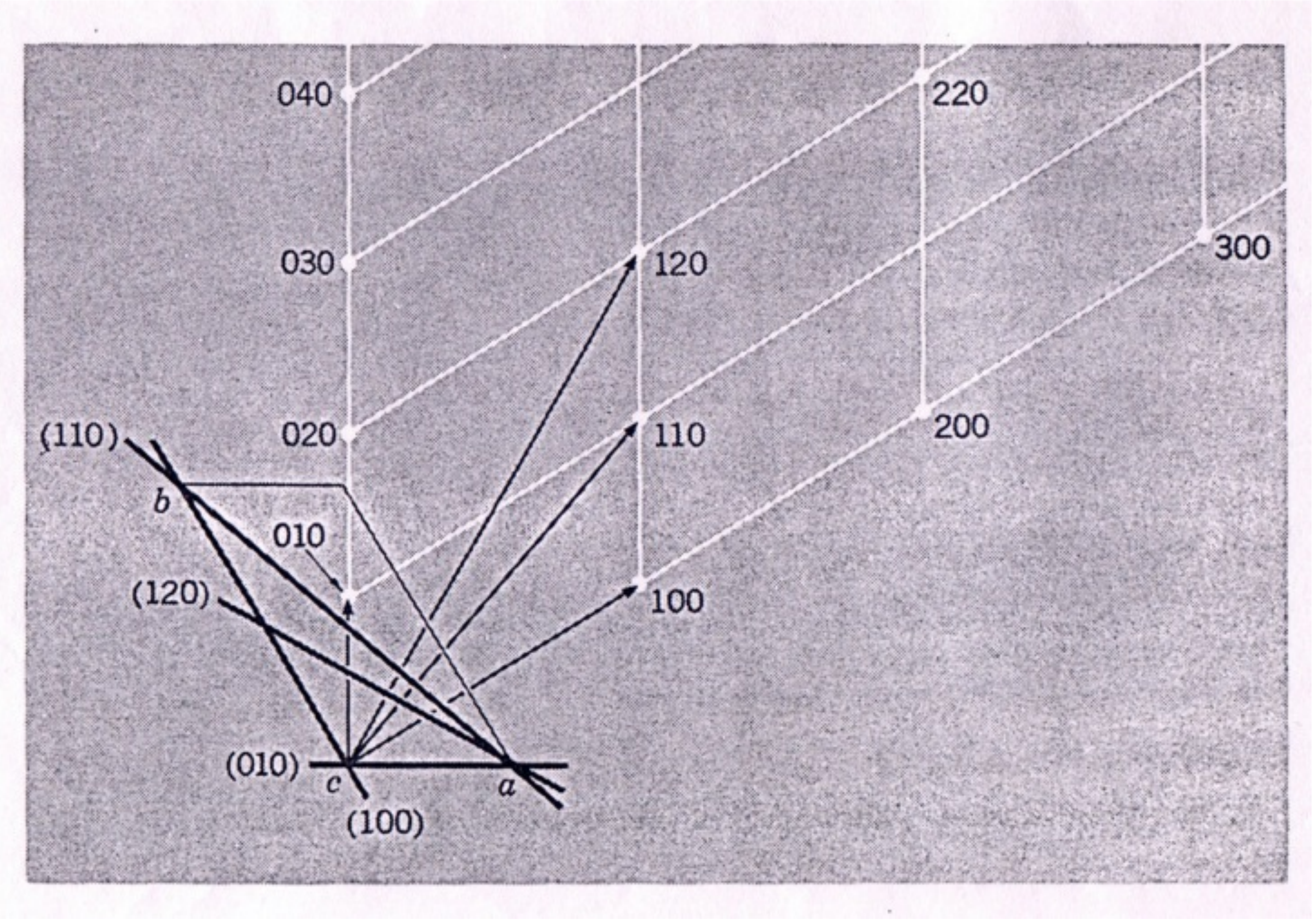
此函數只在k=1/a 時有∞的值

倒空間

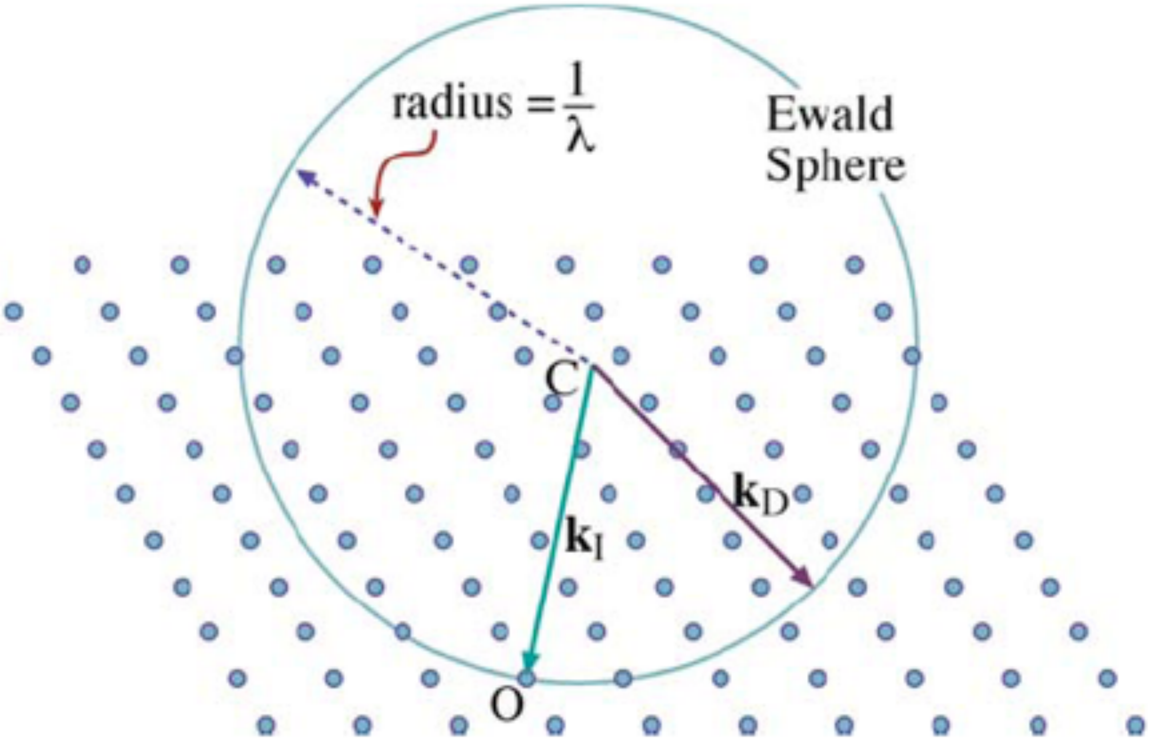
1) 倒空間: 與實空間一樣真實

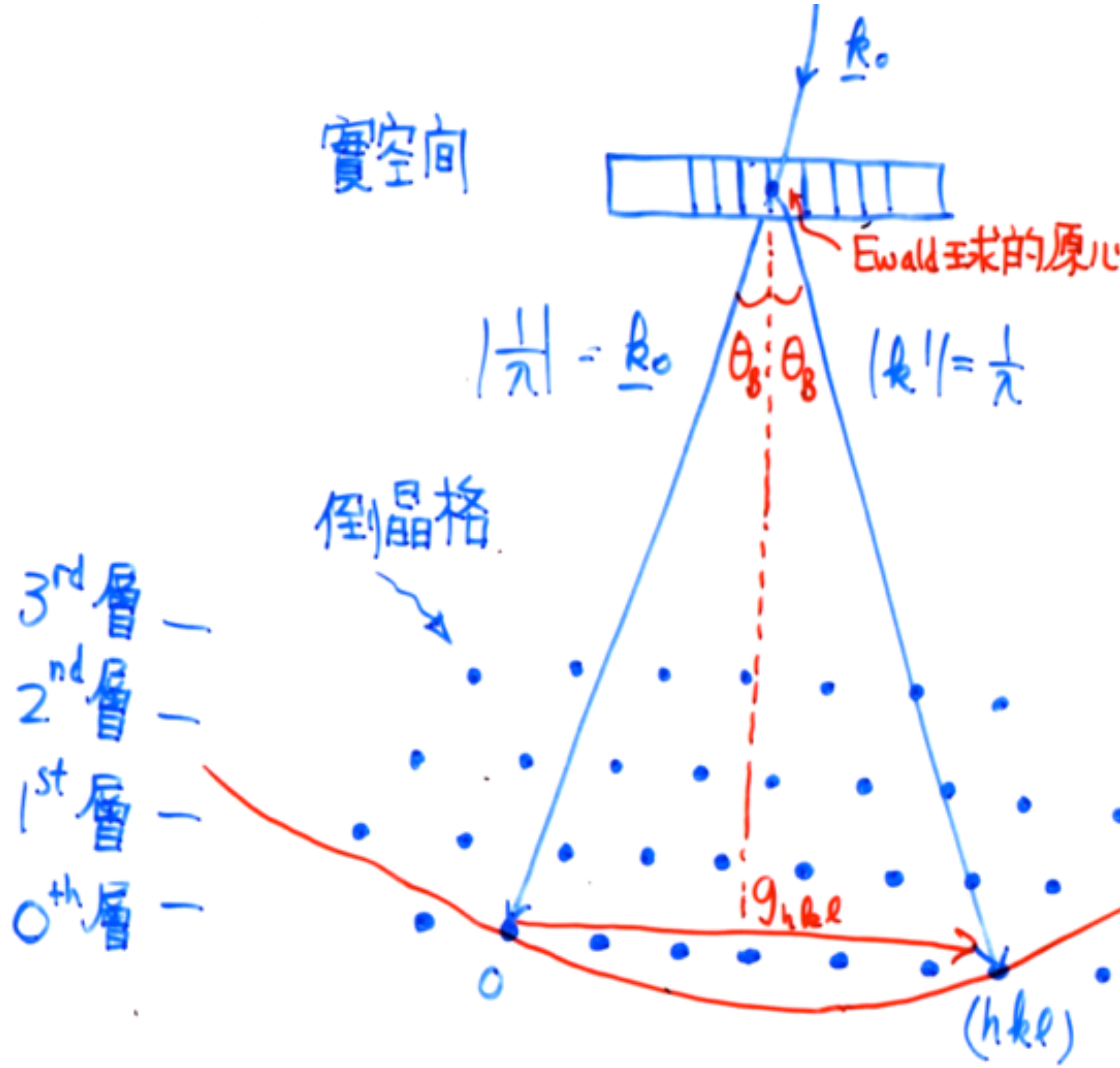
2) 倒空間的一點相對於實空間的一平面

3)倒空間的一點至原點的距離等於平面間距的倒數



3.3.2 Ewald Sphere and Laue Zone





- 以k_0方向通過晶格原點以畫一球,稱為Ewald球

- K_0方向改變Ewald球亦跟著改變

- 倒晶格就如同事與晶體(時空間)是訂在一起的.晶體傾斜,則倒晶格亦被傾斜.

•對電子繞射而言，　$|k_0| \approx |k| >> |g_{hkl}|$

$$|k_0| = \frac{1}{\lambda} = \frac{1}{0.037\text{Å}} \cong 25\ \frac{1}{\text{Å}}$$

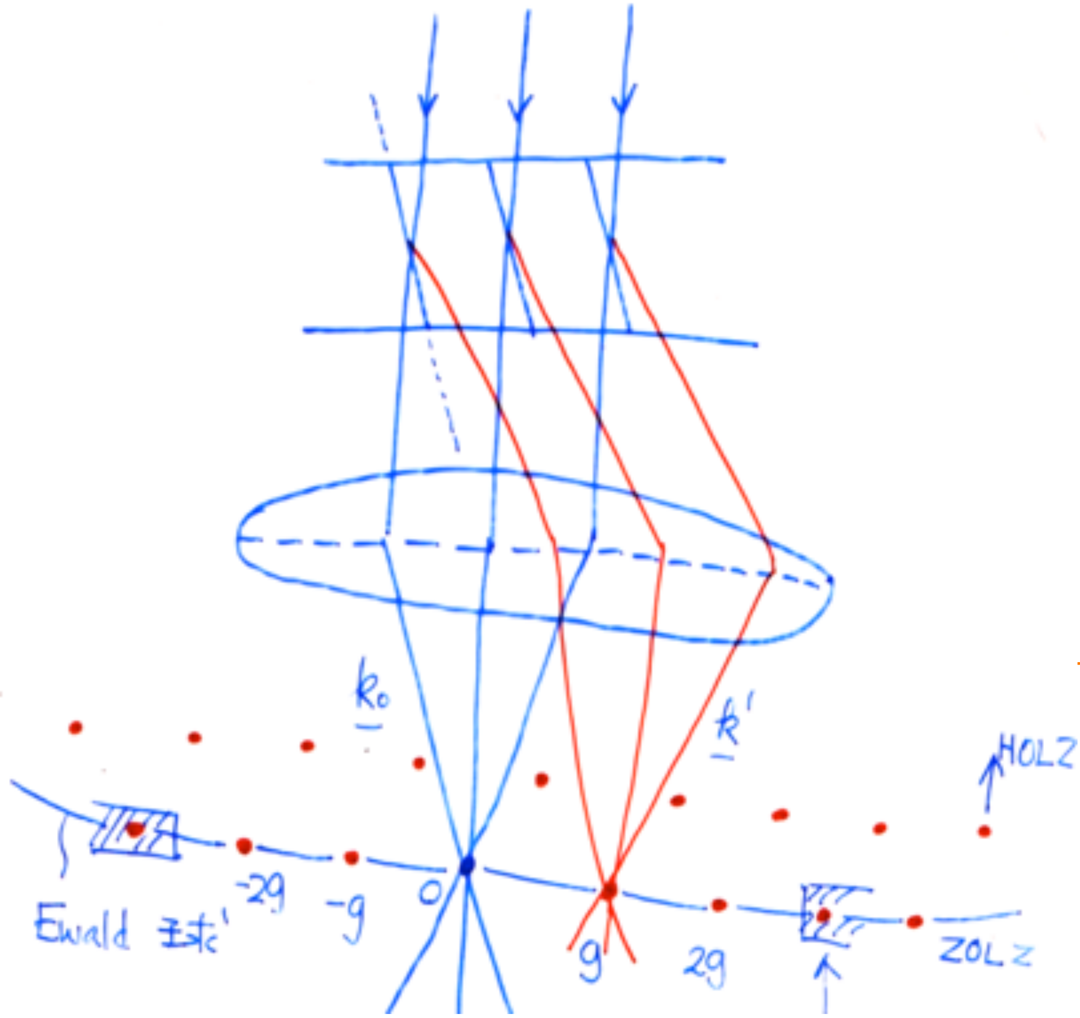
$$|g_{hkl}| \approx \frac{1}{d_{hkl}} = \frac{1}{2}\frac{1}{\text{Å}} = 0.5\frac{1}{\text{Å}}$$

$$|k_0| \cong 50|g_{hkl}|$$

•Ewald 球切過第0層的勞厄區時幾乎近似一平面(而非球面)
因此在原點附近的倒晶格點幾乎都作落在Ewald球上,也就是
有很多組平面都近似滿足Bragg's繞射條件

•我們觀察到的繞射花樣事實上是第0層的倒空間中原點附近的點陣

3.3.3 倒晶格與繞射圖形



•一點代表實空間一平面

•倒晶格點至原點的距離正比面間距的“倒數”

(倒空間之 Zero “Laue Zone”)

•在ZOLZ的倒晶格點幾乎作落在Ewald球上,也就是近似的滿足Bragg’s繞射條件

$g=k'-k_0$ or $2d\sin\theta_B=\lambda$

$|g| = \dfrac{1}{d}$ g⊥原子平面軌跡

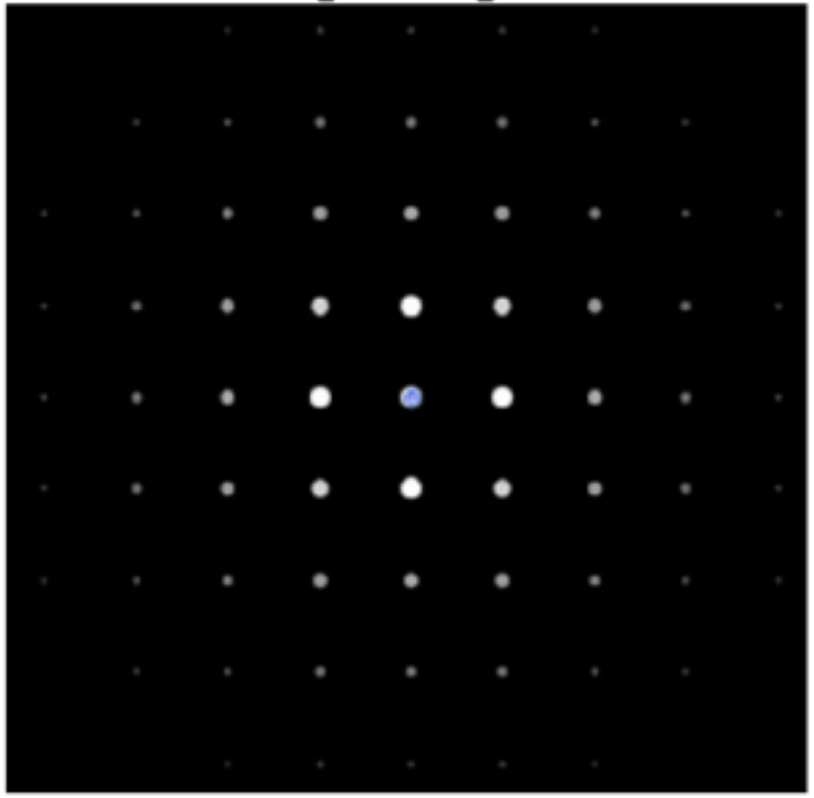
•在電子繞射的繞射條件下,我們在後聚焦面看到的其實是二維的ZOLZ.

3.3.4 EXAMPLES

Zone axis SADPs have symmetry closely related to symmetry of crystal lattice

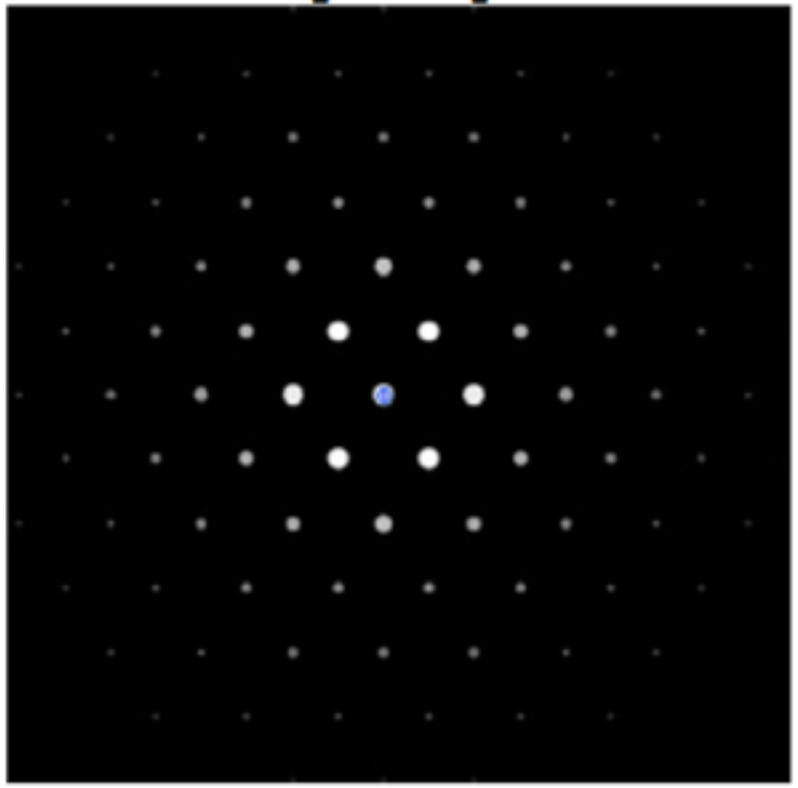
Example: FCC aluminium

[0 0 1]



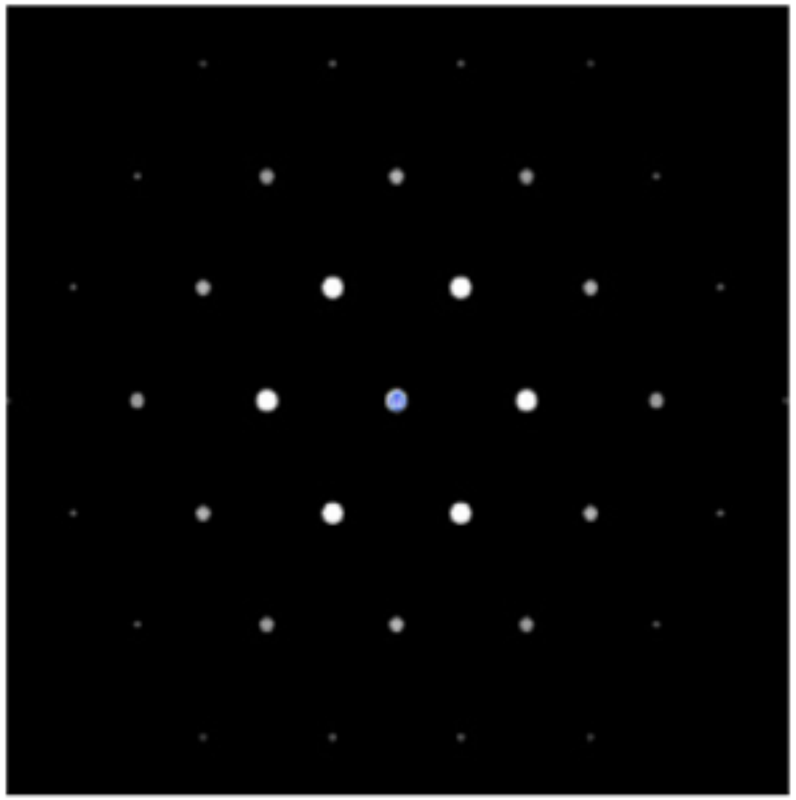
4-fold rotation axis

[1 1 0]



2-fold rotation axis

[1 1 1]



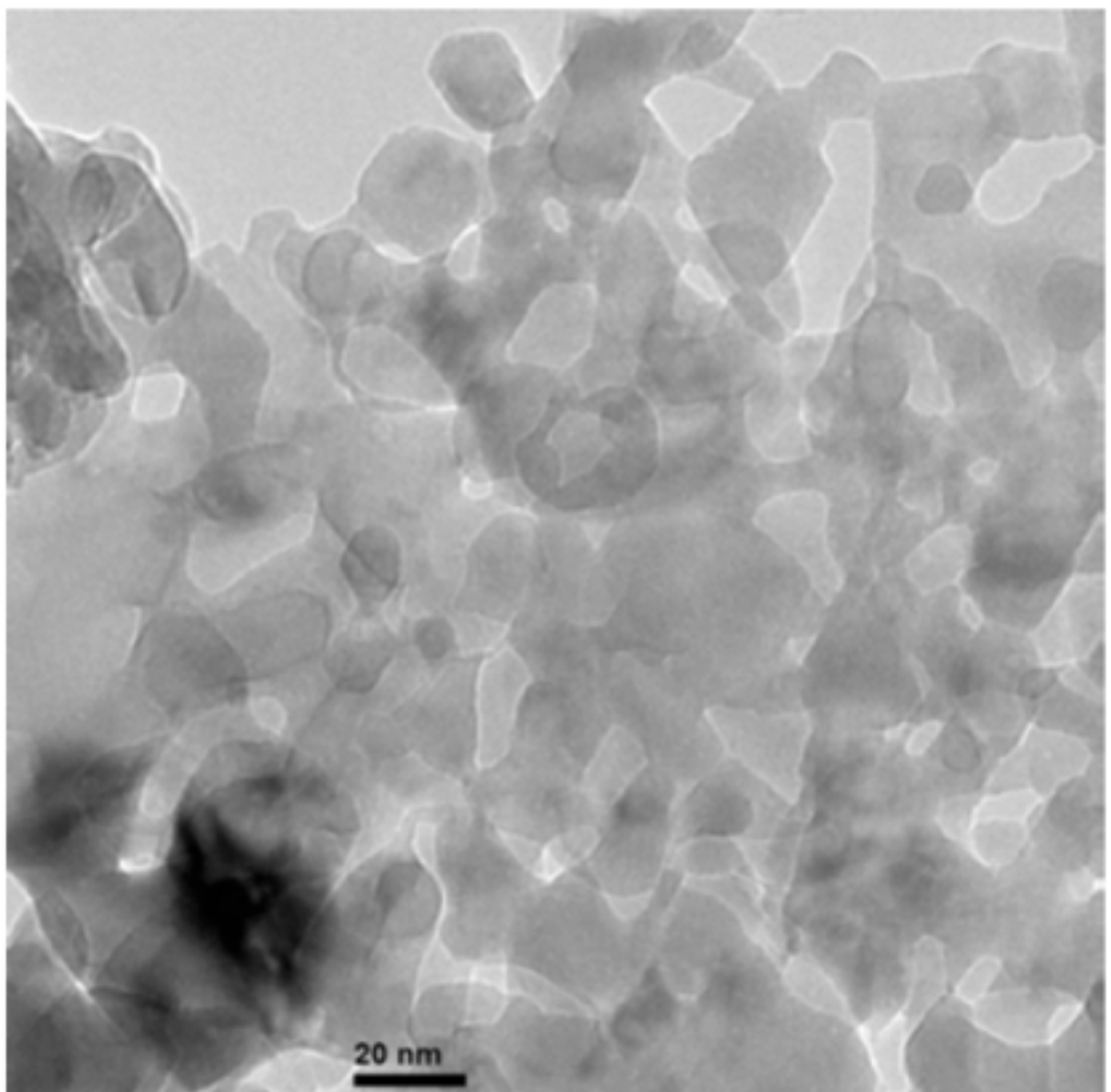
6-fold rotation axis - but [1 1 1] actually 3-fold axis

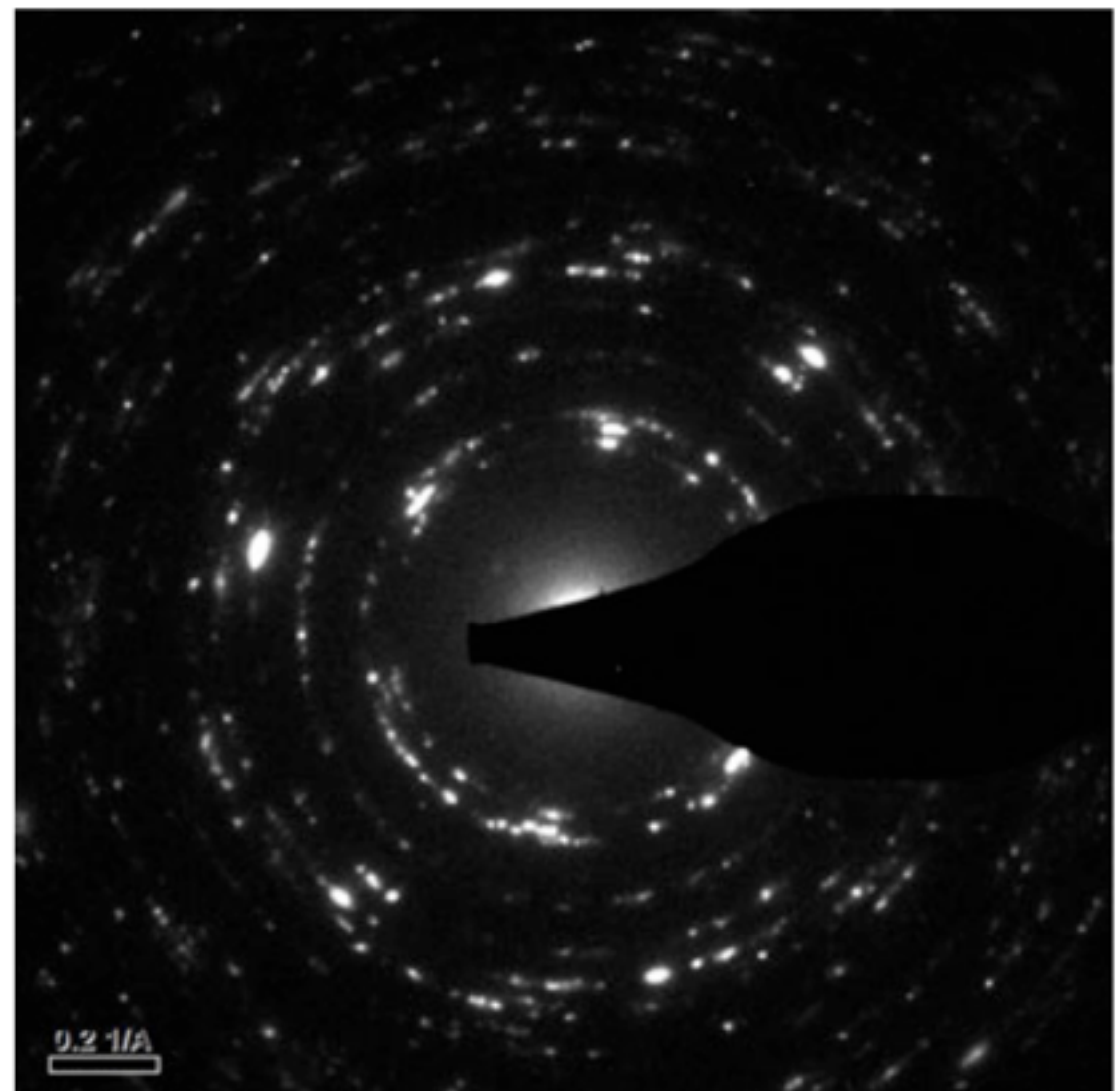
Need third dimension for true symmetry!

Ring diffraction patterns

Larger crystals => more "spotty" patterns

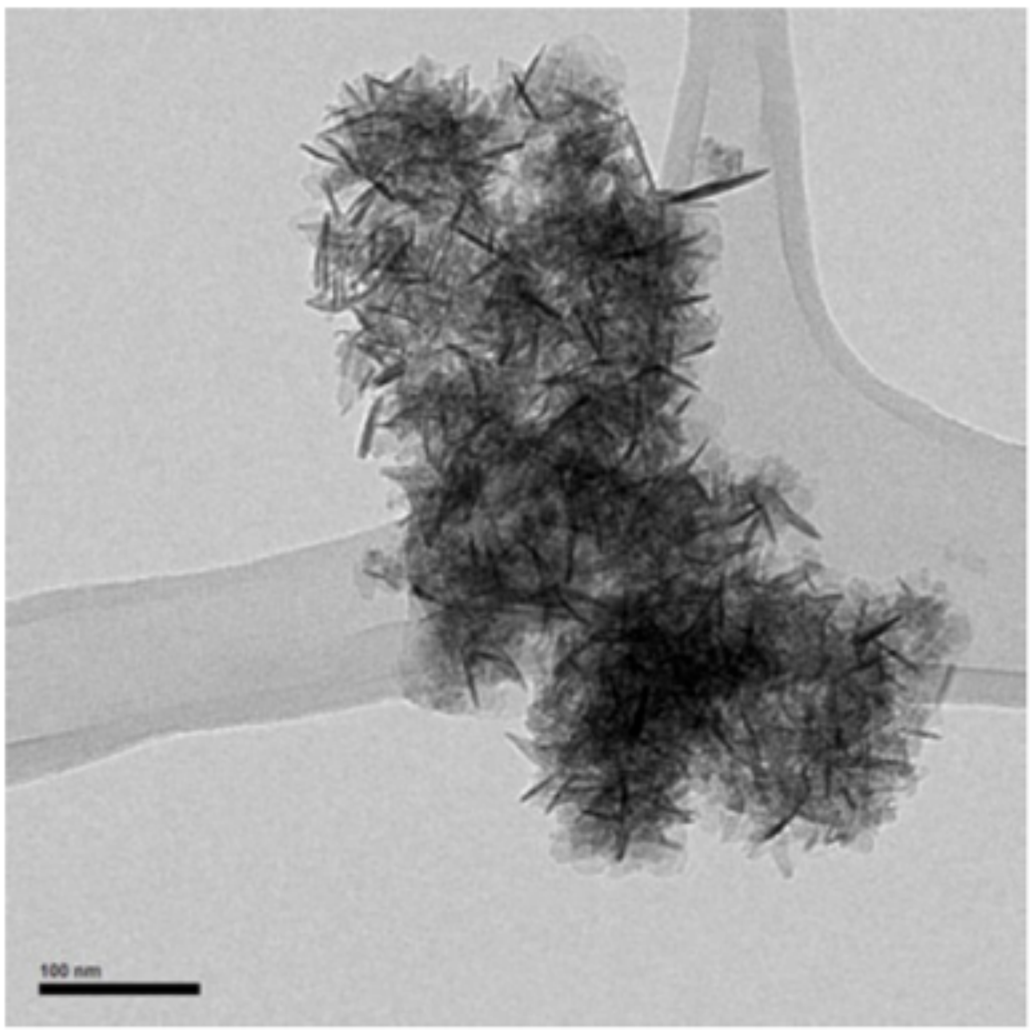
Example: ZnO nanocrystals ~20 nm in diameter

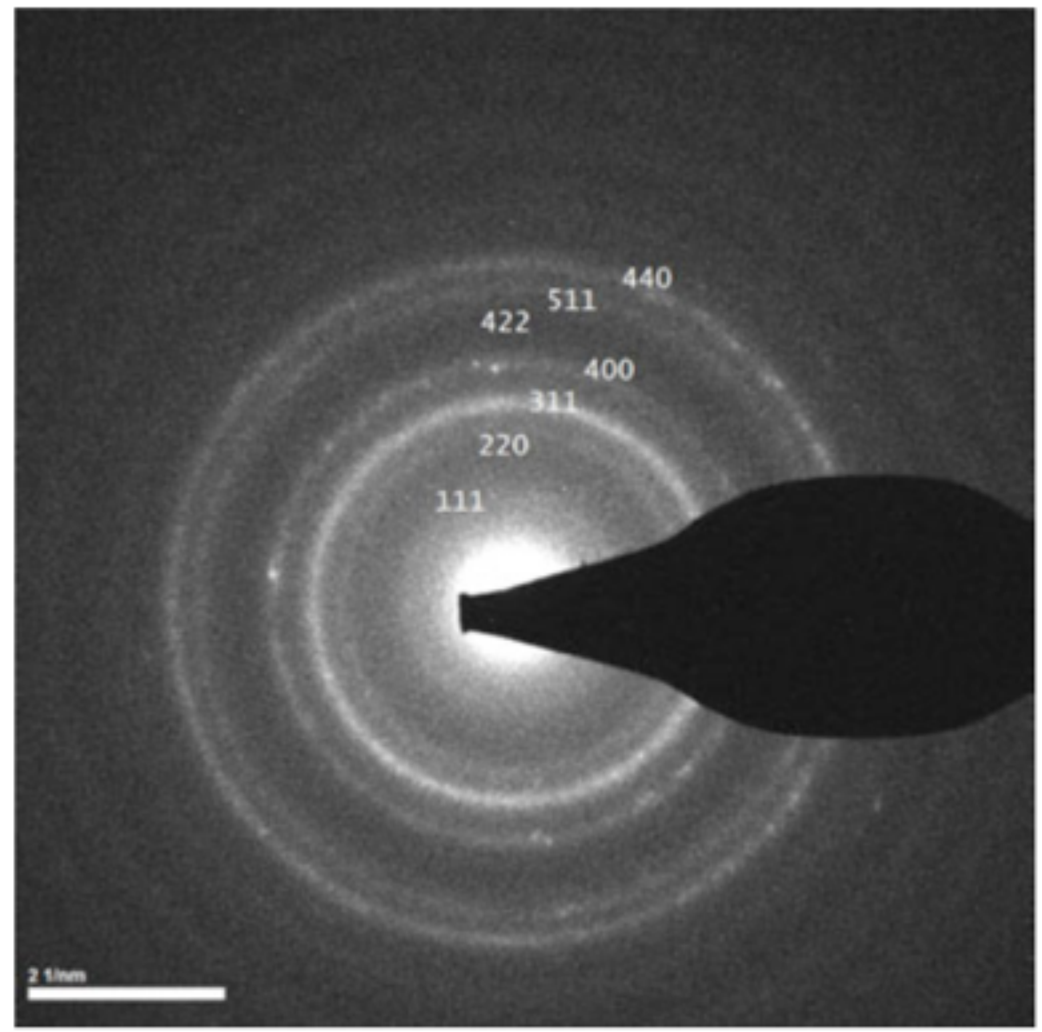




Ring diffraction patterns

If selected area aperture selects numerous, randomly-oriented nanocrystals,
SADP consists of rings sampling all possible diffracting planes
- like powder X-ray diffraction





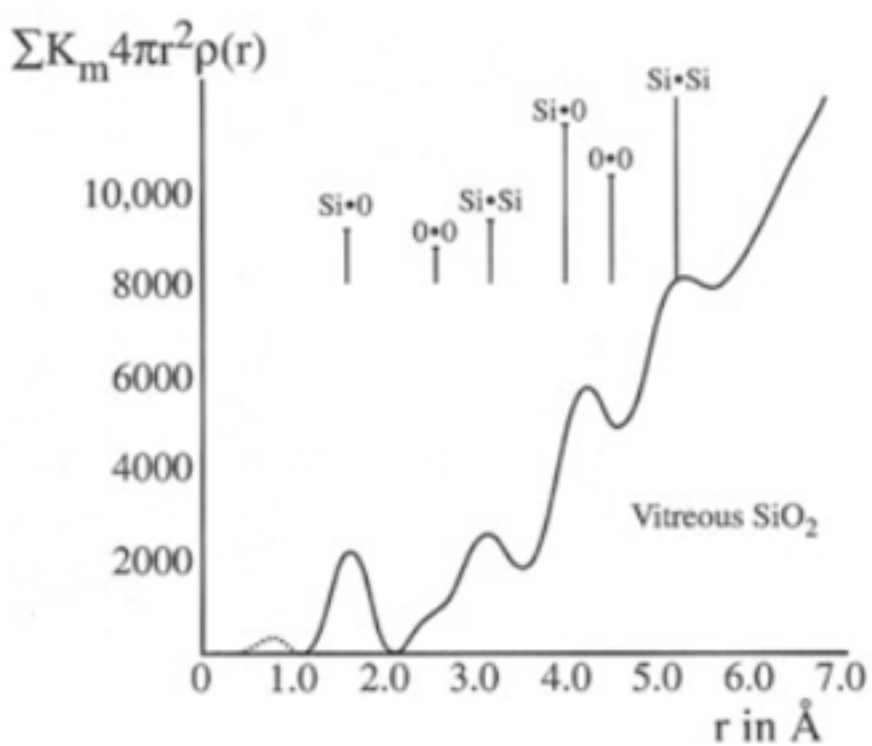
Example: “needles” of contaminant cubic $MnZnO_3$ - which XRD failed to observe!
Note: if scattering sufficiently kinematical, can compare intensities with those of X-ray PDF files

Amorphous diffraction pattern

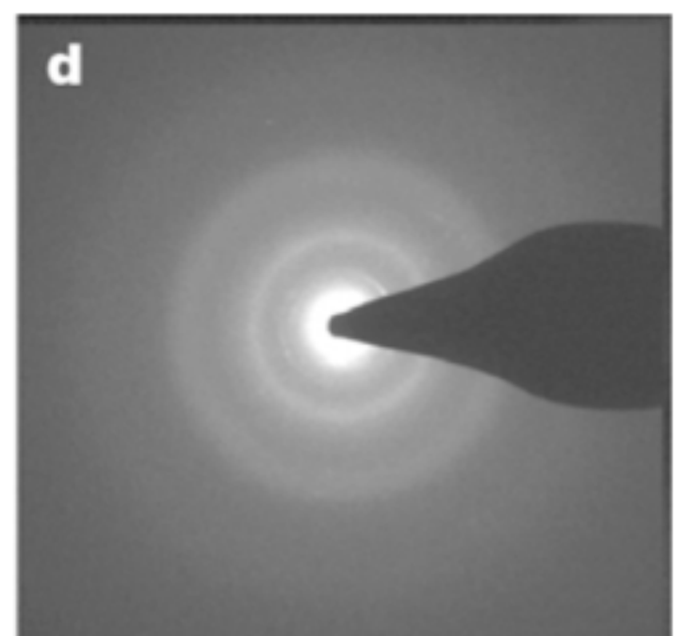
Crystals: short-range order *and* long-range order

Amorphous materials: no long-range order, but do have short-range order (roughly uniform interatomic distances as atoms pack around each other)

Short-range order produces diffuse rings in diffraction pattern



Example:



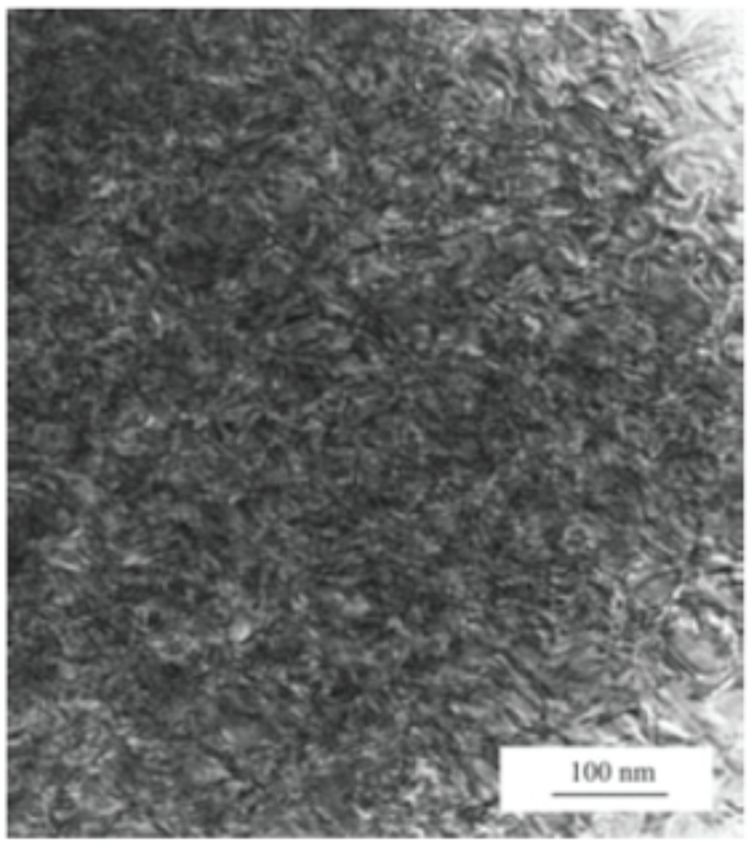
Vitrified germanium

(M. H. Bhat *et al.* Nature **448** 787 (2007)

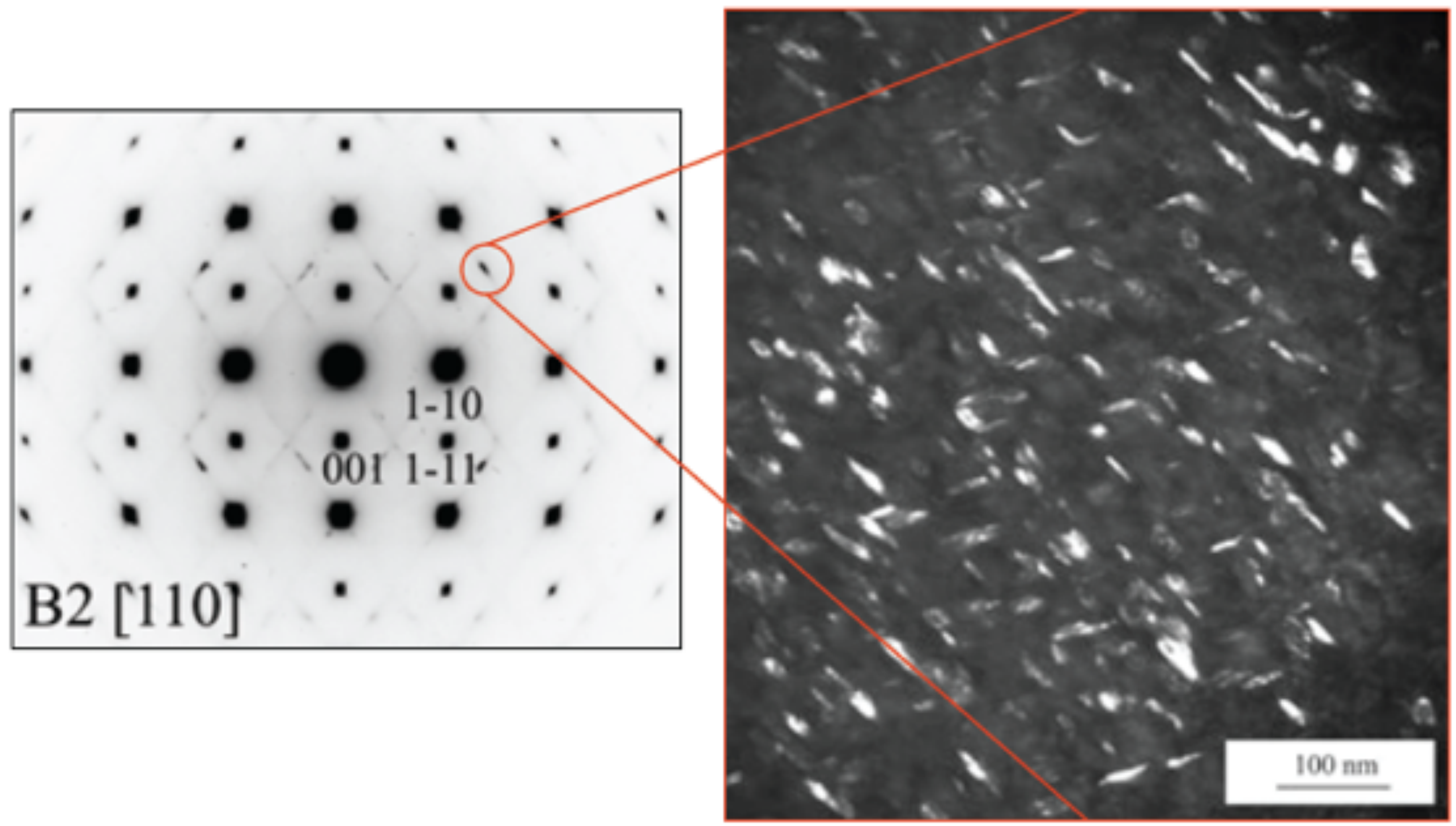
Crystallographically-oriented precipitates

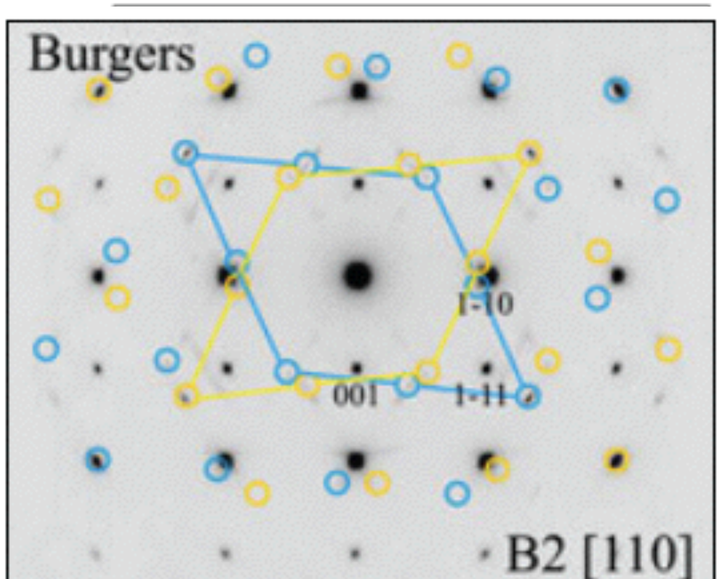
Co-Ni-Al shape memory alloy, austenitic with Co-rich precipitates

Bright-field image



Dark-field image





Burgers relationship:

1^{st} variant of *h.c.p. ε-Co* $(110)_{B2}//(001)_{h.c.p.}$; $[-11\text{-}1]_{B2}//[110]_{h.c.p.}$

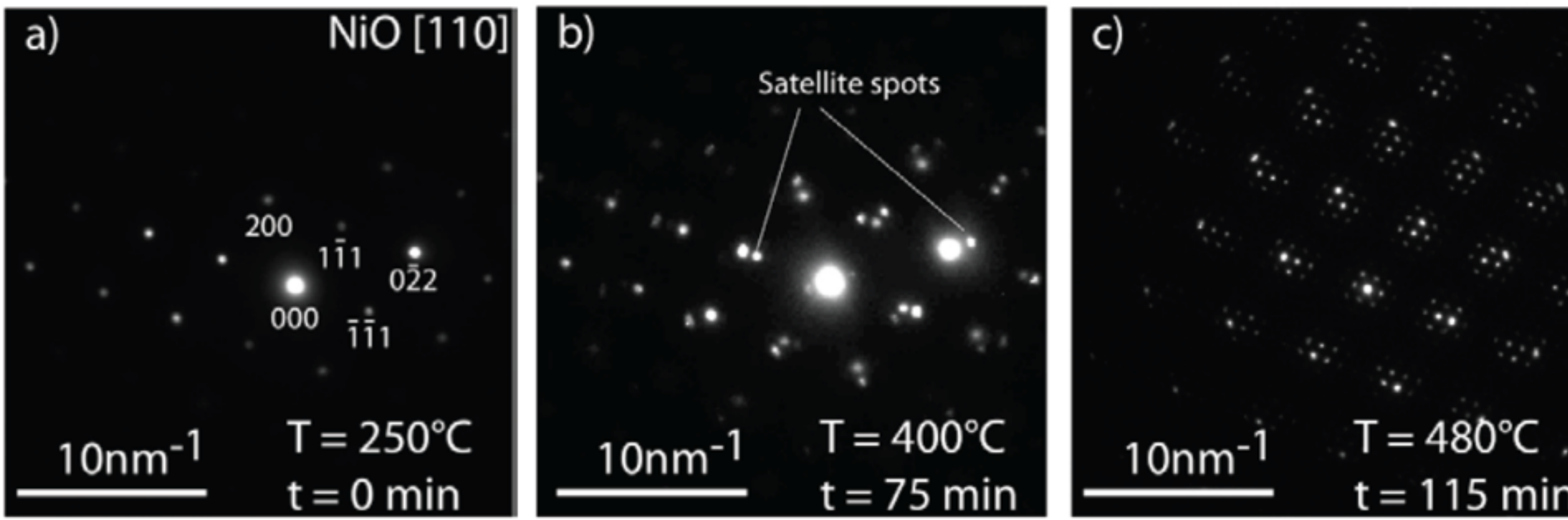
2^{nd} variant of *h.c.p. ε-Co* $(110)_{B2}//(001)_{h.c.p.}$; $[-111]_{B2}//[110]_{h.c.p.}$

Double diffraction

Special type of multiple elastic scattering: diffracted beam travelling through a crystal is rediffracted

Example 1: rediffraction in different crystal - NiO being reduced to Ni in-situ in TEM

Epitaxial relationship between the two FCC structures (NiO: a = 0.42 nm Ni: a = 0.37 nm)



Formation of satellite spots around Bragg reflections

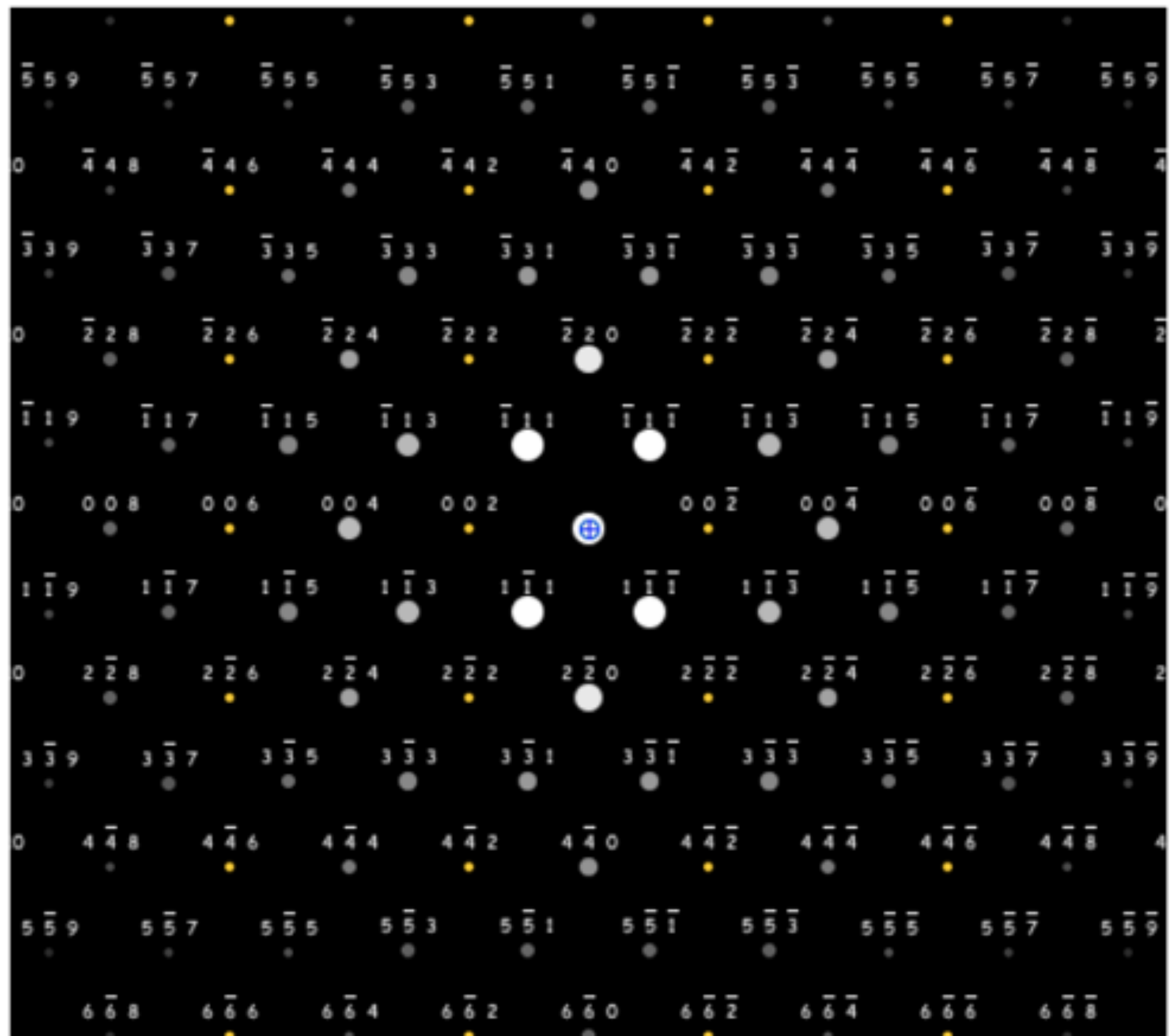
Double diffraction

Example II: rediffraction in the same crystal; appearance of forbidden reflections

Example of silicon; from symmetry of the structure {2 0 0} reflections should be absent

However, normally see them because of double diffraction

Simulate diffraction pattern on [1 1 0] zone axis:

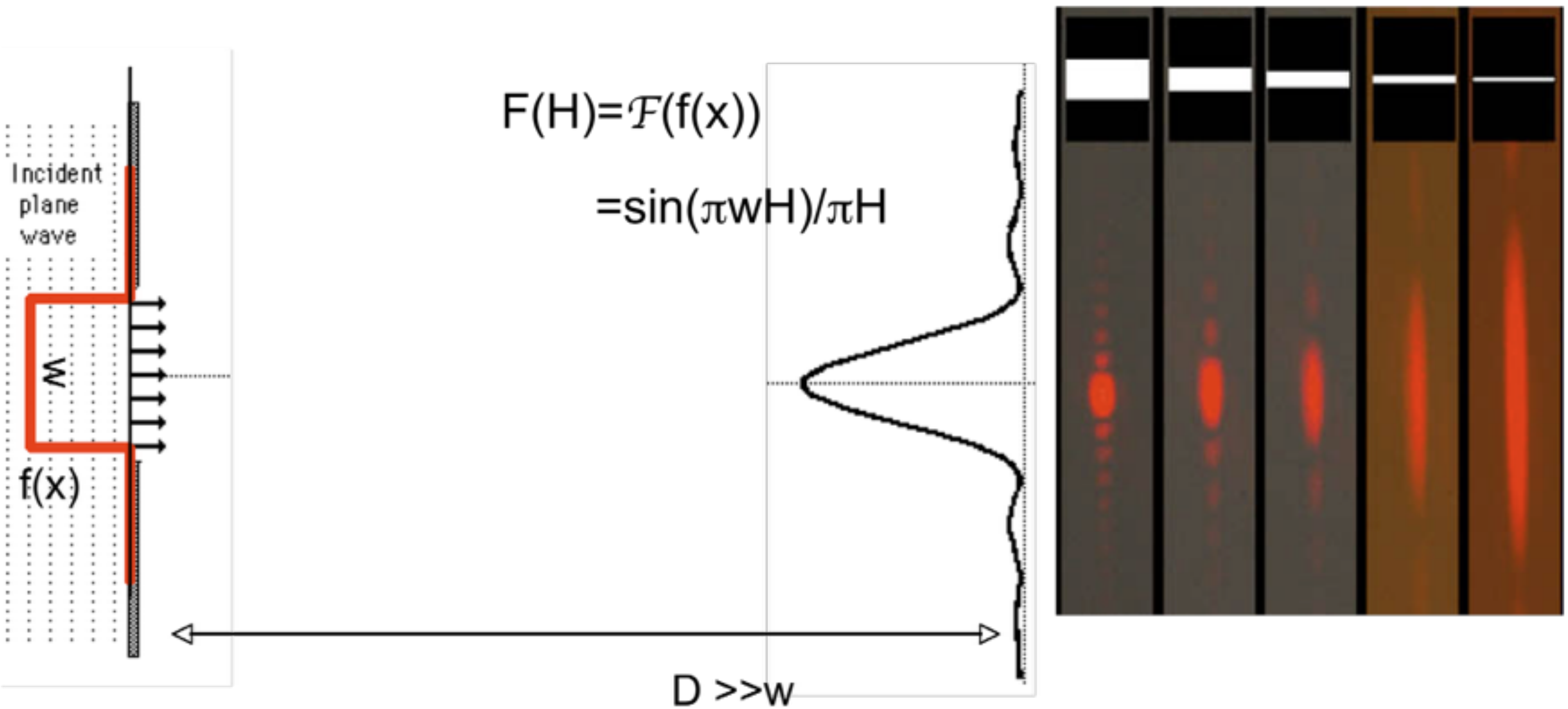


Fourier Transform of Top-Hat Function

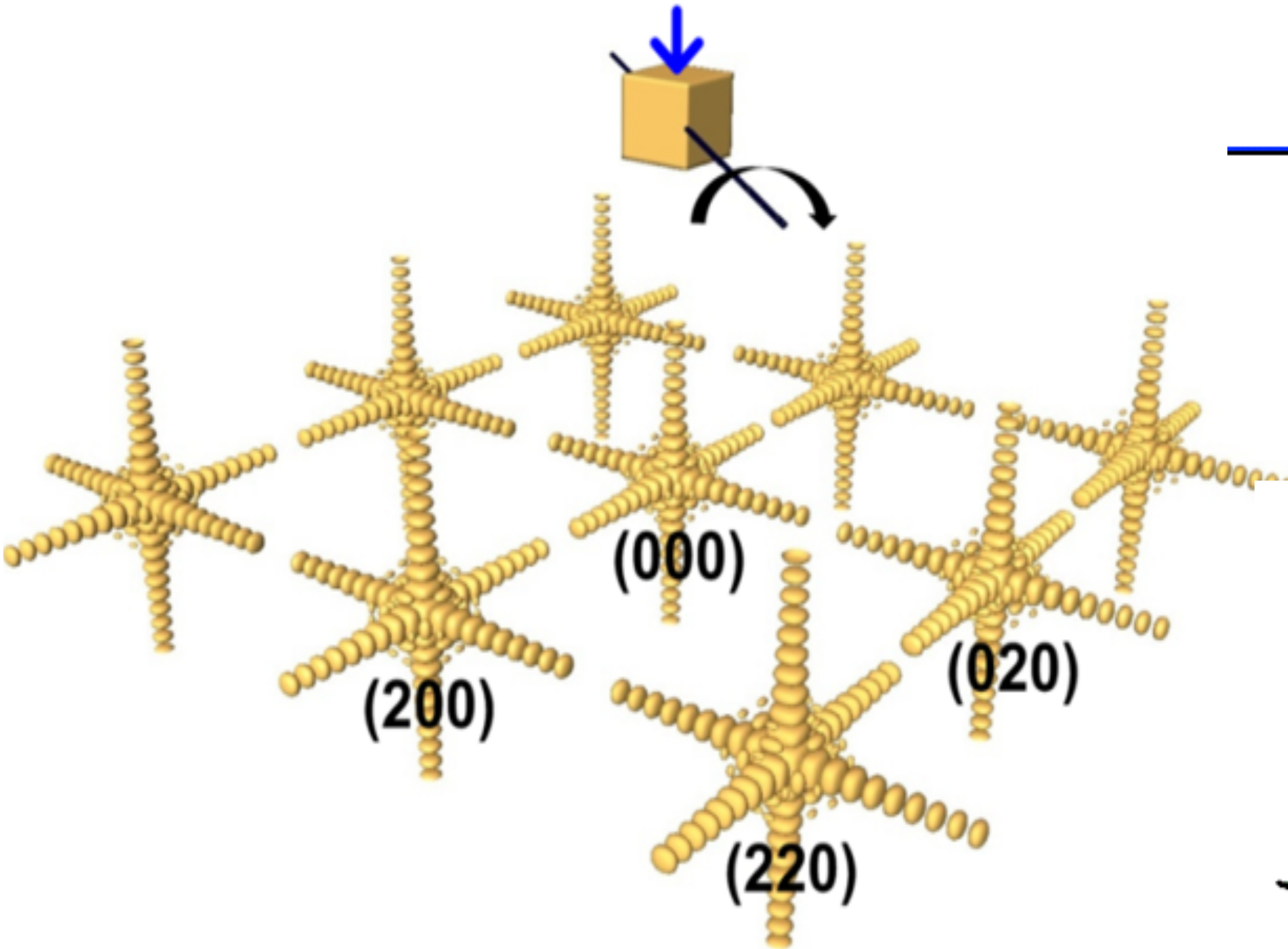
Fraunhofer Diffraction

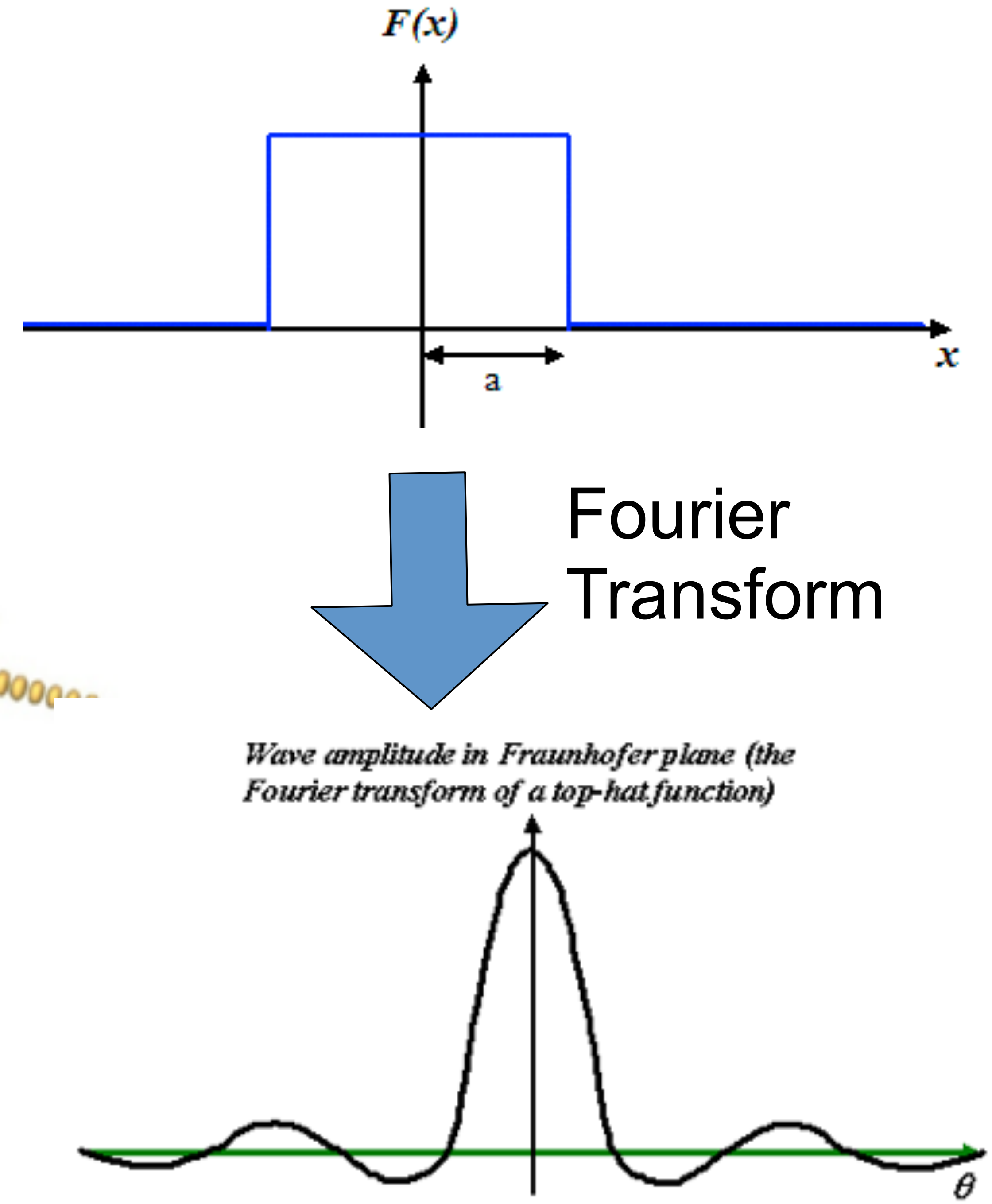
NTHU

$$F(H) = \mathcal{F}(f(x))$$
$$= \sin(\pi w H)/\pi H$$



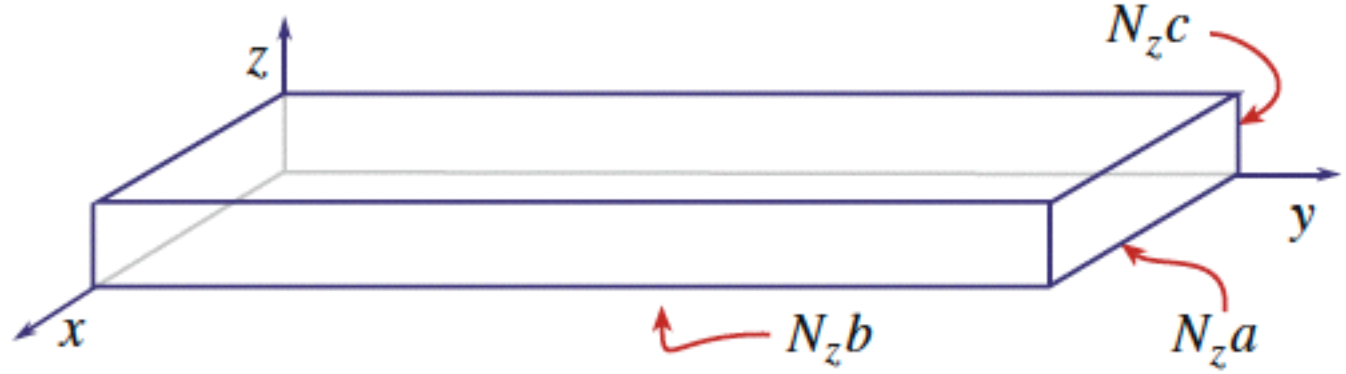
3.3.4 Shape Effect for nano-object





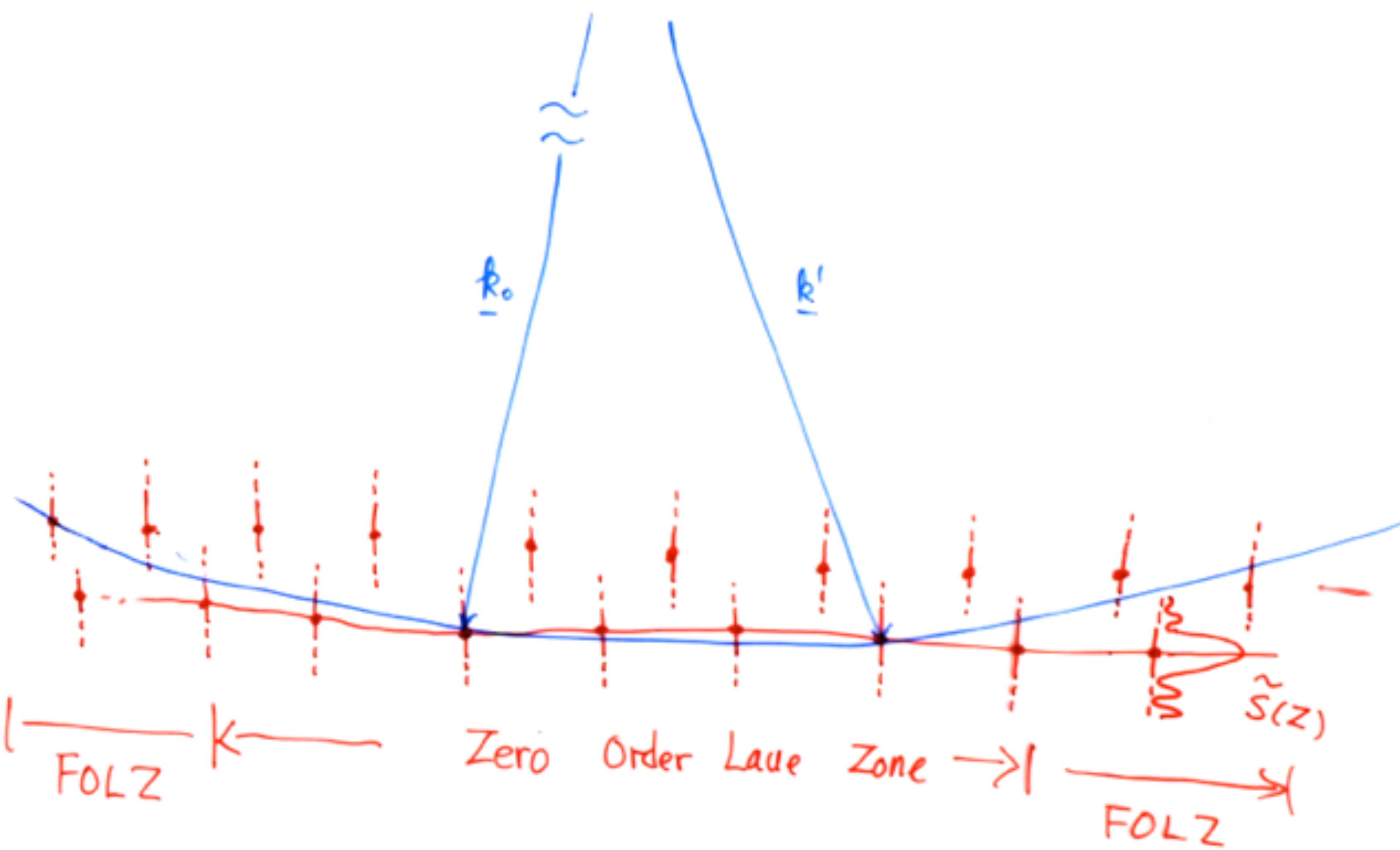
$$I = |A|^2 = |F|^2 \left(\frac{\sin^2(\pi N_x \mathbf{K}.\mathbf{a})}{\sin^2(\pi \mathbf{K}.\mathbf{a})}\right) \left(\frac{\sin^2(\pi N_y \mathbf{K}.\mathbf{b})}{\sin^2(\pi \mathbf{K}.\mathbf{b})}\right) \left(\frac{\sin^2(\pi N_z \mathbf{K}.\mathbf{c})}{\sin^2(\pi \mathbf{K}.\mathbf{c})}\right)$$

3.3.5 Thin Foil Effect

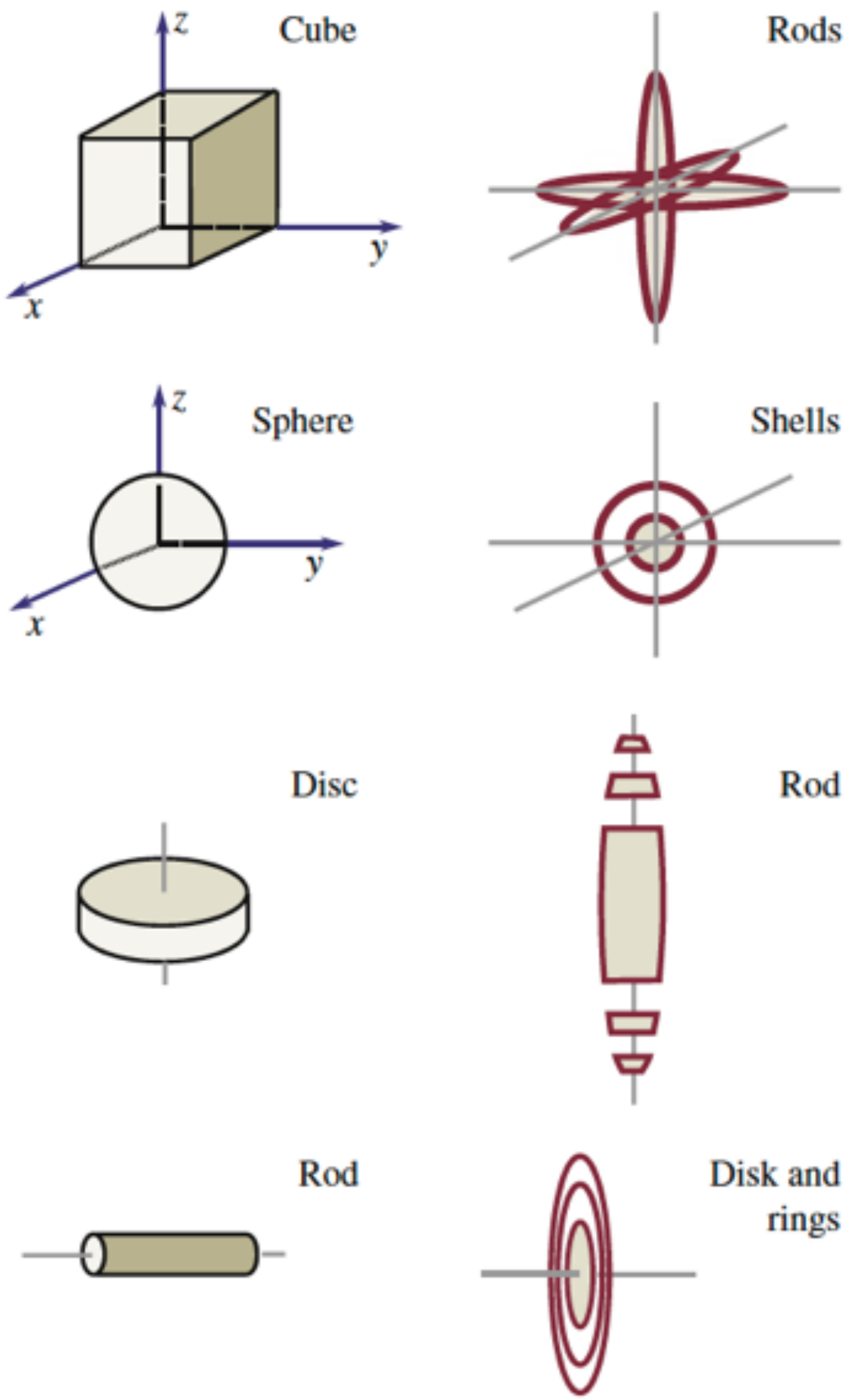


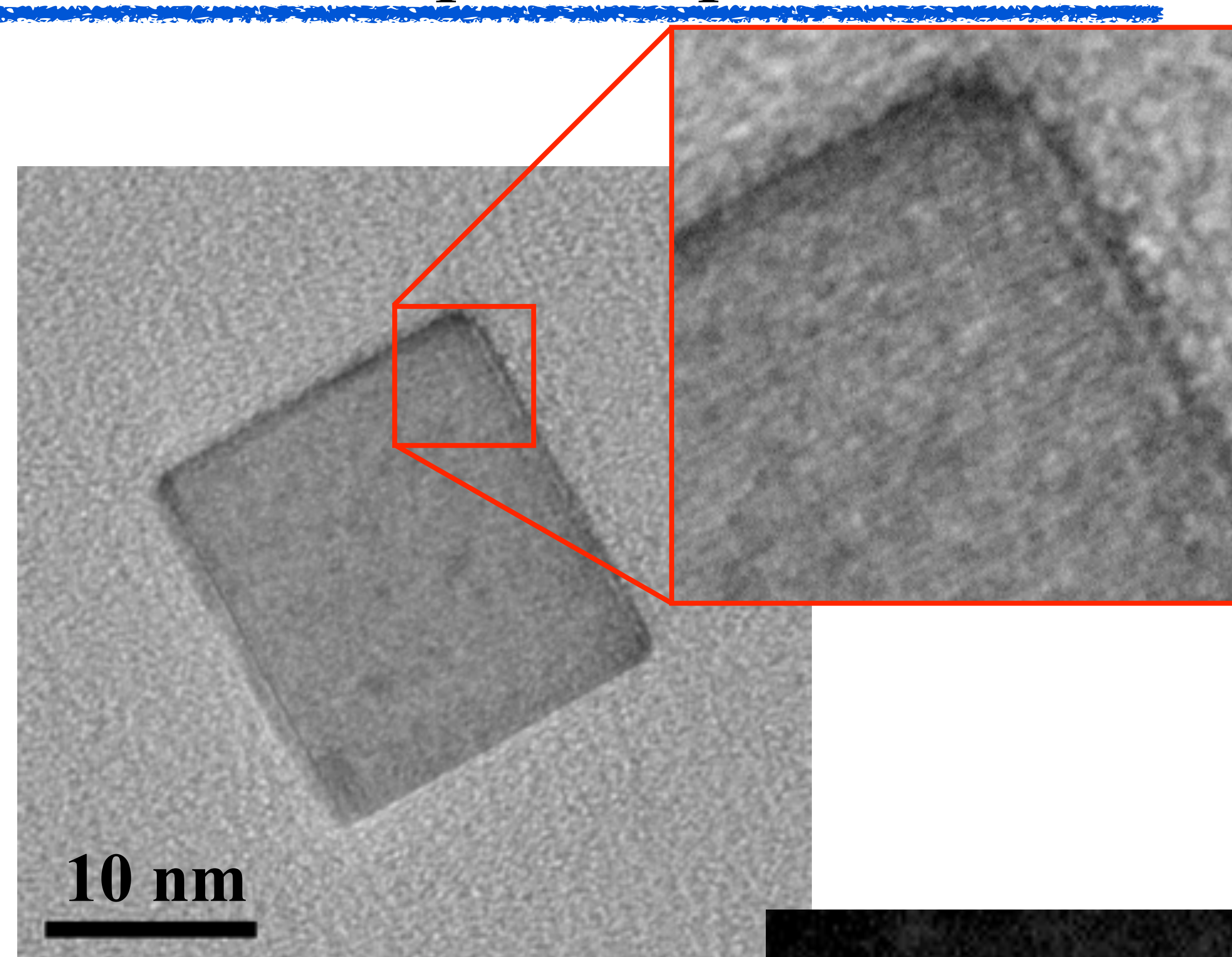
• 每一晶格點沿著Z方向(i.e 垂直試片表面)被一棍狀函數代替.

每一晶格點沿著Z方向(i.e. 垂直試片表面)被一棍狀函數代替.

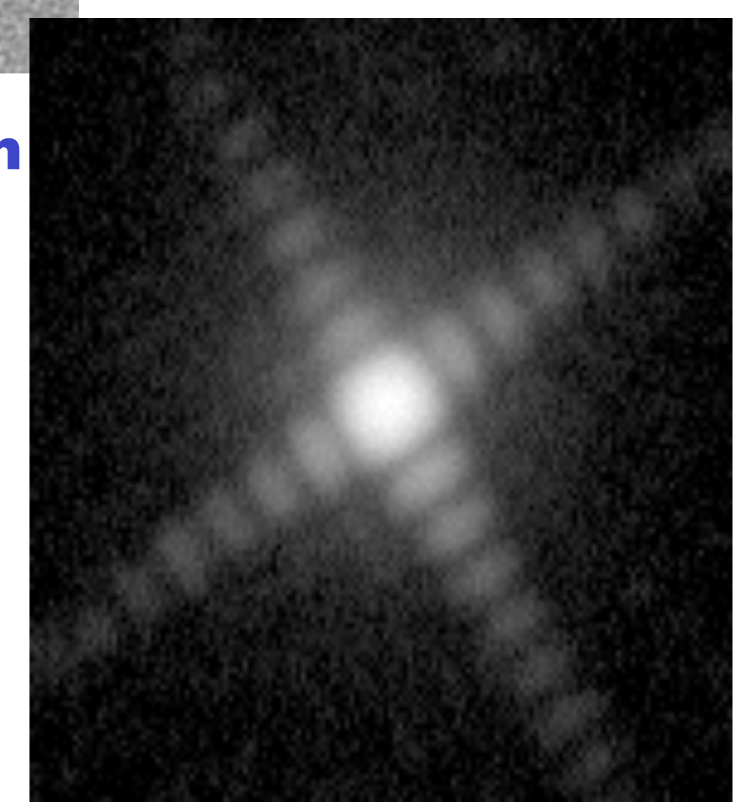


3.3.4 Diffraction from nano-Precipitates, particles



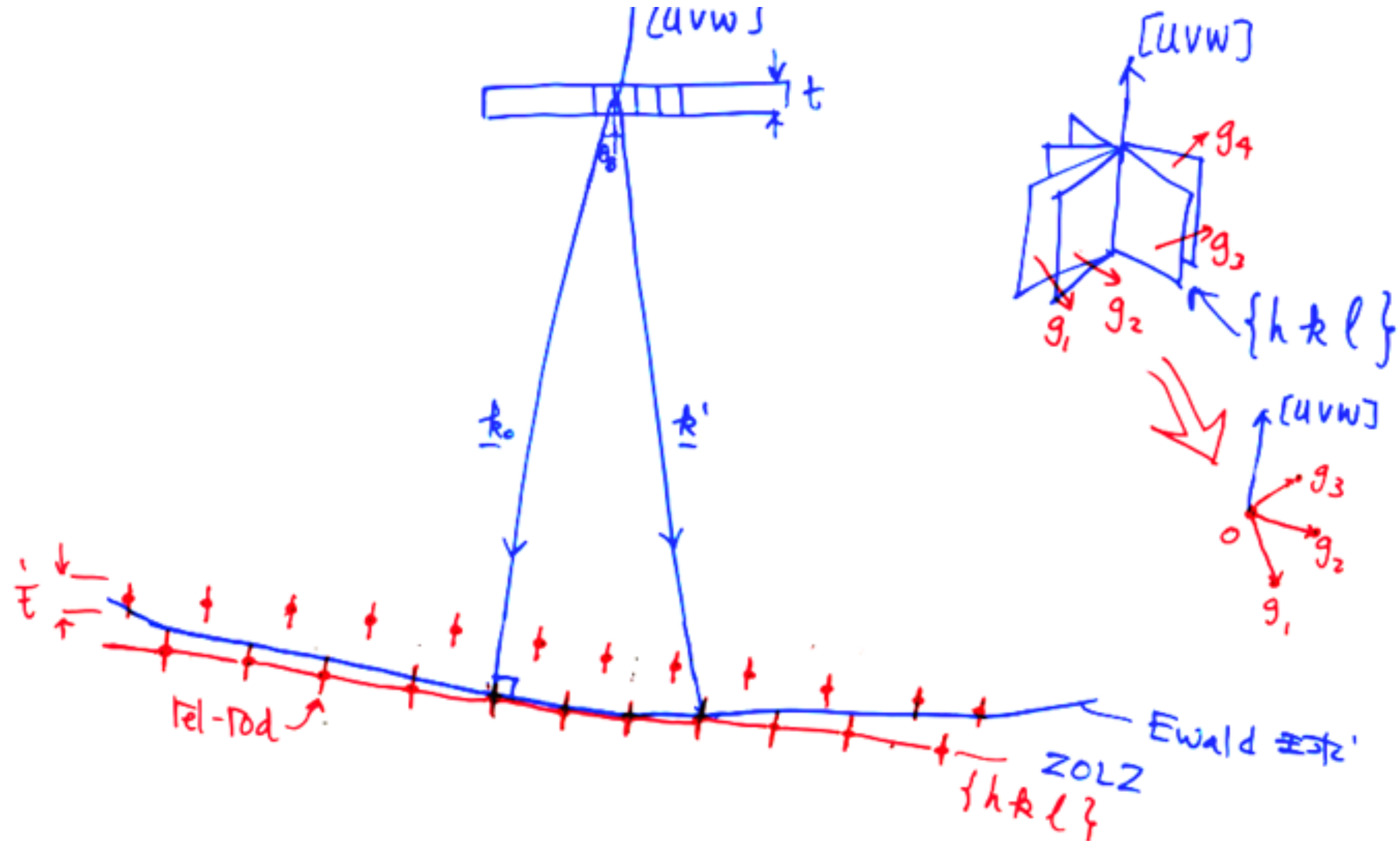


HRTEM image of 17nm MgO cube after preparation



Diffuse scattering around [200] Bragg peak

3.3.5 晶軸” (Zone axis)

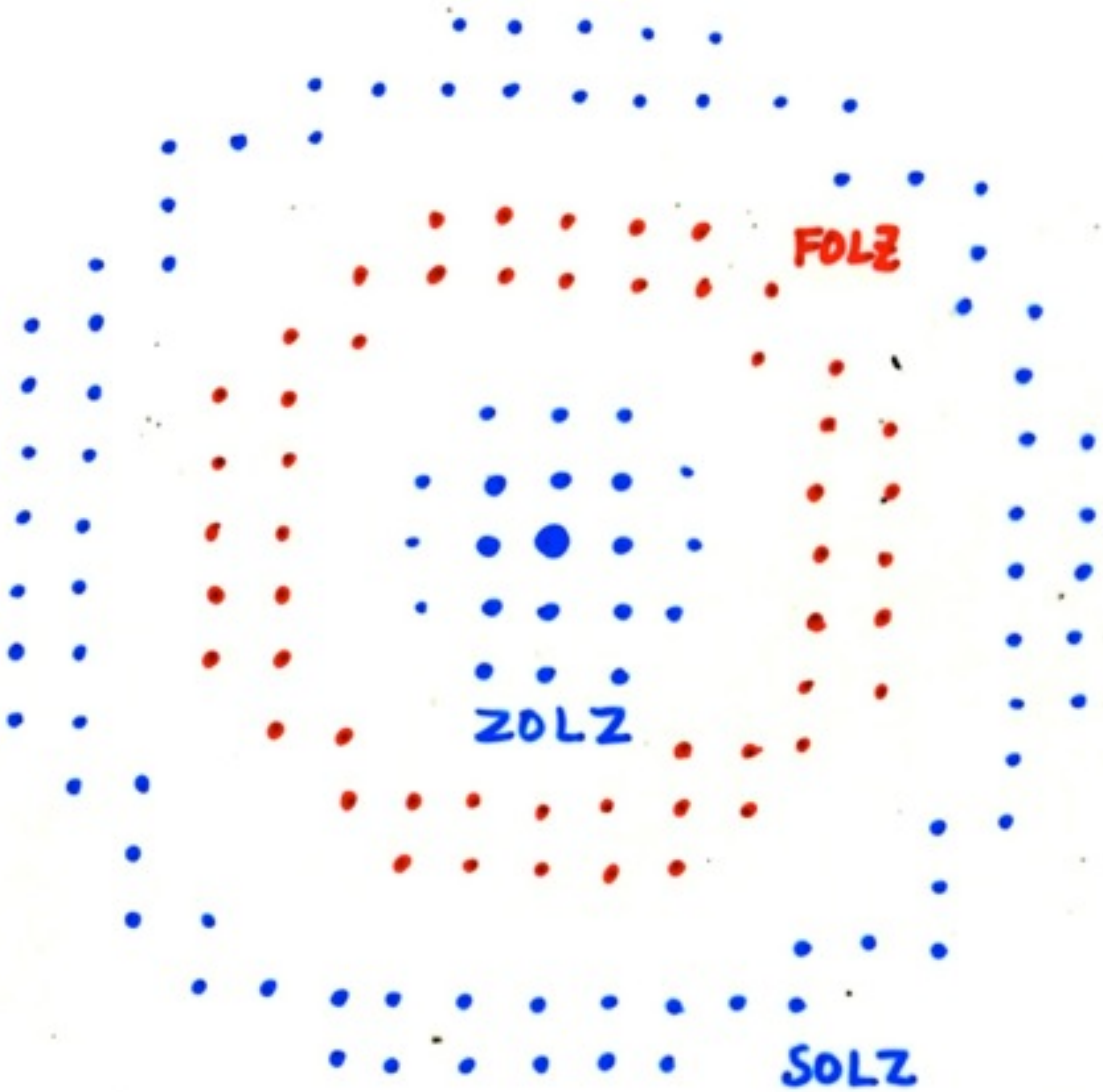


•rel-rod 的長度與晶體的厚度成反比

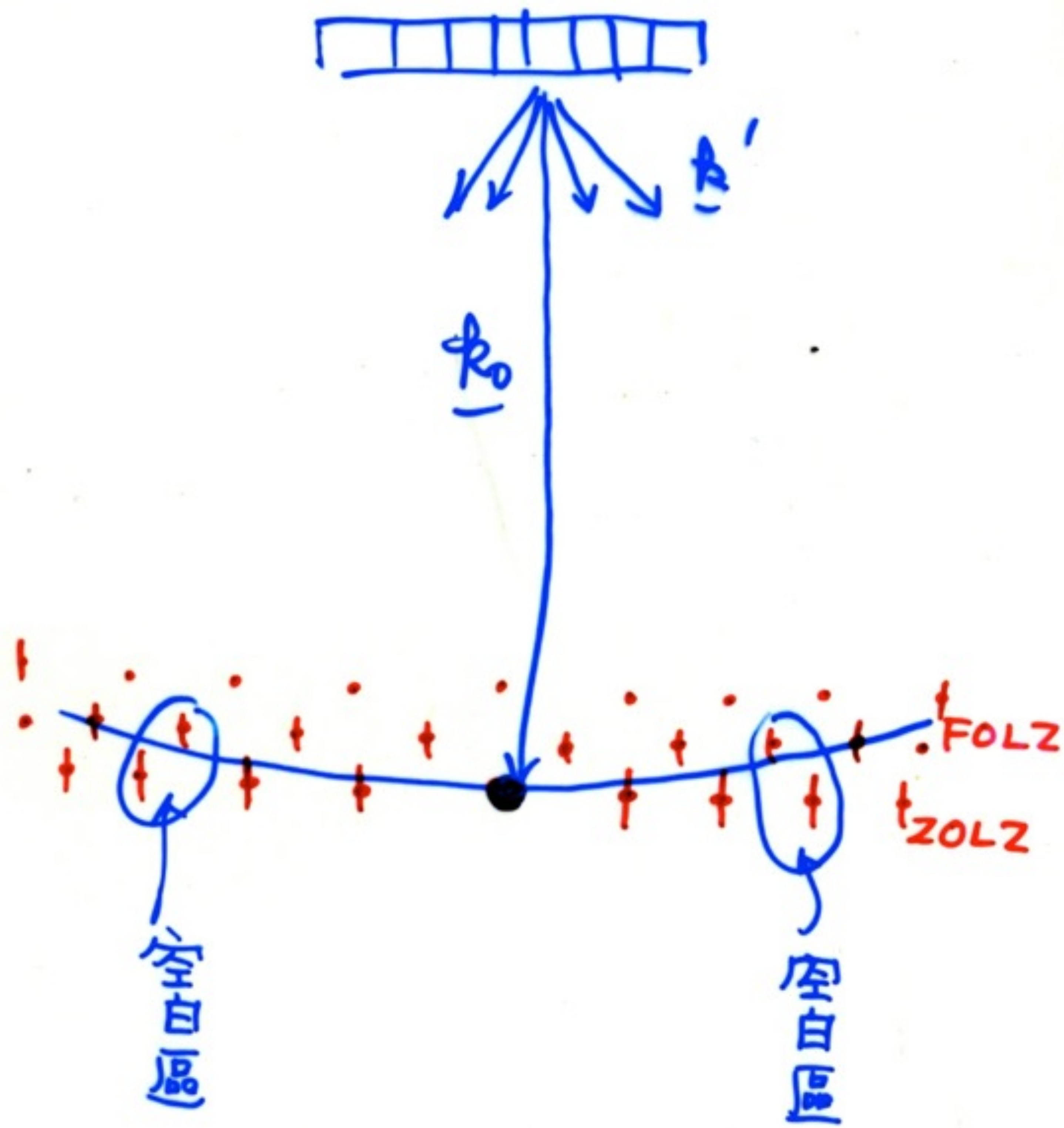
•[u v w]是所有{h k l}平面的交線,稱為“晶軸” (Zone axis)

晶軸為各平面之交線晶軸方向垂直於各平面之法向量

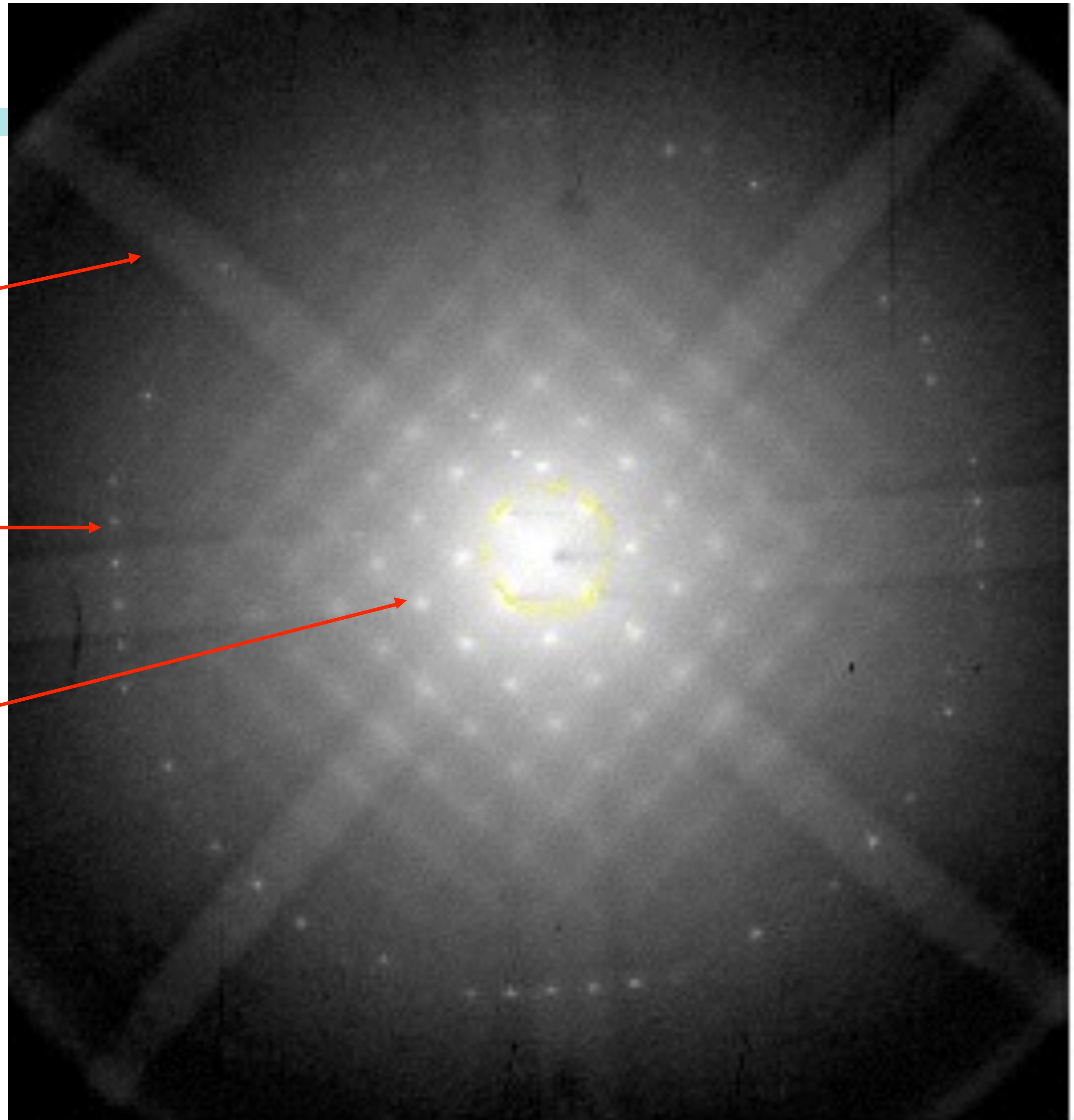
*•事實上若電子束平行於晶軸沒有任何一組平面是滿足繞射條件。（都是薄樣品的條件下而近似滿足Bragg’s條件）



晶軸繞射花樣



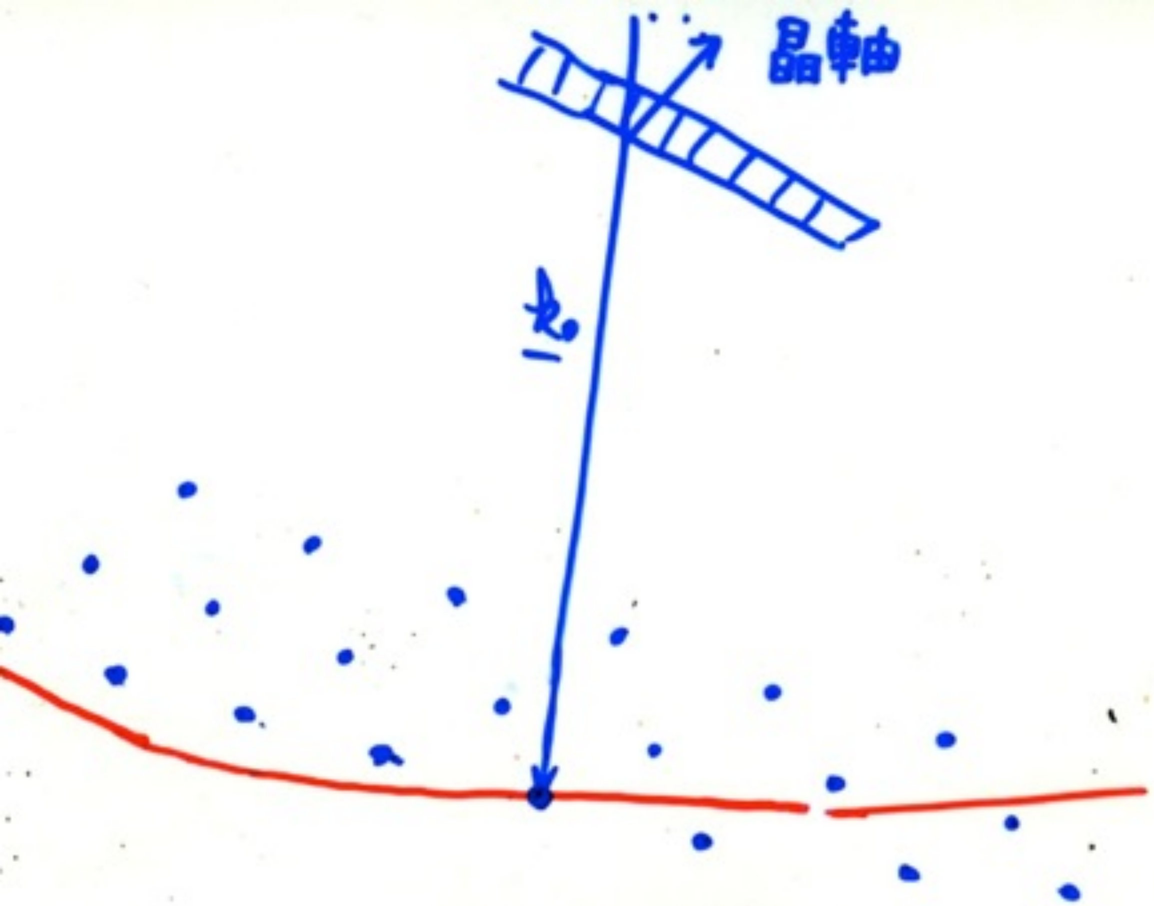
• 在正晶軸時偏離參數($s < 0$)



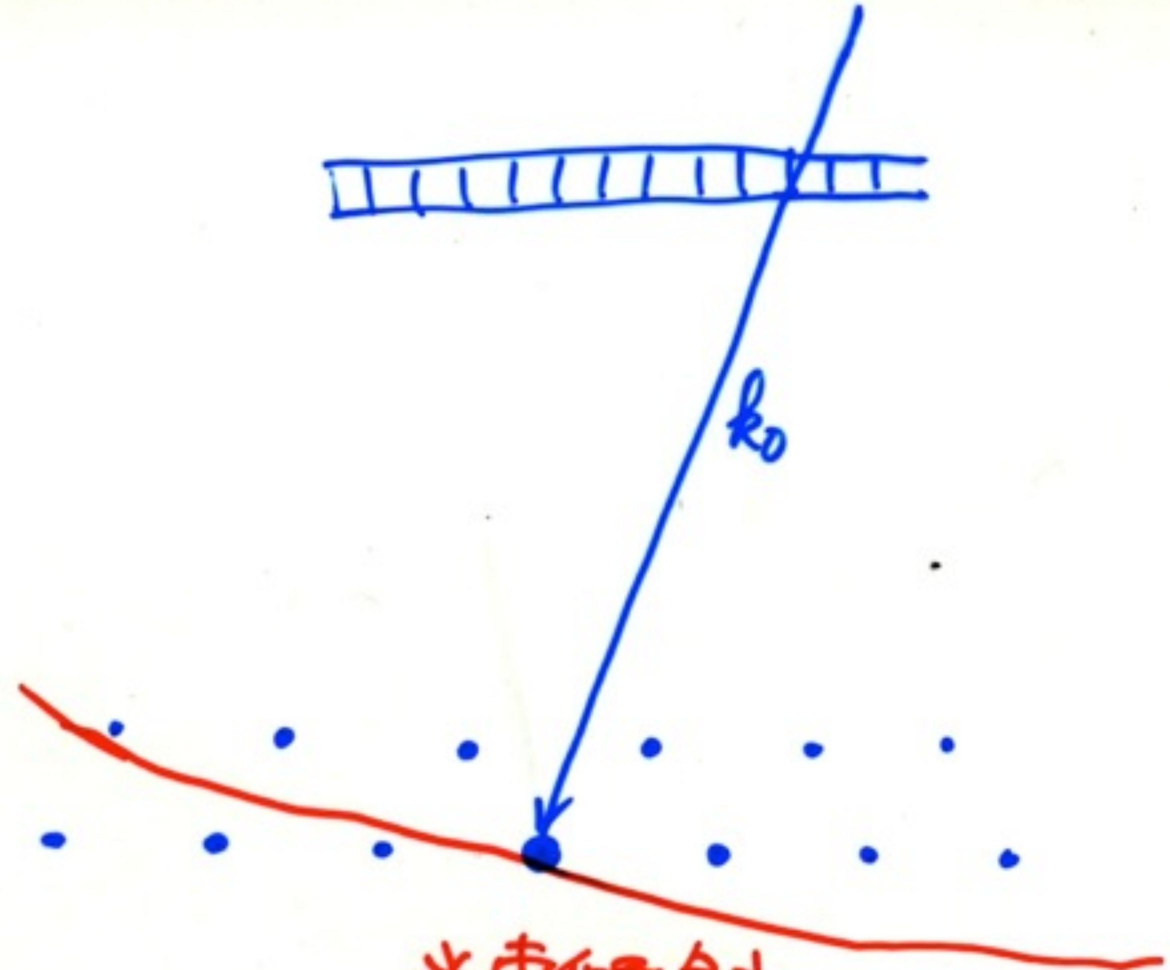
Kikuchi Lines

HOLZ

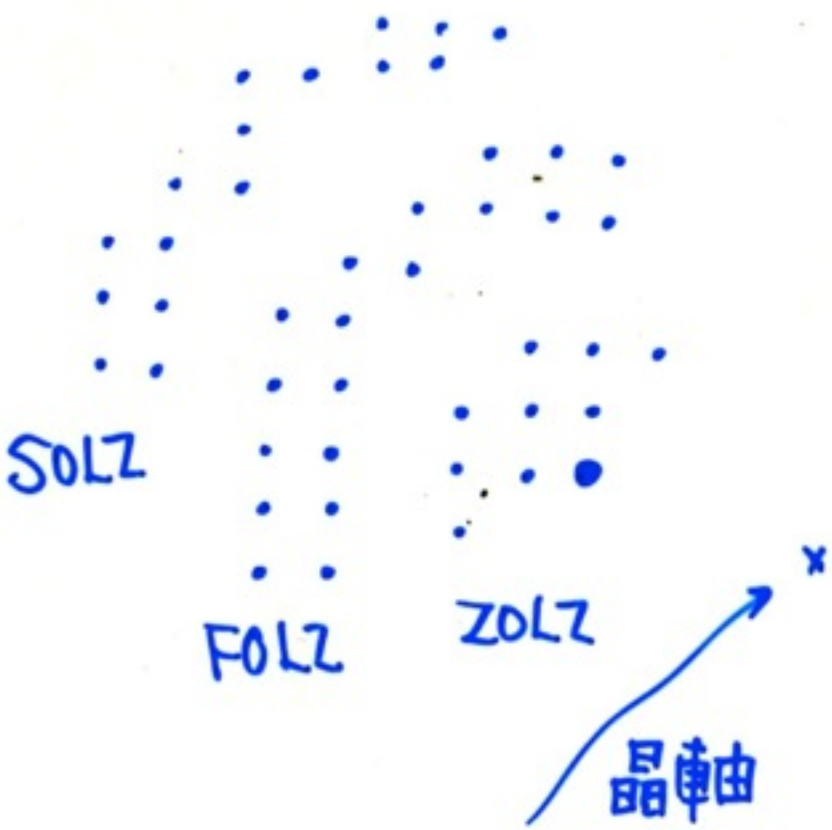
ZOLZ

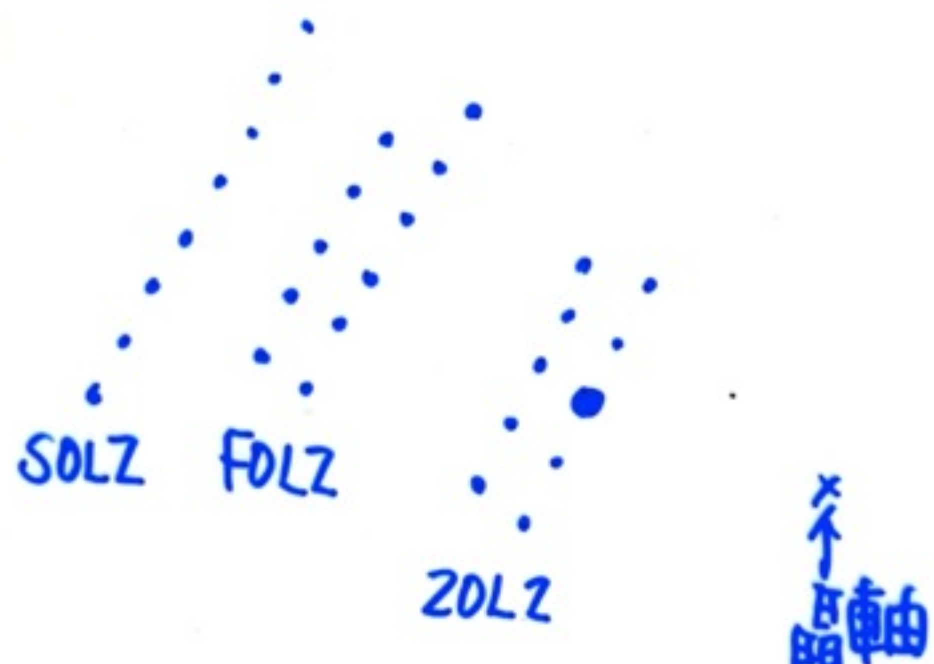


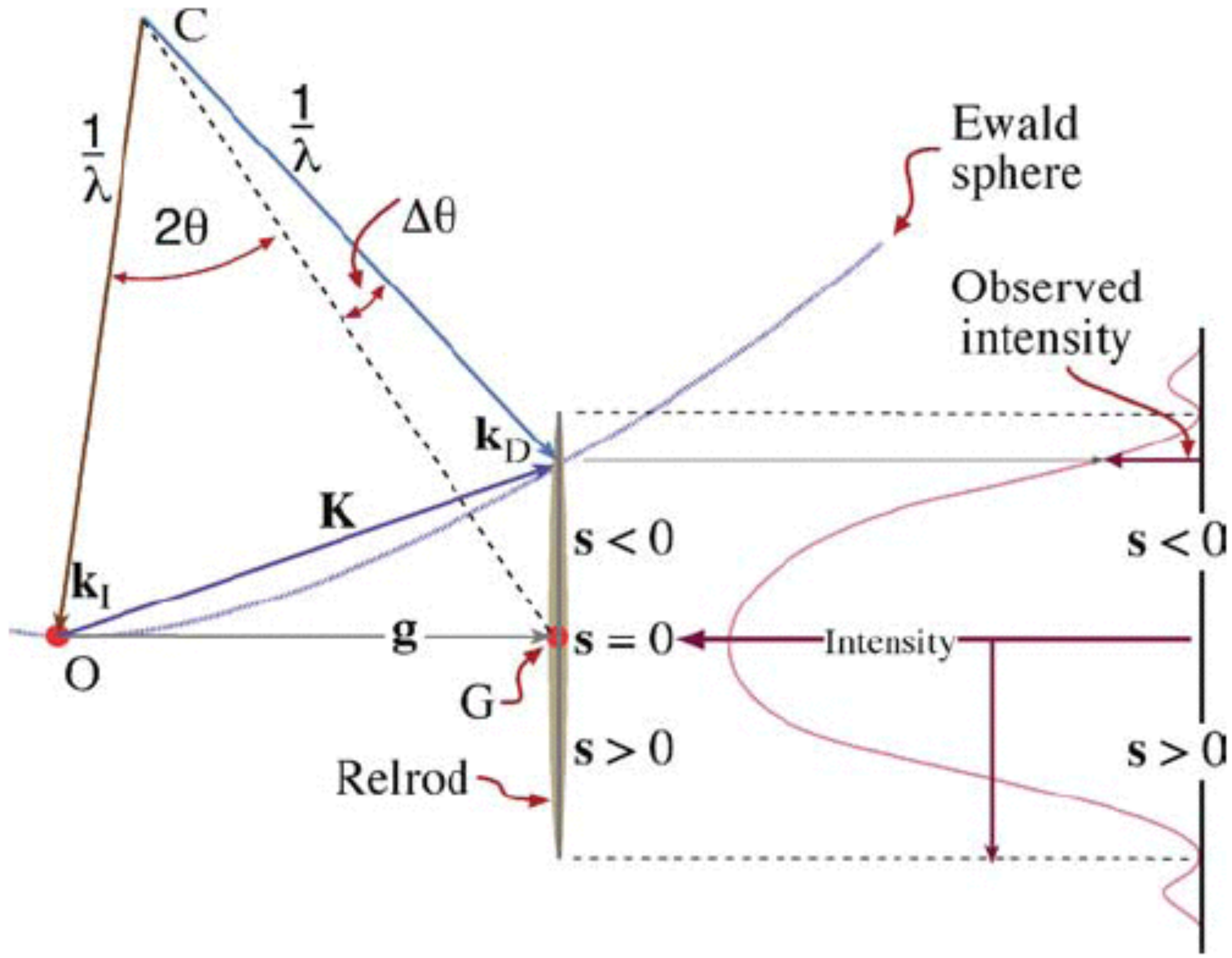
晶体傾斜
(倒晶格傾斜)



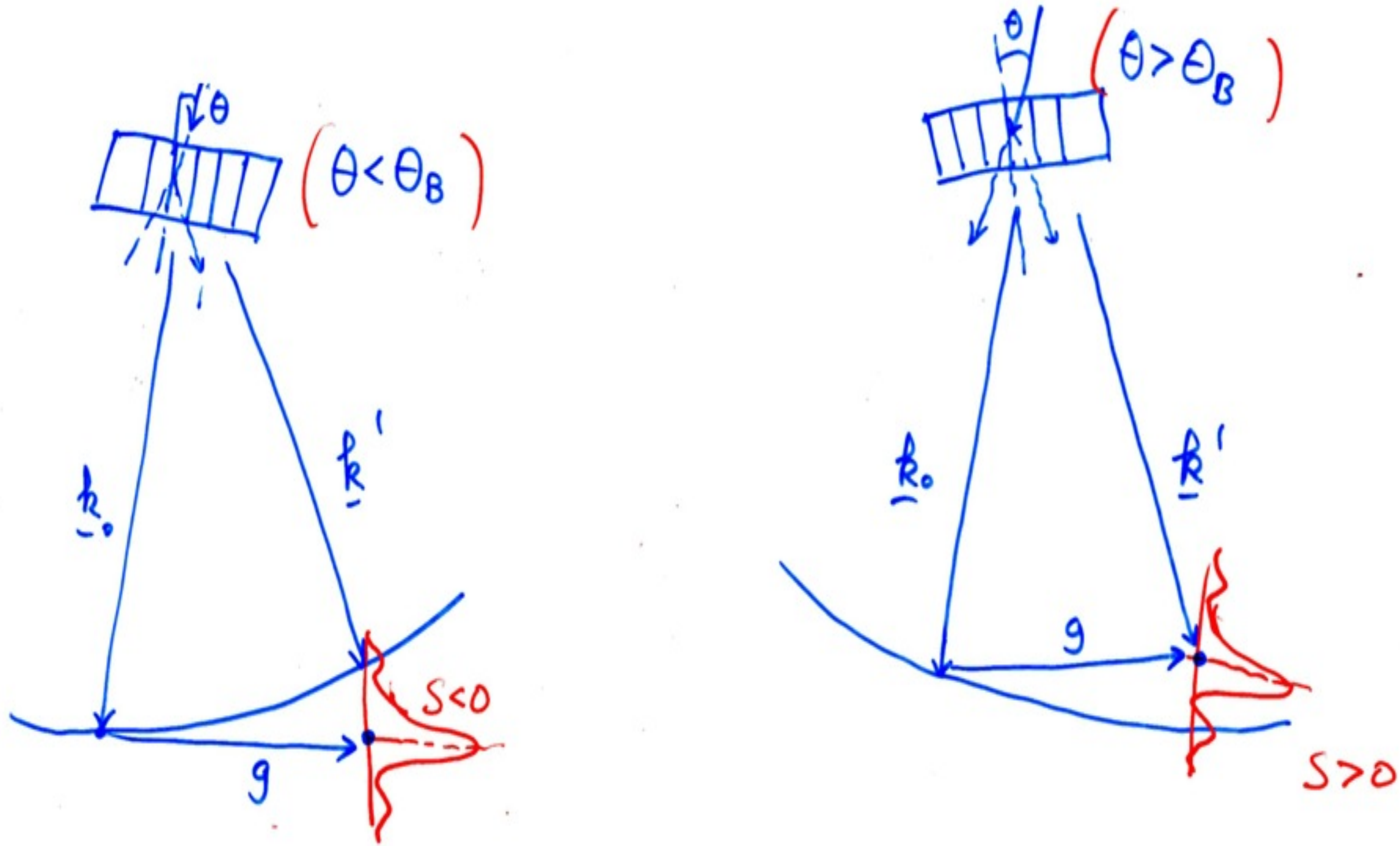
光束傾斜
(Ewald球傾斜)

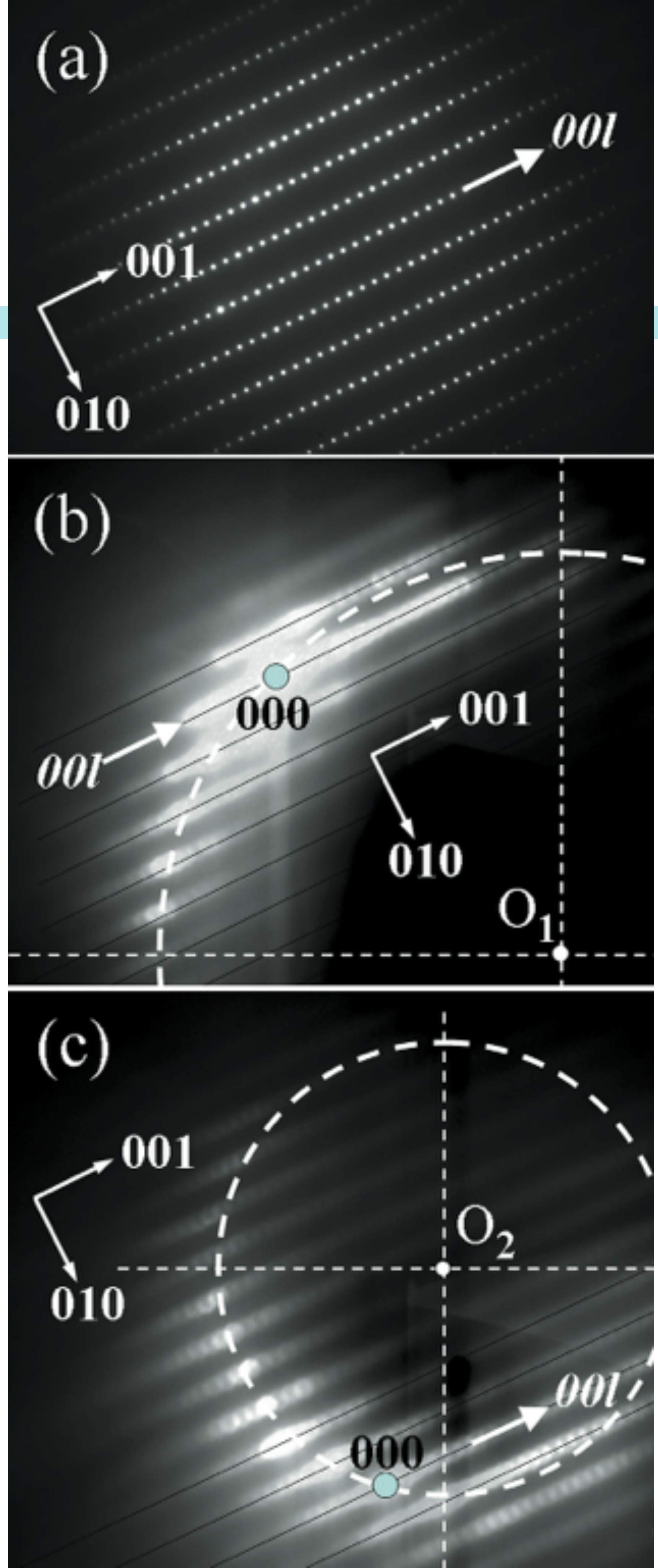


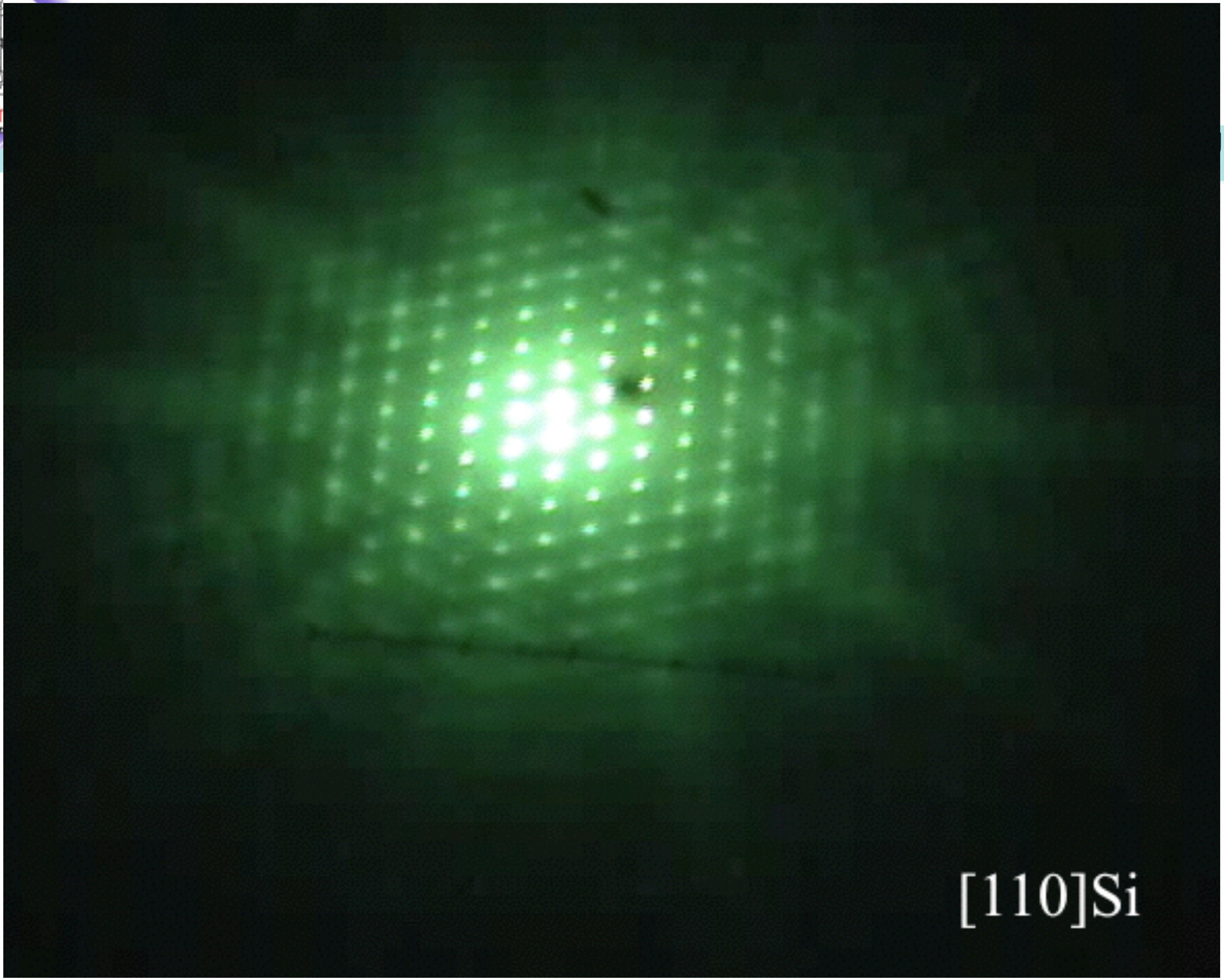


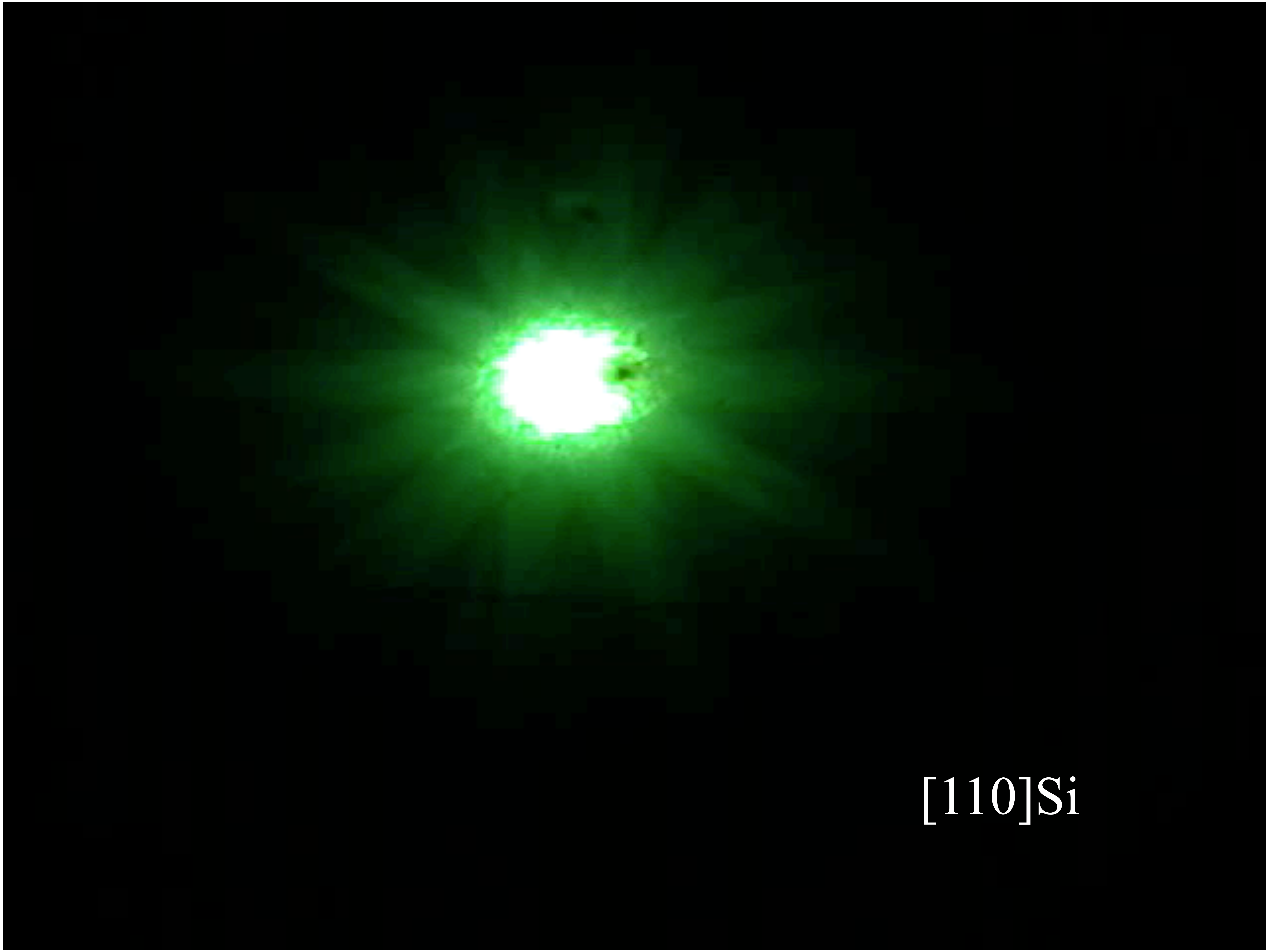

C
$\frac{1}{\lambda}$
$\frac{1}{\lambda}$
2θ
$\Delta\theta$
Ewald sphere
Observed intensity
$\mathbf{k}_D$
$\mathbf{K}$
$\mathbf{k}_I$
$\mathbf{g}$
O
G
Relrod
$\mathbf{s} < 0$
$\mathbf{s} = 0$
$\mathbf{s} > 0$
Intensity
$\mathbf{s} < 0$
$\mathbf{s} > 0$

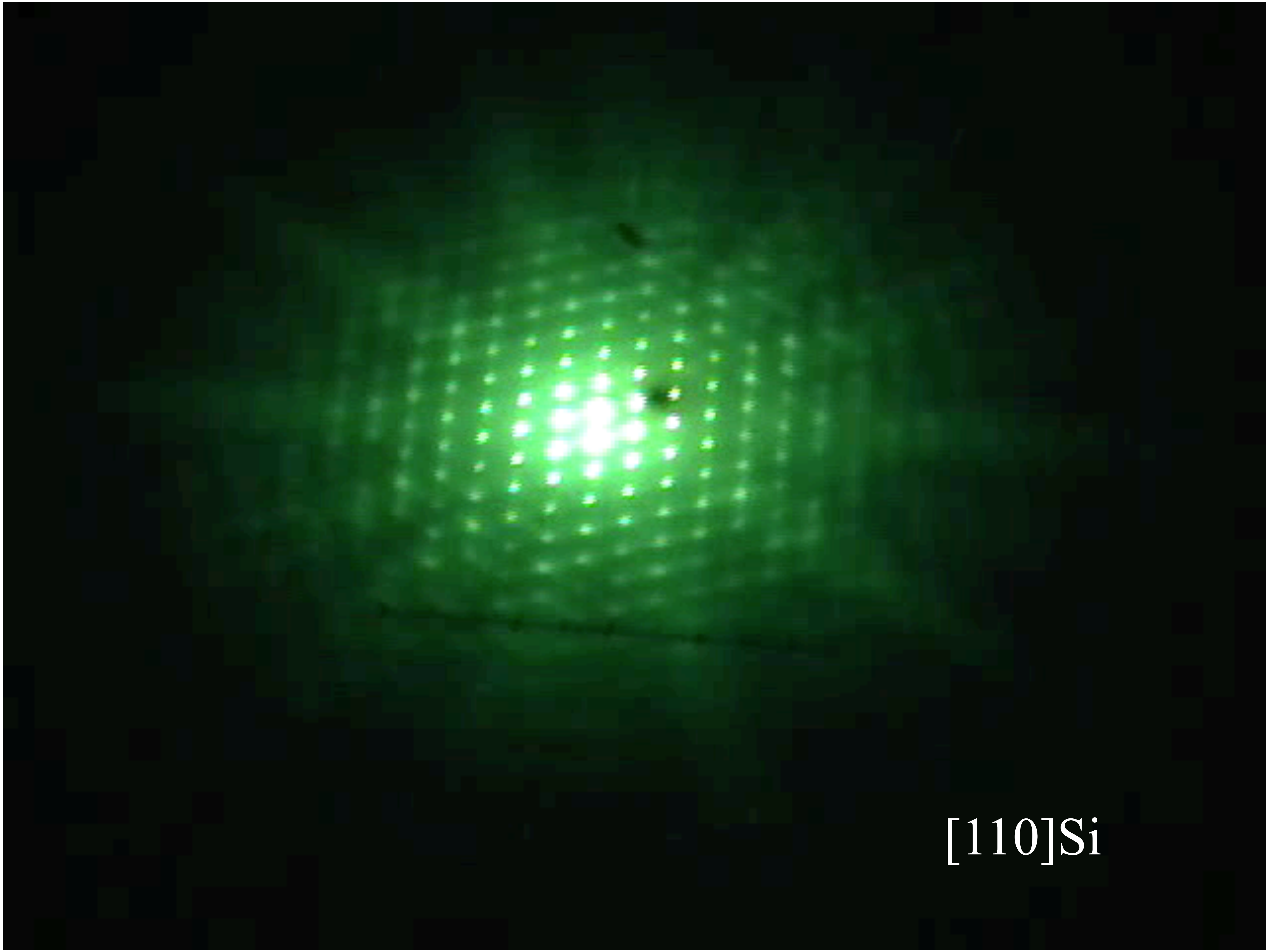
習慣上，S>0倒晶格點在Ewald球內部；S<0倒晶格點在Ewald球內部




(a)
00l
001
010
(b)
000
001
00l
010
O1
(c)
001
010
O2
00l
000


[110]Si


[110]Si


[110]Si