

# 1.5 晶体结构的实验研究

一. X射线衍射

二. X射线衍射的几何理论

三. 影响X射线衍射强度的因素

四. X射线衍射实验方法简介

五. X射线衍射研究实例

六. X射线的产生

七. 电子衍射和中子衍射

八. 原子结构的直接观察

## • 与晶体结构分析有关的部分诺贝尔奖获得者名单

年份	学科	得奖者	内 容
1901	物理	伦琴Wilhelm Conral Rontgen	X射线的发现
1914	物理	劳埃Max von Laue	晶体的X射线衍射
1915	物理	亨利. 布拉格Henry Bragg	晶体结构的X射线分析
		劳伦斯. 布拉格Lawrence Bragg.	
1917	物理	巴克拉Charles Glover Barkla	元素的特征X射线
1924	物理	卡尔. 西格班Karl Manne Georg Siegbahn	X射线光谱学
1937	物理	戴维森Clinton Joseph Davisson	电子衍射
		汤姆孙George Paget Thomson	
1954	化学	鲍林Linus Carl Pauling	化学键的本质
1962	化学	肯德鲁John Charles Kendrew	蛋白质的结构测定
		帕鲁兹Max Ferdinand Perutz	
1962	生理医学	Francis H. C. Crick、JAMES d. Watson、Maurice h. f. Wilkins	脱氧核糖核酸DNA测定
1964	化学	Dorothy Crowfoot Hodgkin	青霉素、B12生物晶体测定
1985	化学	霍普特曼Herbert Hauptman	直接法解析结构
		卡尔Jerome Karle	
1986	物理	鲁斯卡E. Ruska	电子显微镜
		宾尼希G. Binnig	扫描隧道显微镜
		罗雷尔H. Rohrer	
1994	物理	布罗克豪斯 B. N. Brockhouse	中子谱学
		沙尔 C. G. Shull	中子衍射

# History of X-Ray Diffraction

1895

X-rays discovered by Roentgen



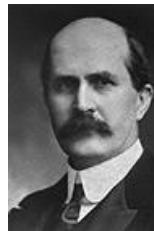
1914

First diffraction pattern of a crystal made by Knipping and von Laue



1915

Theory to determine crystal structure from diffraction pattern developed by Braggs



1924

for his discoveries and research in the field of X-ray spectroscopy – Manne Siegbahn



The first X-ray

1953

DNA structure solved by Watson, Crick, Wilkins



1981

High resolution electron microscopy including X-ray photoelectron spectroscopy



Now

Diffraction improved by computer technology; methods used to determine atomic structures and in medical applications

# 一. X射线衍射

虽然点群和空间群理论以及晶体点阵学说都是19世纪提出的，但直到1912年Laue发现了晶体X射线衍射现象之后才得以从实验上观测到晶体结构并证实了上述理论。普通光学显微镜受分辨率的限制，无法观测原子排列，使用X光源，至今又没有可以使X光聚焦的透镜，所以只能依靠衍射现象来间接观测晶体中的原子排列。**至今为止，晶体内部结构的观测还主要依靠衍射现象来进行。**

目前常使用的方法，除去X射线衍射外，还有中子衍射和电子衍射（德布罗意波长： $\sim 10^{-10}\text{m}$ ），**三种方法原理相同，但各有所长，经常互相配合使用。**

$$\varepsilon = hc/\lambda \quad \lambda(\text{nm}) = \frac{1.24}{\varepsilon(\text{KeV})}$$

为探测晶体微观结构，X射线波长应与原子间距（ $\sim 0.1\text{nm}$ ）相当，要求光子能量约为 $10^4\text{ eV}$

★ 产生衍射的极限条件是： $\lambda \leq 2d$  或：  $d \geq \frac{\lambda}{2}$

常用波长范围： $(0.5 - 2.5) \times 10^{-10}\text{ m}$

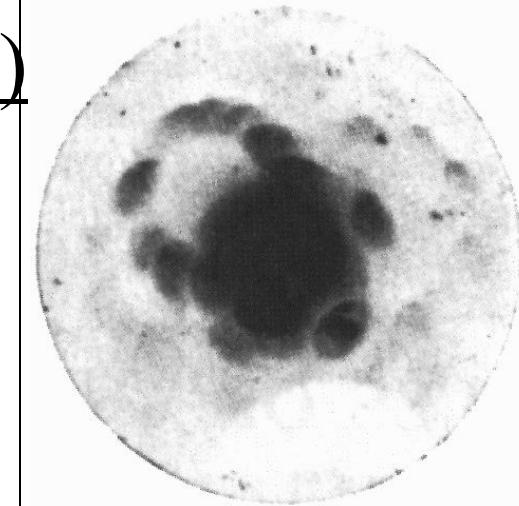
当一束 X射线照射到晶体上时，首先被电子所散射，每个电子都是一个新的辐射源，向空间辐射出与入射波相同频率的电磁波，可以认为一个原子系统的所有电子都近似地从原子中心发出散射波，所以**晶体的 X射线衍射就是晶体中处在不同位置上的原子向外辐射的电磁波相位不同、相互干涉的结果**，是晶体原子的有序排列，使某些方向上散射波始终互相叠加、某些方向上的散射波始终相互抵消，而产生衍射线。因此**每种晶体的衍射花样都反映出晶体内部原子分布的规律**，一个衍射样式的特征可以概括为两个方面：

一方面是衍射线在空间的分布规律（称之为衍射几何）；另一方面是衍射线的强度规律。衍射线在空间的分布规律是由布拉维格子决定的，而衍射线的强度则是由晶胞中原子的种类、数量和位置所决定的。

下面，将按布拉维晶格，晶胞和原子三个层次讨论

# The first x-ray diffraction pattern (1912)

von Laue, was the first person to perform a diffraction experiment with a crystal. He hypothesized that if atoms really existed, and if x-rays really were waves, then the wavelength of x-rays would approximate the distance between atoms in a crystal and diffraction would be observed. His brilliant insight thus proved both atomicity and the wave character of x-rays. This remarkable achievement was recognized by the Nobel prize. Laue did not actually do the experiment himself. Rather, he persuaded a couple of graduate students to do the experiment for him. Laue then set an example that has inspired PIs ever since – he was given all the credit!



The first x-ray diffraction picture, which was taken from a crystal of  $\text{CuSO}_4$  by von Laue's students, and dubbed the "beerstein" pattern.

W. L. (Lawrence) Bragg realized that von Laue's diffraction pattern could be modeled as reflection from Miller planes -- i.e. the angle of incidence wrt Miller planes = the angle of reflection. This is the reason why diffracted x-rays are generally called reflections. Bragg published this work in 1913. His insight further substantiated the wave character of x-rays (thereby contradicting his father's theory that x-rays are particles). This work also allowed the Bragg's (father and son) to determine the first atomic resolution structures. The Bragg's were jointly awarded the Nobel prize in 1915 – at which time W.L. Bragg was 25 years old and fighting in the trenches of world war I.

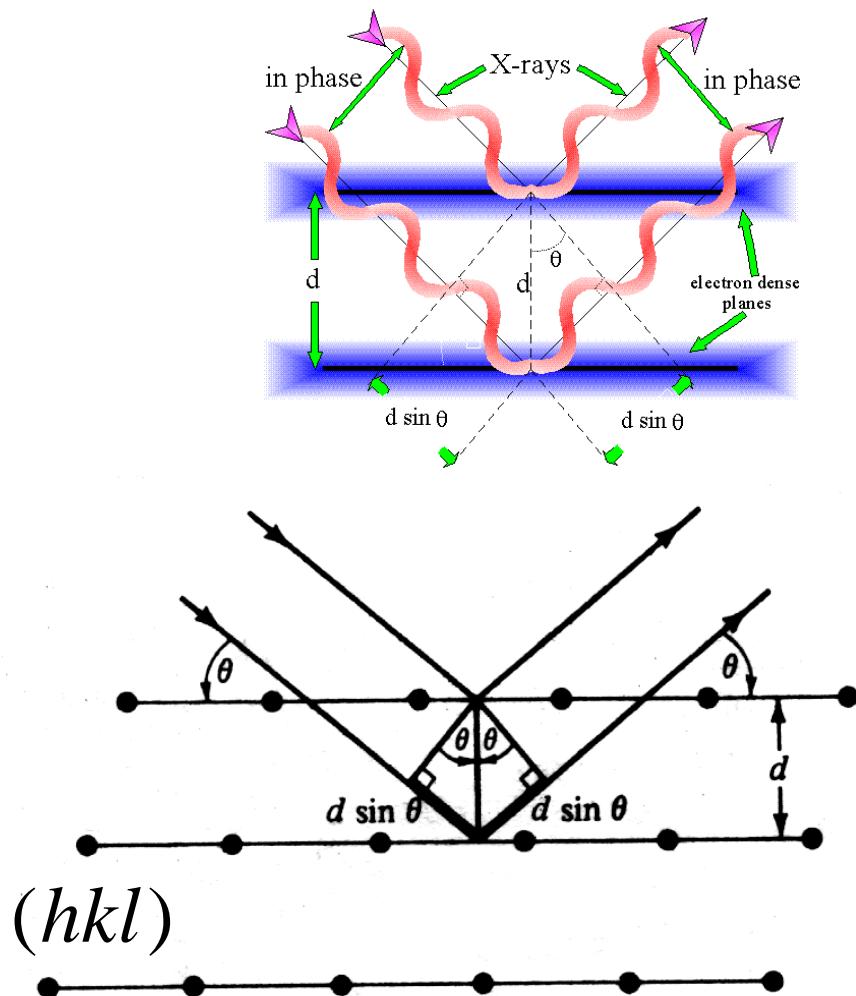
## 二. 晶体衍射的几何理论：发生衍射的条件

入射波波长  $\lambda$

### 1. 衍射条件的Bragg定律

Bragg 把晶体对 X光的衍射当作由原子平面的反射，在反射方向上，一个平面内所有原子的散射波位相相同、相互叠加，当不同原子平面间的辐射波符合Bragg关系时，散射波在反射方向得到加强，形成衍射。

$$2d_{hkl} \sin \theta = n\lambda$$



## 对Bragg定律的一些理解：

Bragg 假定每个晶面都像镀了一层薄银的镜子一样，只对入射波反射很小的一部分，只有在某些  $\theta$  值，来自所有平行晶面的反射才会同相位地增加，产生一个强的反射束。实际上，每个晶面只能反射入射辐射的  $10^{-3}$ — $10^{-5}$  部分，因而对于一个理想晶体，会有来自  $10^3$ — $10^5$  个晶面的原子对形成 Bragg 反射束有贡献。（对 X 射线而言）

发生衍射的 Bragg 条件清楚地反映了衍射方向与晶体结构之间的关系。

但衍射的实质是晶体中各原子散射波之间相互干涉的结果，只是由于衍射线的方向恰好相当于原子面对入射波的反射，才得以使用 Bragg 条件，不能因此混淆平面反射和晶体衍射之间的本质区别。

## 衍射花样和晶体结构的关系：

由 Bragg 方程可知，在一定波长下，衍射方向是晶体面间距的函数，根据1.4节中给出的面间距公式，有：

立方晶系：

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (H^2 + K^2 + L^2)$$

正方晶系：

$$\sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{H^2 + K^2}{a^2} + \frac{L^2}{c^2} \right)$$

斜方晶系：

$$\sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{H^2}{a^2} + \frac{K^2}{b^2} + \frac{L^2}{c^2} \right)$$

六方晶系：

$$\sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{4H^2 + HK + K^2}{3a^2} + \frac{L^2}{c^2} \right)$$

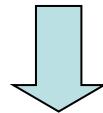
由此关系式可以看出，**不同晶系的晶体，或者同一晶系而晶胞大小不同的晶体，其衍射线的花样（角度分布）是不相同的**。但是，它无法反映出晶胞内原子的品种、数量及位置的分布。

2. 衍射条件的Laue 解释：在晶体中任选一点 O为原点，考虑 O点处的原子与距离它  $\vec{R}_n$  处原子散射波之间的光程差发生衍射的条件是： $\vec{R}_n \cdot \vec{S}_0 - \vec{R}_n \cdot \vec{S}_1 = n\lambda$        $\vec{S}_0, \vec{S}_1$  为单位方向矢量

$$\because \vec{k}_0 = \frac{2\pi}{\lambda} \vec{S}_0, \vec{k}_1 = \frac{2\pi}{\lambda} \vec{S}_1$$

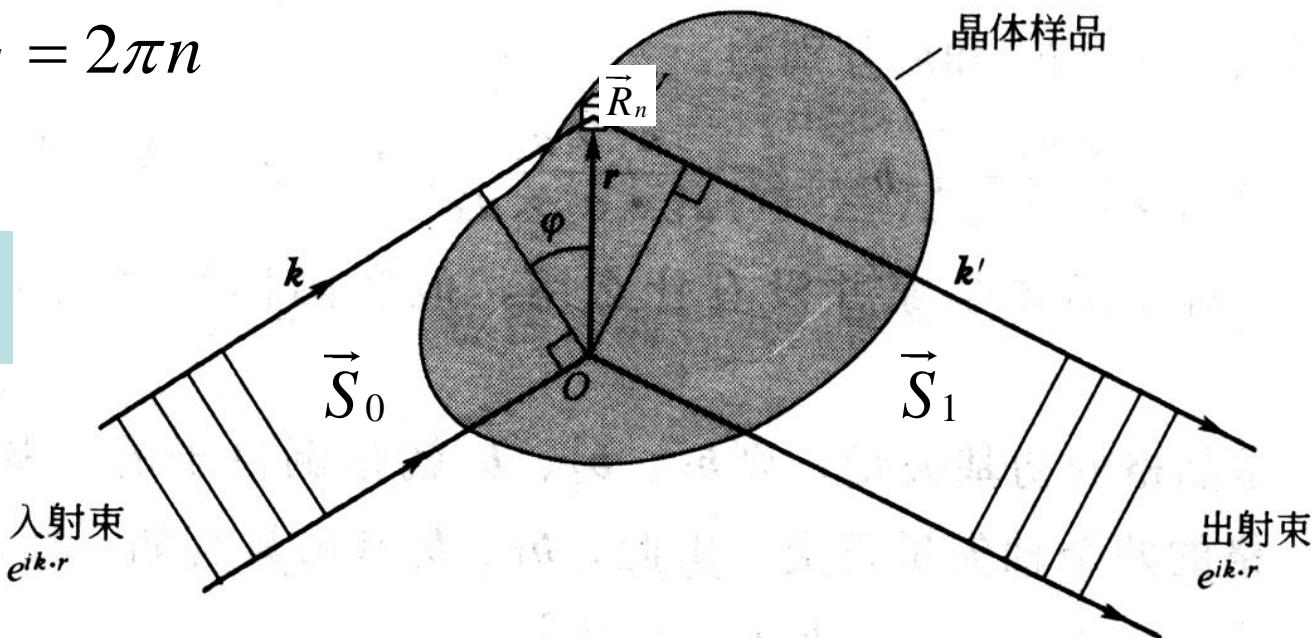
$$\vec{R}_n \cdot (\vec{k}_0 - \vec{k}_1) = 2\pi n$$

$$\text{又} \because \vec{R}_n \cdot \vec{G}_{hkl} = 2\pi n$$



$$\vec{k}_0 - \vec{k}_1 = \vec{G}_{hkl}$$

**Laue 条件**



**Laue**衍射条件：当入射波矢和散射波矢相差一个倒格矢矢量时将发生衍射。kittel说：“一组倒格矢**G** 决定了可能存在的X射线反射”。Laue方程还有其它表示方式：

$$\therefore -\vec{k}_1 = \vec{G}_h - \vec{k}_0 \quad (\text{移项后两边平方得到下式})$$

$$\therefore k_1^2 = G_h^2 - 2\vec{G}_h \cdot \vec{k}_0 + k_0^2$$

$$\therefore k_0 = k_1 \quad \text{弹性散射，波长数值不变，即波矢绝对值不变。}$$

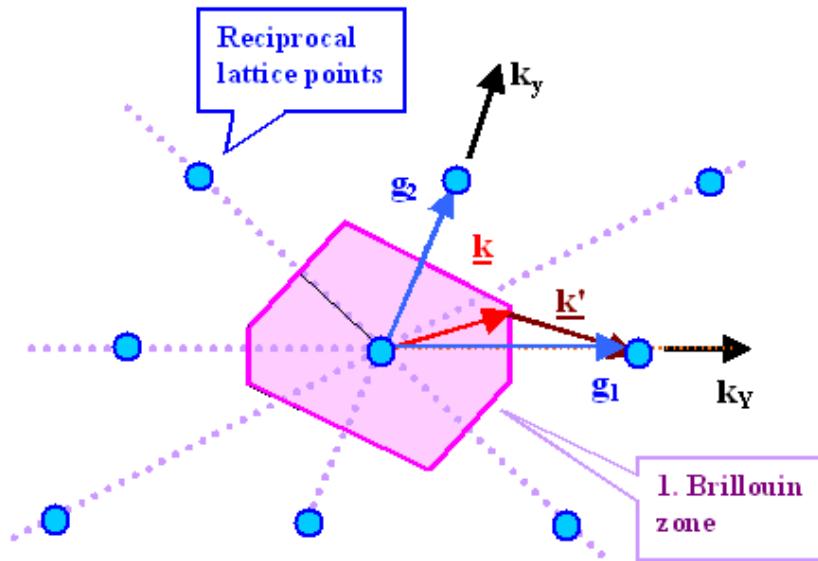
$$\therefore G_h^2 - 2\vec{G}_h \cdot \vec{k}_0 = 0$$

即：

$$2\vec{k} \cdot \vec{G}_h = G_h^2$$

$$\vec{k} \cdot \vec{G}_h = \frac{1}{2} G_h^2$$

**Laue** 衍射条件就是布里渊区边界方程。换句话说：布里渊区界面是由 **Laue**方程决定的。



布里渊边界方程（Laue条件）的意义：

- 1) 从某倒格点出发，凡是满足布里渊边界方程的波矢的端点集合构成布里渊区界面
- 2) 从某倒格点出发，凡波矢  $\underline{k}_0$  端点落在布里渊区界面上的X射线，都满足衍射极大条件，而且其衍射束在  $\underline{k}_0 - \mathbf{G}$  方向上

由Laue条件推出Bragg定律：

$$\vec{k}_0 - \vec{k}_1 = \vec{G}_h$$

$$\because k_0 = k_1 = k$$

$$\therefore G_h = 2k \sin \theta$$

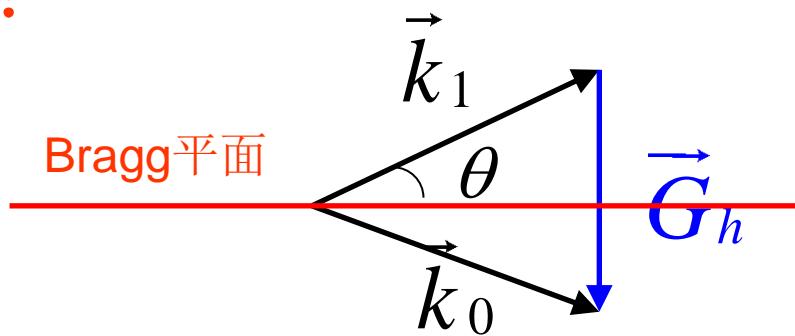
假定  $\vec{G}_h$  方向最短倒格矢为  $\vec{G}_0$   $\rightarrow \vec{G}_h = n\vec{G}_0, n$  为整数

而  $G_0 = 2\pi/d$ ,  $d$  为面间距,  $k = 2\pi/\lambda$

$$nG_0 = 2k \sin \theta$$

$$n2\pi/d = 2 \cdot (2\pi/\lambda) \sin \theta$$

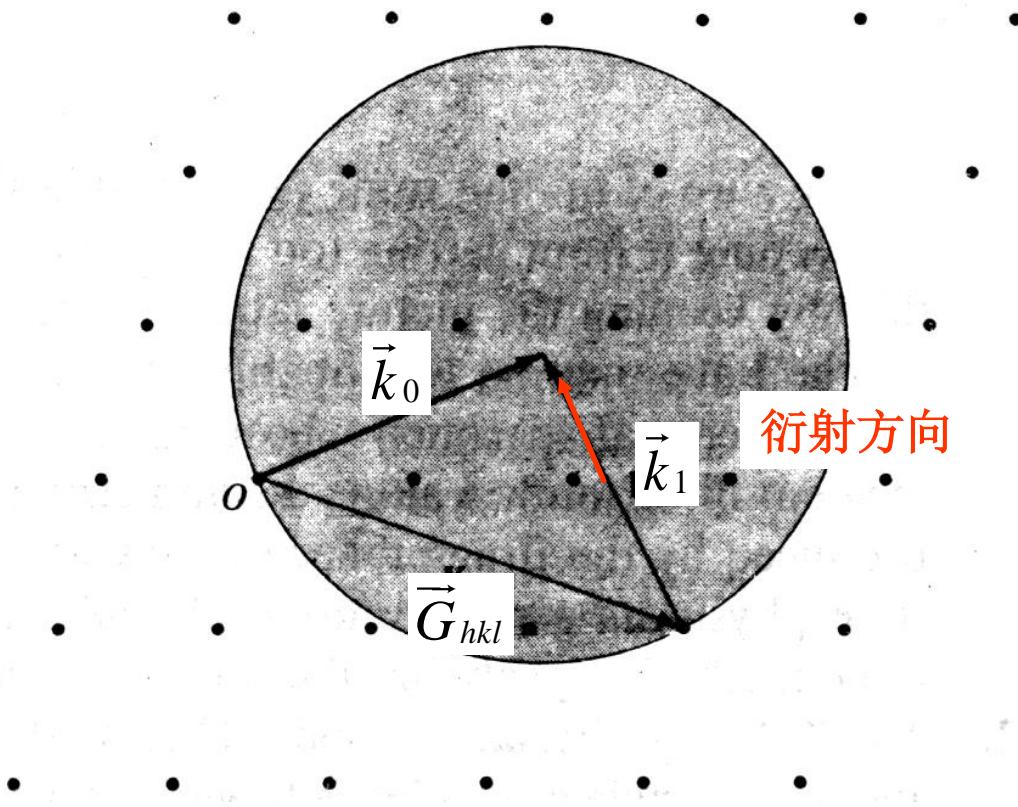
$$\longrightarrow n\lambda = 2d \sin \theta \quad \text{Bragg定律}$$



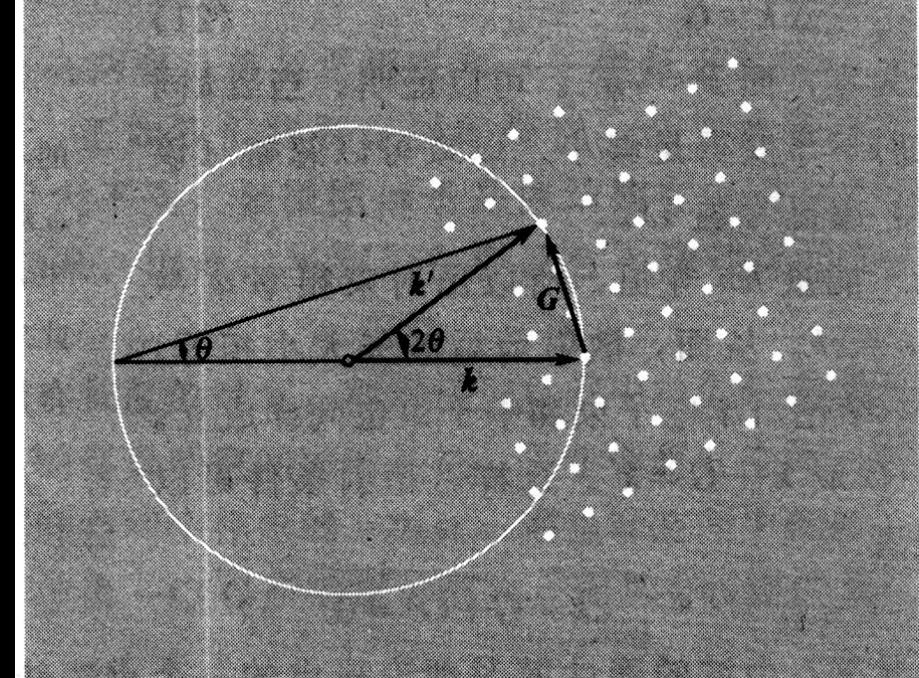
### 3. Ewald球 图解法:

对于给定的晶体，当入射波矢确定后，究竟在哪些方向可以观察到衍射呢？Ewald 利用反射球作图法给出了符合 Laue 条件的答案：

以入射波矢端点为圆心，以  $k$  为半径做反射球，凡落在球面上的倒格点都会满足 Laue 方程，因为原点必然落在反射球上，所以从原点到落在反射球上的其它格点恰好是一个倒格矢，故  $\vec{k}_1$  方向发生衍射。

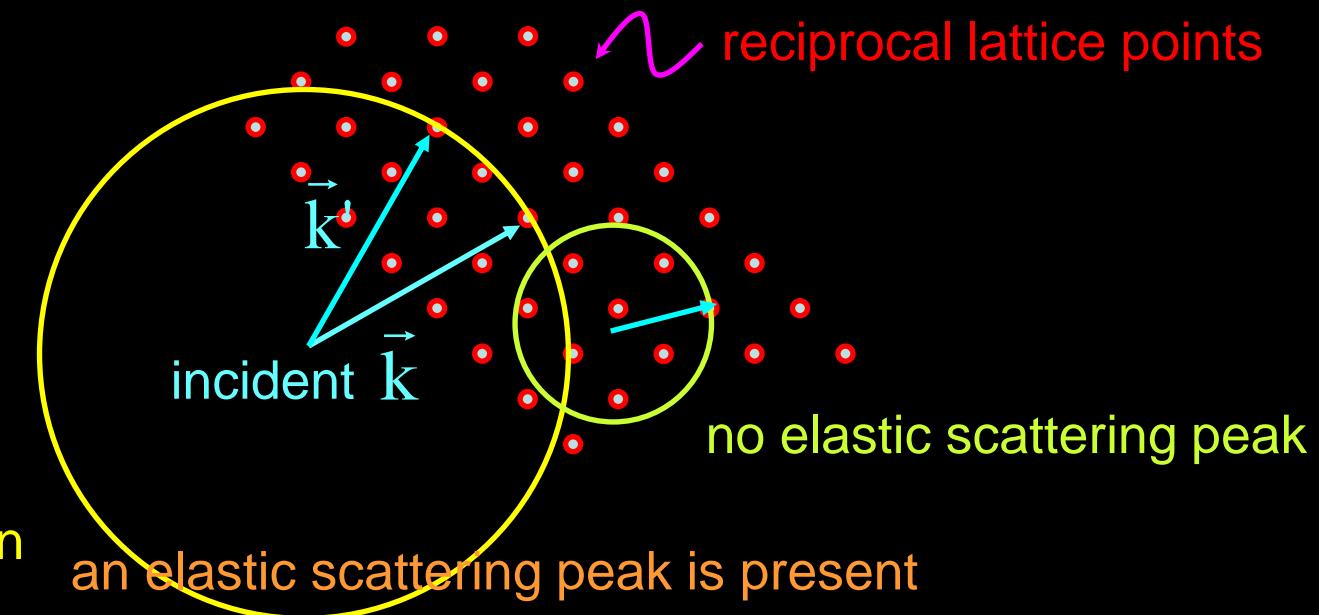


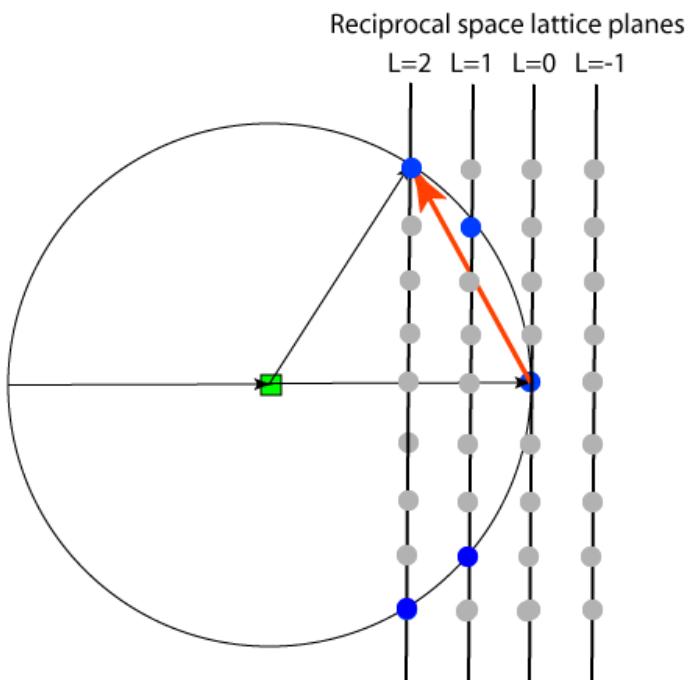
# Ewald球另一种形式的作图法



1913 Ewald

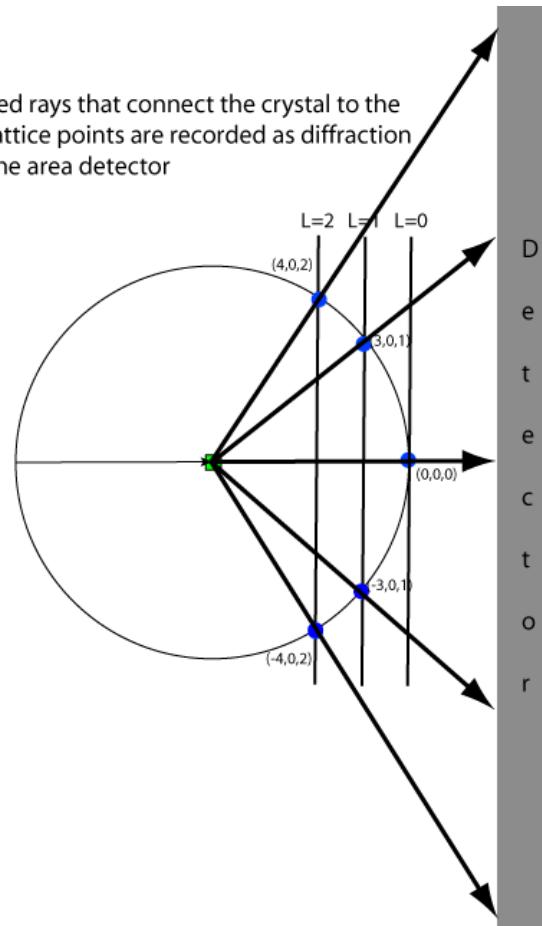
An Ewald construction





A perfectly-aligned crystal shooting down the  $C^*$  axis  
Only spots lying on the Ewald sphere are diffracting

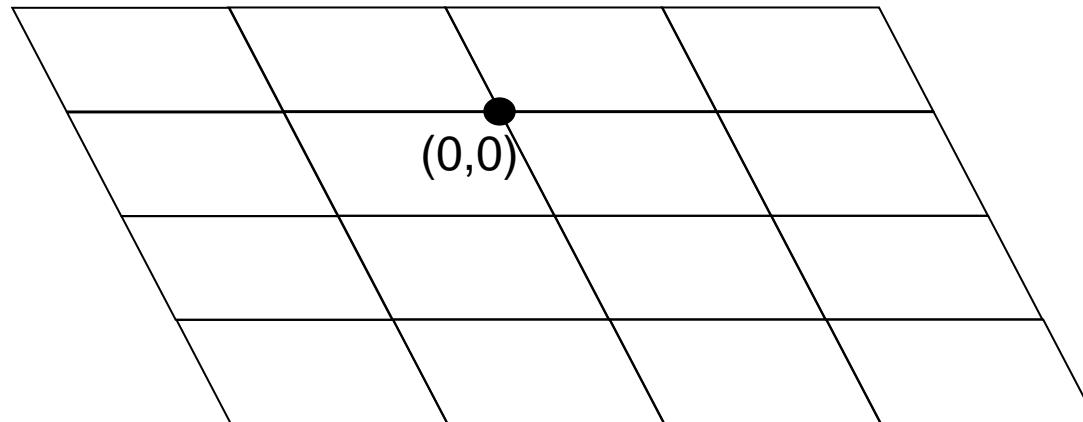
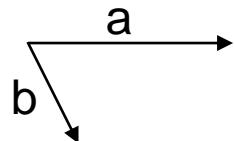
The diffracted rays that connect the crystal to the reciprocal lattice points are recorded as diffraction "spots" on the area detector



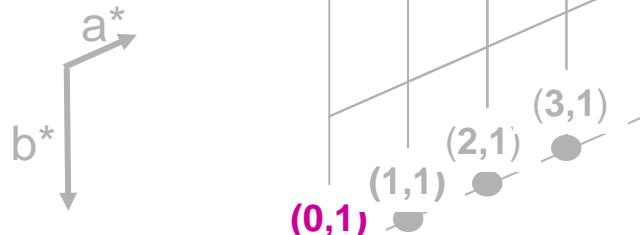
## RECIPROCAL LATTICE



## REAL LATTICE

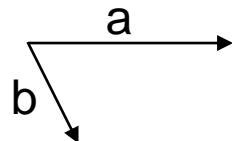


## RECIPROCAL LATTICE



length= $1/d_{0,1}$

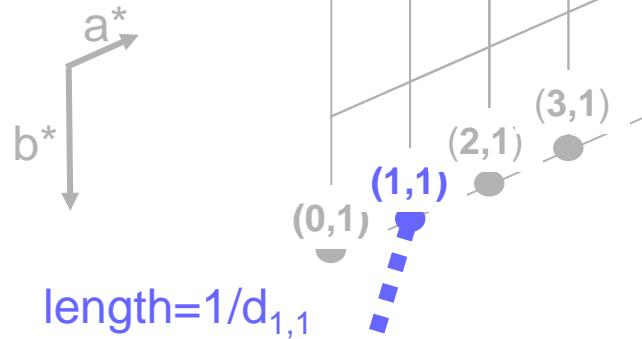
## REAL LATTICE



$(0,0)$

$(0,1)$  planes

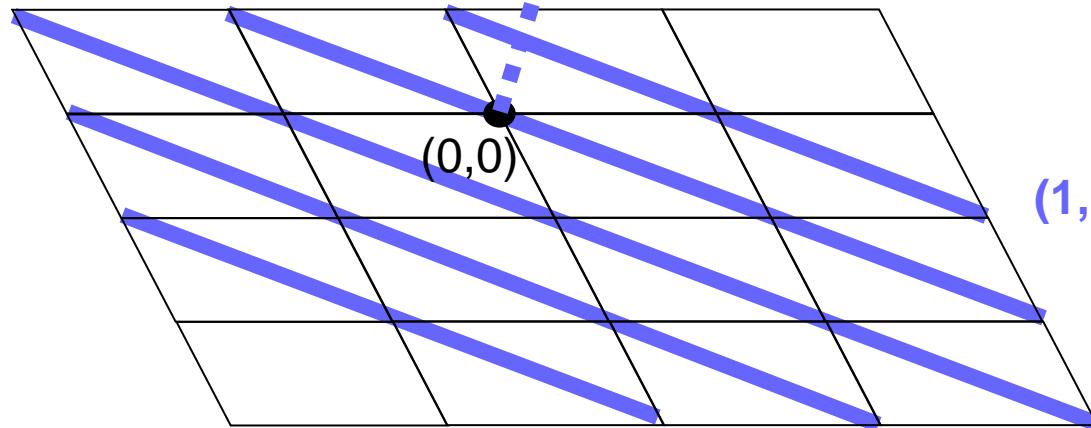
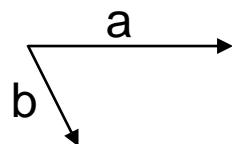
## RECIPROCAL LATTICE



$$\text{length} = 1/d_{1,1}$$

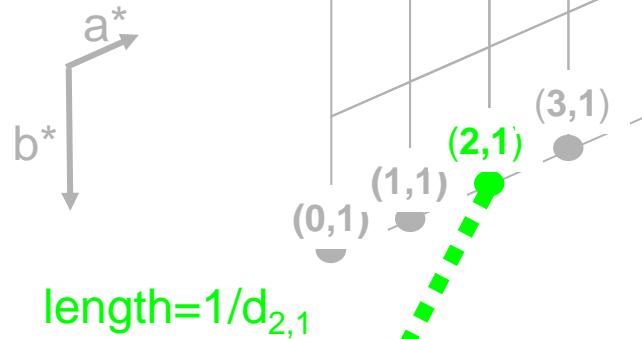
length is longer than  $(0,1)$  since spacing between  $(1,1)$  planes is smaller.

## REAL LATTICE



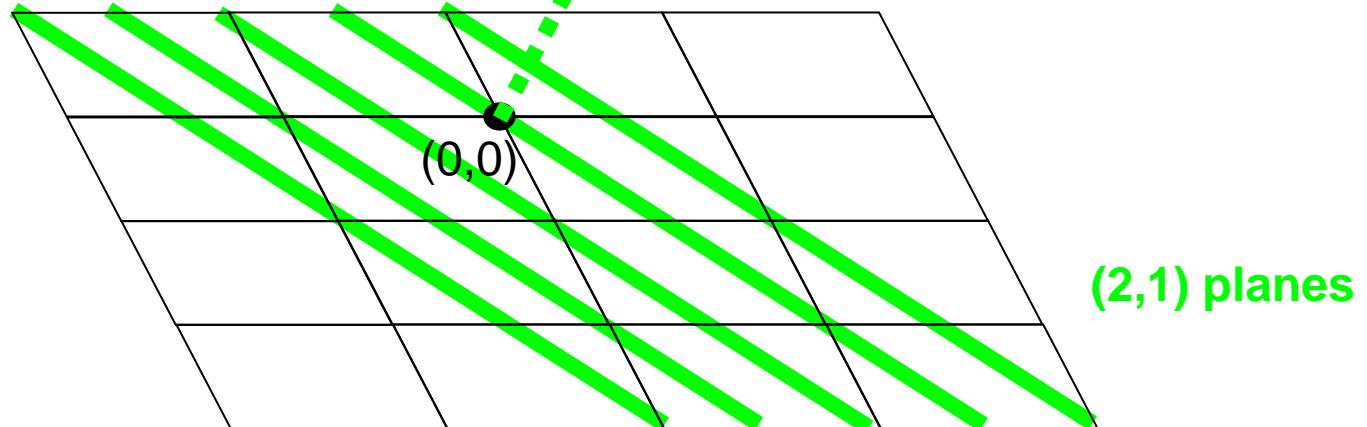
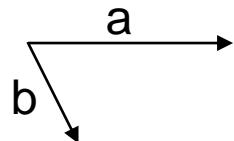
$(1,1)$  planes

## RECIPROCAL LATTICE



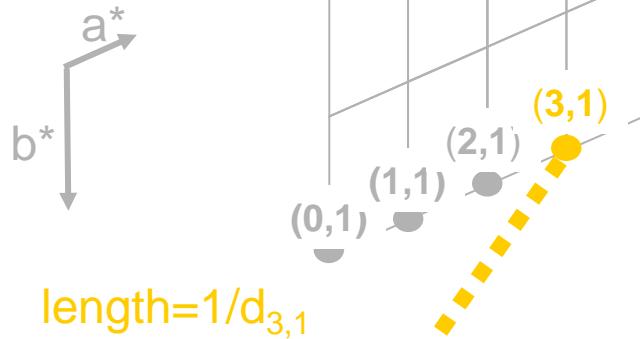
length= $1/d_{2,1}$

## REAL LATTICE

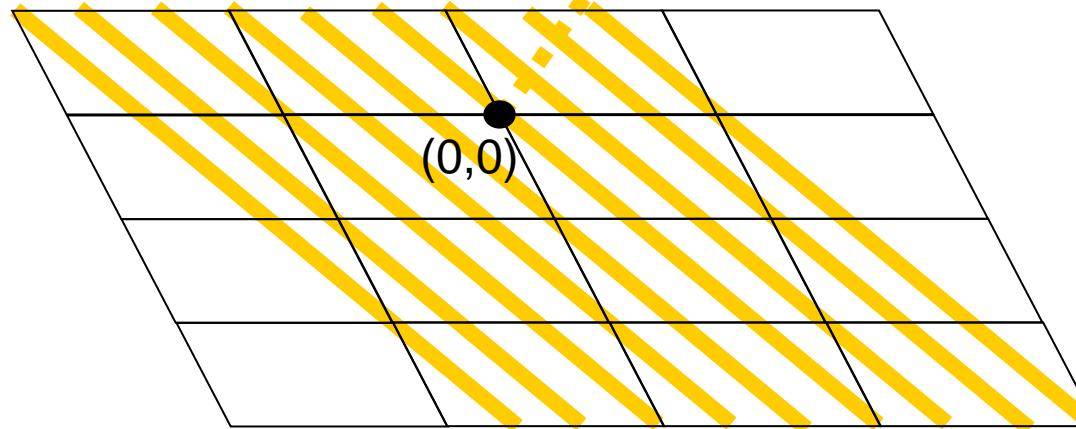
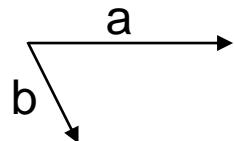


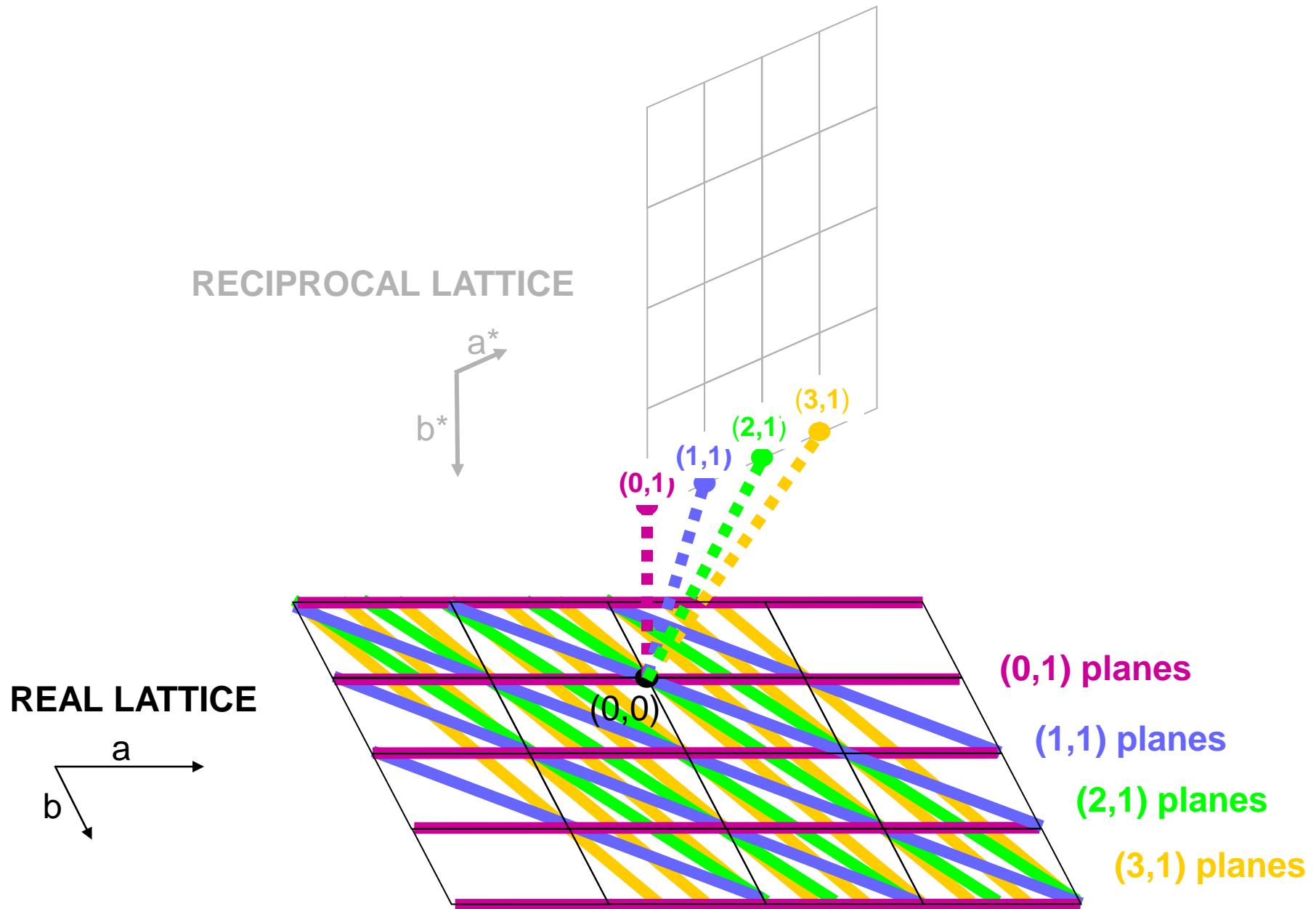
$(2,1)$  planes

## RECIPROCAL LATTICE

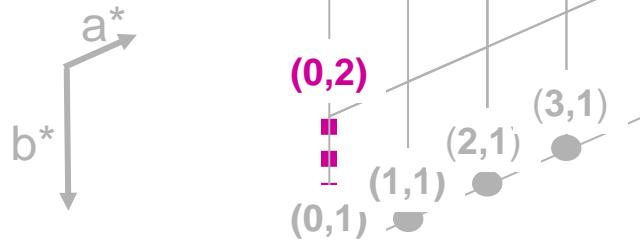


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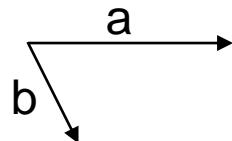


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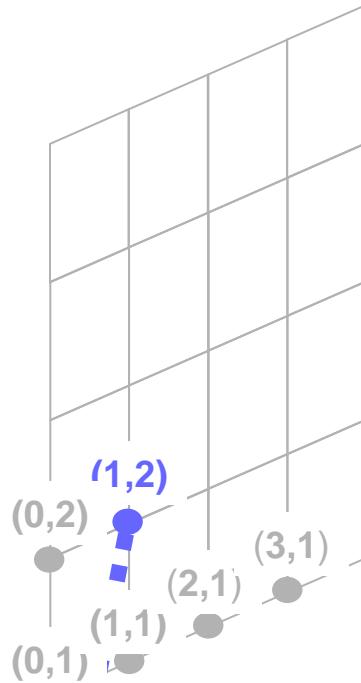
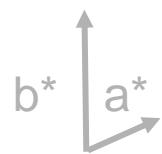
## REAL LATTICE



$(0,0)$

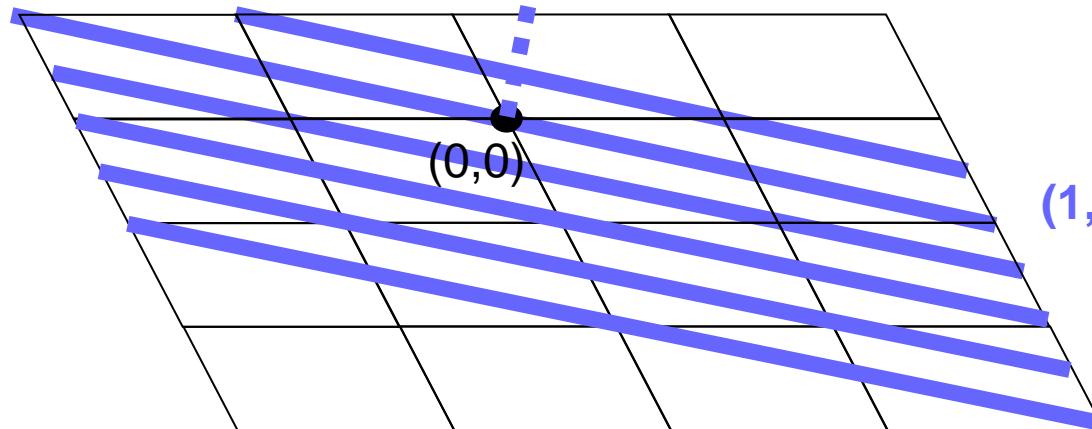
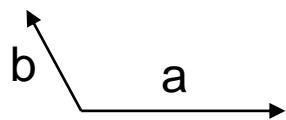
$(0,2)$  planes

## RECIPROCAL LATTICE



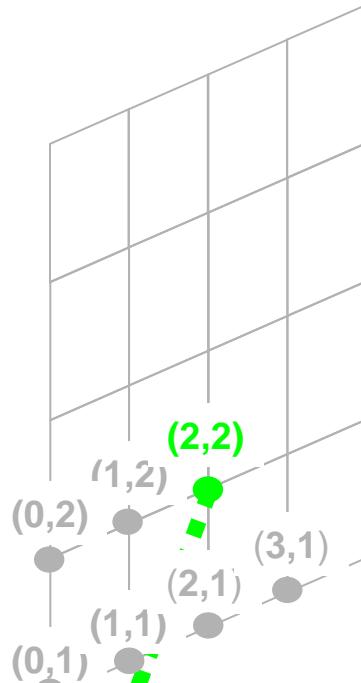
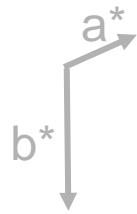
length =  $1/d_{1,2}$

## REAL LATTICE



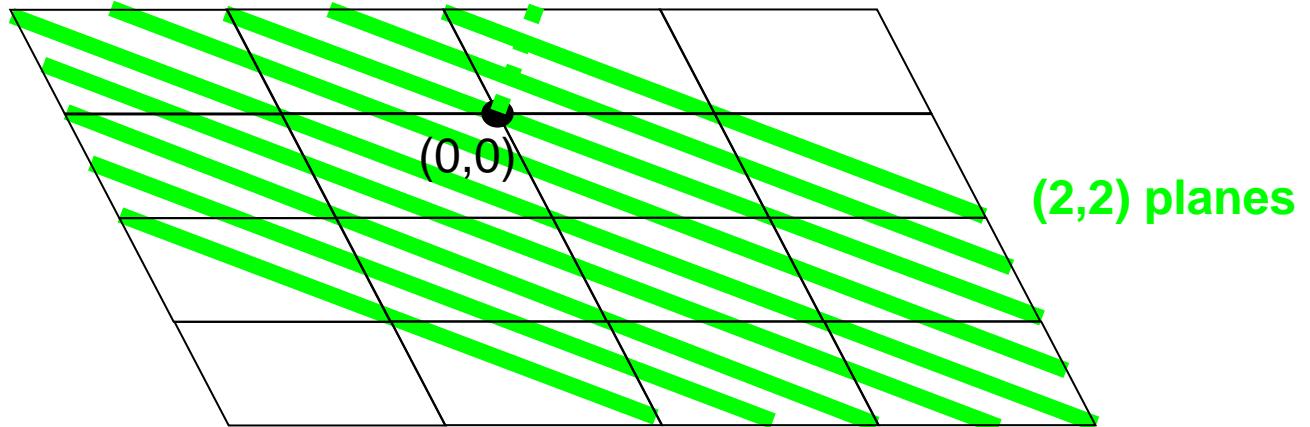
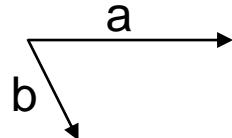
$(1,2)$  planes

## RECIPROCAL LATTICE

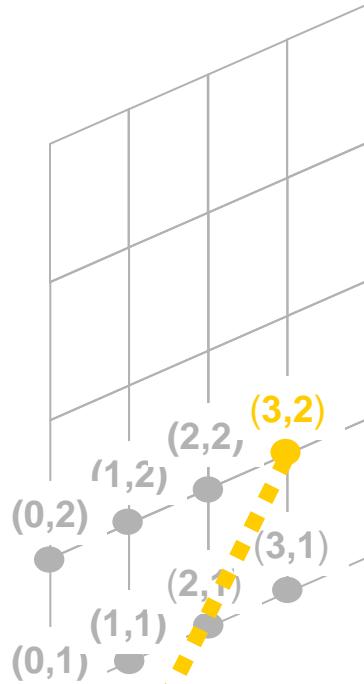
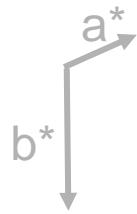


length= $1/d_{2,2}$

## REAL LATTICE

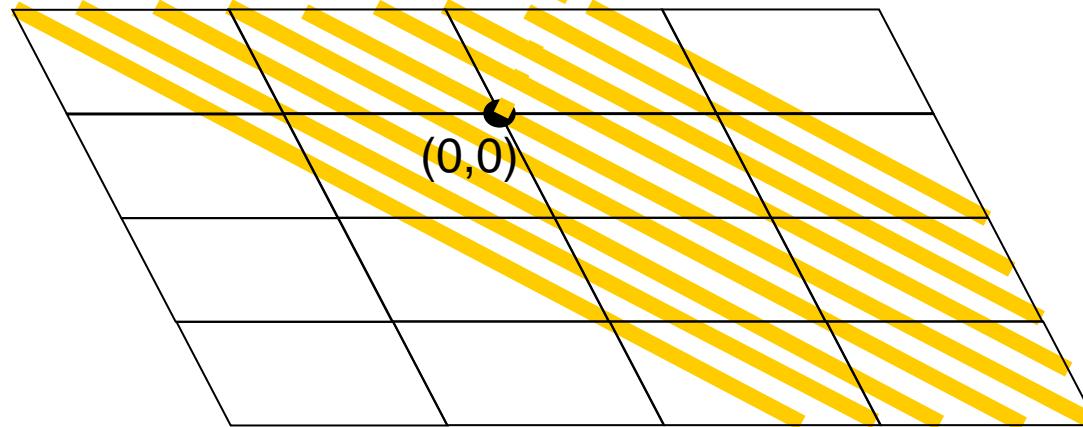
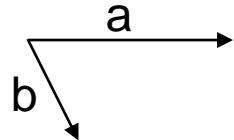


## RECIPROCAL LATTICE



length =  $1/d_{3,2}$

## REAL LATTICE



(3,2) planes

## RECIPROCAL LATTICE

$a^*$   
 $b^*$

(0,1)  
(0,2)  
(1,1)  
(1,2)  
(2,1)  
(2,2),  
(3,1)  
(3,2)

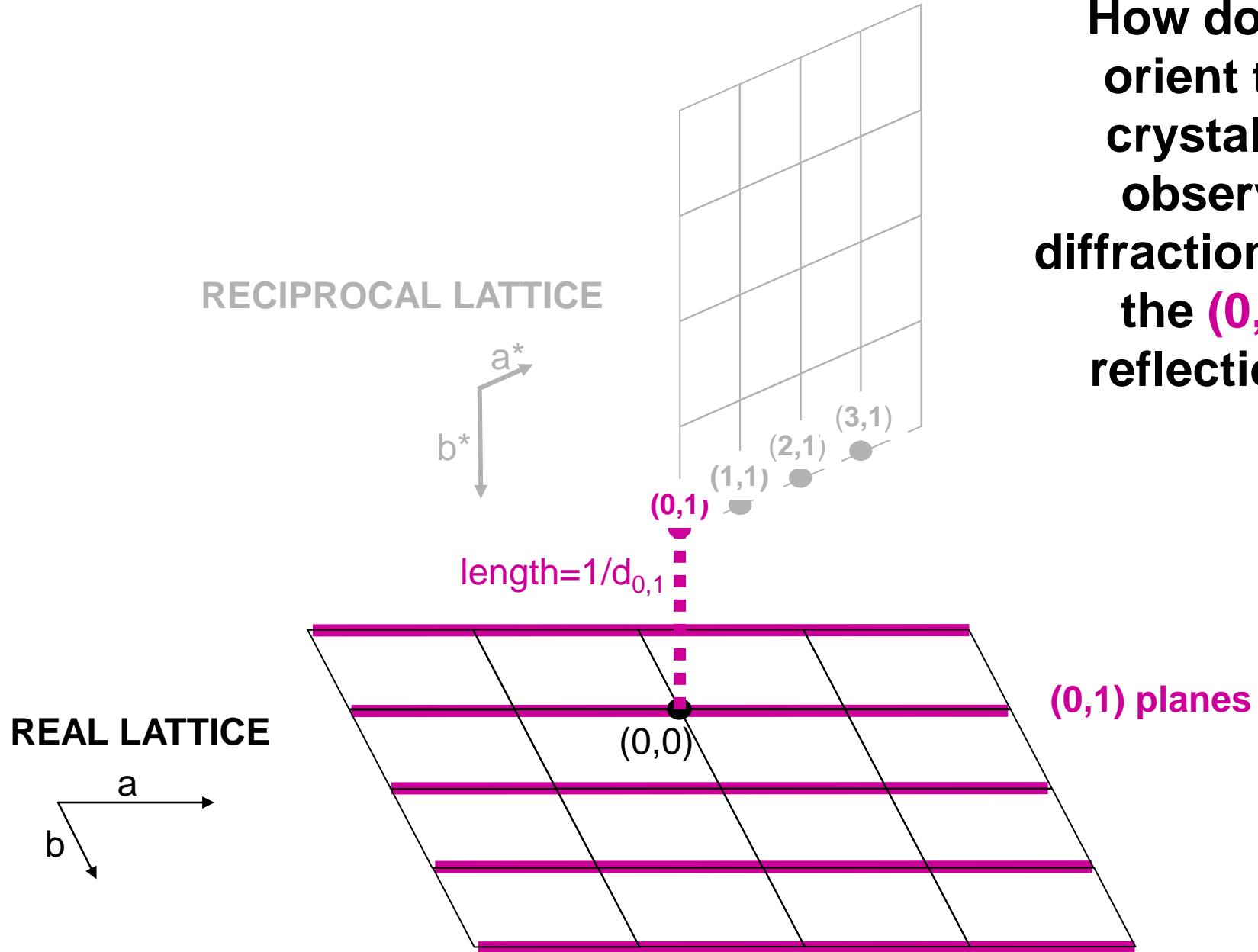
## REAL LATTICE

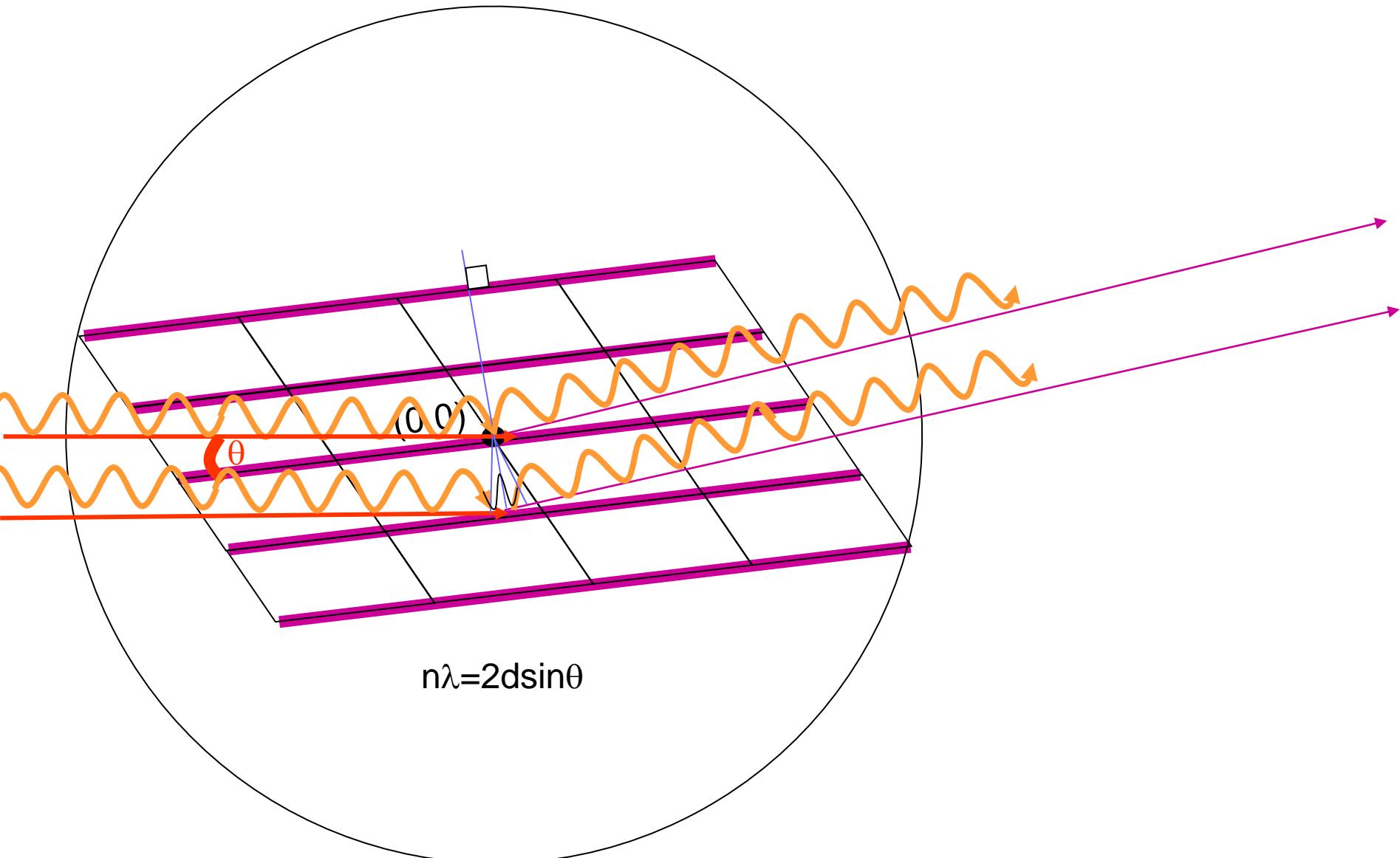
$a$   
 $b$

(0,0)

(0,1) planes  
(0,2) planes  
(1,1) planes  
(1,2) planes  
(2,1) planes  
(2,2) planes  
(3,1) planes  
(3,2) planes

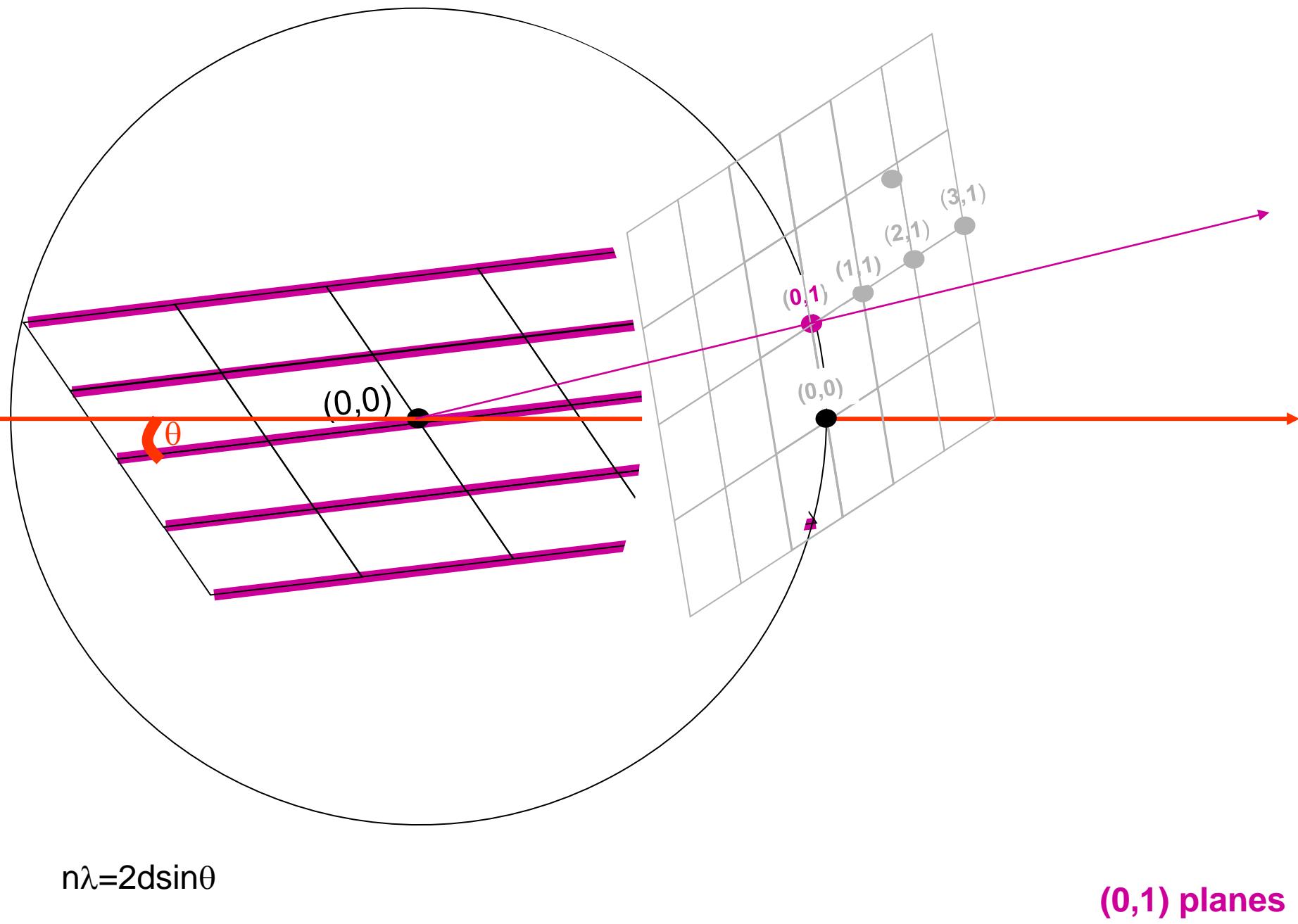
**How do we  
orient the  
crystal to  
observe  
diffraction from  
the (0,1)  
reflection?**

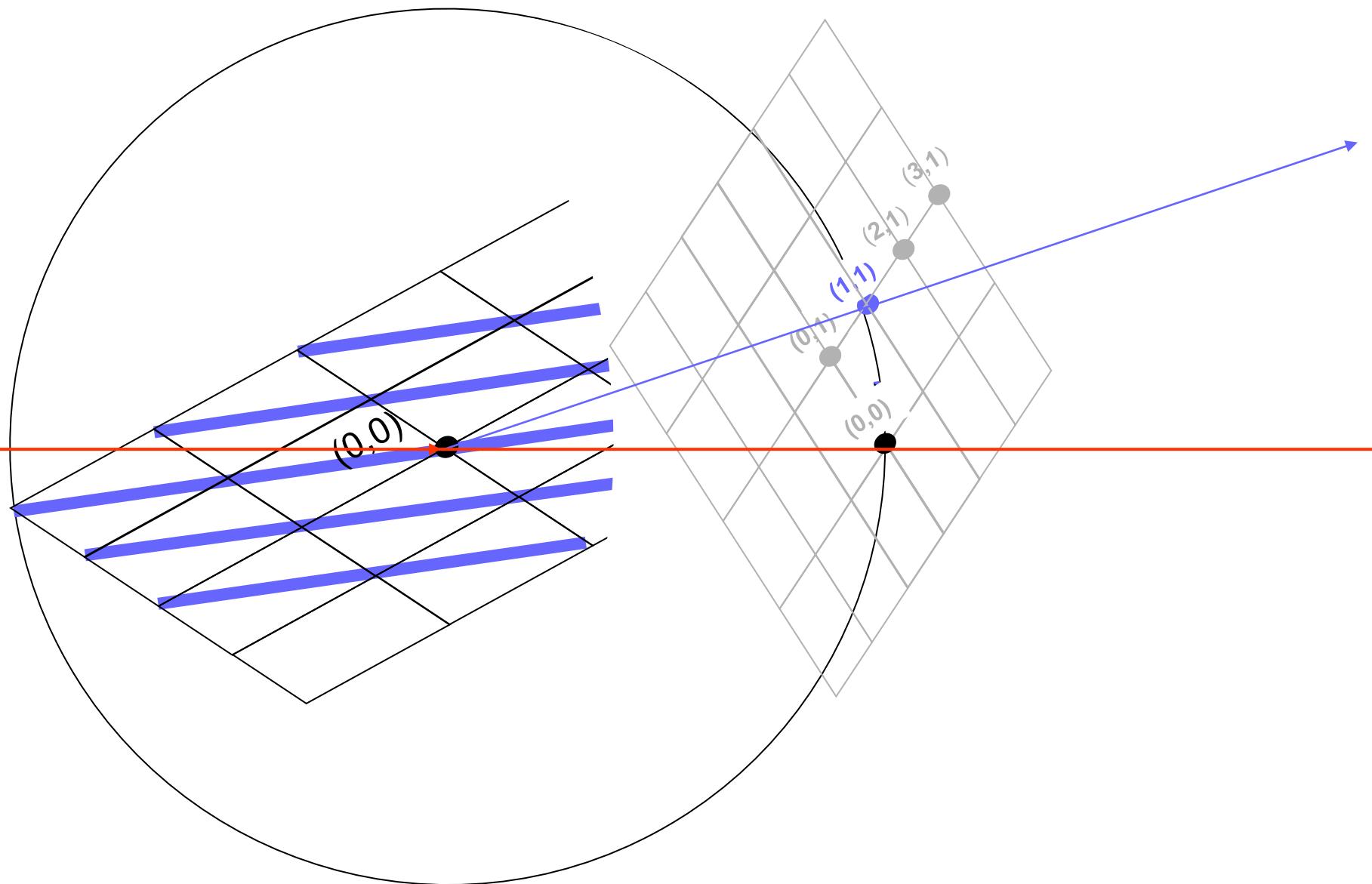




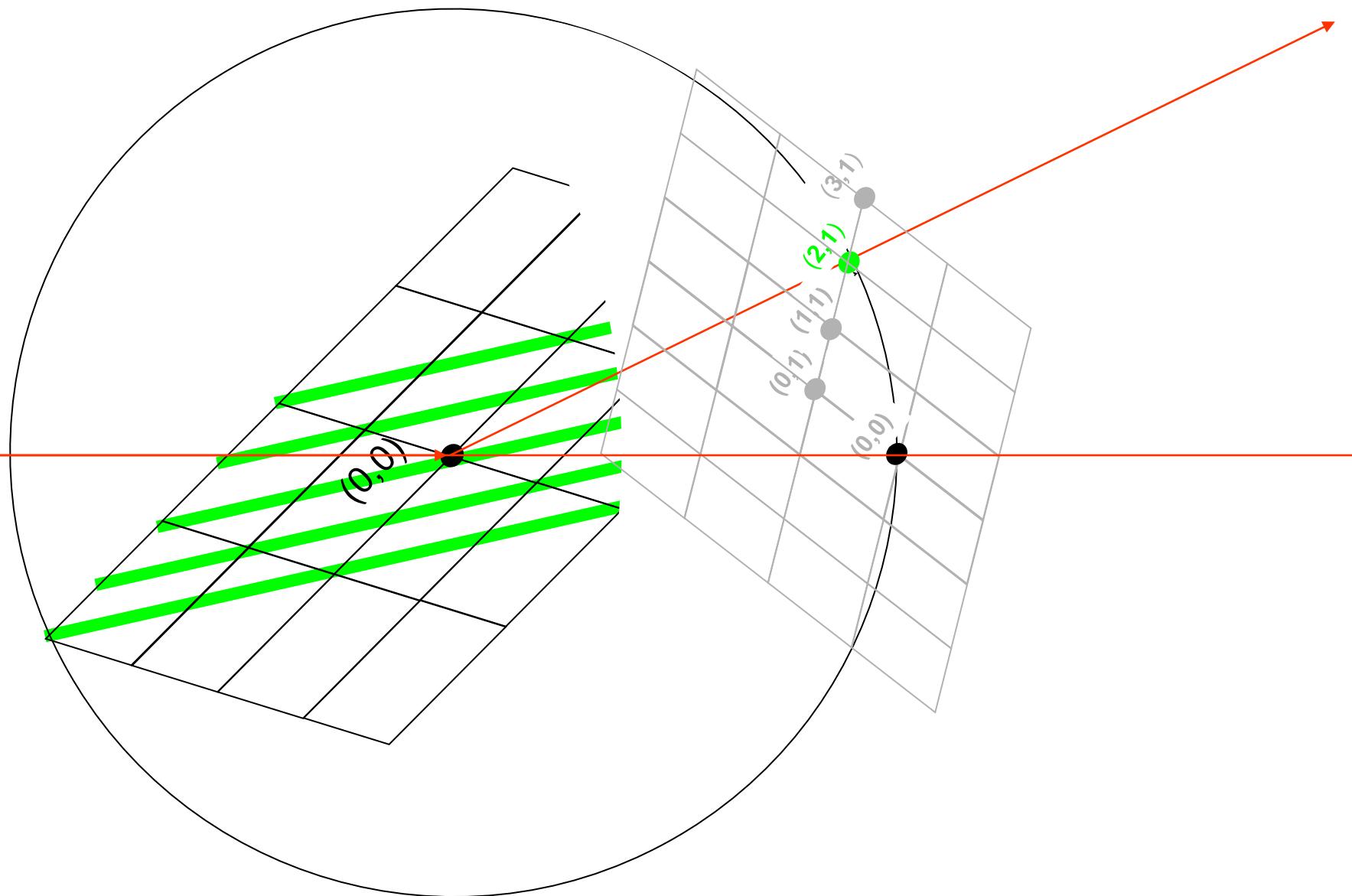
Bragg condition-- upper beam has to be an integral number of wavelengths from the lower beam for constructive interference.

**(0,1) planes**

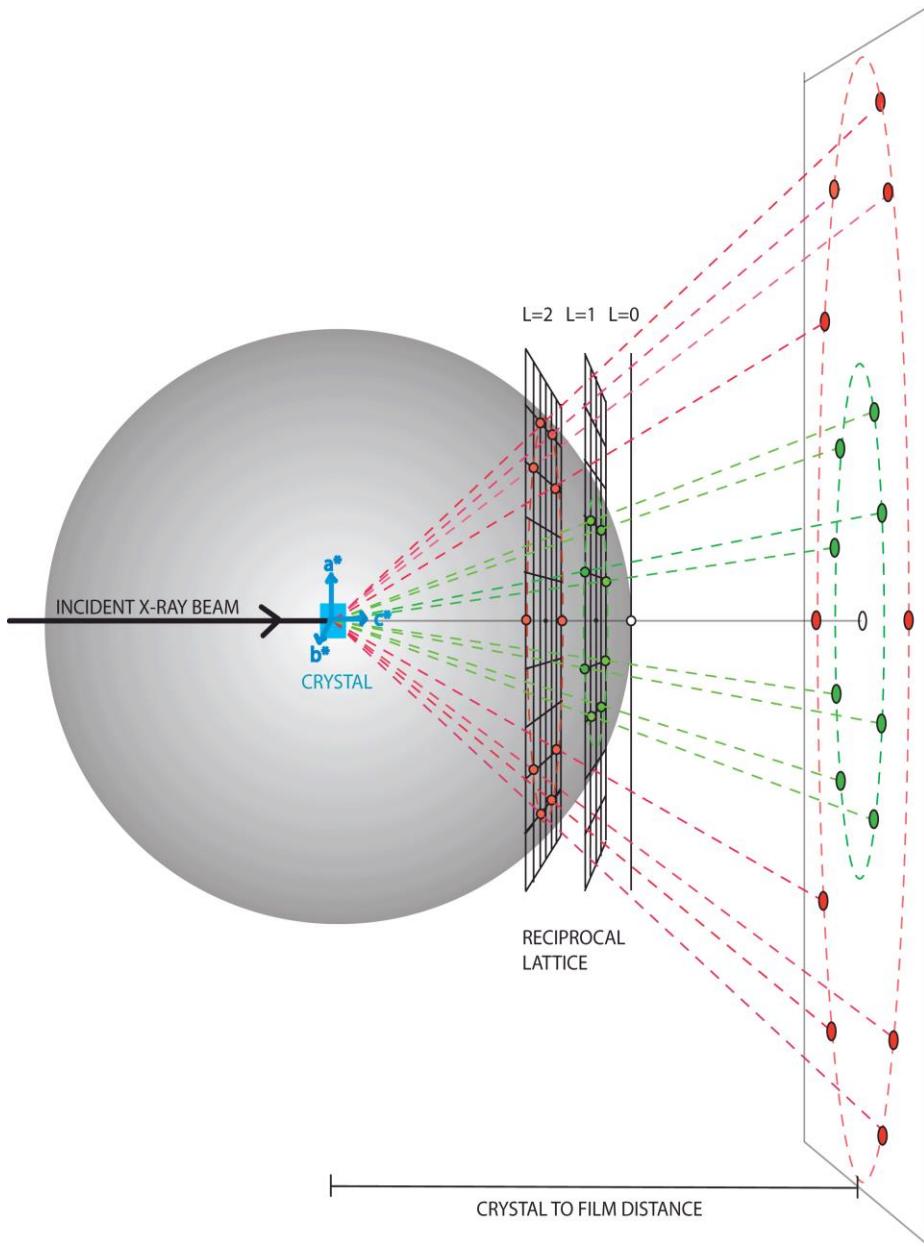




**(1,1) planes**



(2,1) planes



### 三. 影响衍射强度的因素：可以分2个层次进行分析

1. 原子散射因子：根据经典理论，电子受到电磁辐射，会发生强迫振动，而辐射出与入射电磁波相同波长的电磁波，其强度

由Thomson 公式给出： $I_e = I_0 \frac{e^4}{m^2 c^4} \left( \frac{1 + \cos^2 2\theta}{2} \right)$  强度和方向有关。

一个原子有许多电子，它的原子散射因子定义为：一个原子的相干散射振幅和一个电子的相干散射振幅之比：

$$f_a = \frac{A_a}{A_e} = f_a(\theta, \lambda \dots)$$

它和原子中电子的分布、数目、X射线的波长、以及发射角有关，各原子的原子散射因子数值可以在有关书中查到。

一个原子的散  
射波强度：

$$I_a = f_a^2 I_e \quad \theta = 0, I_a = z^2 I_e$$

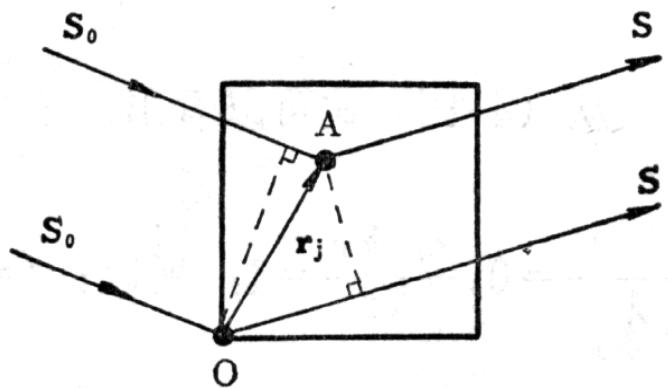
## 2. 几何结构因子：

如果晶胞内只含有一个原子时，Bragg公式或 Laue 条件给出的d 值即可确定出晶胞大小和原子位置，但当晶胞包含两个以上的原子时，如 fcc 或 bcc 结构，金刚石，NaCl,CsCl 等情形就不同了，必须考虑晶胞中原子的相对位置和原子种类不同而带来的差异，因而定义一个原胞内所有原子的散射振幅和一个电子的散射振幅之比为晶胞几何结构因子：

$$F = \frac{A_b}{A_e}$$

如何确定各种晶体结构的几何结构因子是一件重要的事情，对了解晶体结构十分重要。

下面我们分析晶胞内原子的相干散射，给出几何结构因子的一般表达式。



$\vec{S}_0, \vec{S}_1$  为单位方向矢量

晶胞内两个原子的相干散射

假定O是晶胞的一个顶点，同时作为坐标原点，处在晶胞A处的第j个原子与处在O点的原子散射波之间的光程差为：

$$\delta_j = \vec{r}_j \cdot (\vec{S}_0 - \vec{S}_1) \quad \overrightarrow{OA} = \vec{r}_j = x_j \vec{a}_1 + y_j \vec{a}_2 + z_j \vec{a}_3$$

其相位差：  $\phi_j = \frac{2\pi}{\lambda} \delta_j = \vec{r}_j \cdot (\vec{k}_0 - \vec{k})$

如果发生衍射的是  $(HKL)$  晶面，则：

$$\vec{k}_0 - \vec{k}_1 = \vec{G}_{HKL} = H\vec{b}_1 + K\vec{b}_2 + L\vec{b}_3$$



$$\phi_j = \vec{G}_{HKL} \cdot \vec{r}_j$$

所以，一个晶胞内所有原子的相干散射振幅需要对所有原子求和： $A_b = A_e \sum_{j=1}^n f_j e^{i\phi_j}$  根据几何结构因子的定义，有：

$$F_{HKL} = \frac{A_b}{A_e} = \sum_{j=1}^n f_j \exp(i\phi_j) = \sum_{j=1}^n f_j \exp(i\vec{G}_{HKL} \cdot \vec{r}_j)$$

因为衍射测量的是衍射强度，它正比于： $|F_{HKL}|^2$   
只需要将上式乘以共轭复数再开方即为结构因子的表达式

$$|F_{HKL}| = \left\{ \left[ \sum_{i=1}^n f_i \cos(\vec{G}_{HKL} \cdot \vec{r}_i) \right]^2 + \left[ \sum_{i=1}^n f_i \sin(\vec{G}_{HKL} \cdot \vec{r}_i) \right]^2 \right\}^{\frac{1}{2}}$$

在X射线衍射分析中，晶体的特殊对称性起着重要作用，因此一般采用惯用晶胞。fcc和bcc可以看作是sc加基元的结果

对于边长为 $a$ 的立方格子，倒格矢可以写成：

$$\vec{G}_{HKL} = H\vec{b}_1 + K\vec{b}_2 + L\vec{b}_3 = \frac{2\pi}{a} (Hx + Ky + Lz)$$

$$F_{HKL} = \sum_{j=1}^n f_j \exp[i \frac{2\pi}{a} (Hx_j + Ky_j + Lz_j)]$$

- 1) 简立方情形：只有1个原子，坐标为：000，所以  
 $HKL$  为任意整数时，都能产生衍射。 $F_{HKL} = f_a$

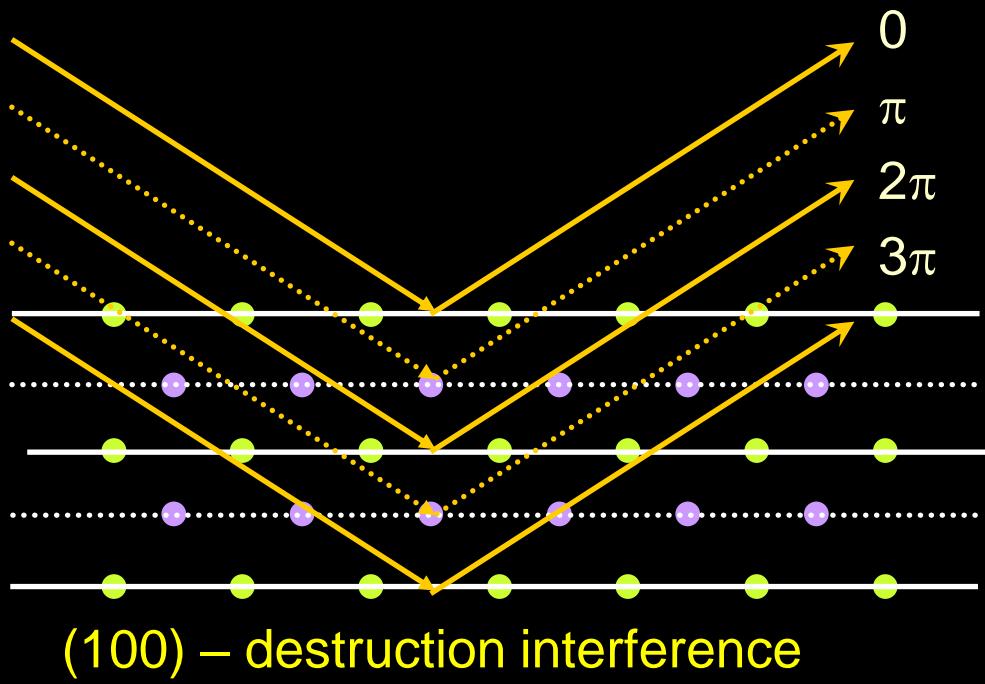
2) 体心立方情形: 晶胞内有 2个原子:  $000, \frac{1}{2} \frac{1}{2} \frac{1}{2}$

$$\begin{aligned} F_{HKL} &= f_a [1 + \exp(i\pi(H + K + L))] \\ &= f_a [1 + \cos \pi(H + K + L)] \end{aligned}$$

显然,  $H+K+L =$  偶数时  $F_{HKL} = 2f_a$

$H+K+L =$  奇数时  $F_{HKL} = 0$

所以只有  $H+K+L =$  偶数的晶面才会显现衍射峰, 而  
 $(100), (111), (210), (300), (221), (311)$  等晶面的衍射峰消失。



3) 面心立方情形: 四个原子:  $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$ ,

$$F_{HKL} = f_a [1 + \exp(i\pi(H+K)) + \exp(i\pi(K+L)) + \exp(i\pi(L+H))]$$

$$F_{HKL} = f_a [\cos \pi(0) + \cos \pi(H+K) + \cos \pi(H+L) + \cos \pi(L+K)]$$

显然  $H, K, L$  为全奇、全偶时,  $H+K, H+L, K+L$  均为偶数。

$$F_{HKL} = 4f_a$$

$H, K, L$  奇偶混杂时 (2奇1偶或2偶1奇)  $H+K, H+L, K+L$  必定有2个奇数, 1个偶数, 所以:

$$F_{HKL} = f_a [1 - 1 + 1 - 1] = 0$$

只有当  $H, K, L$  为全奇或全偶的晶面才会显现衍射峰。  
 $(100), (110), (210), (211), (300)$  等晶面衍射峰消失。

## Selection Rules for Reflection in Cubic Crystals

$(hkl)$	$h^2+k^2+l^2$	SC	BCC	FCC
100	1	✓	✗	✗
110	2	✓	✓	✗
111	3	✓	✗	✓
200	4	✓	✓	✓
210	5	✓	✗	✗
211	6	✓	✓	✗
220	8	✓	✓	✓
300	9	✓	✗	✗
310	10	✓	✓	✗
311	11	✓	✗	✓
222	12	✓	✓	✓
320	13	✓	✗	✗
321	14	✓	✓	✗
400	16	✓	✓	✓

### 3. 影响衍射强度的其它因素：

晶体的不完整性：对周期性的偏离，引起衍射峰展宽。

温度影响：使衍射峰值降低。

吸收影响：晶体原子对入射波的吸收。

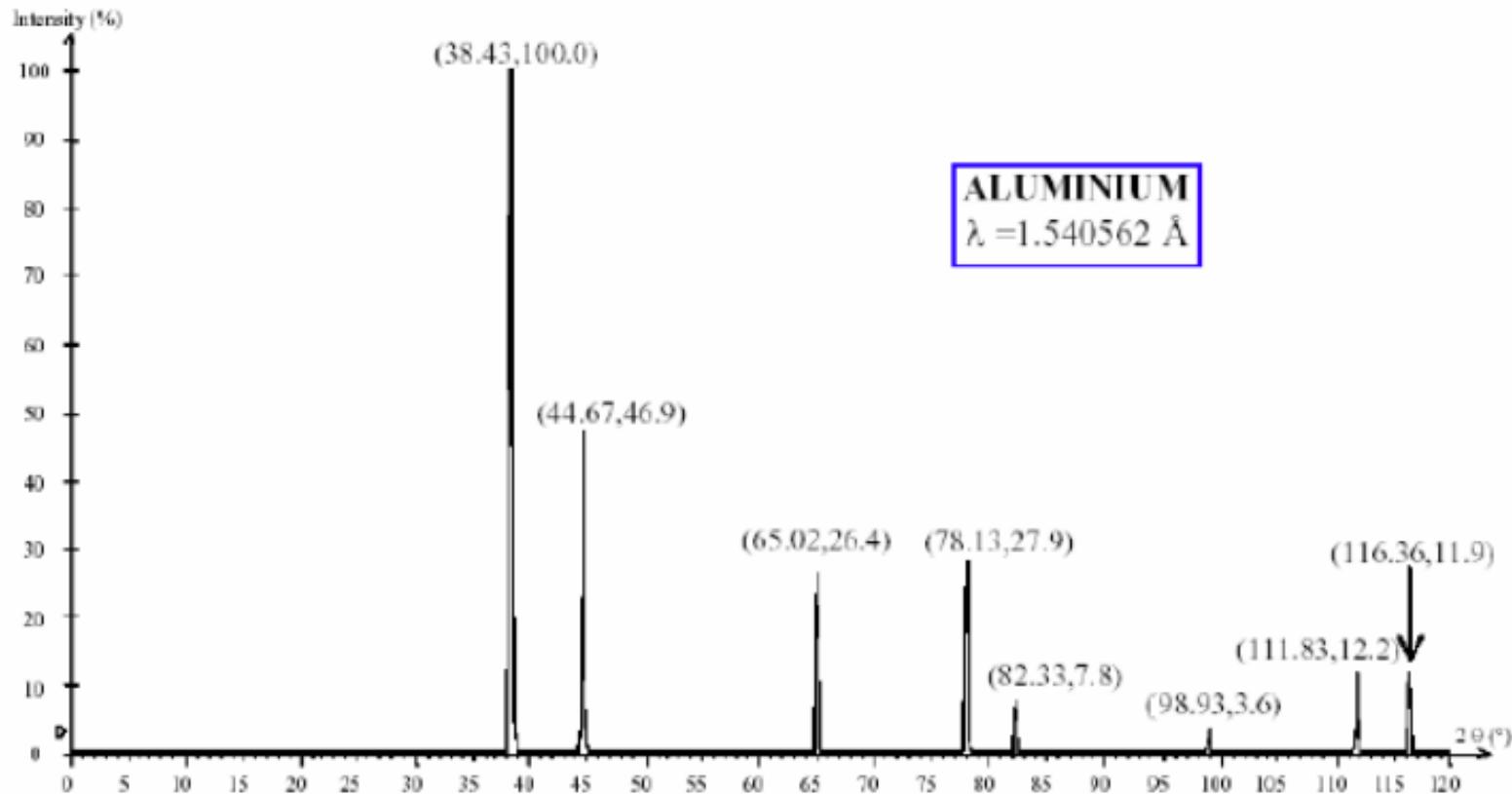
消光效应：X射线在晶体内部多次反射引起的相消干涉。

等等

以上在晶体结构的实际测量中都是要注意到的。

# Worked Example

Consider the following XRD pattern for Aluminum, which was collected using CuK $\alpha$  radiation.



Index this pattern and determine the lattice parameters.

# Worked Example cont...

## Steps:

- (1) Identify the peaks.
- (2) Determine  $\sin^2 \theta$
- (3) Calculate the ratio  $\sin^2 \theta / \sin^2 \theta_{min}$  and multiply by the appropriate integers.
- (4) Select the result from (3) that yields  $h^2 + k^2 + l^2$  as an integer.
- (5) Compare results with the sequences of values  $h^2 + k^2 + l^2$  to identify the Bravais lattice, e.g. BCC  $h^2 + k^2 + l^2 = 2, 4, 6, 8 \dots$
- (6) Calculate lattice parameters.

# Worked Example cont...

**Step 1:** Identify the peaks and their proper  $2\theta$  values. Eight peaks for this pattern

Peak No.	$2\theta$	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	$hkl$	$a (\text{\AA})$
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

# Worked Example cont...

**Step 1:** Determine  $\sin^2 \theta$

Peak No.	$2\theta$	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	$hkl$	$a (\text{\AA})$
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						
8	116.36	0.7220						

# Worked Example cont...

**Step 3:** Calculate the ratio  $\sin^2 \theta / \sin^2 \theta_{min}$  and multiply by the appropriate integers.

Peak No.	$2\theta$	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$h^2+k^2+l^2$	$hkl$	$a (\text{\AA})$
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

# Worked Example cont...

**Step 4:** Select the result from (3) that yields  $h^2 + k^2 + l^2$  as a series of integers.

Peak No.	$2\theta$	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	$hkl$	$\alpha (\text{\AA})$
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

# Worked Example cont...

**Step 5:** Compare results with the sequences of  $h^2 + k^2 + l^2$  values to identify the Bravais lattice.

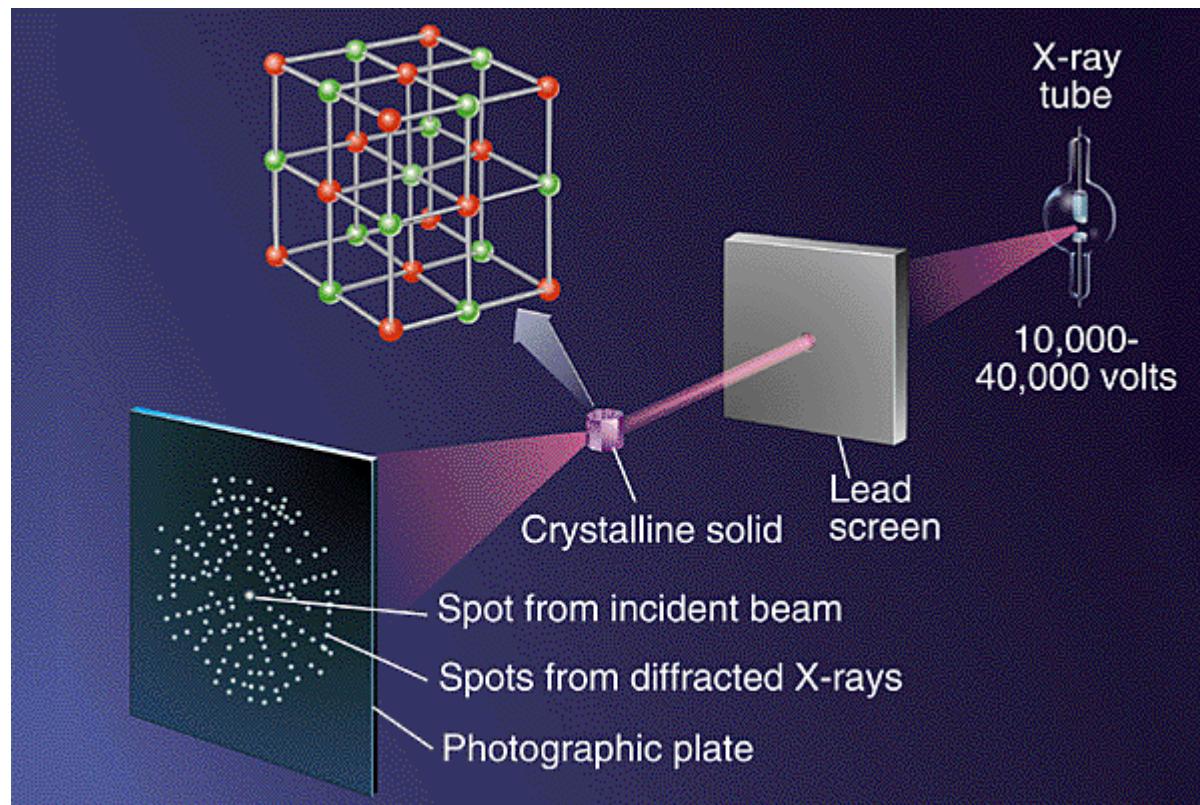
Peak No.	$2\theta$	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	$hkl$	$a (\text{\AA})$
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Bravais lattice is Face-Centred Cubic

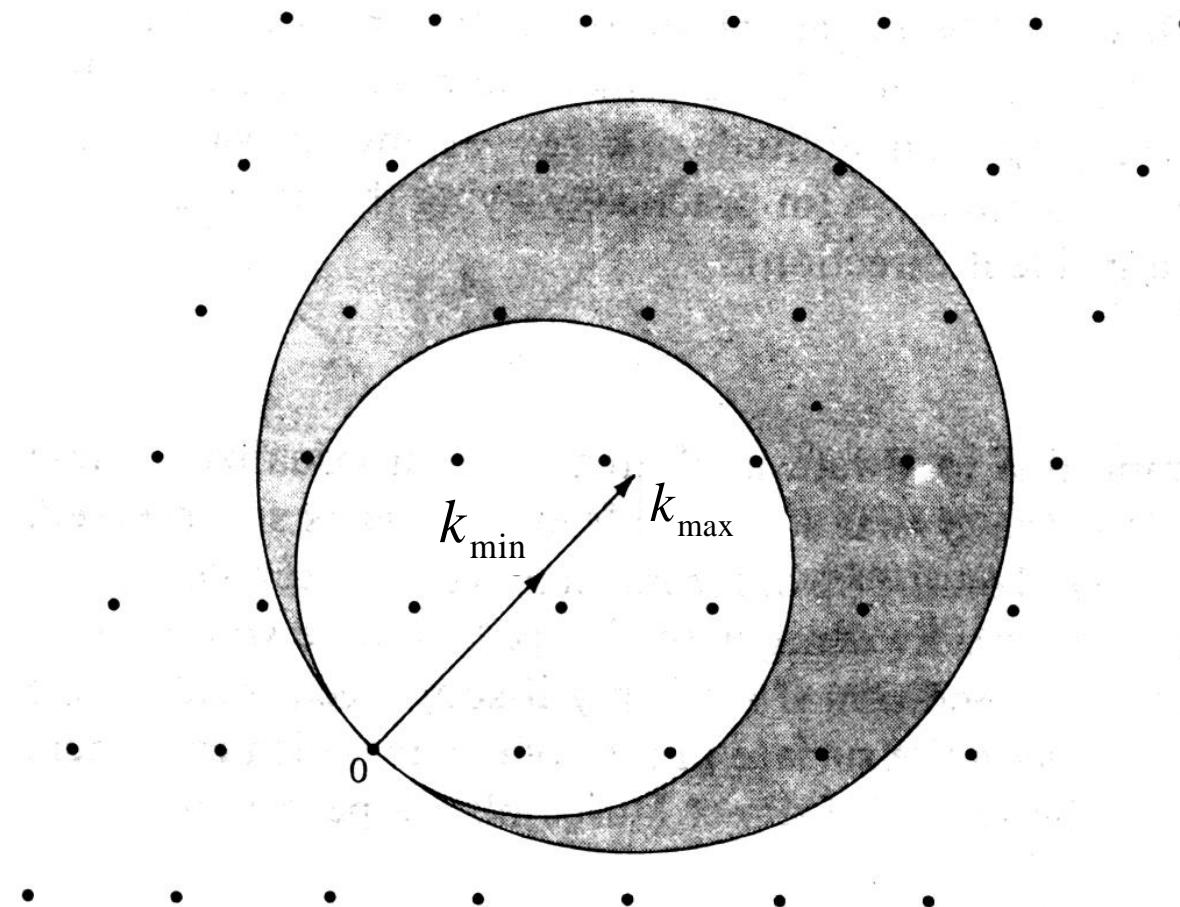
$$\sin^2 \theta = \left( \frac{\lambda^2}{4a^2} \right) (h^2 + k^2 + l^2)$$

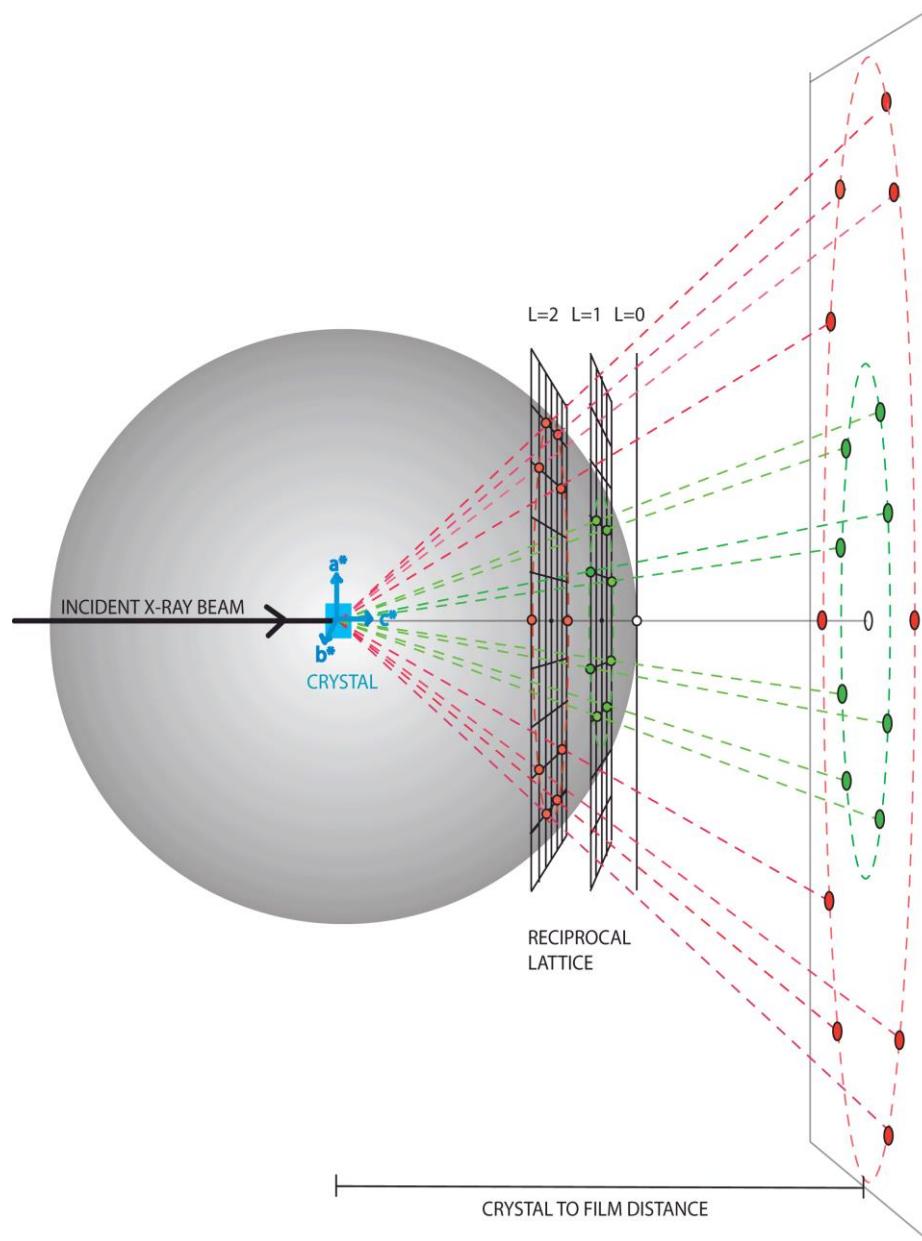
### 三. 实验方法简介:

1. **Laue** 方法: 一个单晶固定在一束**连续波长的X射线**中,会在一些方向产生衍射斑点,在某些特定方向可以表现出明显的对称特点,常用于单晶样品的定向。

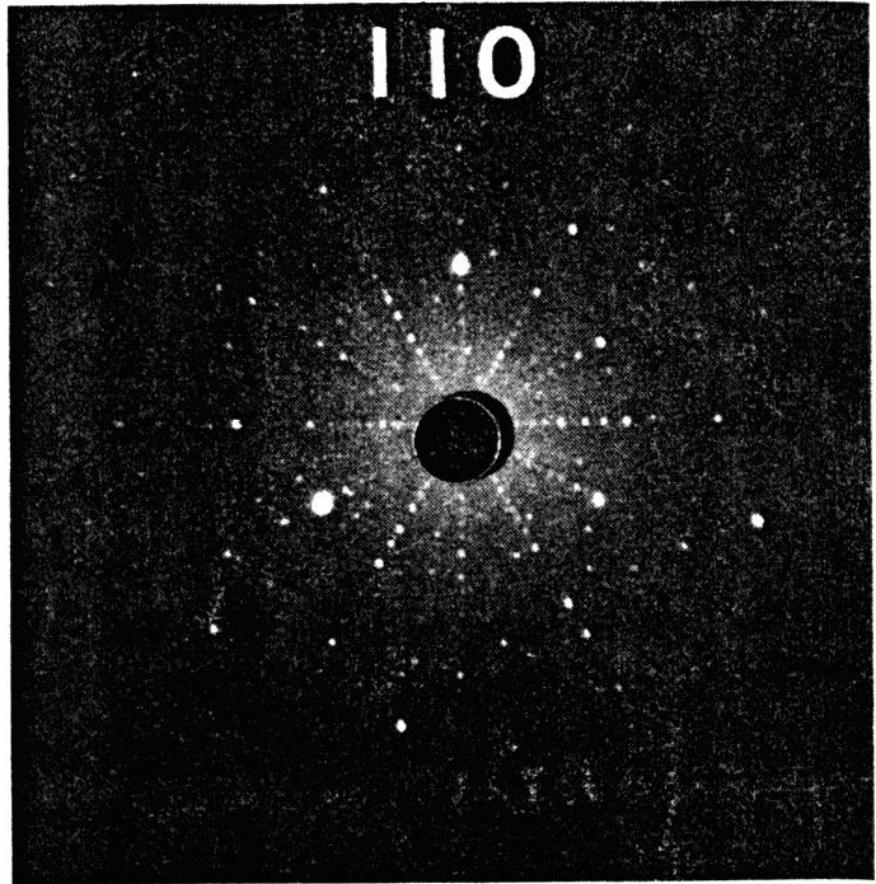
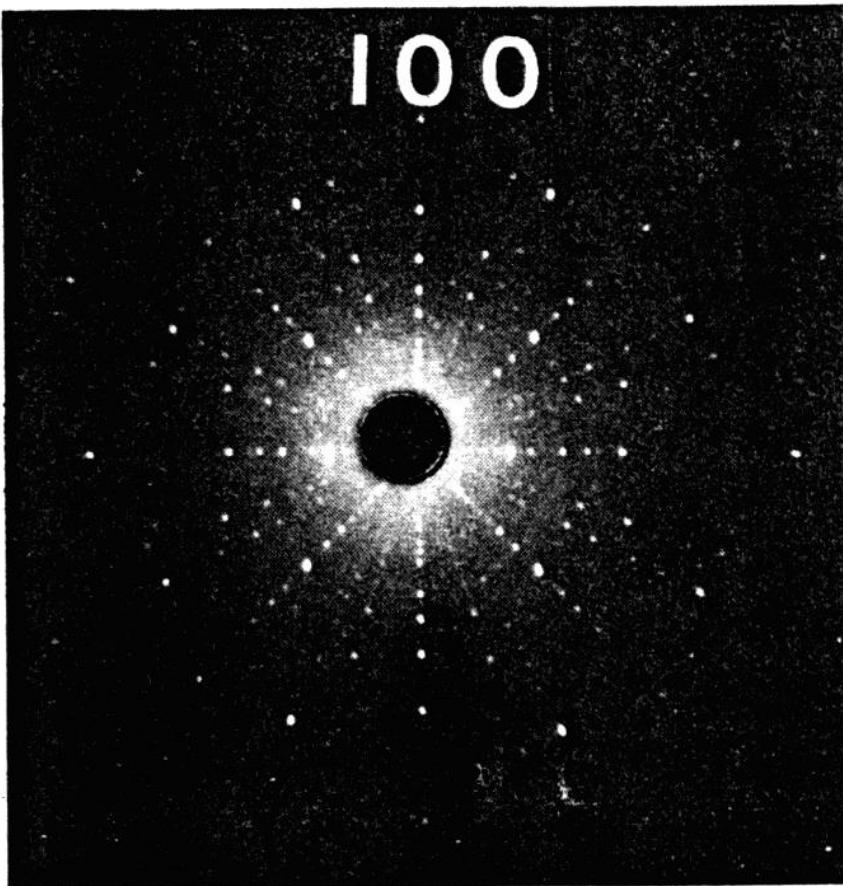


坐落在最小波矢  $k_{\min}$  和最大波矢  $k_{\max}$  两个球中间的倒格点所代表的晶面族都会发生衍射。





# FeS<sub>2</sub> 单晶 Laue X 射线衍射图

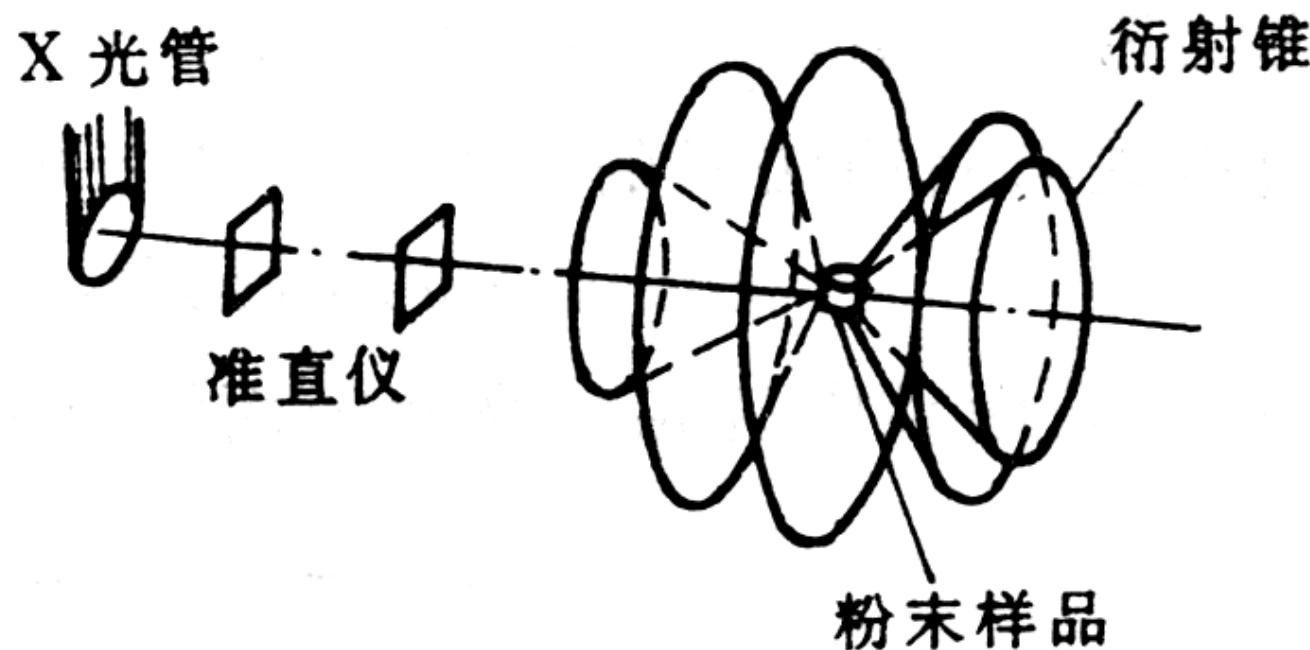


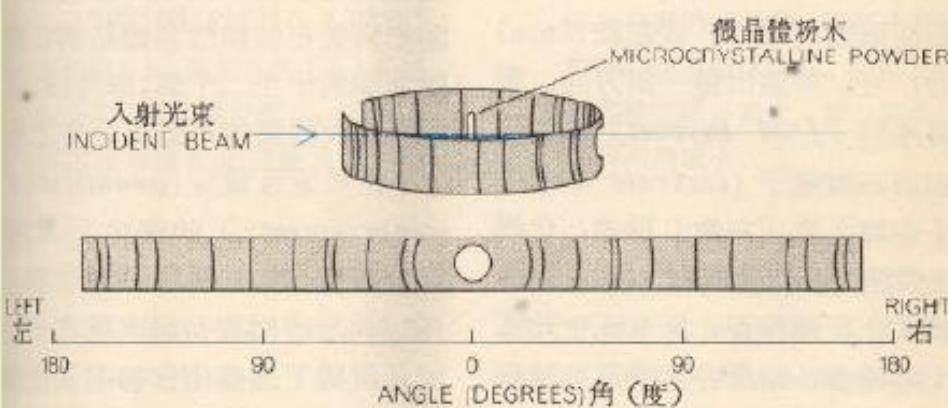
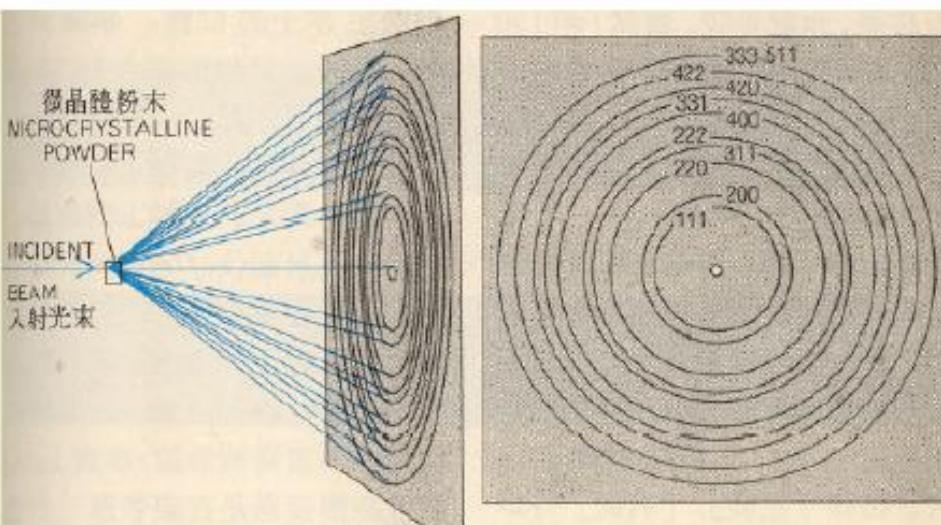
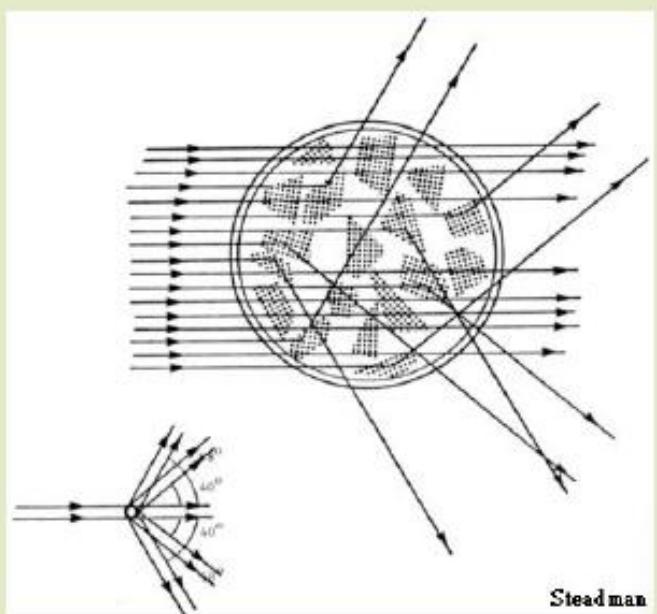
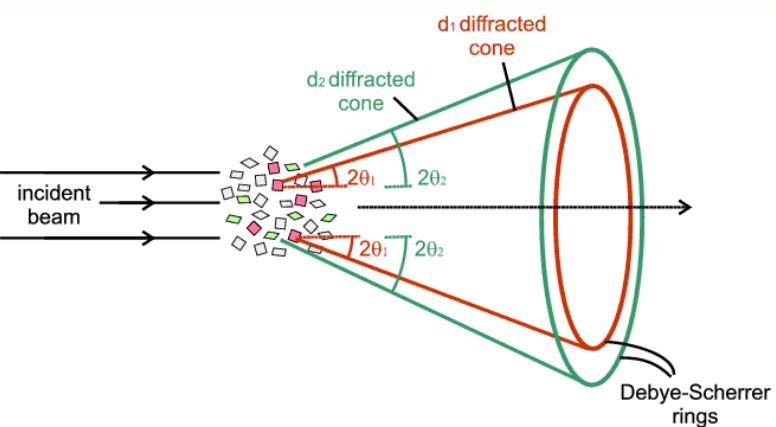
FeS<sub>2</sub> 有两种晶型：立方晶系的黄铁矿和斜方晶系的白铁矿。

X—衍射图具有立方对称性，因而是点群为T<sub>h</sub>的黄铁矿  $T_h^6(P_{a3})$

## 2. 粉末衍射方法 (X-ray powder diffraction)

使用单色 X 射线照射粉末样品，由于粉末的随机分布，可以同时满足各晶面族发生衍射的条件。常用于材料的物相分析等。已经收集到超过25000多种晶体材料的标准粉末衍射图，只需要将衍射结果和标准图进行比较，即可知道被测材料的结构。





[圖八] 粉末式攝影 (POWDER PHOTOGRAPHS)

作粉末式照像時，X光照射在一塊許多向任意方向排列的小晶體上，每一階次( $hkl$ )的繞光束組成一圓椎體，如以垂直於入射光之平面感光板記錄，每一階次以圍繞中心的圓環狀出現；(上)。

本圖的這些環的位置是面心正方晶格的典型式。為了比較方便，經常使用圓柱形底片，其軸垂直於入射光(下)。圓柱體與圓柱相交照出的弧線，差不多可以包括所有角度直至 $180^\circ$ ；底片可打開成條形。

## X-rays are scattered in a sphere around the sample

- Each diffraction peak is actually a Debye diffraction cone produced by the tens of thousands of randomly oriented crystallites in an ideal sample.
  - A cone along the sphere corresponds to a single Bragg angle  $2\theta$
- The linear diffraction pattern is formed as the detector scans along an arc that intersects each Debye cone at a single point
- Only a small fraction of scattered X-rays are observed by the detector.

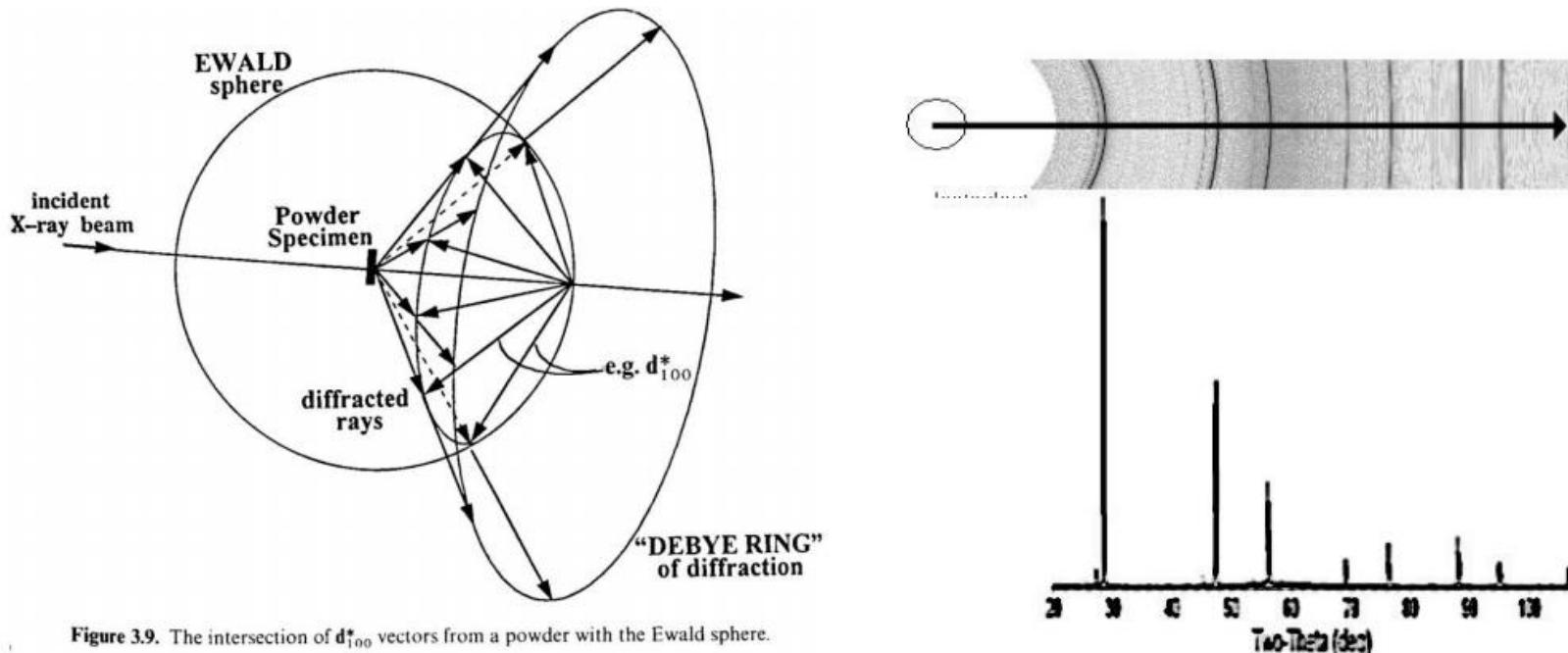
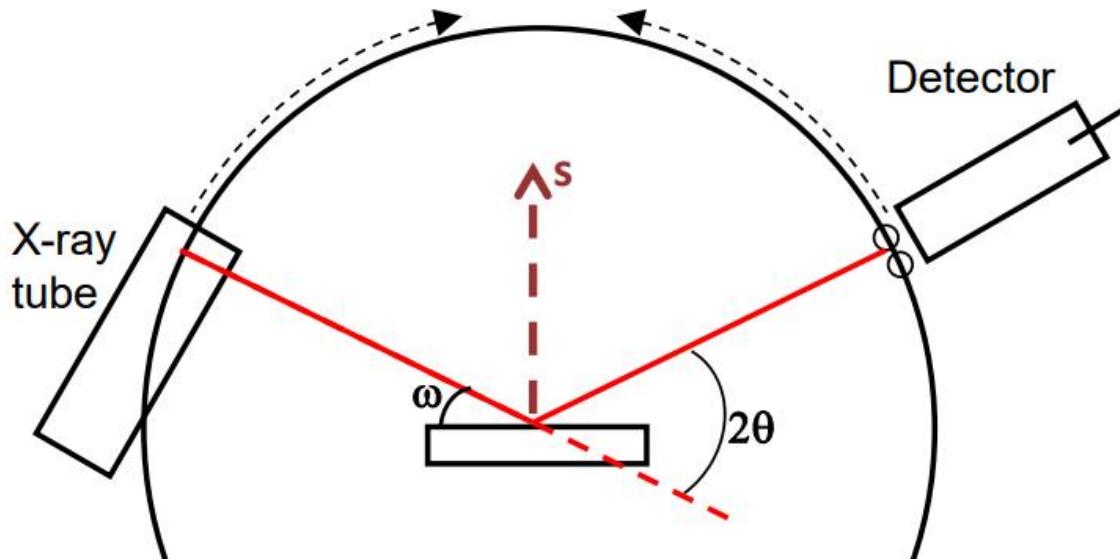
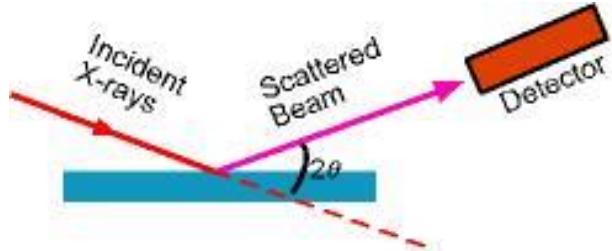


Figure 3.9. The intersection of  $d_{100}^*$  vectors from a powder with the Ewald sphere.

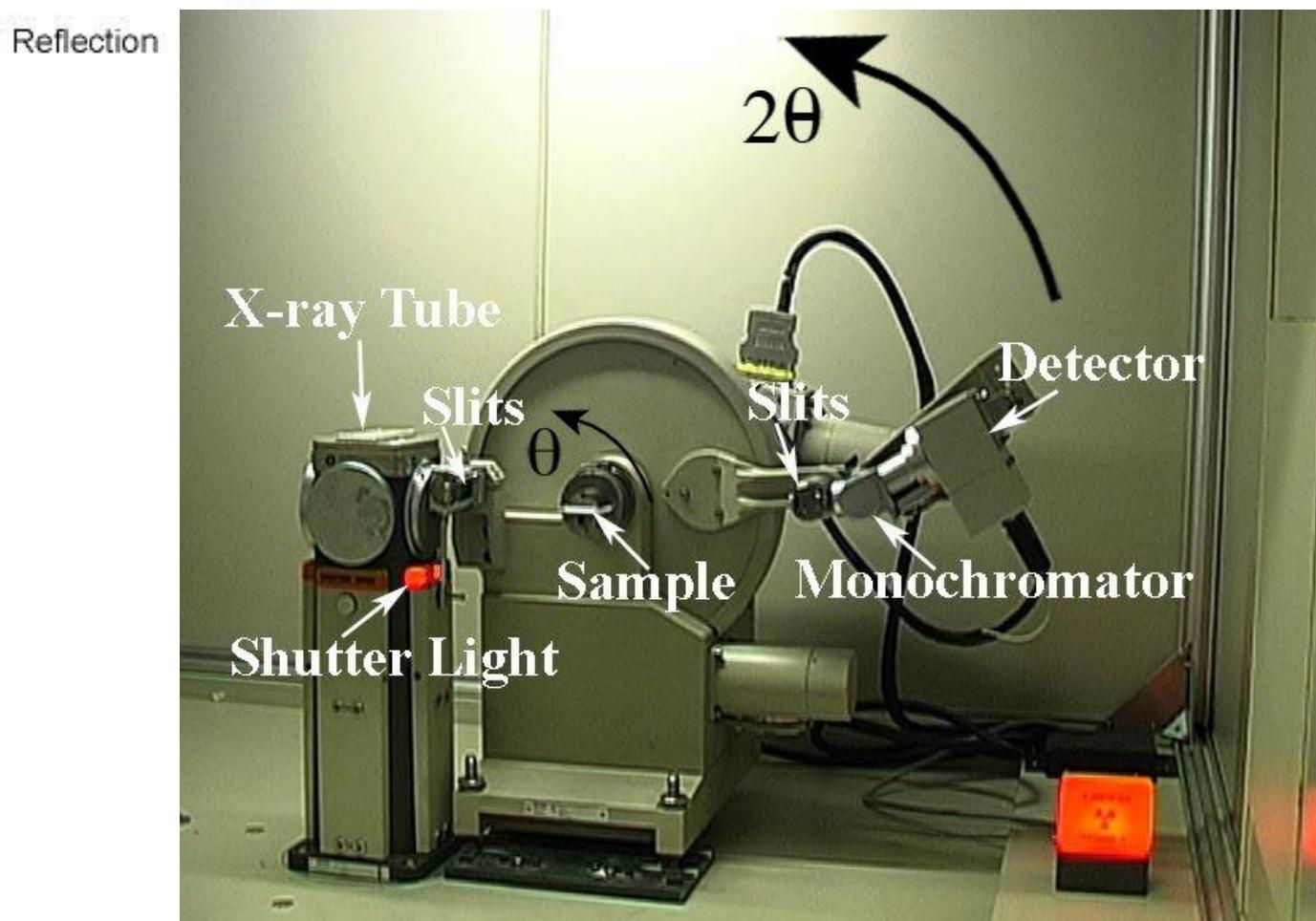
# Many powder diffractometers use the Bragg-Brentano parafocusing geometry.



- The incident angle,  $\omega$ , is defined between the X-ray source and the sample.
- The diffraction angle,  $2\theta$ , is defined between the incident beam and the detector.
- The incident angle  $\omega$  is always  $\frac{1}{2}$  of the detector angle  $2\theta$ .
  - In a  $\theta:2\theta$  instrument (e.g. Rigaku H3R), the tube is fixed, the sample rotates at  $\theta$  °/min and the detector rotates at  $2\theta$  °/min.
  - In a  $\theta:\theta$  instrument (e.g. PANalytical X'Pert Pro), the sample is fixed and the tube rotates at a rate  $-\theta$  °/min and the detector rotates at a rate of  $\theta$  °/min.
- **In the Bragg-Brentano geometry, the diffraction vector ( $s$ ) is always normal to the surface of the sample.**
  - The diffraction vector is the vector that bisects the angle between the incident and scattered beam



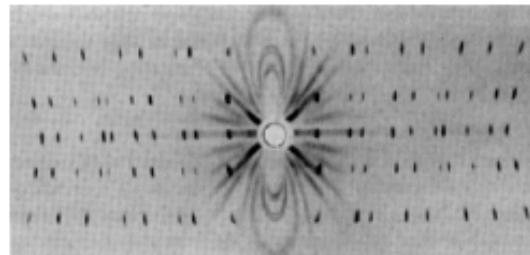
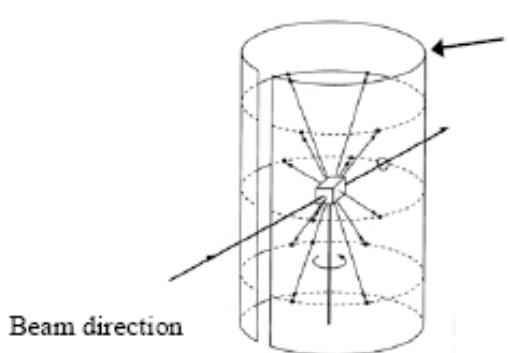
$$n\lambda = 2d \sin Q$$



### 3. 旋转晶体法(Rotating crystal method):

单一波长的 X射线照射放在旋转头上的晶体，晶体通过自身旋转，使各晶面族满足衍射条件。这是用于晶体结构测定、确定原子位置最基本的方法。

- ◆ Aligned crystal is rotated around one axis so helps pass through the Ewald sphere
  - Produces spots lying on layer lines



Rotation photograph of quartz showing spots on layer lines

## 五. 研究实例:

几种立方晶系晶胞几何结构因子的计算结果，可能产生衍射的晶面如下：

sc: (100),(110),(111),(200),(210),(211),(220),(221)(300),(310),(311),(222)

bcc: --- ,(110), --- , (200), --- , (211),(220), --- --- ,(310), --- , (222)

fcc: ---, --- , (111),(200), --- , --- ,(220), --- , --- , ---- , (311),(222)

## 衍射结果实例：

FeCo合金；镍粉；金钢石；NaCl；KCl；KBr

几何结构因子的计算结果和实测曲线结果相符，完全证实了晶体点阵学说对晶体结构的描述。

镍粉末衍射图，面心立方结构，  
只有全奇全偶的晶面族有衍射峰

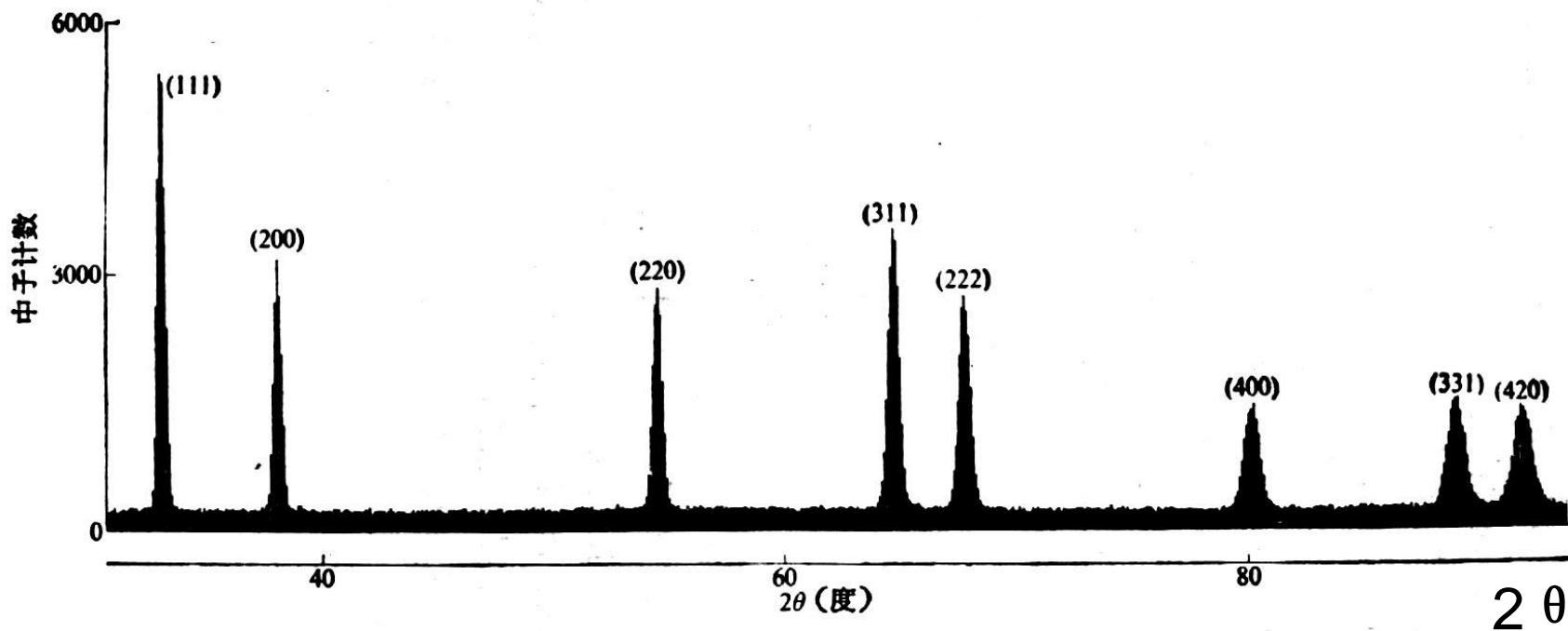
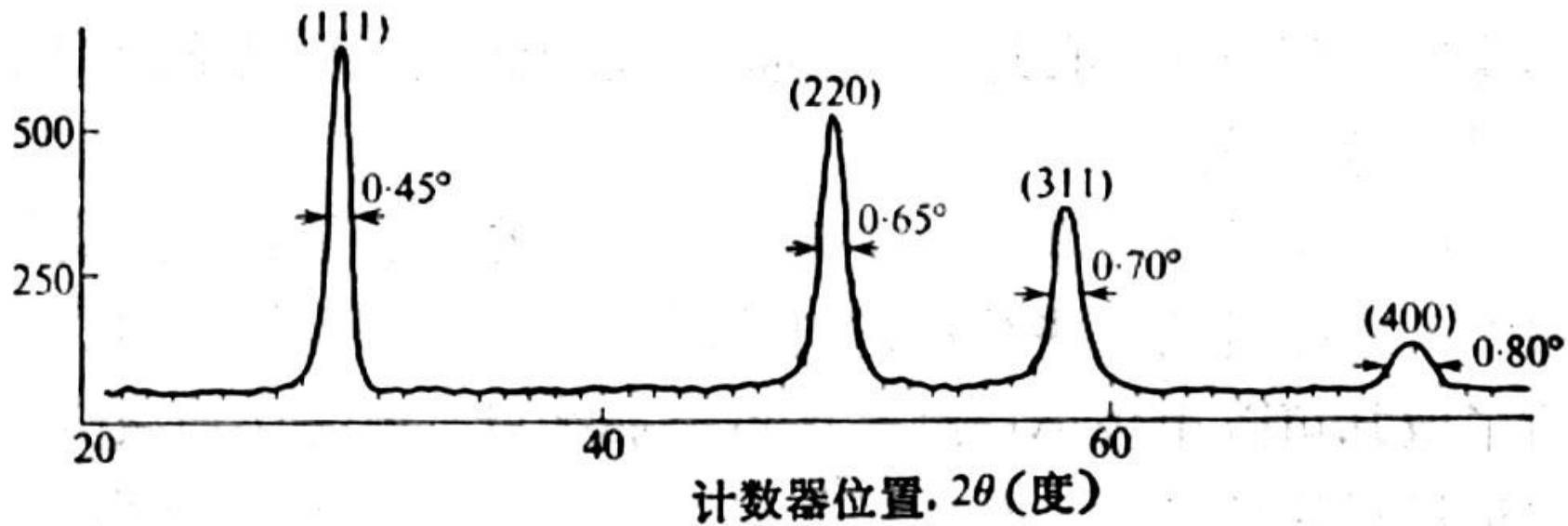


图 58 部分镍粉末衍射图。采用镨单色器,由 A.E.R.E. Harwell 的 PANDA 衍射计记录,  
相应波长 1.14 埃,  $2\theta$  的每  $0.1^{\circ}$  为计数间隔.

# 金钢石的粉末衍射图



可以和金钢石几何结构因子的计算结果比较（作业）

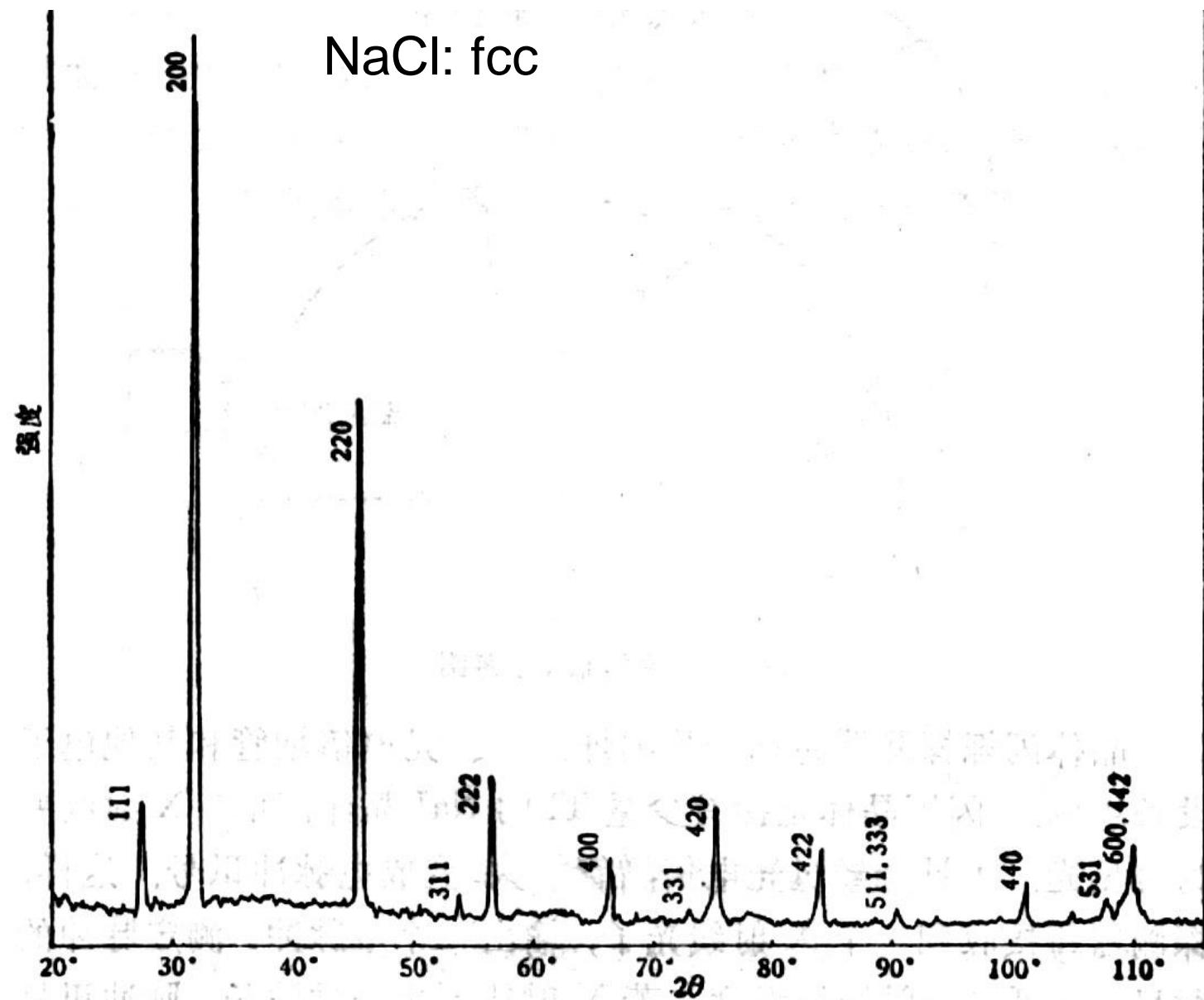


图 9-8 NaCl 晶体的粉末衍射图

# Solving the Structure of DNA: History

- Rosalind Franklin- physical chemist and x-ray crystallographer who first crystallized and photographed BDNA
- Maurice Wilkins- collaborator of Franklin
- Watson & Crick- chemists who combined the information from Photo 51 with molecular modeling to solve the structure of DNA in 1953



Rosalind Franklin

# Solving the Structure of DNA

- Photo 51 Analysis
  - “X” pattern characteristic of helix
  - Diamond shapes indicate long, extended molecules
  - Smear spacing reveals distance between repeating structures
  - Missing smears indicate interference from second helix

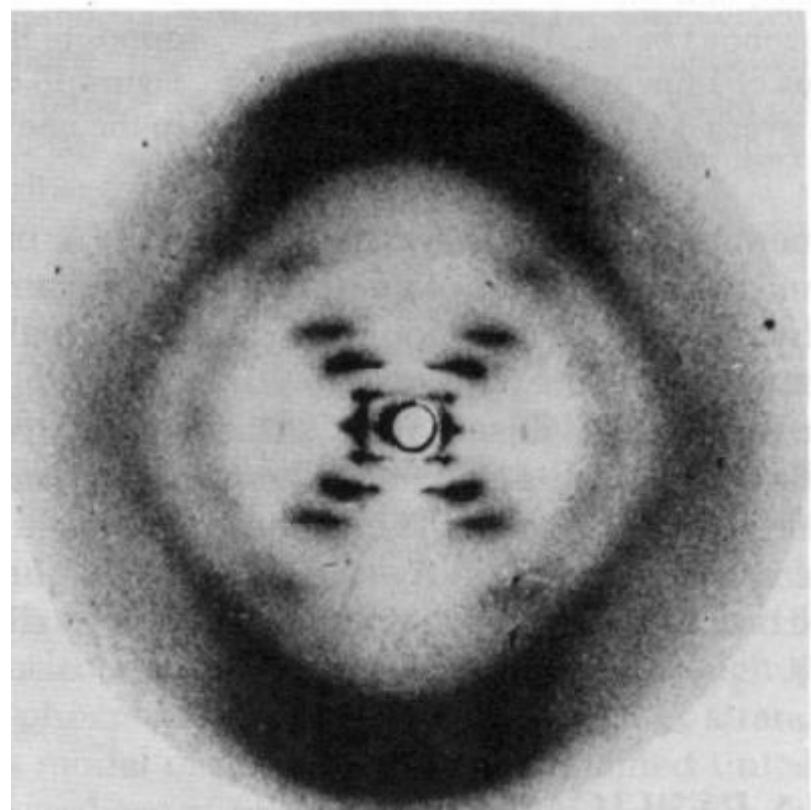


Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

# Solving the Structure of DNA

- Photo 51 Analysis
  - “X” pattern characteristic of helix
  - Diamond shapes indicate long, extended molecules
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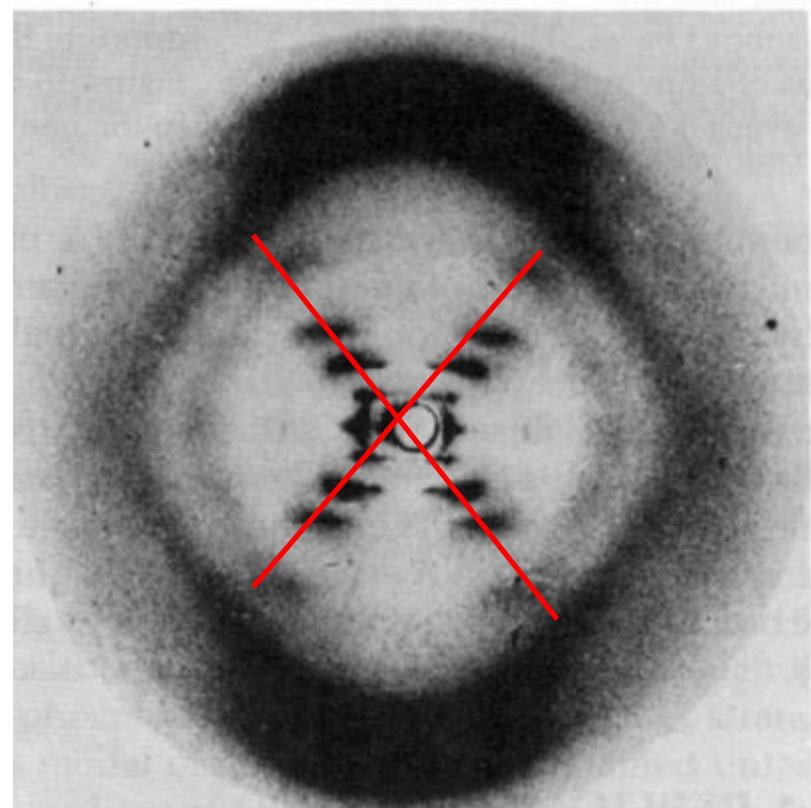


Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

# Solving the Structure of DNA

- Photo 51 Analysis
  - “X” pattern characteristic of helix
  - Diamond shapes indicate long, extended molecules
  - Smear spacing reveals distance between repeating structures
  - Missing smears indicate interference from second helix

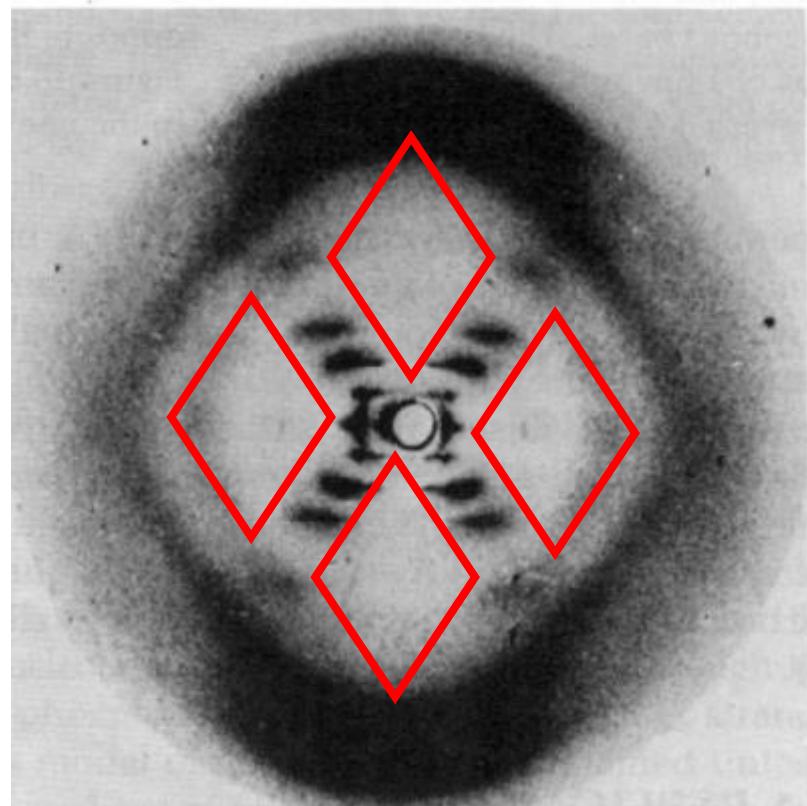


Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

# Solving the Structure of DNA

- Photo 51 Analysis
  - “X” pattern characteristic of helix
  - Diamond shapes indicate long, extended molecules
  - Smear spacing reveals distance between repeating structures
  - Missing smears indicate interference from second helix

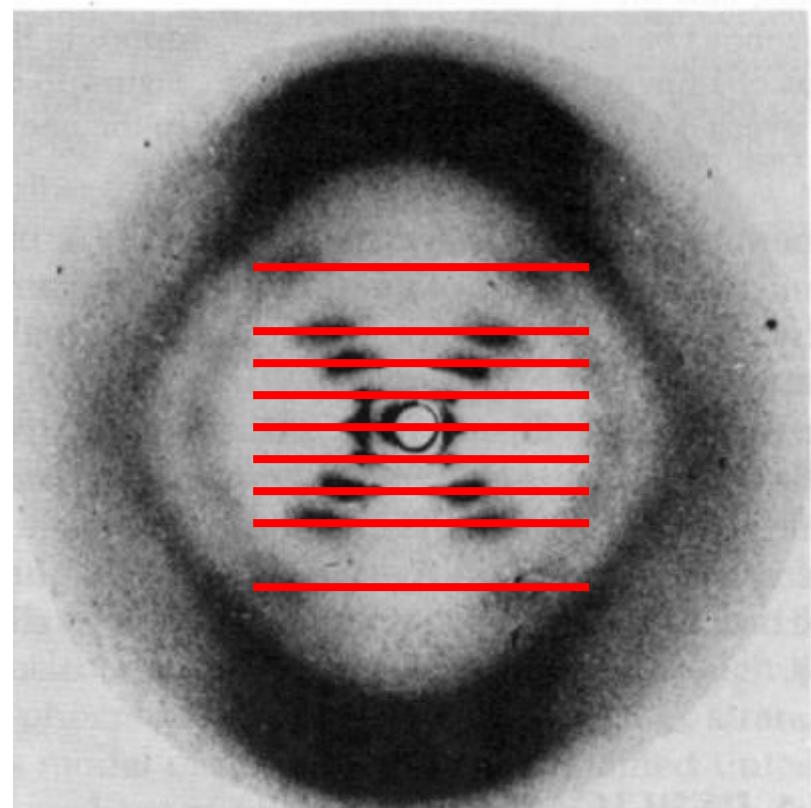


Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

# Solving the Structure of DNA

- Photo 51 Analysis
  - “X” pattern characteristic of helix
  - Diamond shapes indicate long, extended molecules
  - Smear spacing reveals distance between repeating structures
  - Missing smears indicate interference from second helix

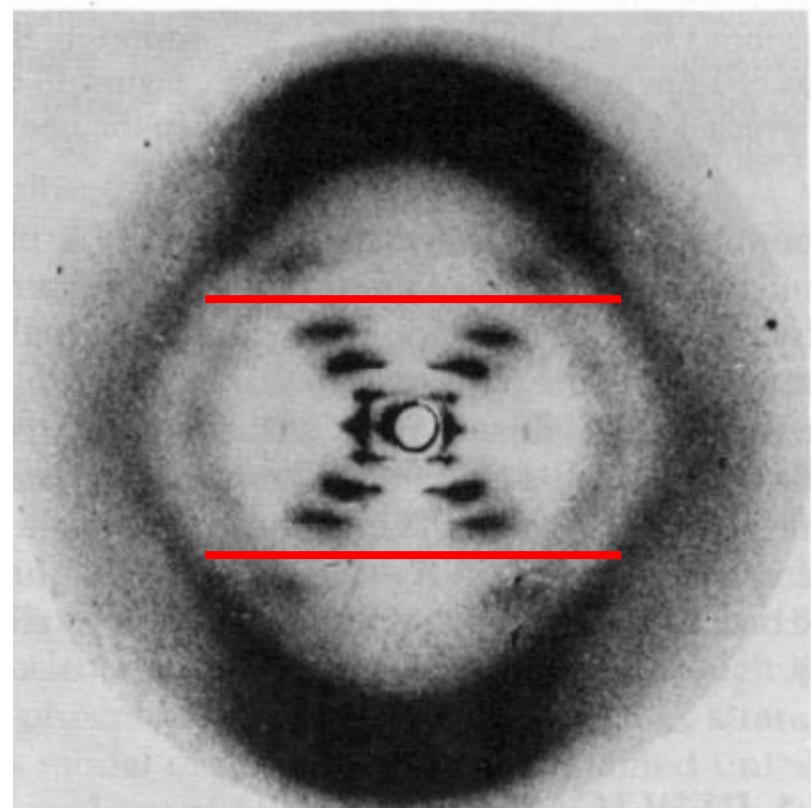
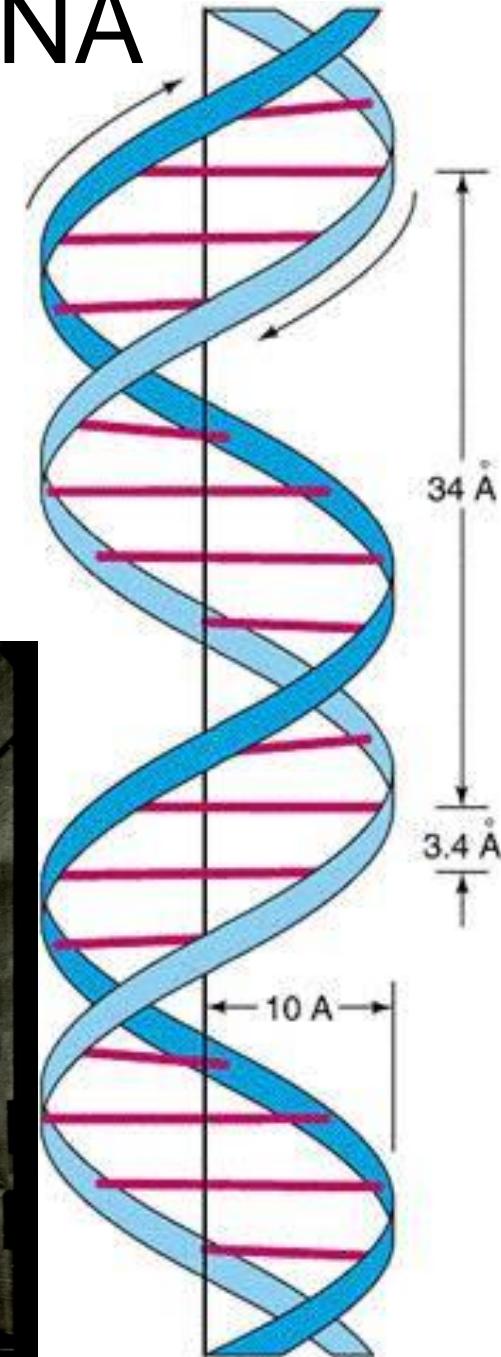
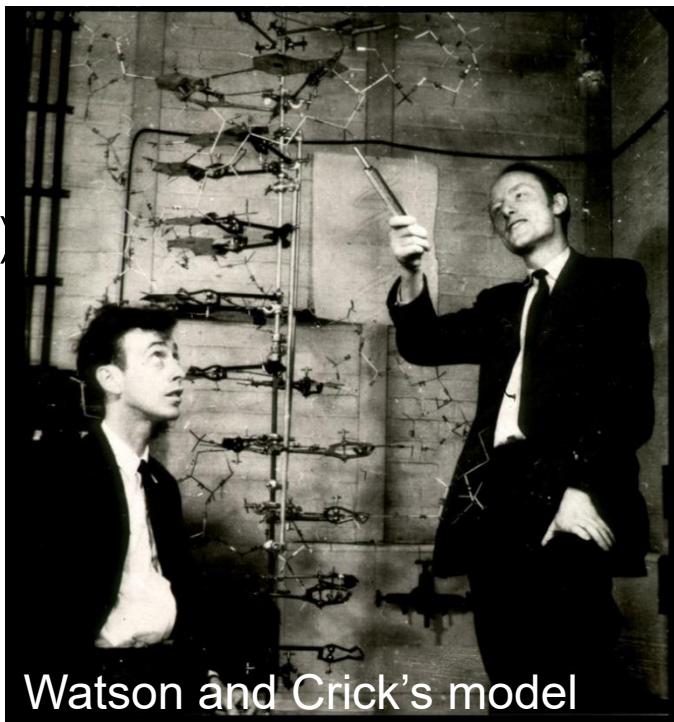


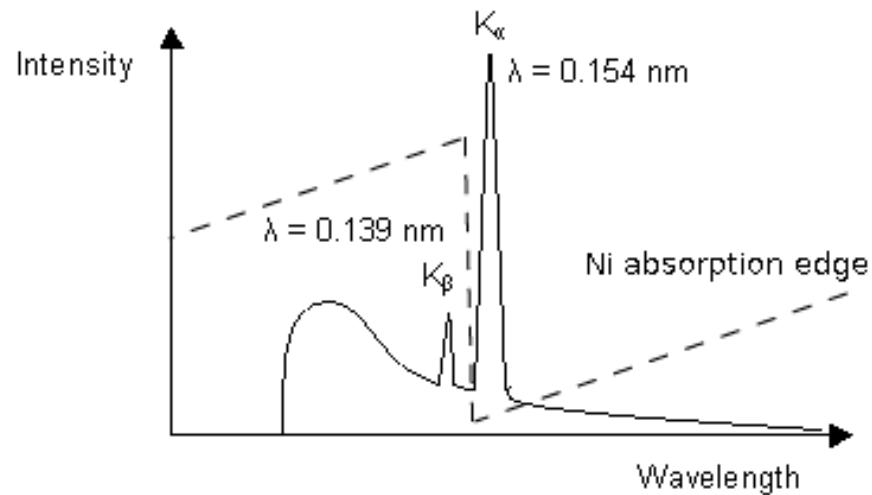
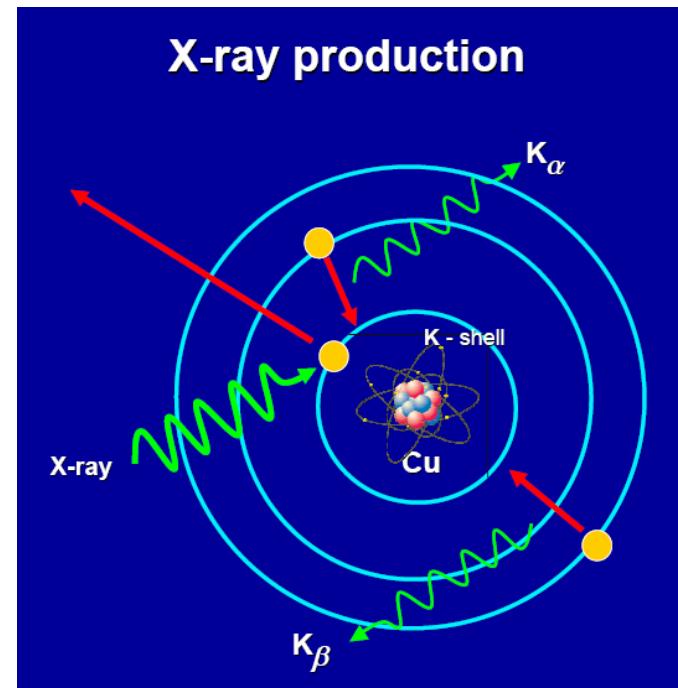
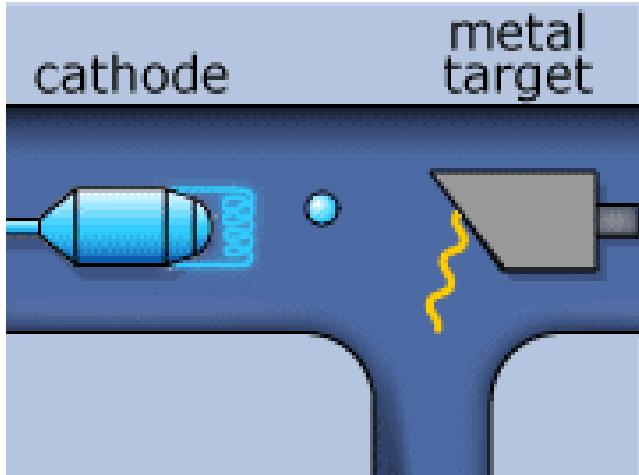
Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

# Solving the Structure of DNA

- Information Gained from Photo 51
  - Double Helix
  - Radius: 10 angstroms
  - Distance between bases: 3.4 angstroms
  - Distance per turn: 34 angstroms
- Combining Data with Other Information
  - DNA made from:
    - sugar
    - phosphates
    - 4 nucleotides (A,C,G,T)
  - Chargaff's Rules
    - $\%A = \%T$
    - $\%G = \%C$
  - Molecular Modeling

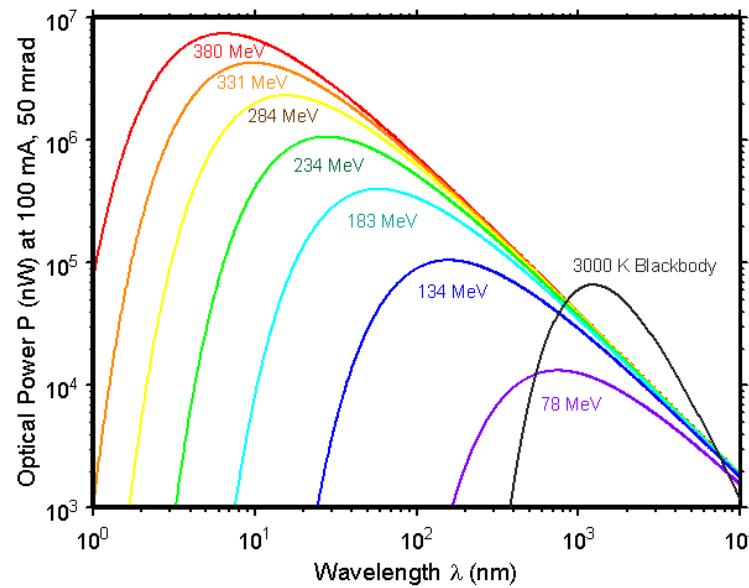
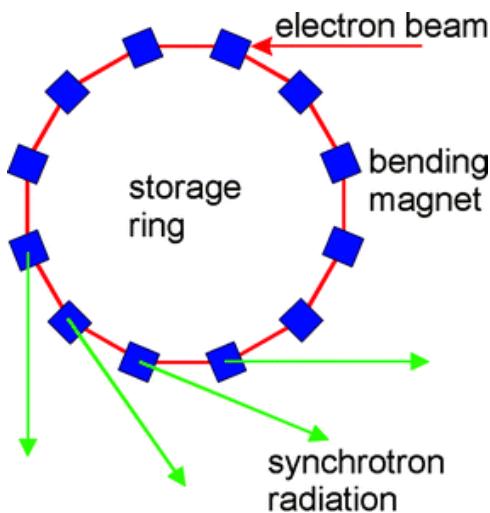


## 六. X射线的产生

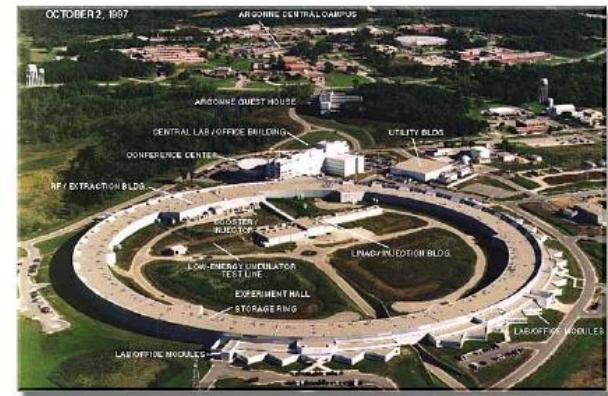
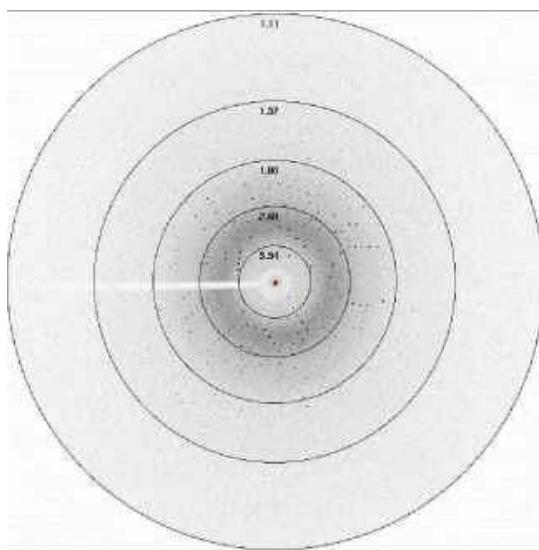


The Ni absorption edge is midway between the  $K_{\beta}$  and  $K_{\alpha}$  lines so that the former is reduced very substantially while the latter is only marginally reduced.. In selecting the thickness of the filter, a compromise has to be reached between eliminating as much as possible of the undesired radiation and maximizing the desired radiation.

# 同步辐射



The Advanced Photon Source



中华眼镜蛇神经毒II蛋白晶体的X射线衍射图， X射线波长为 $1.15162\text{\AA}$



科大同步辐射国家实验室



合肥先进光源

## 七. 电子衍射和中子衍射

微观粒子具有波动性，合适的波长的粒子同样可以用于衍射技术，测定晶体结构。

低能电子衍射（LEED），中子衍射和X光衍射都已经成为测定晶体结构的基本手段。

中子衍射特点：吸收小、核散射，磁散射；

测定含有重元素原子晶体中轻原子的位置

测定原子序数相近的原子组成的晶体结构

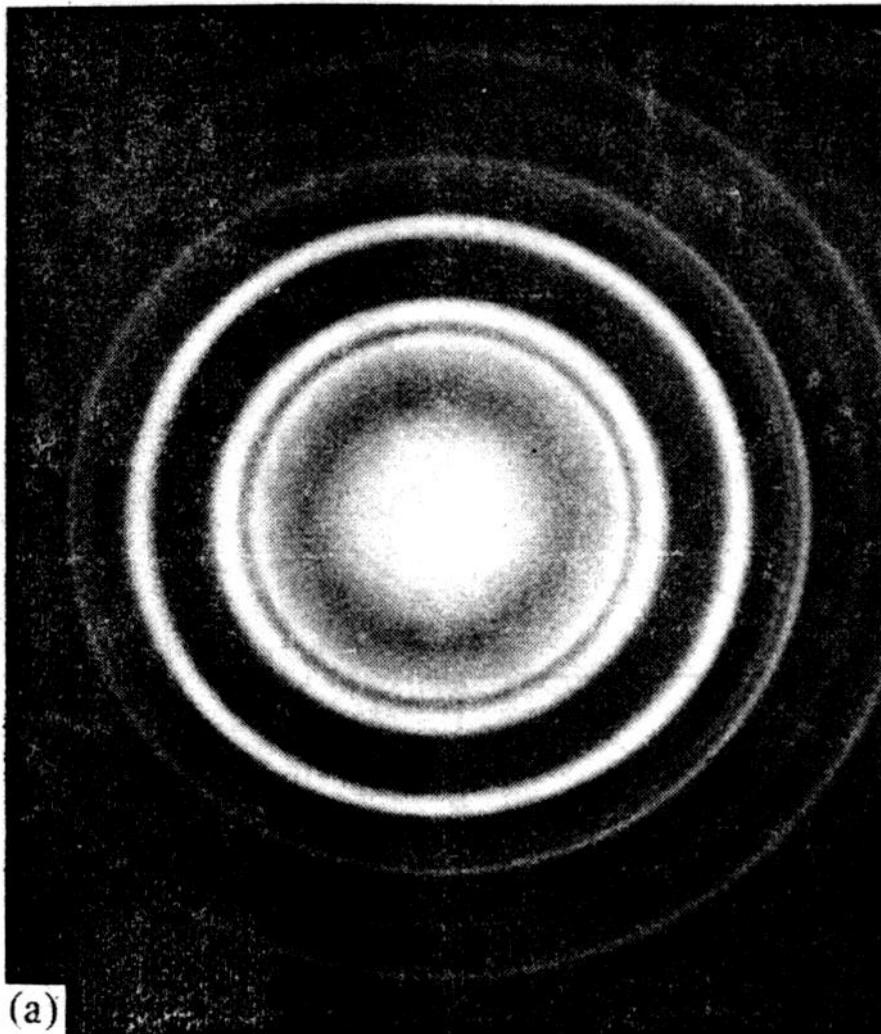
区别出晶体结构中的同位素原子

研究磁结构

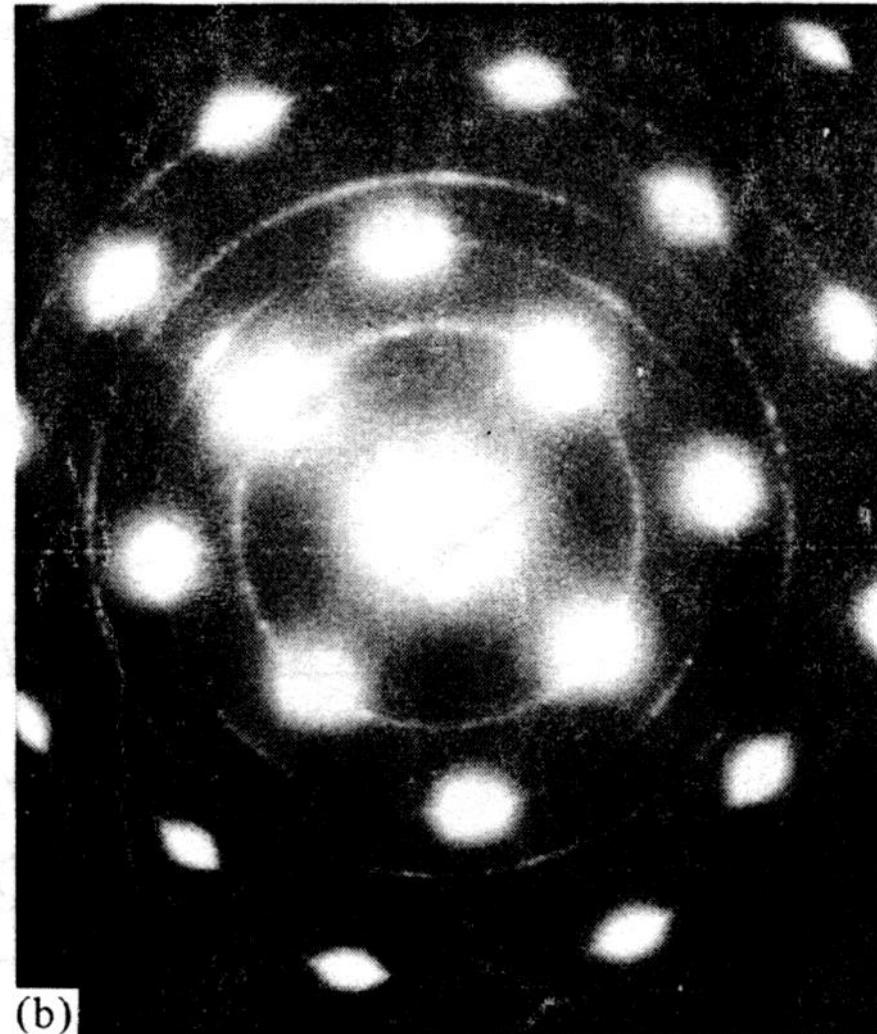
# 1. 晶体的电子衍射

电子衍射与X射线衍射有许多差异。主要差异有(i)在同样的加速电压下,电子波的波长比X射线的波长短的多,因而电子衍射角度比X射线衍射角度小的多。(ii)晶体对电子的散射能力比对X射线的散射能力强的多,因而电子衍射强度比X射线衍射强度高的多。

电子衍射在几何上和光学上的特点主要源于电子束波长短(特别是高能电子)和原子对它的散射能力强。



(a)



(b)

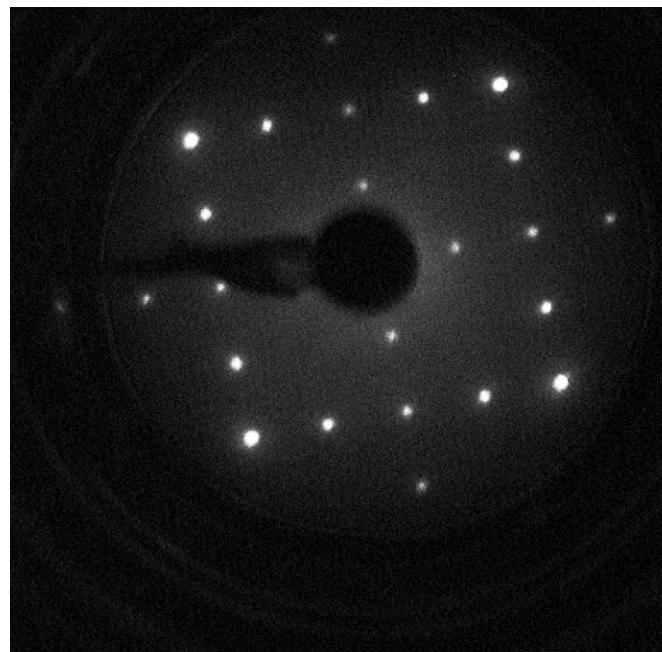
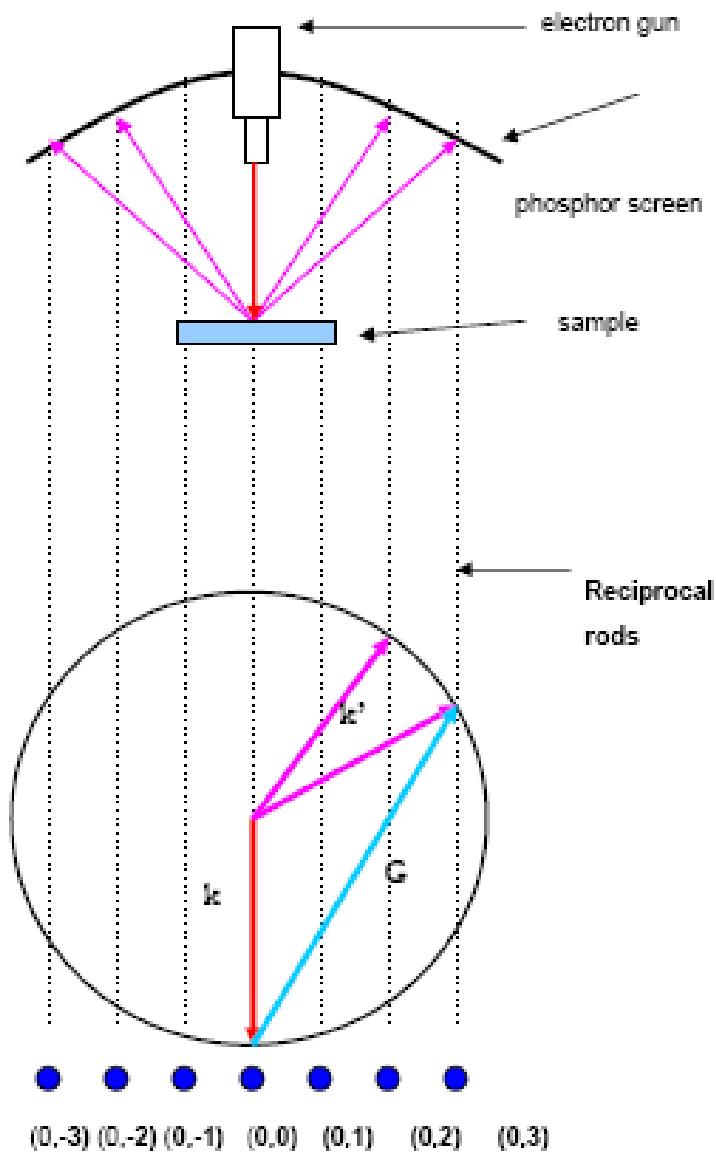
薄膜的电子衍射图：

多晶衍射

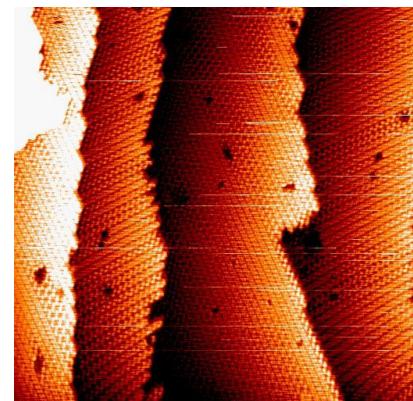
单晶衍射。

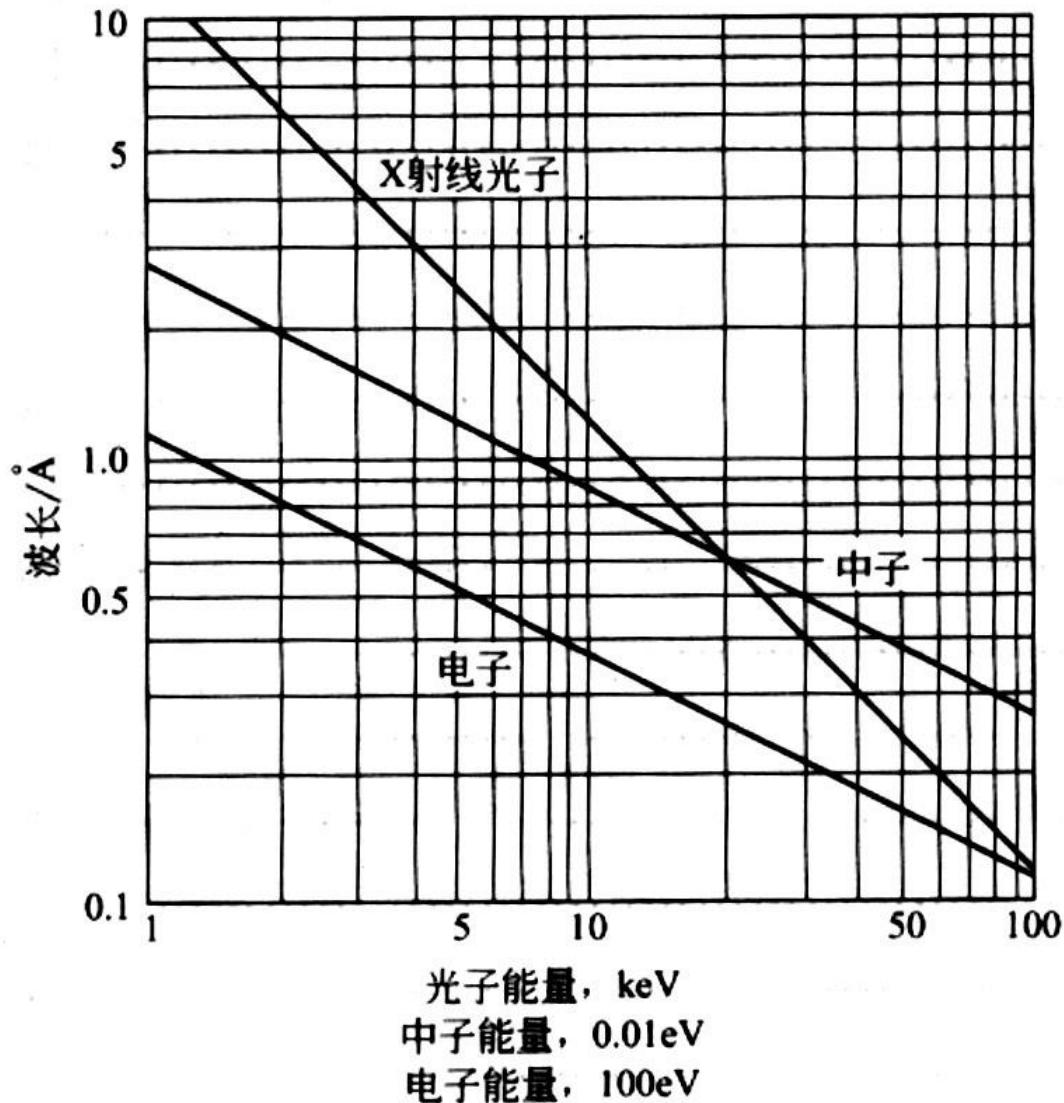
## Low Energy Electron Diffraction

2D-surface lattice forms reciprocal rods



Si(100)-2x1





$$\lambda = h/p$$

$$E = p^2/2m$$

图 1 光子、中子和电子的波长与其能量的关系曲线。

## 2. 晶体的中子衍射

中子是组成原子核的基本粒子，它可由原子能反应堆产生。中子也具有波粒二象性，当与晶体相互作用时也会产生与X射线和电子束类似的衍射现象。

同X射线衍射和电子衍射一样，中子衍射也要两个要素：衍射方向和衍射强度。

中子衍射强度正比与结构因子的平方：

$$I \propto F_{hkl}^2$$

中子衍射除了由于中子和原子核的相互作用外，还由于中子磁矩和原子磁矩的相互作用，这种相互作用称为磁性散射。

$$|F_{hkl}|^2 = \left| \sum f_{N_j} \exp[i2\pi(hx_j + ky_j + lz_j)] \right|^2 + \left| \sum p_j \exp[i2\pi(hx_j + ky_j + lz_j)] \right|^2$$

用中子衍射法测定晶体的结构时，衍射强度即核衍射强度；若晶体为磁性物质，则衍射强度除核衍射强度外，还包括磁衍射强度。

中子衍射在**研究**和**测定**晶体结构中有重要应用：

- (1) **研究**磁性晶体的结构；
- (2) **测定**晶体结构中轻原子的位置；
- (3) **识别**同一化合物中原子序数相近的两种原子。

# 八. 原子的直接观察:

透射电子显微术

TEM

(扫描电子显微术)

(SEM)

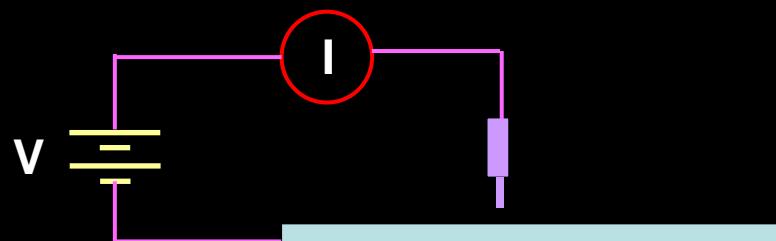
扫描探针显微术

SPM

Direct observation—see atoms directly on surface

**STM**

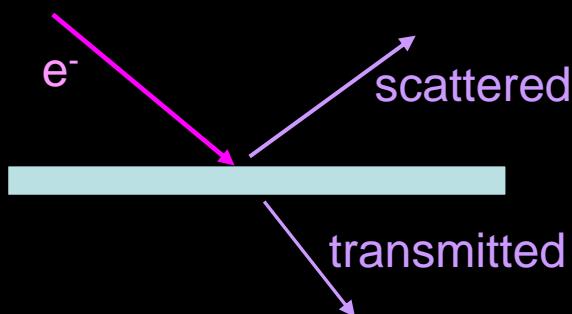
Scanning Tunneling Microscope



*Quantum mechanical  
tunneling*

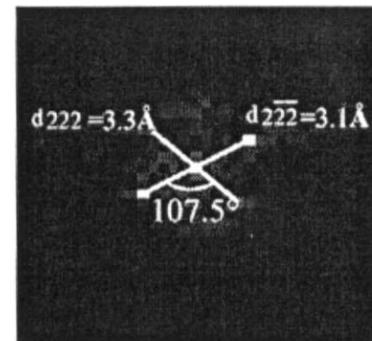
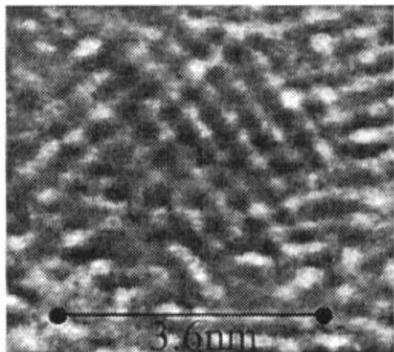
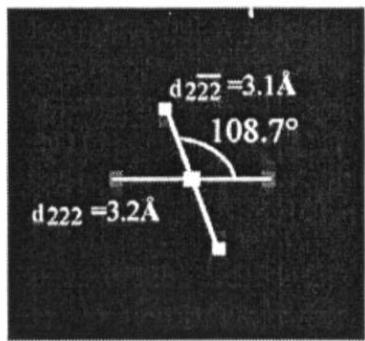
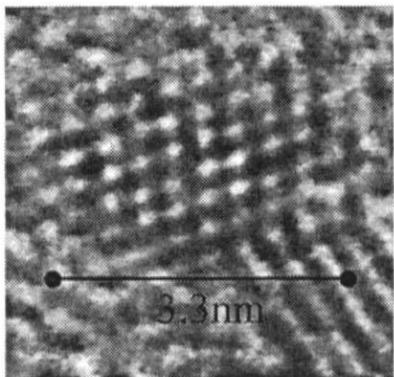
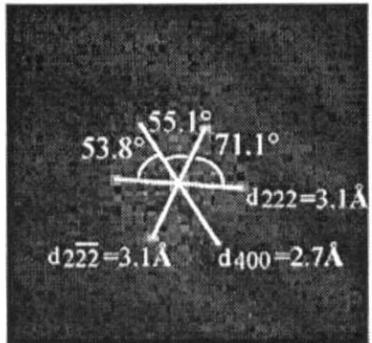
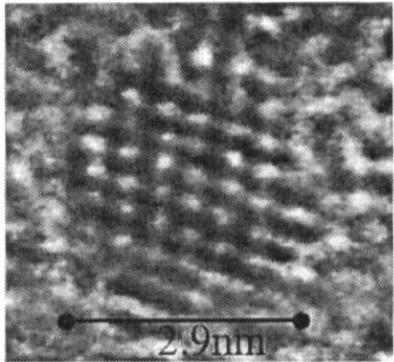
**HREM**

High Resolution Electron Microscope



*Electron wave optics*

# TEM

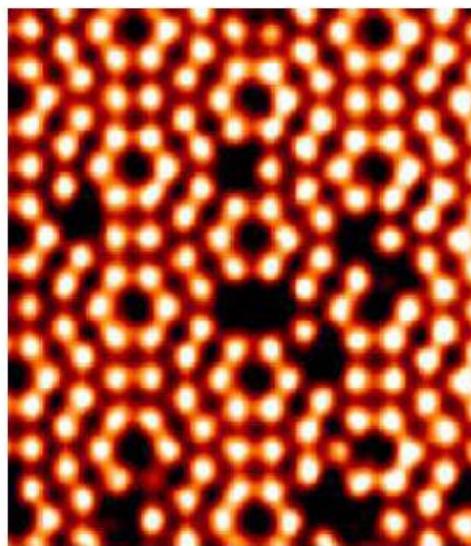


(a)

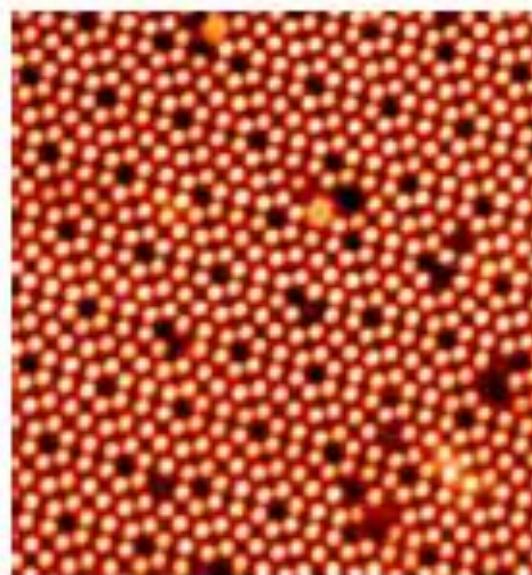
$\text{Eu}_2\text{O}_3$  晶状纳米颗粒  
TEM 照片，从中可以  
清楚地看到原子周期  
排列的特征。

# SPM

AFM (non-contact mode):  
Atomic resolution on Si(111)7x7

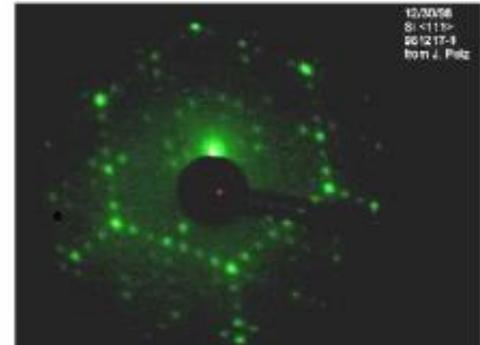


# STM

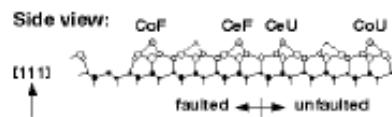
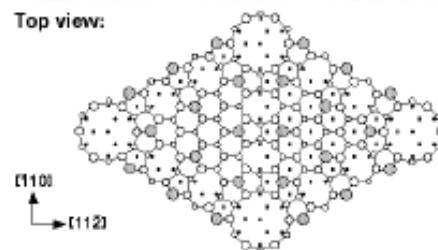


# LEED

Real LEED pattern of Si(111)-7x7



Top view:



习题：

1.15 使用  $\lambda = 1.54 \times 10^{-10} \text{ m}$  的 X 射线照射晶体，

- a. 已知具有 fcc 结构的 Al 多晶 (111) 面的衍射角为 38.4 度，试求出 (111) 面的面间距。
- b. 已知具有 bcc 结构的 Fe 多晶 (110) 面的衍射角为 44.6 度，试求出其晶胞长度。

1.16 试给出金刚石的结构因子，并指出衍射强度消失的晶面  
面指数。

1.17 CsCl 晶体，假定 Cs 原子的原子散射因子是 Cl 原子原子  
散射因子的 3 倍， $f_{\text{Cs}} = 3f_{\text{Cl}}$  试给出其几何结构因子。

表3 元素的晶体结构

[本表所列数据，除特别以单位 K 注明温度的数据之外，其他均为最常见的室温下的数据，更详细的情况，读者可以联机“无机晶体结构数据库（ICSD）”进行检索。]

H <sup>1</sup> 4K hcp 3.75 6.12	Li 78K bcc 3.491	Be hcp 2.27 3.59	Mg hcp 3.21 5.21	Na 5K bcc 4.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br <sub>2</sub> )	Kr 4K fcc 5.64
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn(α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I <sub>2</sub> )	Xe 4K fcc 6.13				
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77	Hf hcp 3.19	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At	Rn				
Fr —	Ra —	Ac fcc 5.31	Ce fcc 5.16	Pr hex. 3.67	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55					
见Kittel书P15			Th fcc 5.08	Pa tetr. 3.92	U complex	Np complex	Pu complex	Am hex. 3.64 ABAC	Cm —	Bk —	Cf —	Esr —	Fm —	Md —	No —	Lr —					