

# Crystal structure determination

利用可见光是否能够直接观察到晶体的结构？

**可见光波长： 400~700 nm**

**X射线波长： 0.1 ~ 10 nm**

**晶体中原子间距 ~ 0.1nm**

衍射学 { X射线衍射  
          电子衍射  
          中子衍射

显微学 { 电子显微镜  
          扫描隧道显微镜

# History of X-Ray Diffraction

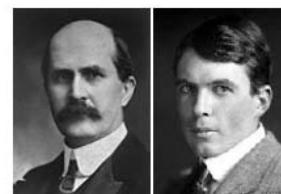
1895 X-rays discovered by Roentgen



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



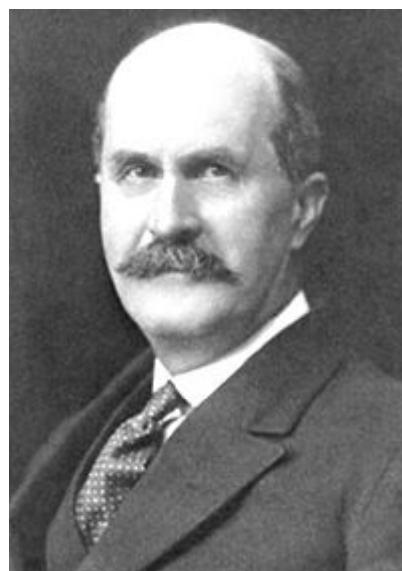
The first X-ray

1953 DNA structure solved by Watson, Crick, Wilkins

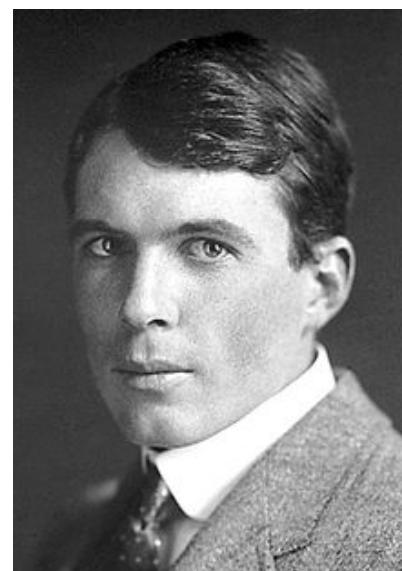


Now Diffraction improved by computer technology;  
methods used to determine atomic structures and  
in medical applications

**Max Theodor Felix von Laue (9 October 1879 – 24 April 1960)**  
was a German physicist who won the Nobel Prize in Physics in 1914 for his discovery of the diffraction of X-rays by crystals.



William H Bragg



William L Bragg

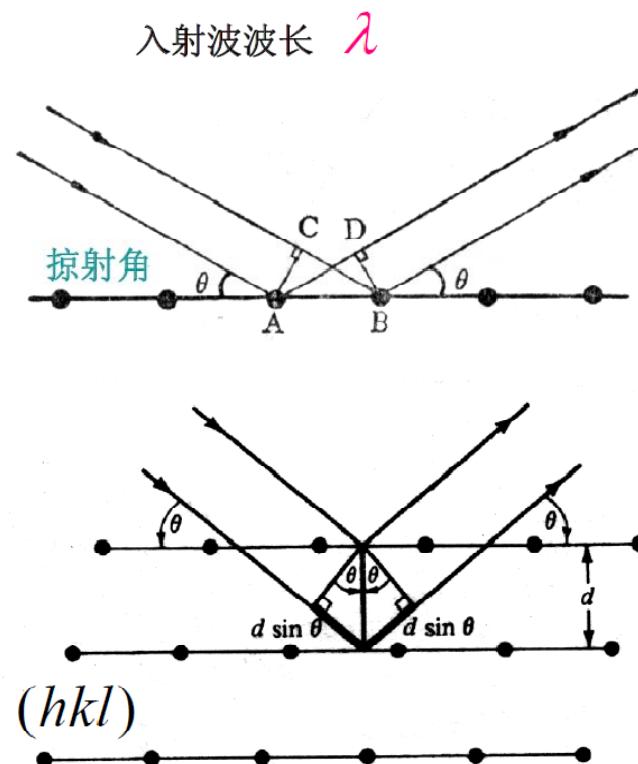
建立了X射线衍射的理论解释，测量了NaCl的晶格常数，并校准了X射线波长。发展了X射线衍射学。在小布拉格的领导下，英国在生物体结构领域的研究后来产生了12位诺贝尔奖获得者。

## 晶体衍射的几何理论 - 发生衍射的条件

Bragg's law 布拉格定律

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。

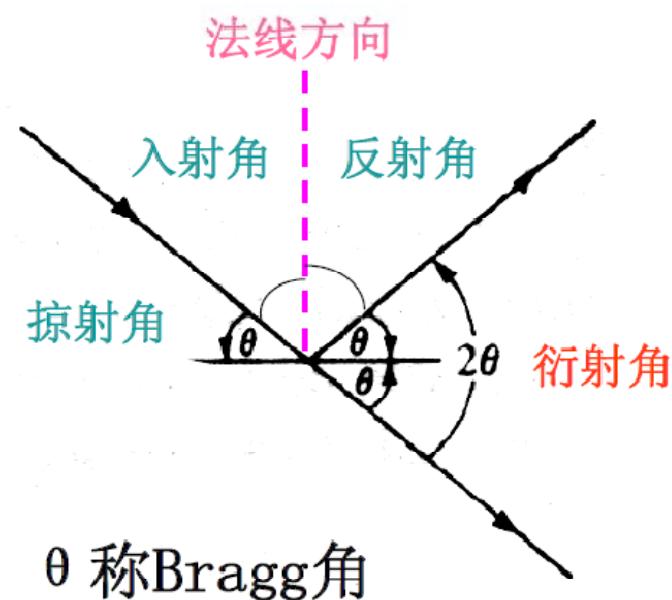
★产生衍射的极限条件是： $\lambda \leq 2d$  或： $d \geq \frac{\lambda}{2}$

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

★为了应用中的方便，经常把公式中的  $n$  隐含在  $d$  中得到简化的Bragg 方程：

$$2d_{HKL} \sin \theta = \lambda$$

此时，我们把  $(hkl)$  晶面的  $n$  级反射看成是与  $(hkl)$  晶面平行、面间距为  $d_{HKL} = \frac{d_{hkl}}{n}$  晶面的1级反射。



## 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 1.3 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：

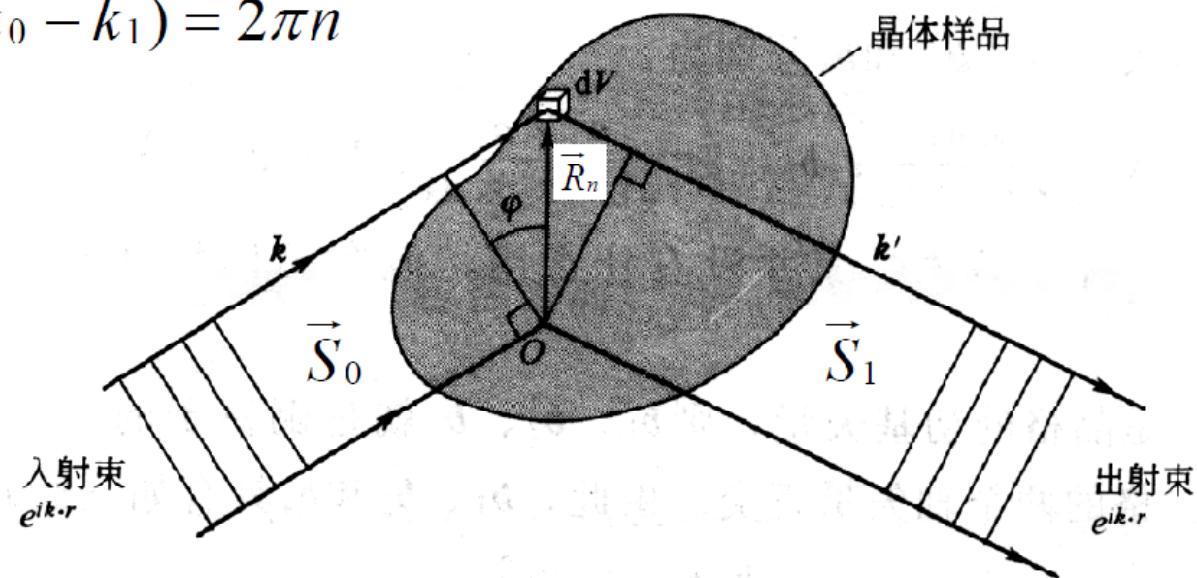
$$\sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{4H^2 + HK + K^2}{3a^2} + \frac{L^2}{c^2} \right)$$

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： $\vec{R}_n \cdot \vec{S}_0 - \vec{R}_n \cdot \vec{S}_1 = n\lambda$        $\vec{S}$  为方向矢量

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

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



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

$$\vec G \bullet \vec R = 2\pi m$$

$$\overrightarrow{k}_0-\overrightarrow{k}_1=\overrightarrow{G}_{HKL}$$

**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 (p24)说：“一组倒格矢  $\mathbf{G}$  决定了可能存在的 X 射线反射”。**Laue**方程还有其它表示方式：

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

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

$\because k_0 = k_1$  弹性散射，波长数值不变，即波矢绝对值不变。

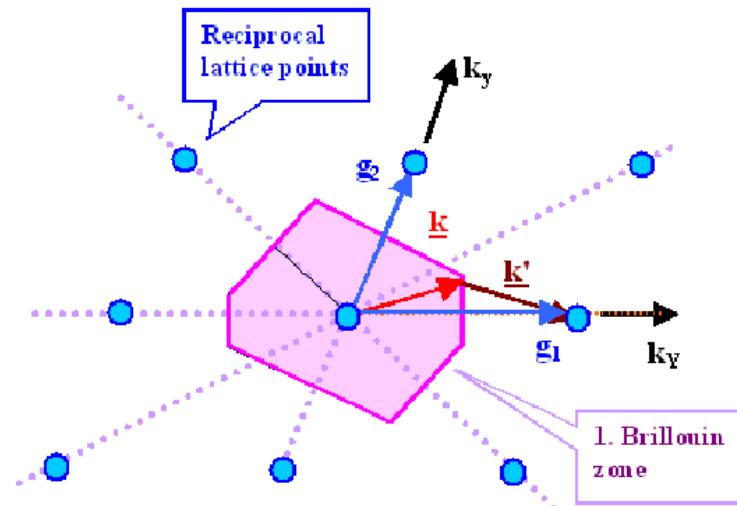
$$\therefore G_h^2 - 2\vec{G}_h \cdot \vec{k}_0 = 0$$

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：

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

$$\therefore k_0 = k_1 = k$$

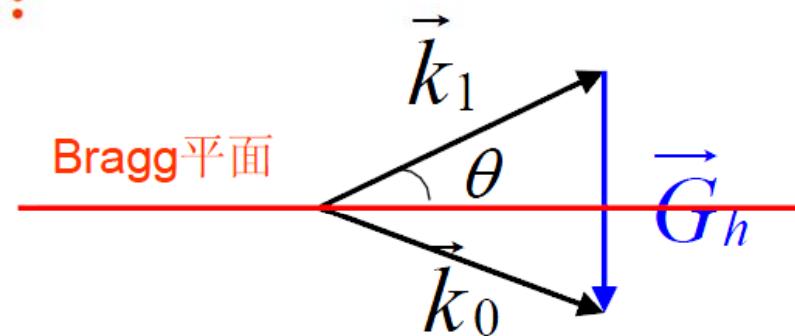
$$\therefore G_h = 2k \sin \theta$$

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,  $k = 2\pi/\lambda$

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

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



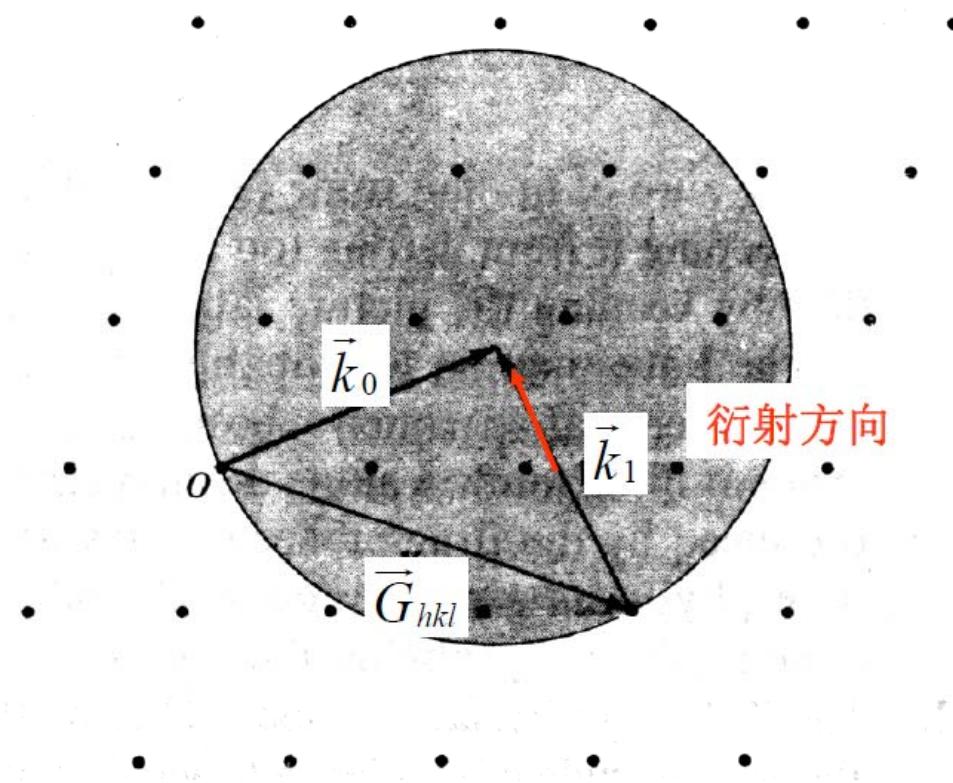
$$\rightarrow n\lambda = 2d \sin \theta \quad \text{Bragg 定律}$$

# Ewald sphere

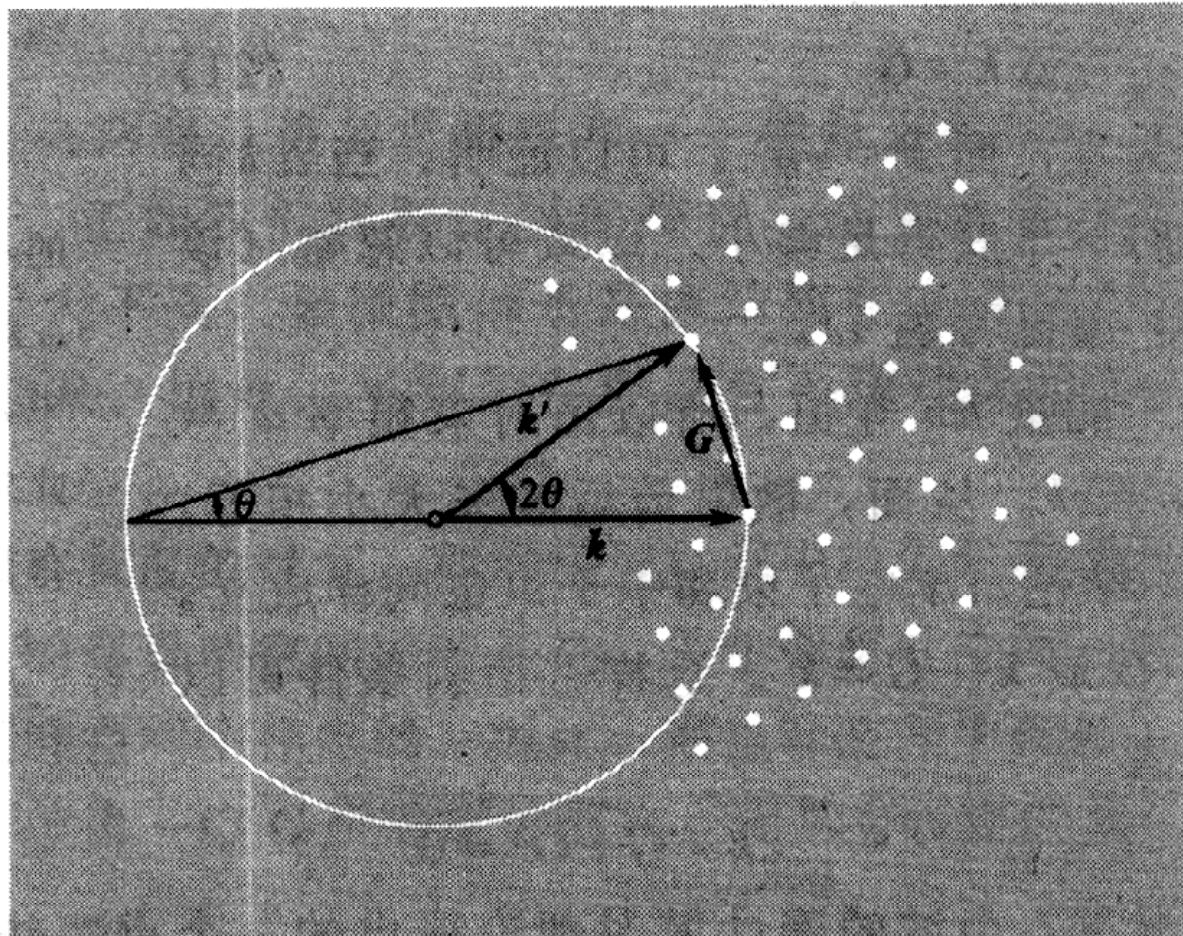
以入射波矢端点为圆心，以  $k$  为半径做反射球，凡落在球面上的倒格点都会满足 **Laue** 方程，因为原点必然落在反射球上，所以从原点到落在反射球上的其它格点恰好是一个倒格矢，故  $\vec{k}_1$  方向发生衍射。

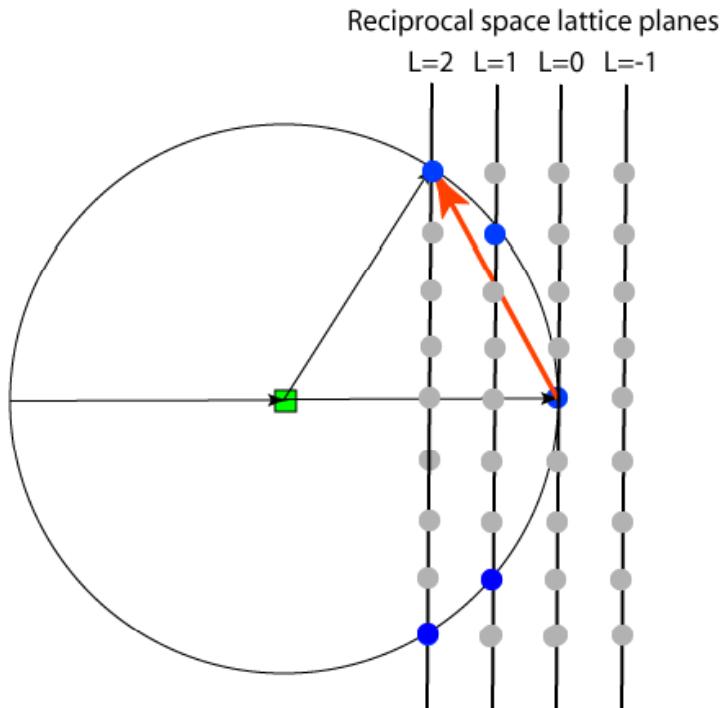
$$k_0 = k_1$$

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



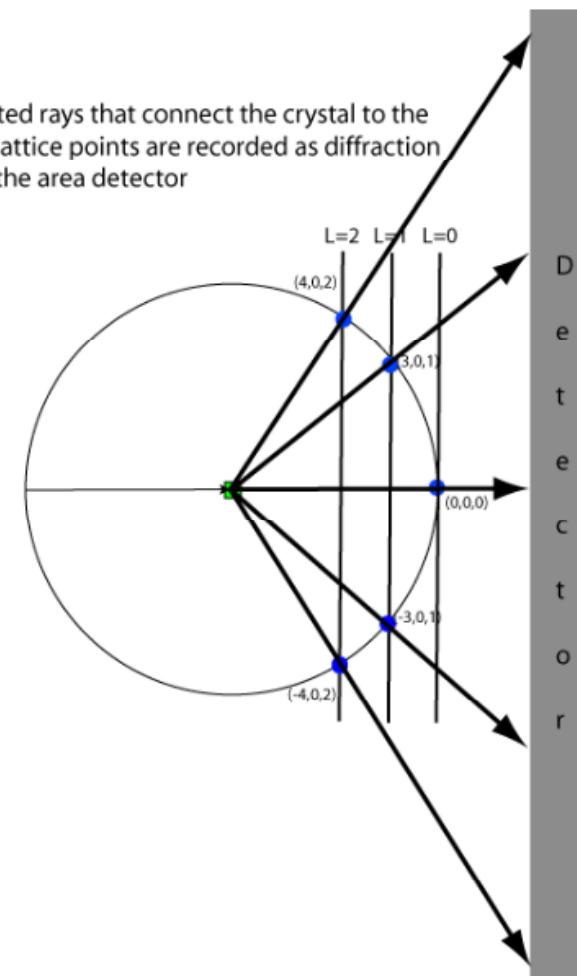
Kittel p26 另一种形式的作图法。





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



除了考虑衍射图样的几何分布外，还需要考虑衍射图样的强度

{ 原子散射因子 **Atomic form factor**  
几何结构因子 **geometrical scattering factor**

原子散射因子：单个原子对入射波的散射本领

几何结构因子：晶胞中所有原子对于入射波的散射本领

# 原子散射因子

## Atomic form factor

原子散射因子: 原子对入射波的散射本领, the scattering amplitude of a wave by an isolated atom, 具体定义为一个原子的相干散射振幅和一个假设位于原子核处的电子相干散射振幅之比

$$\vec{K} = \vec{k} - \vec{k}_0$$

$$f(\vec{K}) = \int \rho(\vec{r}) e^{i\vec{K} \cdot \vec{r}} d^3 r$$

$$\vec{k} = \vec{k}_0$$

$$f(0) = \int \rho(\vec{r}) d^3 r = Z$$

# 几何结构因子

## Geometric scattering factor

$$\vec{K} = \vec{k} - \vec{k}_0$$

$$F = \sum_{j=1}^n f_j \exp(i\vec{K} \bullet \vec{R}_j)$$

$$\vec{R}_j = x_j \vec{a}_1 + y_j \vec{a}_2 + z_j \vec{a}_3$$

若

$$\vec{K} = \vec{G}_{HKL}$$

$$\vec{K} \bullet \vec{R}_j = 2\pi(Hx_j + Ky_j + Lz_j)$$

$$F_{HKL} = \sum_{i=1}^n f_i [\cos 2\pi(Hx_i + Ky_i + Lz_i) + i \sin 2\pi(Hx_i + Ky_i + Lz_i)]$$

因为衍射测量的是衍射强度，与此相关的是： $|F_{HKL}|^2$

$$|F_{HKL}| = \left\{ \left[ \sum_{i=1}^n f_i \cos 2\pi(Hx_i + Ky_i + Lz_i) \right]^2 + \left[ \sum_{i=1}^n f_i \sin 2\pi(Hx_i + Ky_i + Lz_i) \right]^2 \right\}^{\frac{1}{2}}$$

$$F_{HKL}^2 = \left[ \sum_{i=1}^n f_j \cos 2\pi(Hx_j + Ky_j + Lz_j) \right]^2 + \left[ \sum_{i=1}^n f_j \sin 2\pi(Hx_j + Ky_j + Lz_j) \right]^2$$

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

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

$$F_{HKL}^2 = f_a^2 [1 + \cos \pi(H + K + L)]^2$$

显然，  $H+K+L=$  偶数时  $F_{HKL}^2 = 4f_a^2$

$H+K+L=$  奇数时  $F_{HKL}^2 = 0$

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。

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

$$F_{HKL}^2 = f_a^2 [\cos 2\pi(0) + \cos \pi(H+K) + \cos \pi(H+L) + \cos \pi(L+K)]^2 \\ + f_a^2 [\sin 2\pi(0) + \sin \pi(H+K) + \sin \pi(H+L) + \sin \pi(L+K)]^2$$

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

$$F_{HKL}^2 = 16f_a^2$$

$H, K, L$  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：

$$F_{HKL}^2 = f_a^2 [1 - 1 + 1 - 1] = 0$$

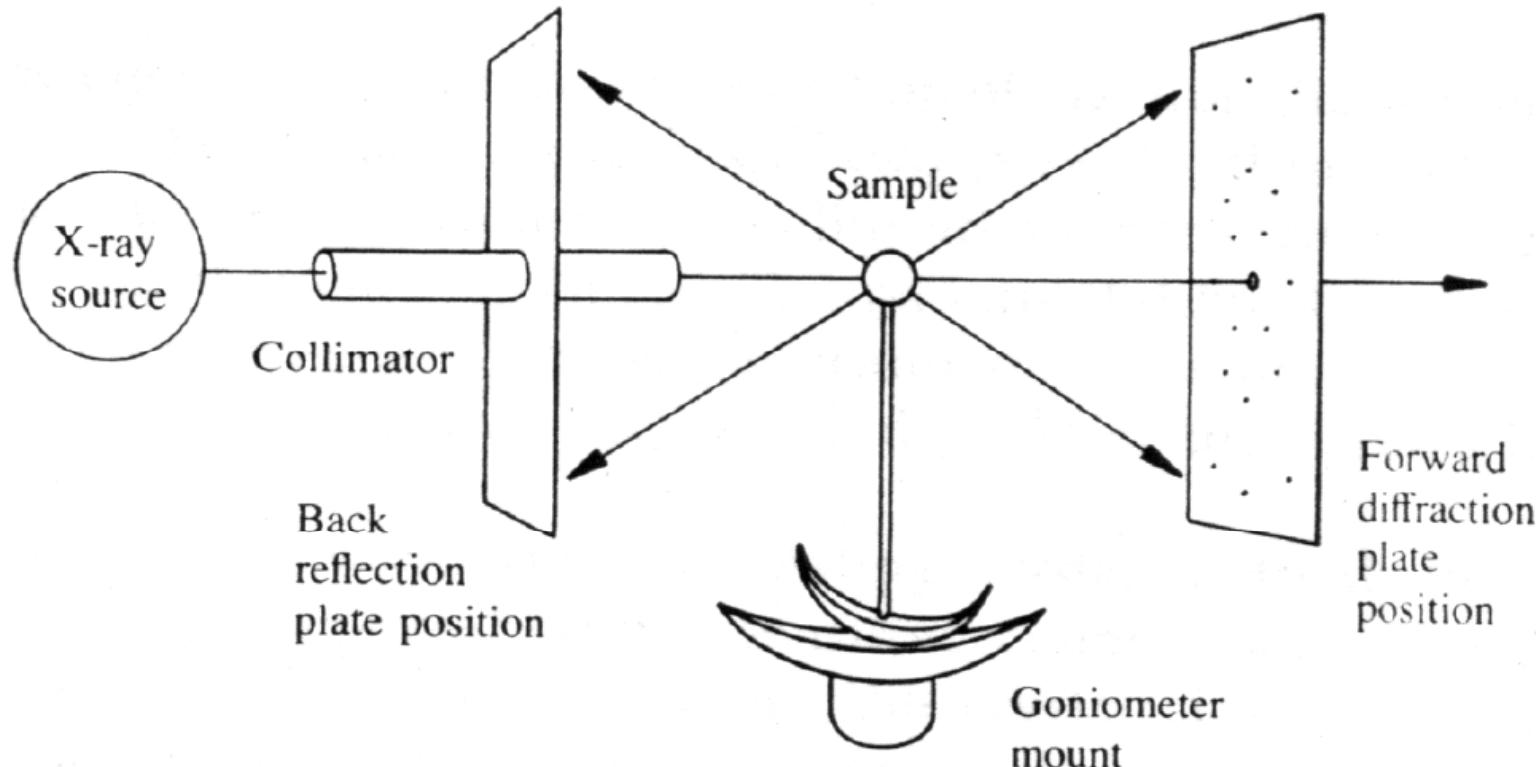
只有当  $H, K, L$  为全奇或全偶的晶面才会显现衍射峰。  
 $(100), (110), (210), (211), (300)$  等晶面衍射峰消失。

## 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	✓	✓	✓

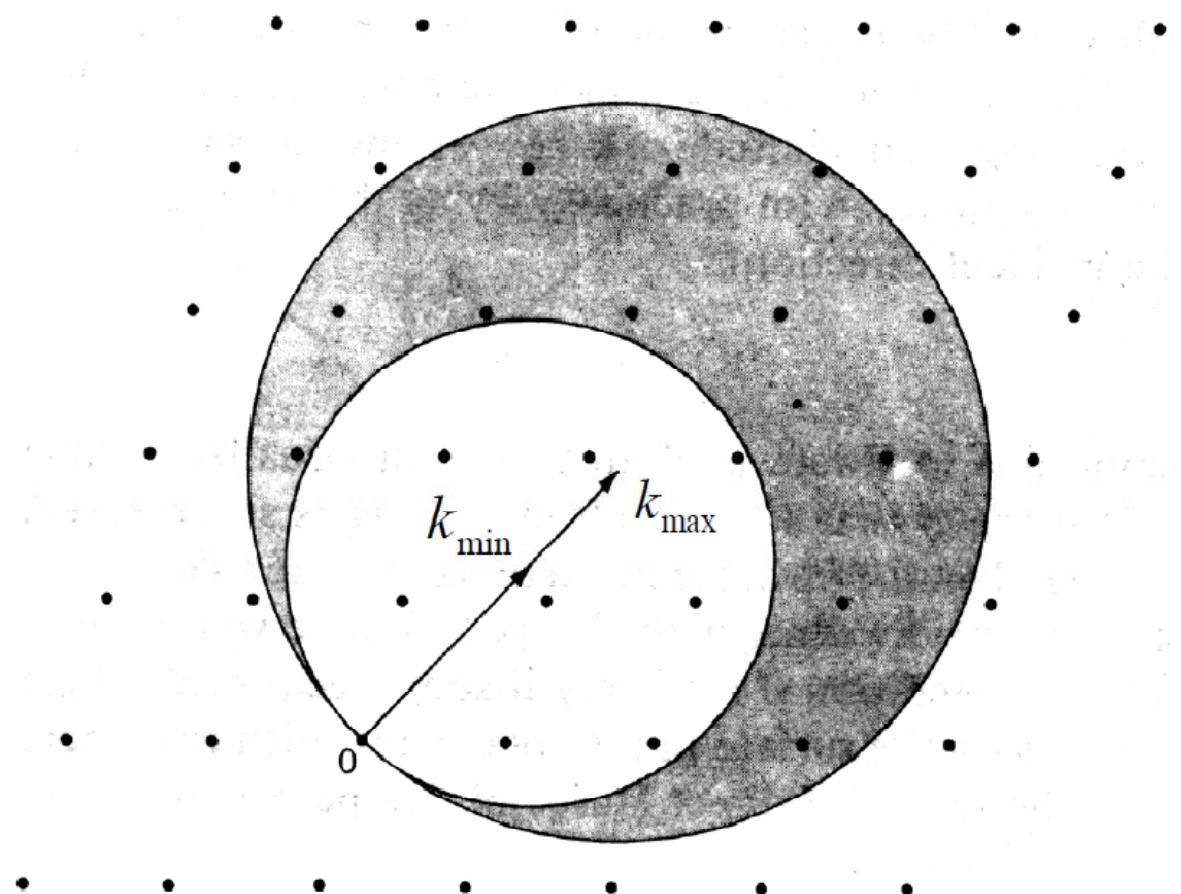
# X射线实验方法

**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。

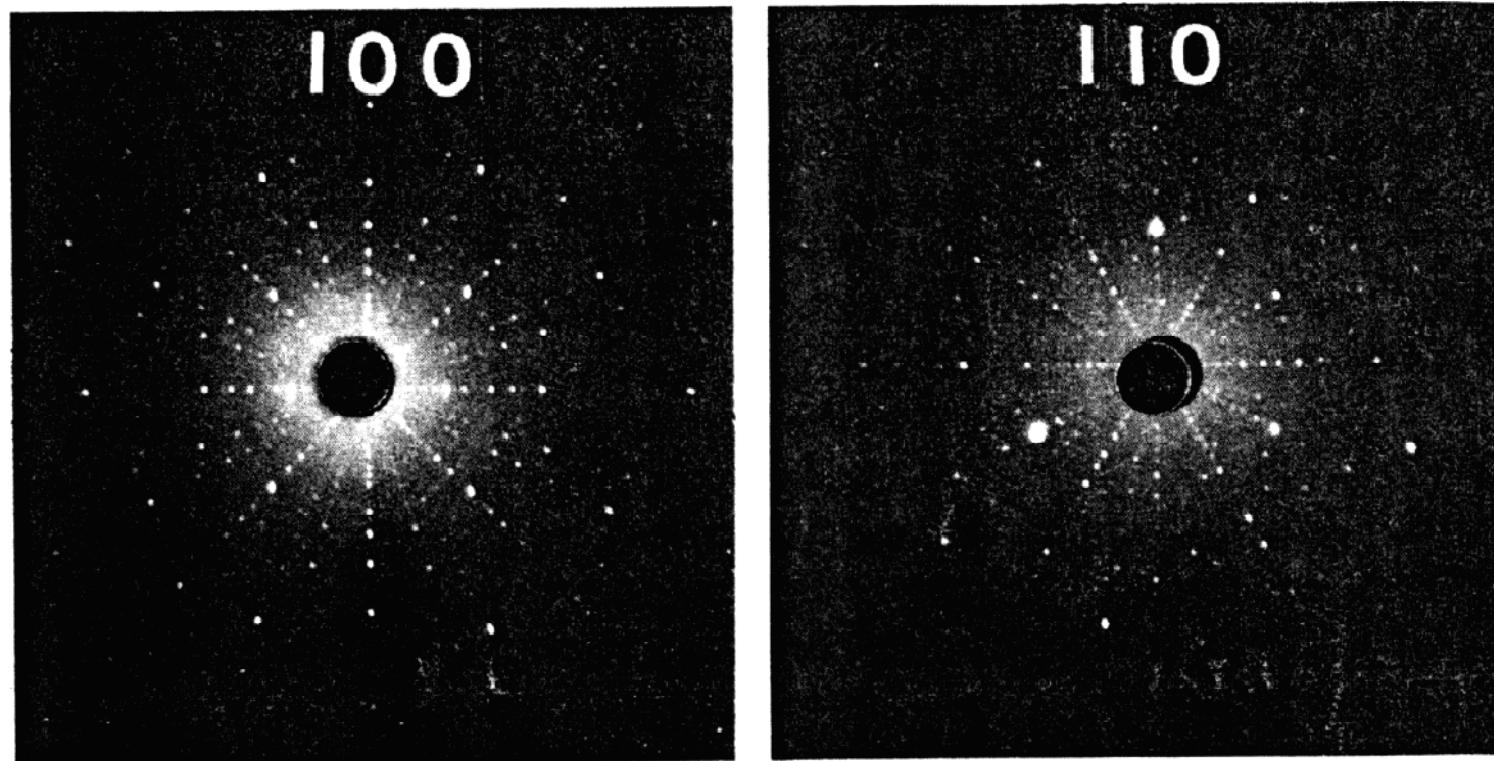


缺陷：无法获得具体的晶格常数

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。

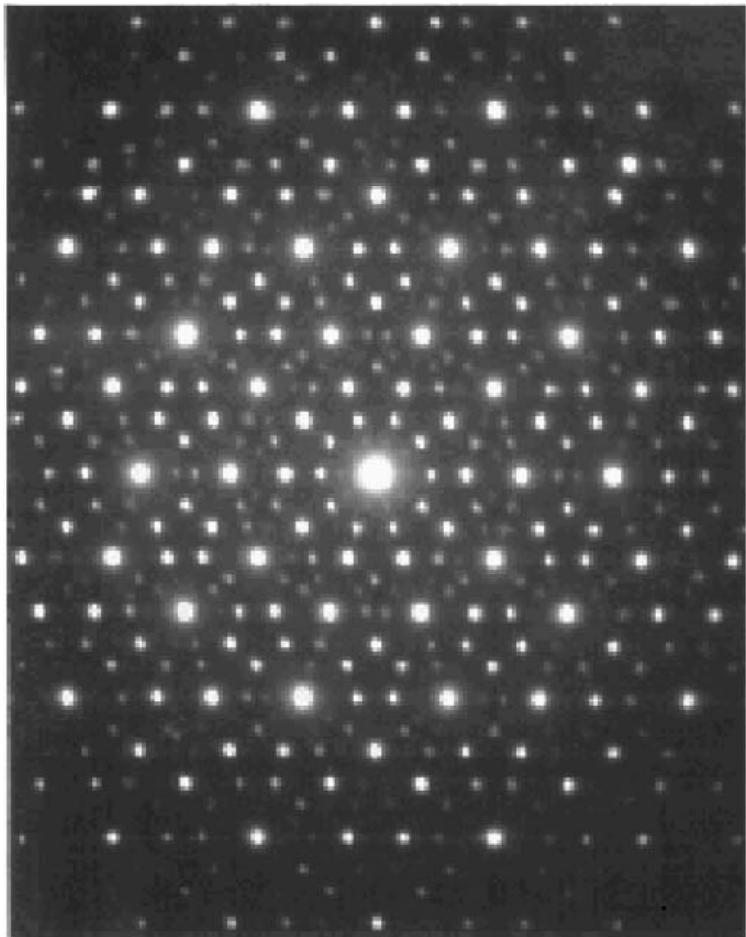


## $\text{FeS}_2$ 单晶 Laue X 射线衍射图

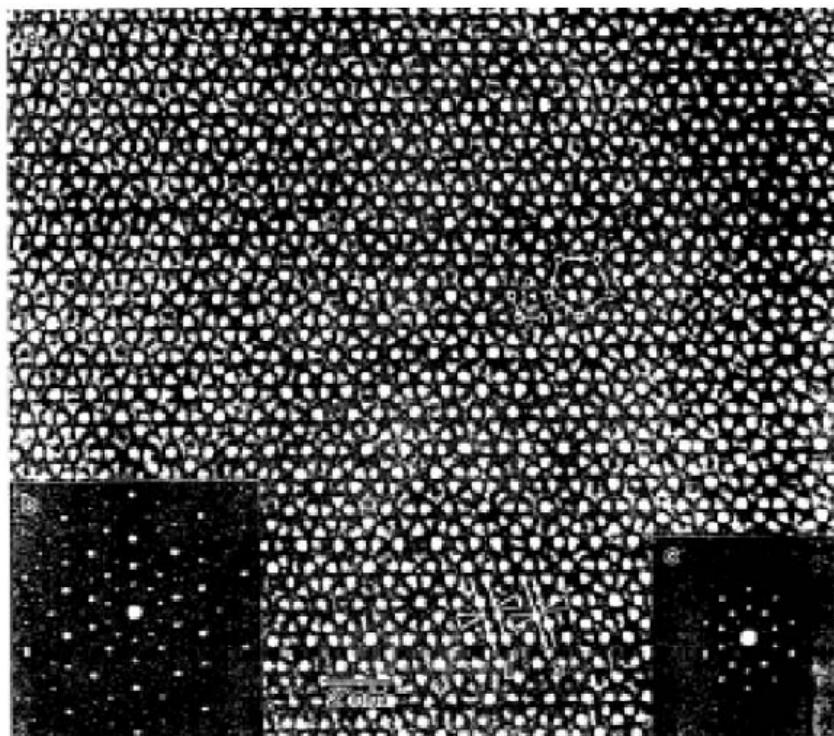


$\text{FeS}_2$  有两种晶型：立方晶系的黄铁矿和斜方晶系的白铁矿。

X—衍射图具有立方对称性，因而是点群为 $T_h$ 的黄铁矿  $T_h^6(P_{a3})$   
见 Blakemore p52



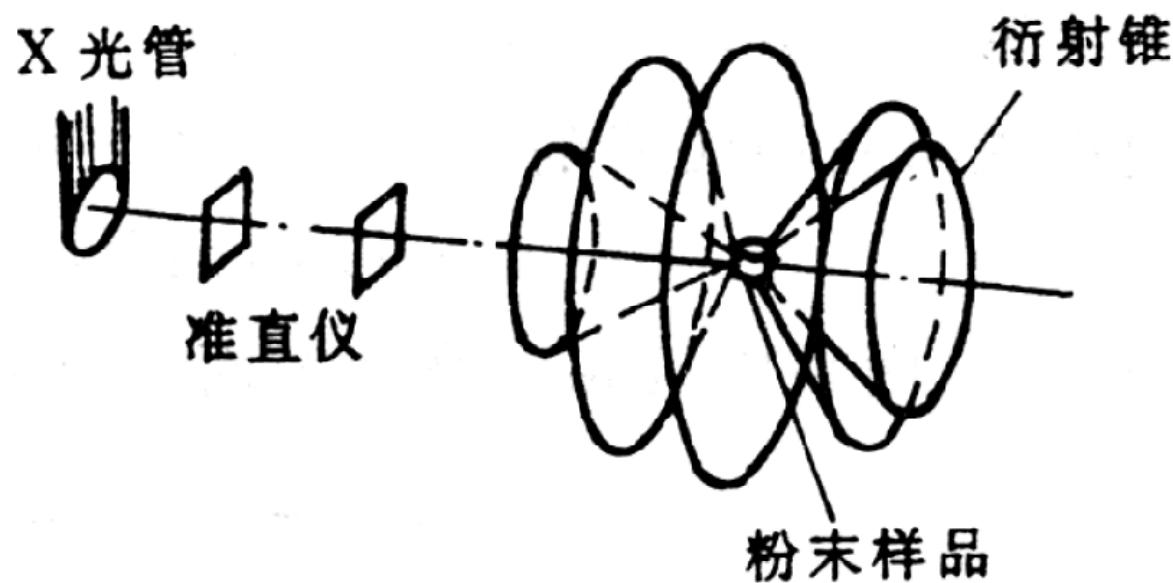
准晶的电子衍射照片  
显示出5次对称性。

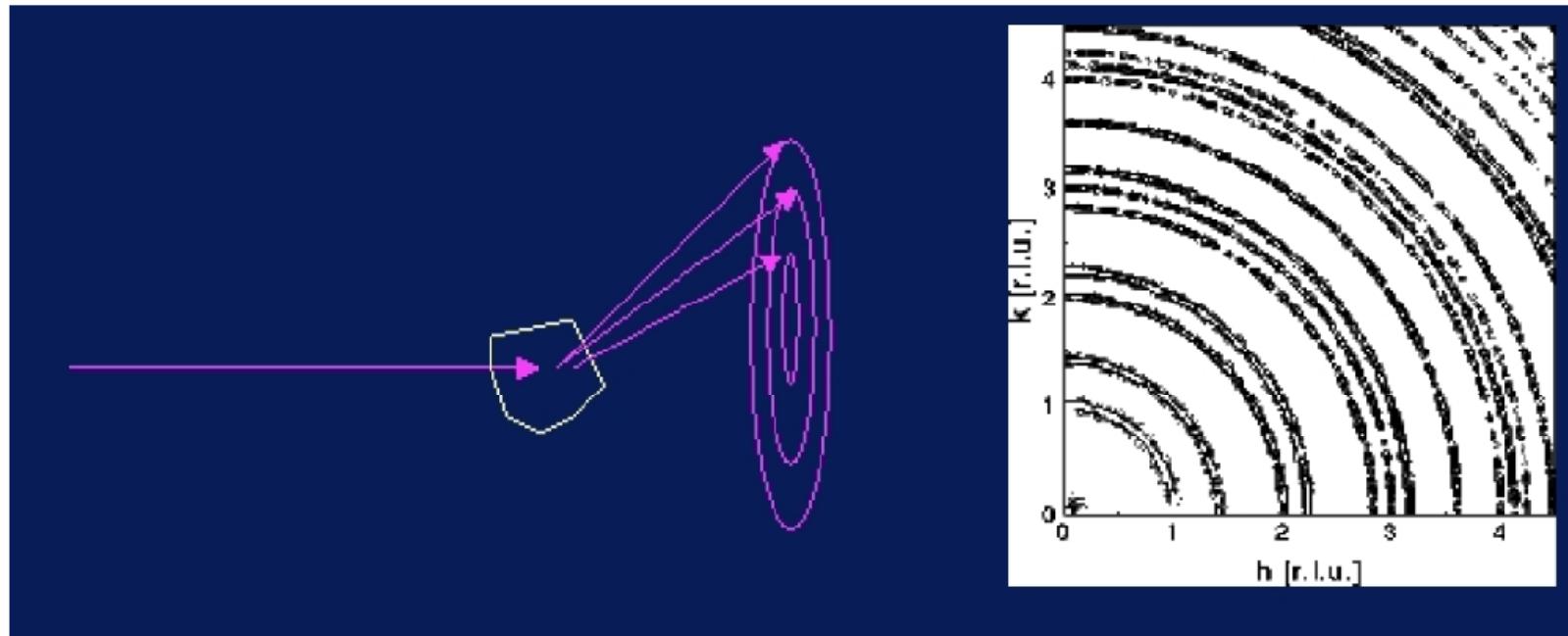


Al-Mn-Si准晶的高  
分辨照片。

## 2. 粉末衍射方法：Debye-Scherrer 方法

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。

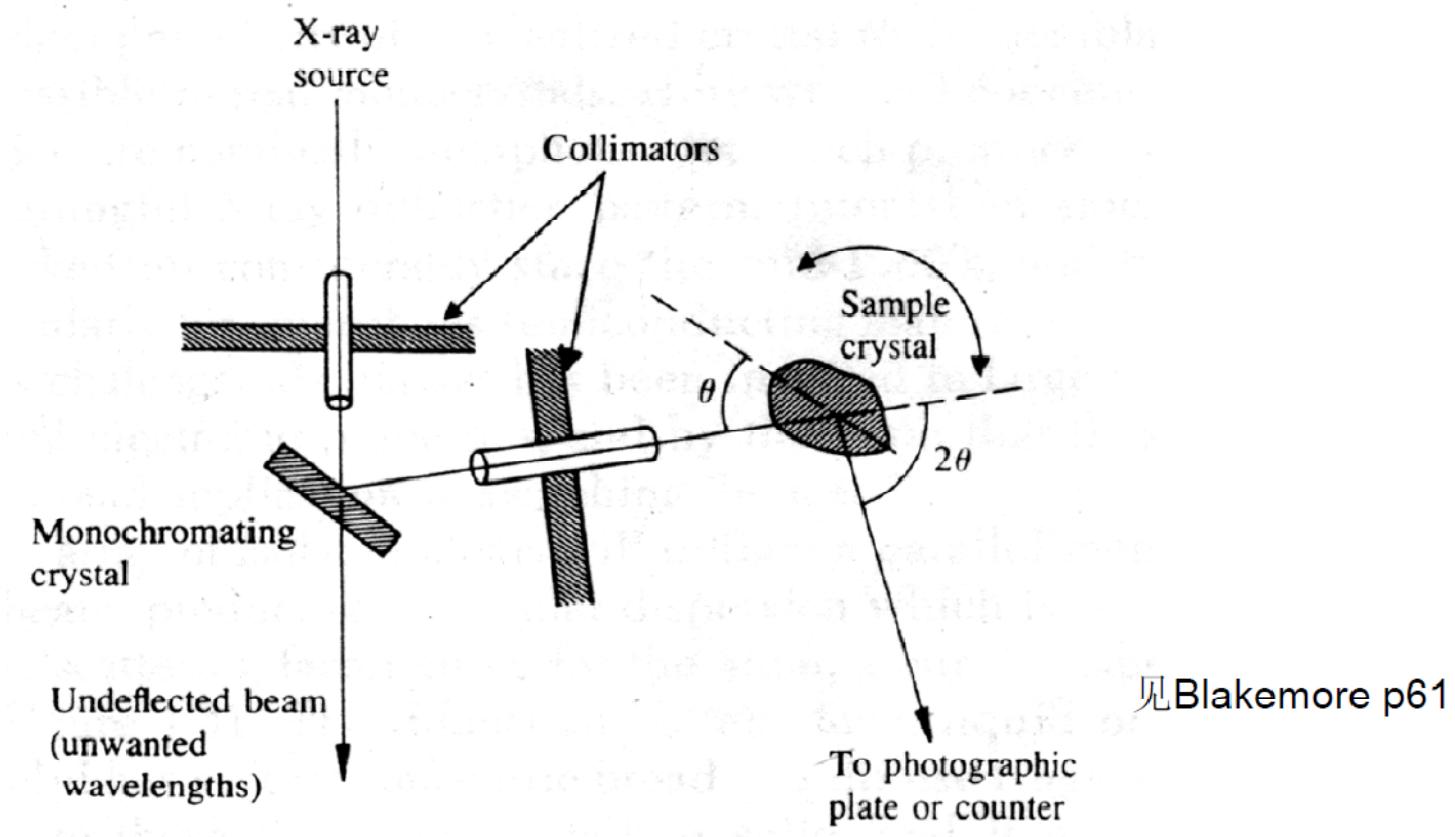




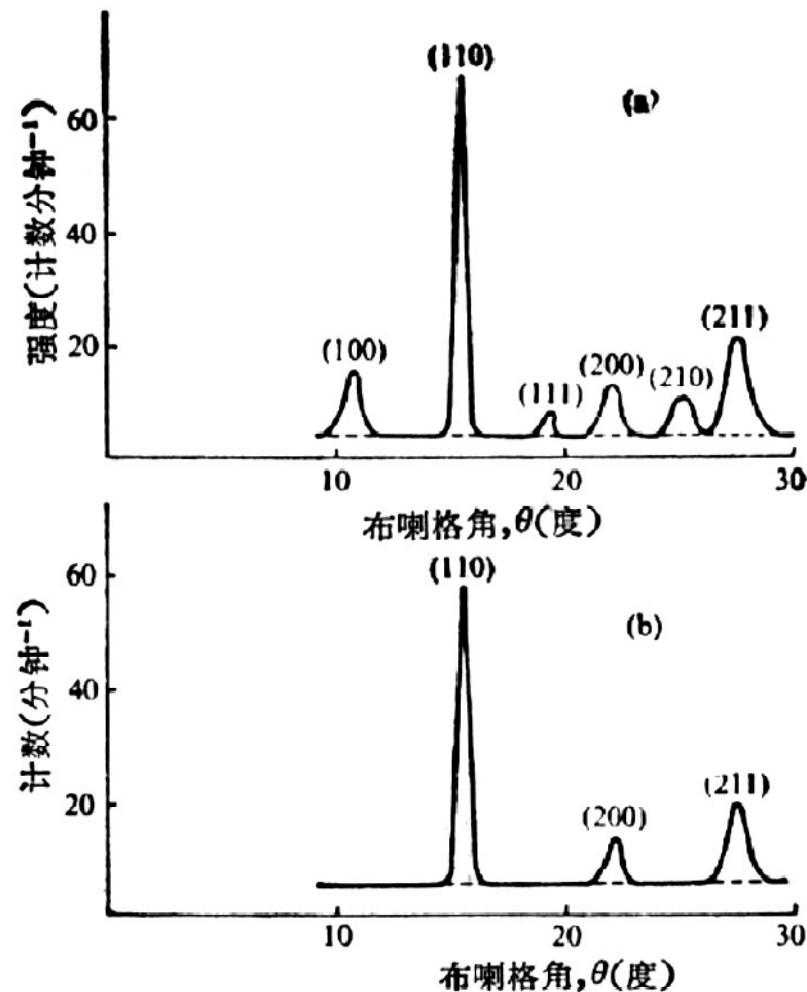
## 粉末（多晶材料）X-Ray衍射的例子

衍射环出现条件：满足Bragg 衍射条件以及几何结构因子不为0

**3. 旋转晶体法：**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。



见 Blakemore p61



FeCo 有序 (a) 和无序 (b) 样品的中子衍射图.

1023K下缓慢冷却  
FeCo 有序分布  
是简立方结构

1023K下淬火后  
FeCo 无序分布  
是体心立方结构

见Bacon书P347

见Bacon: 《中子衍射》 P110图  
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

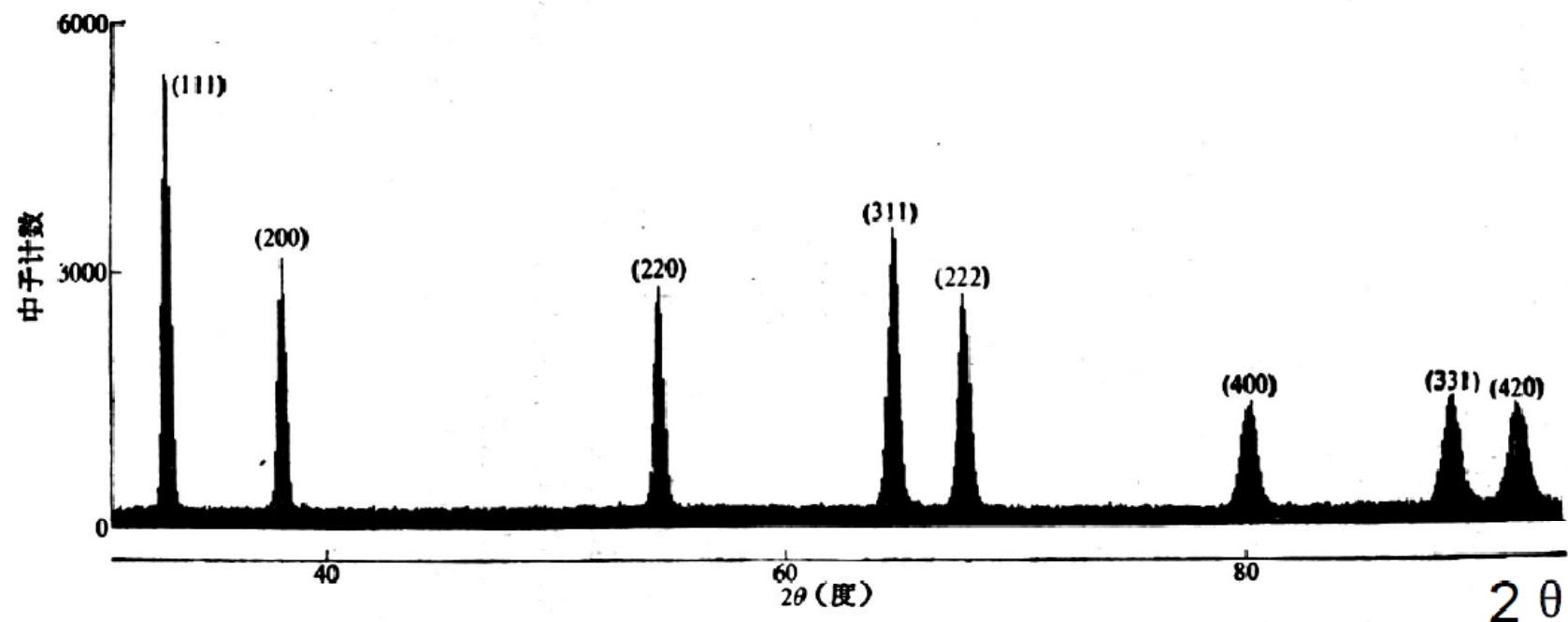


图 58 部分镍粉末衍射图. 采用镥单色器, 由 A.E.R.E. Harwell 的 PANDA 衍射计记录,  
相应波长 1.14 埃,  $2\theta$  的每  $0.1^\circ$  为计数间隔.

## Solving the Structure of DNA: History

- Rosalind Franklin- physical chemist and x-ray crystallographer who first crystallized and photographed B-DNA
- 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

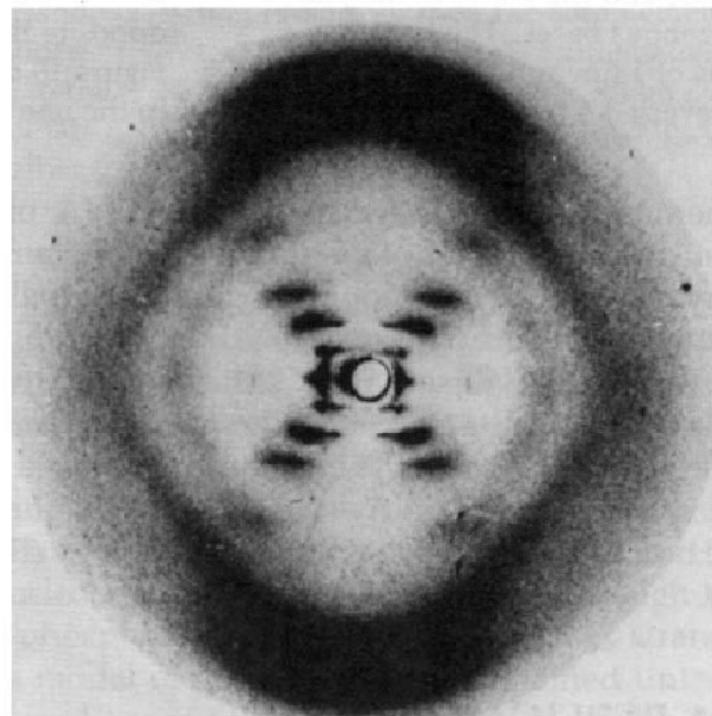
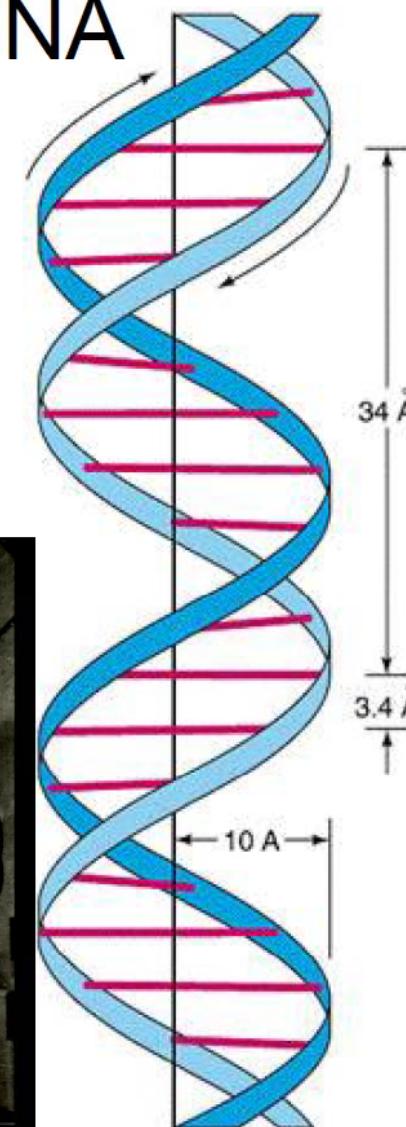


Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

[www.pbs.org/wgbh/nova/photo51](http://www.pbs.org/wgbh/nova/photo51)

# 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

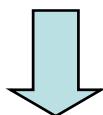


X 射线衍射

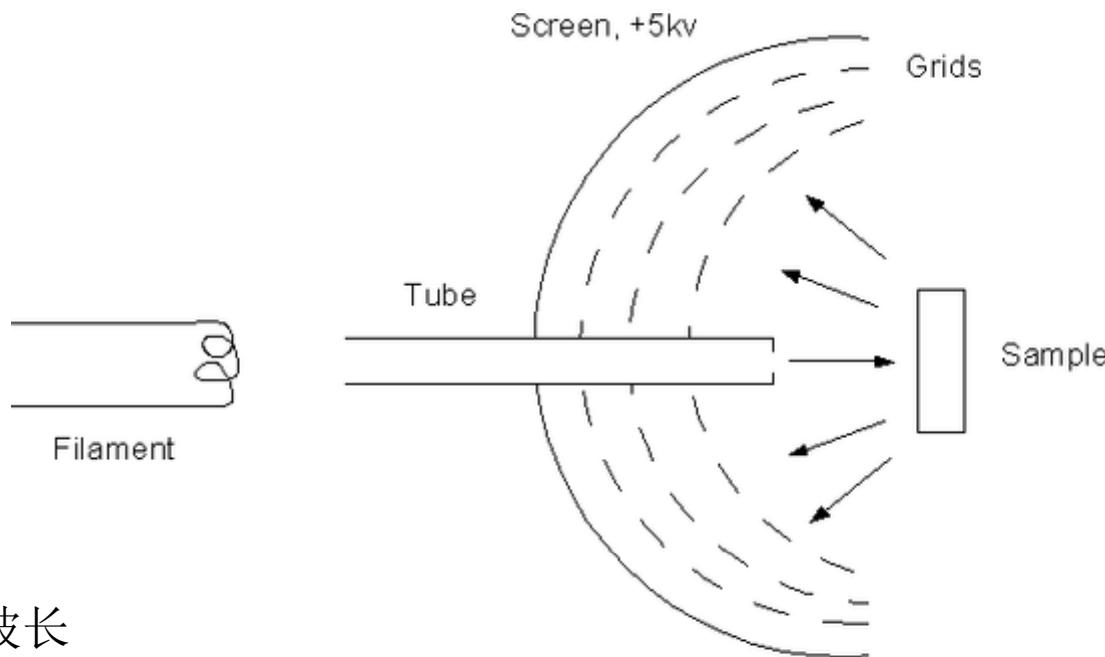
电子衍射

中子衍射

Louis Victor de Broglie 一个基本粒子在本质上是一种波  
 $E=hv$  (1924)



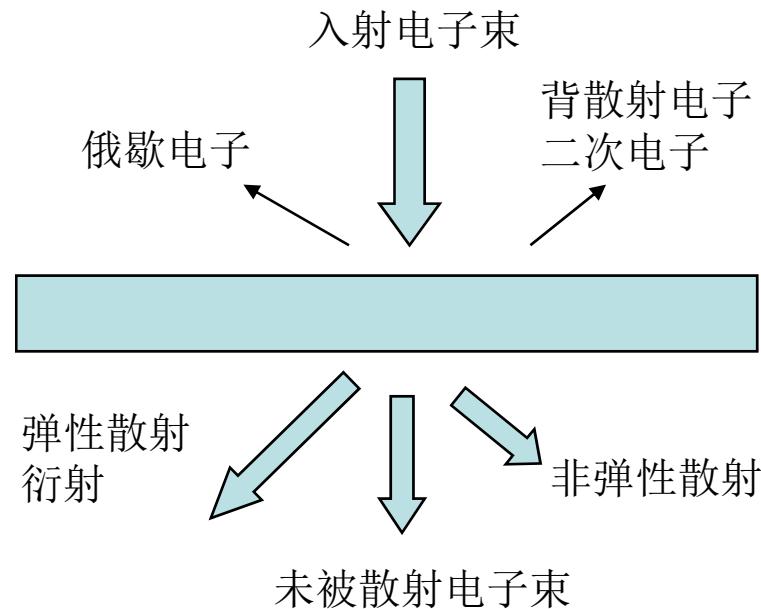
Clinton Joseph Davisson low energy electron diffraction (LEED) 低能电子衍射(1924)  
LEED衍射斑与Bragg预言的X射线衍射峰位置吻合 (1927)



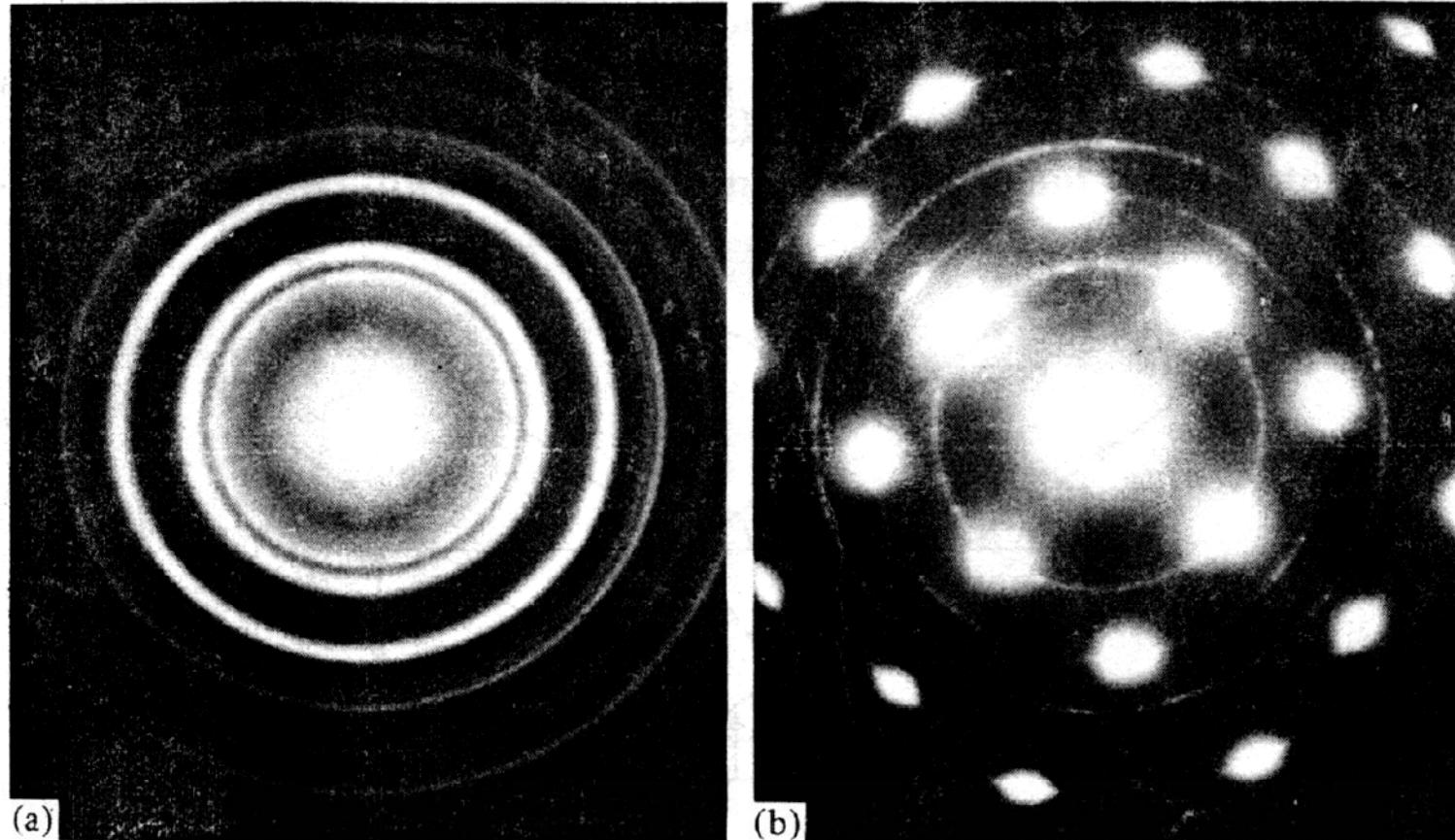
电子的波长

$$\lambda = \frac{h}{p} = \frac{2\pi}{\sqrt{2m_e E / \hbar^2}} = \frac{12.25 \text{ \AA}}{\sqrt{E / eV}}$$
$$E = 20 \sim 60000 \text{ eV}$$
$$\lambda = 2.7 \sim 0.05 \text{ \AA}$$

G.P. Thomson 使用了一种新的实验方法，得到的衍射图样同样与X射线衍射吻合



Max Knoll and Ruska 根据这种方法制造了第一台透射电镜(transmission electron microscope (TEM)) (1931)，并已经实现工业化生产  
并在此基础上制造出了第一台扫描电镜(STEM) (scanning transmission electron microscope (STEM)) 分辨率0.2nm左右

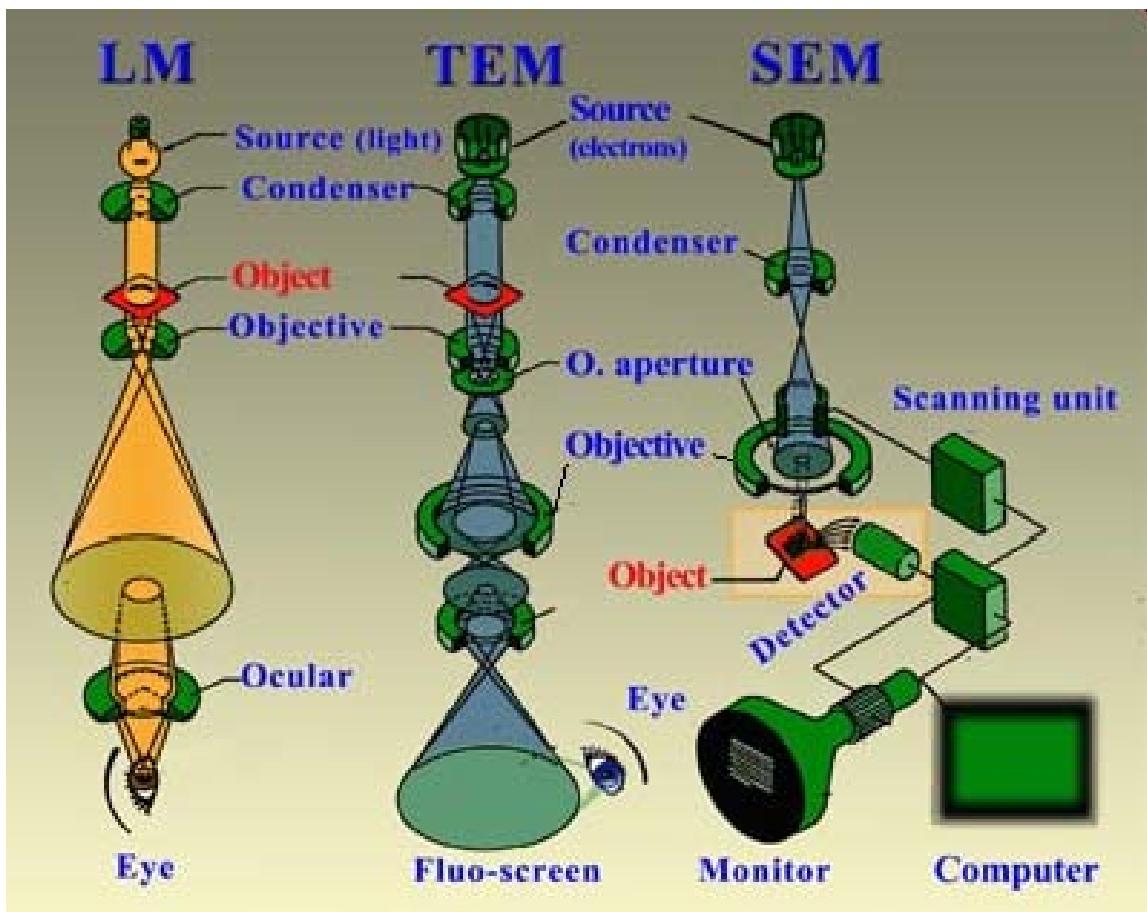


见Blakemore p53

薄膜的电子衍射图：

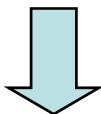
多晶衍射

单晶衍射。

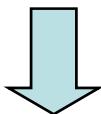




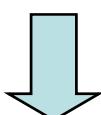
Louis Victor de Broglie 一个基本粒子在本质上是一种波  
 $E=hv$  (1924)



James Chadwick 发现基本粒子中子 (1932)



Clifford G. Shull 开始用中子探测凝聚态物质中H原子的位置 (1946)



Bertram N. Brockhouse 用中子探测固体中原子振动 (声子) 、自旋波 (spin wave) (1950)

中子衍射的机制：中子与核子之间的强相互作用，这与X射线衍射或电子衍射中的电磁相互作用是不同的。

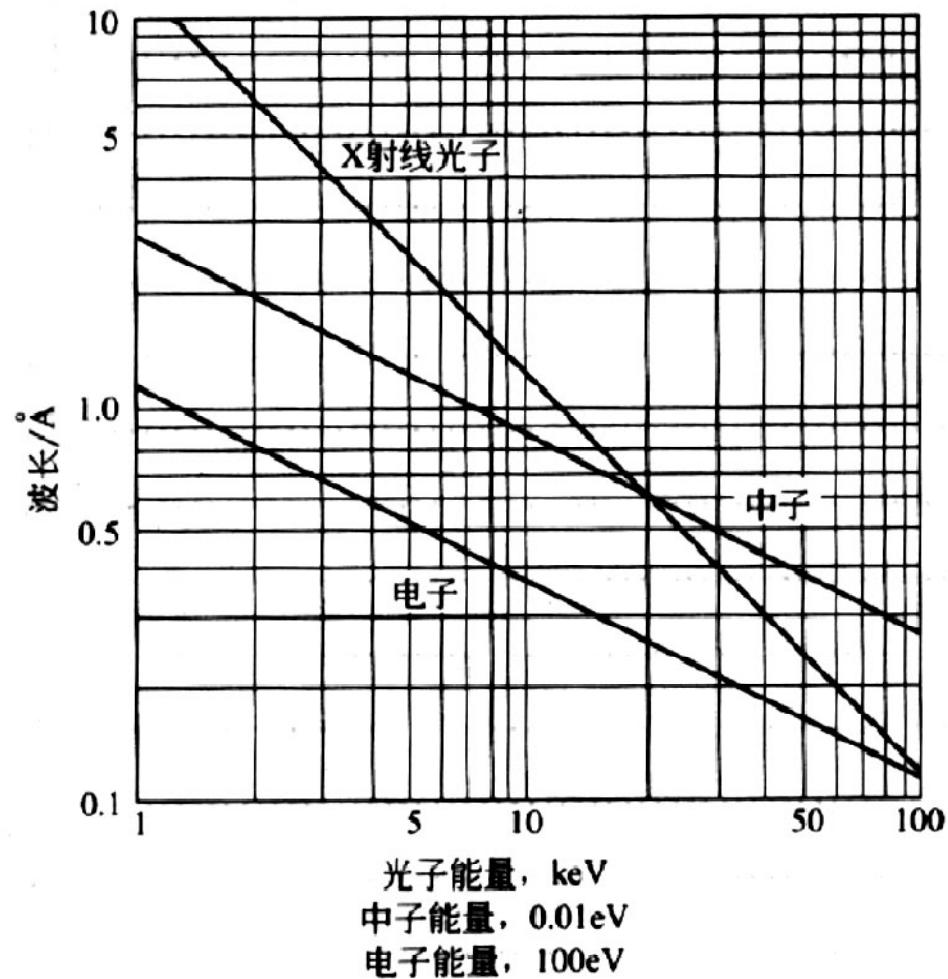


图 1 光子、中子和电子的波长与其能量的关系曲线。

$$\lambda = h/p$$

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

见Kittel书P20

衍射法	优势	劣势
X射线	仪器设备最简单；很广的应用范围	不适用于分析非常薄的薄膜和探测固体中的准粒子
电子	正、倒空间图像同时获得，适用于研究表面和薄膜物理	很难探测很轻的元素；不适合探测固体中某些类型的准粒子或集体运动方式
中子	很适合探测轻元素；可以分辨同位素；可以探测各种准粒子	很大的仪器设备（核反应堆）； 中子数的探测非常困难； 很低的亮度，很长的实验时间

**Neutron scattering** { Elastic scattering – neutron diffraction  
Inelastic scattering

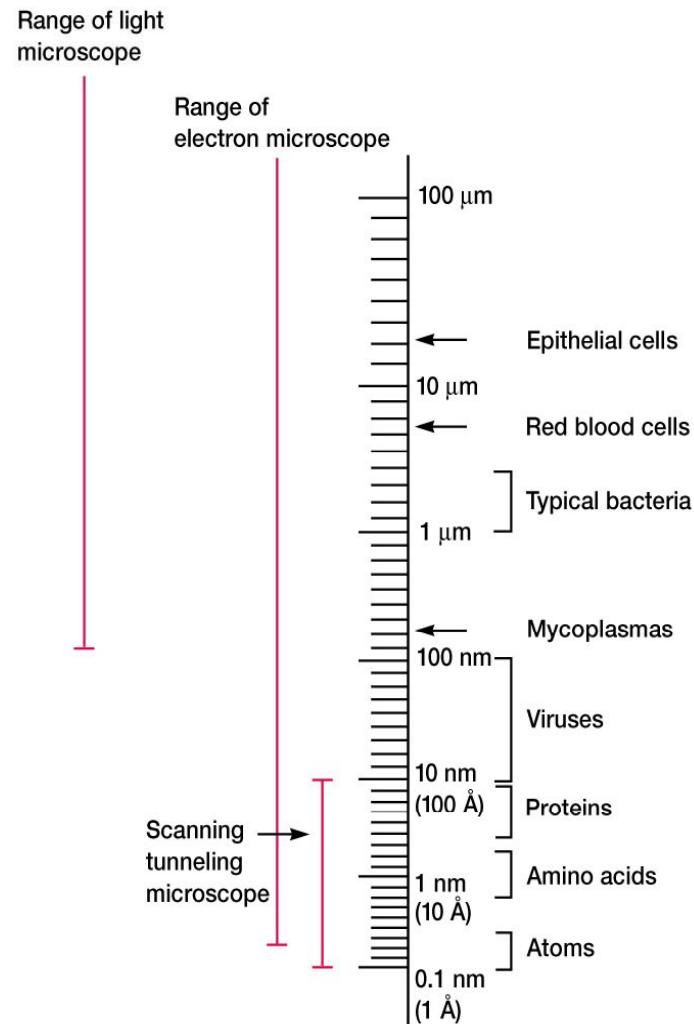
X射线更容易与原子核周围的电子相互作用,而种子更容易与原子核相互作用.

中子非弹性散射可以测量晶格振动, 室温热平衡下中子能量~25meV, 与中子能量匹配

由于中子具有磁矩, 因此可以测量磁性材料中磁结构, 以及spin wave等。

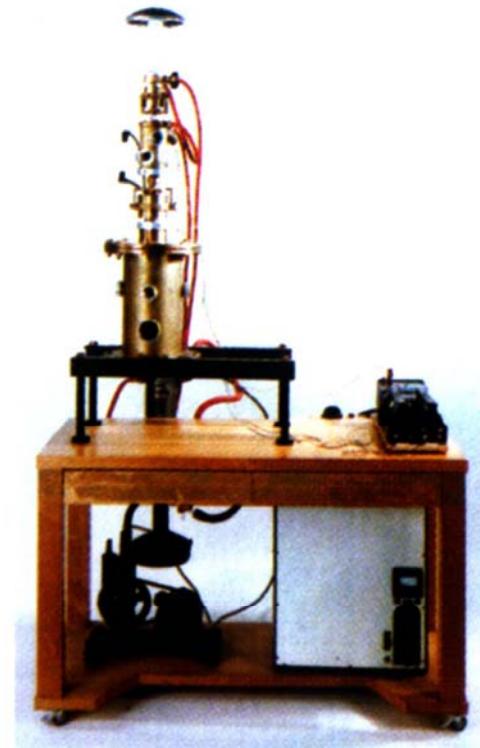
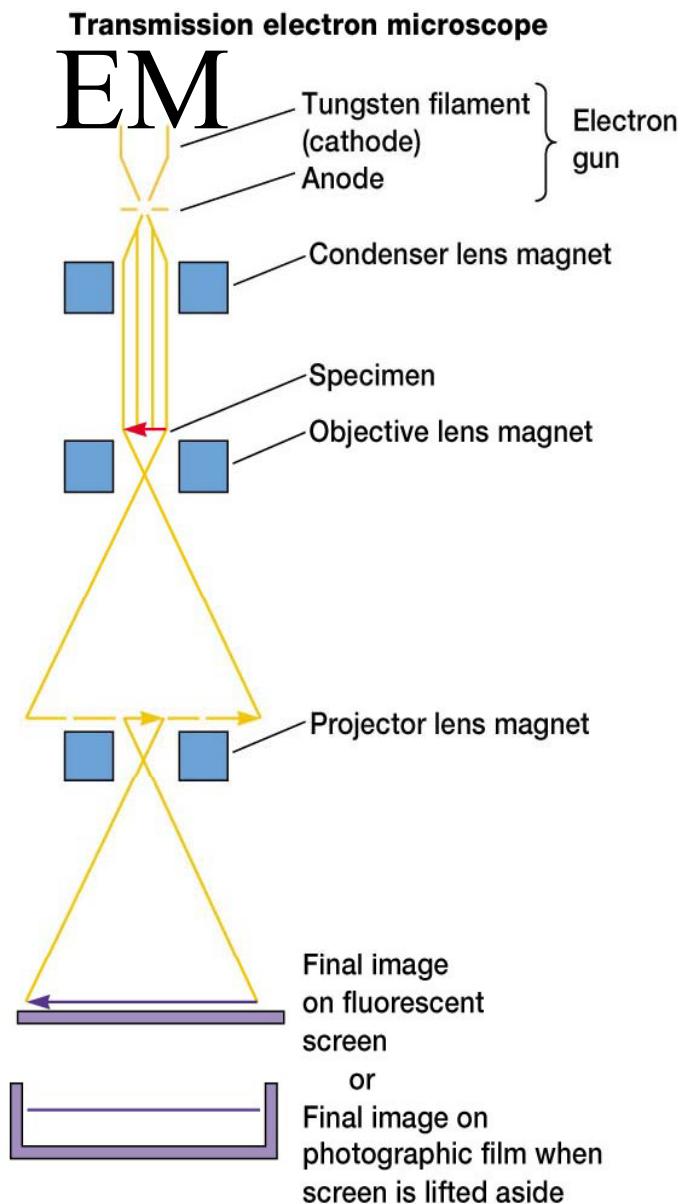
# Electron Microscopy

- **beams of electrons are used to produce images**
- **wavelength of electron beam is much shorter than light, resulting in much higher resolution**



# The Transmission Electron Microscope (TEM 透射电镜)

- electrons scatter when they pass through thin sections of a specimen
- transmitted electrons (those that do not scatter) are used to produce image
- denser regions in specimen, scatter more electrons and appear darker



**Ernst Ruska**

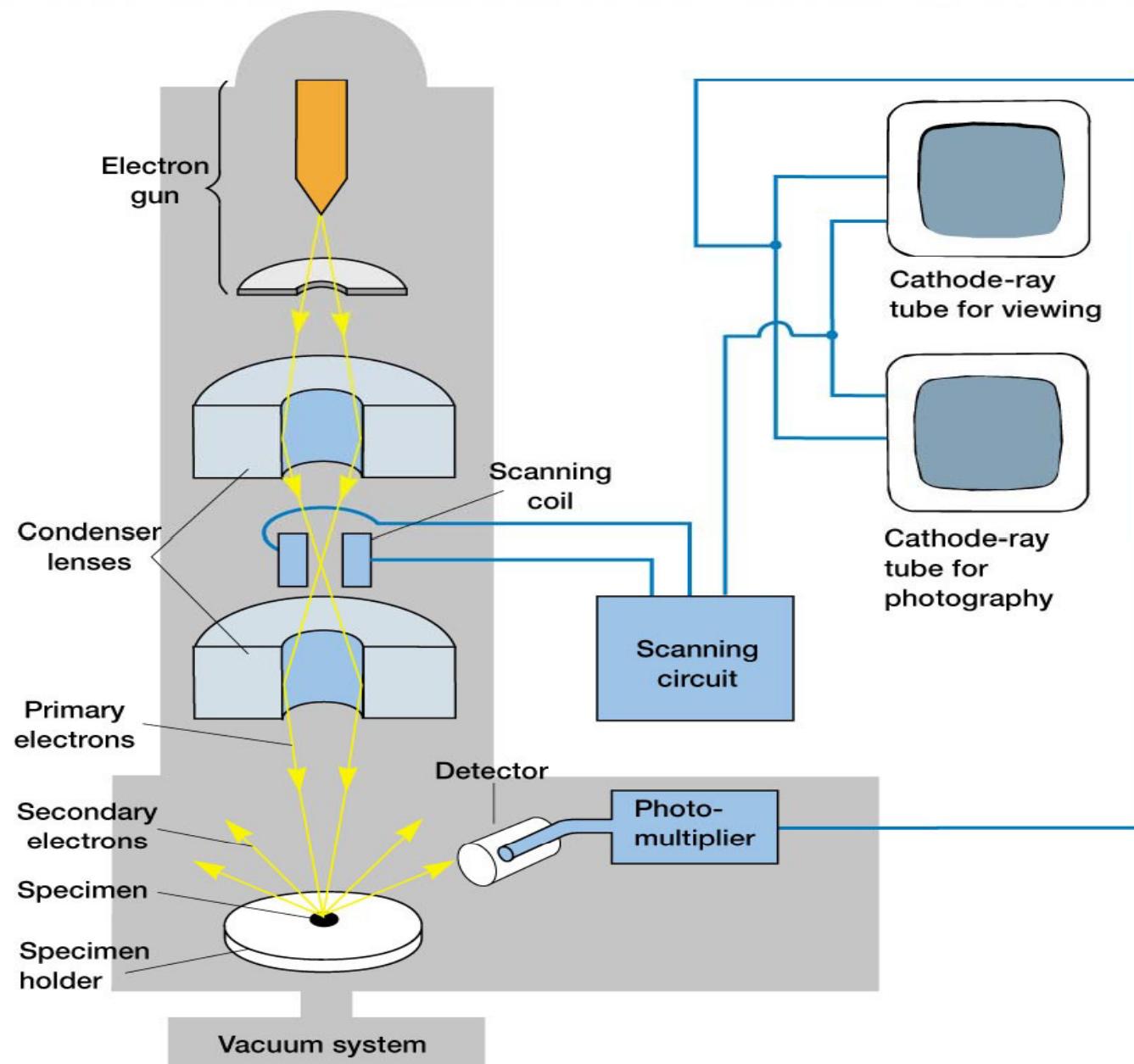
分辨率：约1纳米  
**1931年**

A black and white transmission electron micrograph showing several spherical and filamentous viral particles. In the upper left, a cluster of spherical particles is visible. A prominent, roughly circular filamentous particle occupies the lower right portion of the frame, characterized by its internal structural details and a distinct outer envelope membrane. The background consists of a granular, cellular ultrastructure.

Ebola

# The Scanning Electron Microscope

- uses electrons reflected from the surface of a specimen to create image
- produces a 3-dimensional image of specimen's surface features



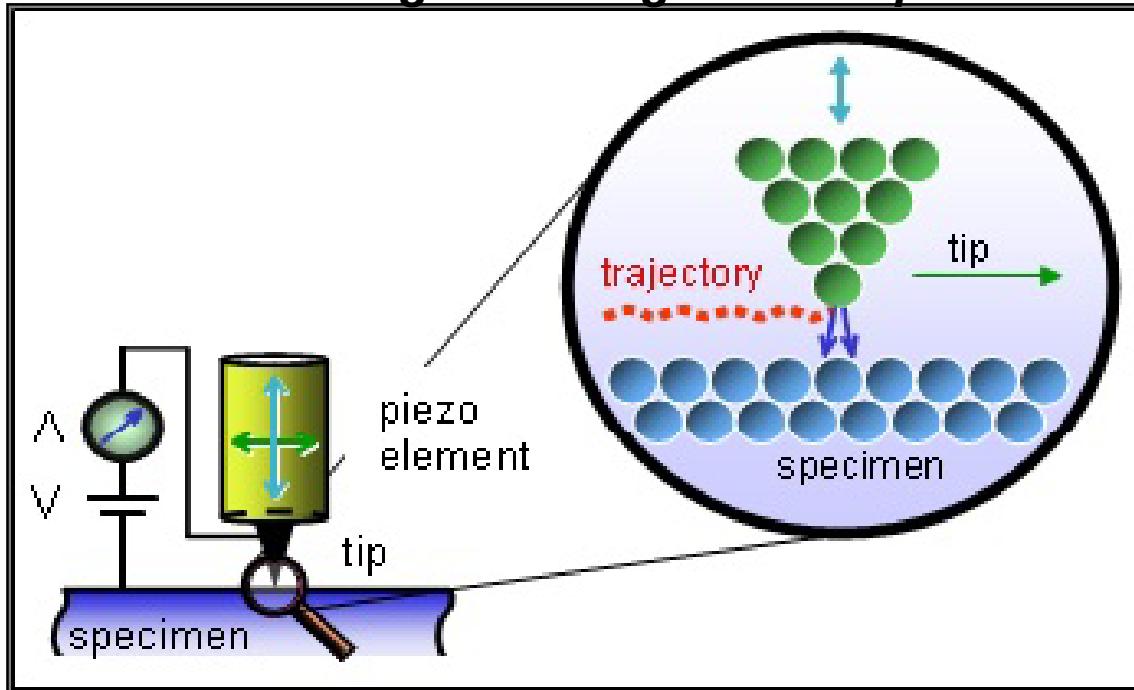


a coloured scanning electron micrograph (SEM) of the head of a fruit fly

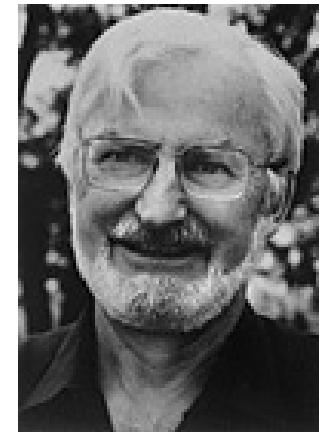
# **Scanning Probe Microscopy(SPM)**

- **scanning tunneling microscope (STM)**
  - **steady current (tunneling current) maintained between microscope probe and specimen**
  - **up and down movement of probe as it maintains current is detected and used to create image of surface of specimen**

*The Scanning Tunneling Microscope works like a record player...*



Gerd Binnig



Heinrich Rohrer



分辨率：约0.01纳米

1981年

APL 40, 178 (1982)



## The Nobel Prize in Physics 1986

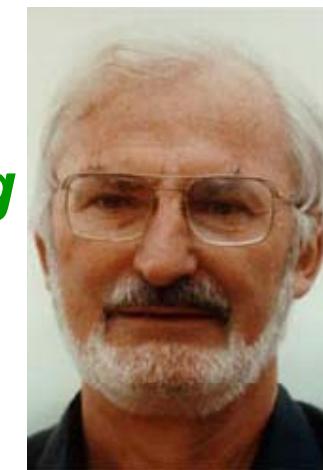


*Ernst Ruska(1906-1988)*

***"for his fundamental work in electron optics, and  
for the design of the first electron microscope"***



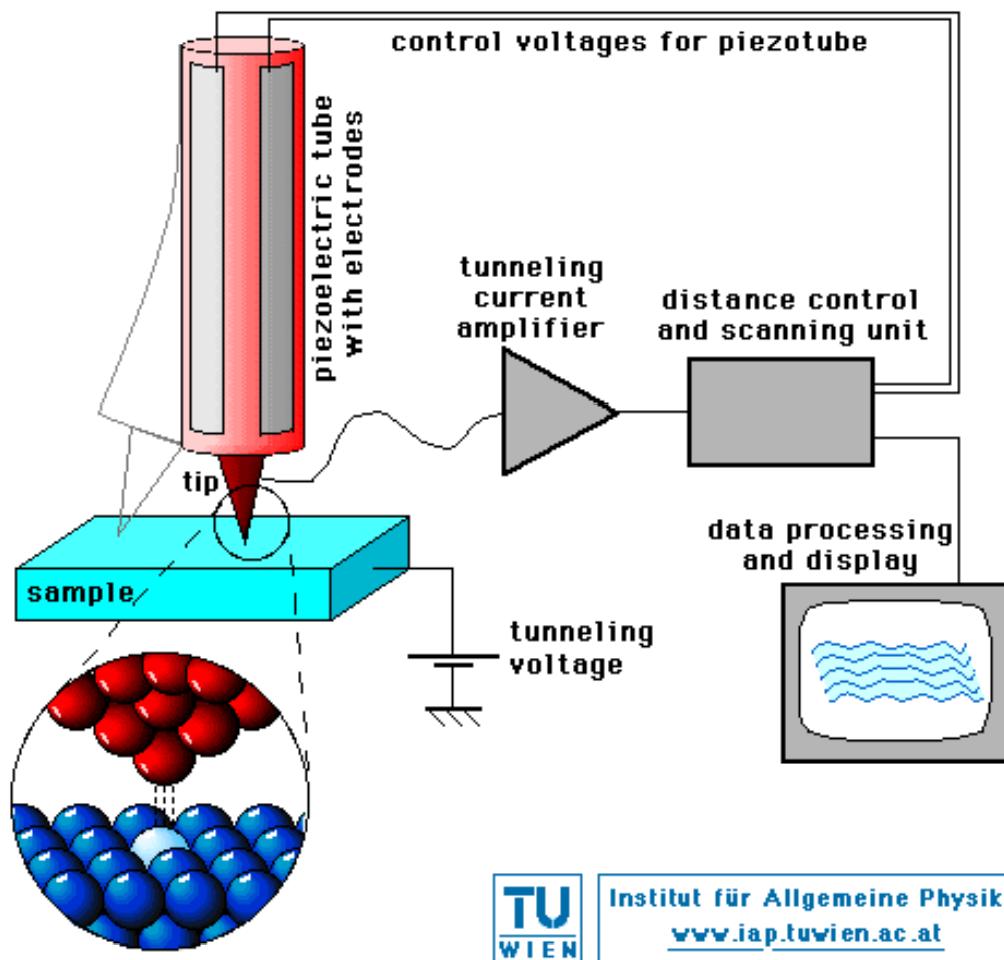
*Gerd Binnig  
(1947-)*



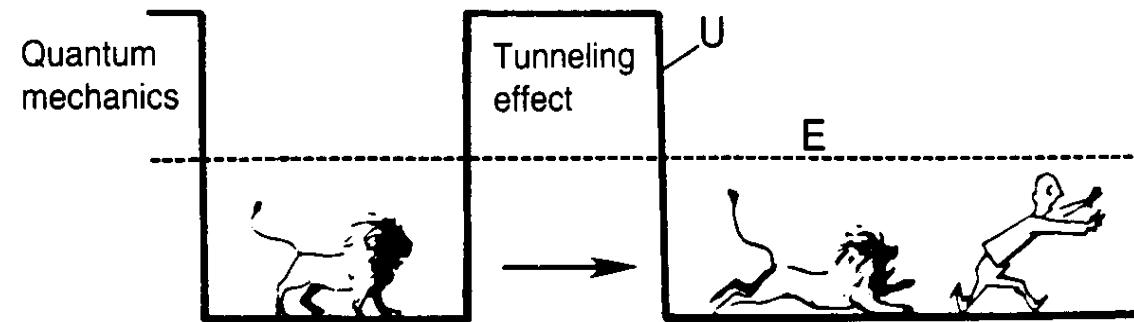
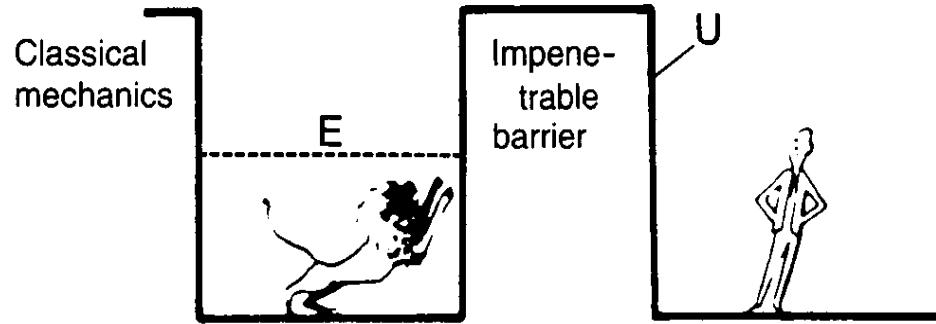
*Heinrich Rohrer  
(1933-)*

***"for their design of the scanning tunneling microscope"***

# Scanning Tunneling Microscope(STM)



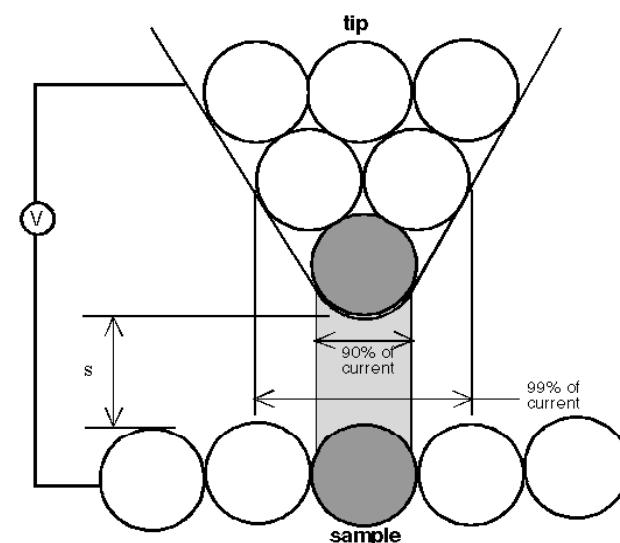
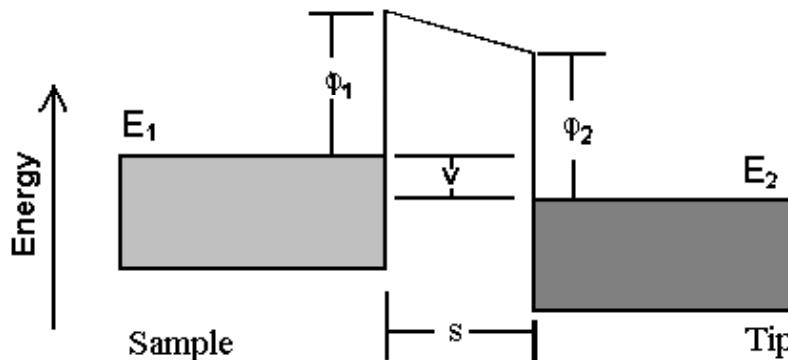
## STM的基本原理-量子隧穿



Chen, C.J. In *Introduction to Scanning Tunneling Microscopy*; Oxford University Press: New York, 1993; p 3.

## Electron Tunneling

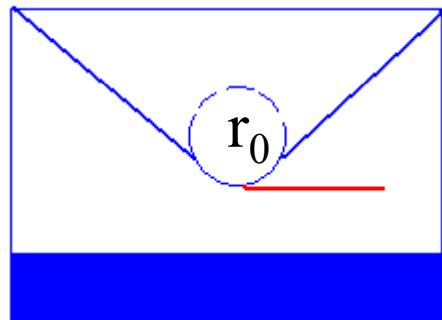
- Apply bias voltage,  $V$ , to sample to raise electron energies
- Electrons in the filled energy states ( $E_1 - V$ ) tunnel into the empty states ( $E_2 + V$ )
- Tunneling current depends exponentially on tip to sample separation
- Exponential dependence leads to fantastic resolutions. Order of  $10^{-12}$  m in the perpendicular direction and  $\sim 10^{-10}$  m in the parallel directions



# Tersoff—Hamann模型

$$I = \frac{2\pi e}{\hbar} \sum_{\mu\nu} f(E_\mu) [1 - f(E_\nu + eV)] |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu)$$

$$|M|_{\mu\nu} = \frac{\hbar^2}{2m} \int_s (\psi_\mu^* \nabla \psi_\nu - \psi_\nu \nabla \psi_\mu^*) \cdot d\vec{s}$$



隧道电流正比于针尖曲率中心处( $\vec{r}_0$ )费米能级附近的样品的局域态密度(LDOS)。

STM实验中有(x,y,z,V,I)五个变量。

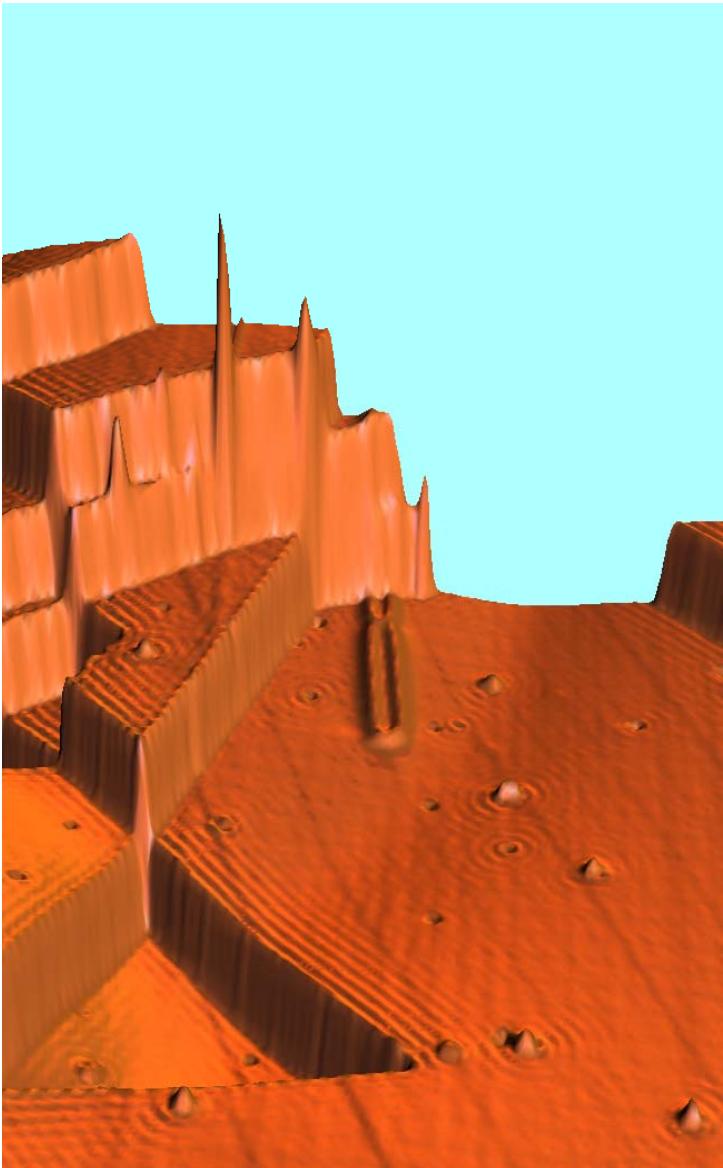
通常扫描图象时常保持V恒定。

测量I(V)谱（扫描隧道谱STS）时，V是变化的。

STM的工作模式

- 恒流模式  $(V, I) = \text{const.}$   $(x, y) / z$ , 测量电子态的空间分布
- 等高模式  $(V, Z) = \text{const.}$   $(x, y) / I$ , 测量态的分布与贡献

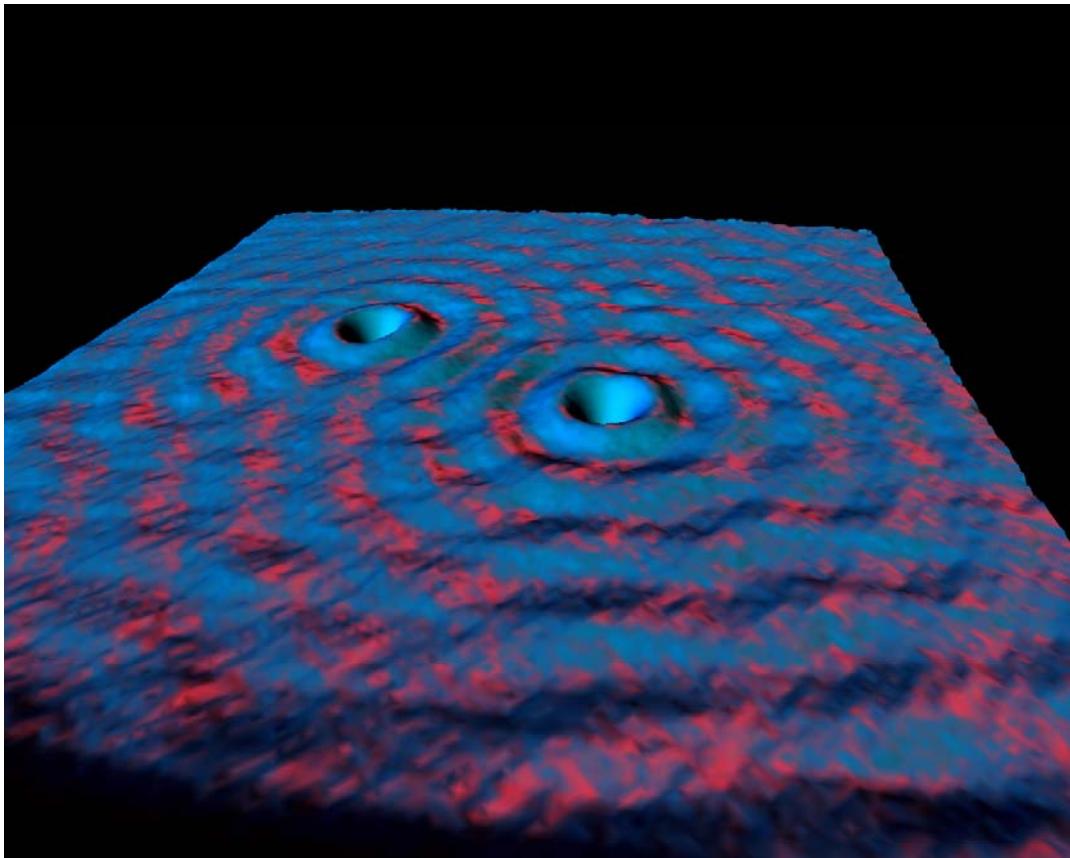
## *A Copper Perspective*



Reminiscent of formal Japanese rock gardens, here we see ripples surrounding features on the copper (111) surface. The artists' fortunes took a major turn upward when they determined that the ripples were due to "surface state electrons." These electrons are free to roam about the surface but not to penetrate into the solid. When one of these electrons encounters an obstacle like a step edge, it is partially reflected. The ripples extending away from the step edges and the various defects in the crystal surface are just the standing waves that are created whenever a wave scatters off of something. The standing waves are about 15 Angstroms (roughly 10 atomic diameters) from crest to crest. The amplitude is largest adjacent to the step edge where it is about 0.04 Angstroms from crest to trough.

M.F. Crommie, C.P. Lutz, D.M. Eigler. **Imaging standing waves in a two-dimensional electron gas.** *Nature* 363, 524-527 (1993).

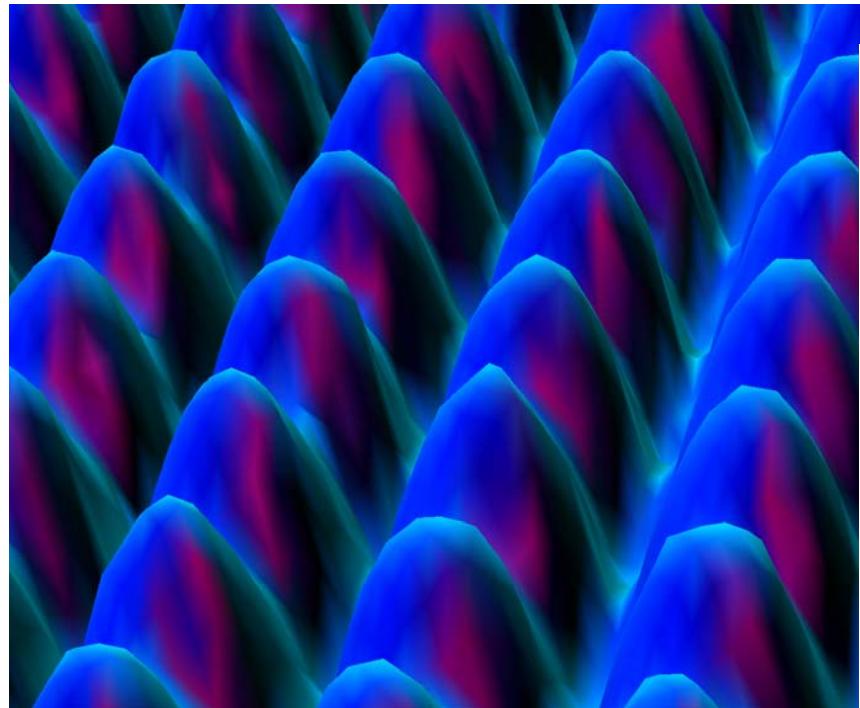
## *Circles on Circles (Unknown on Copper (111) )*



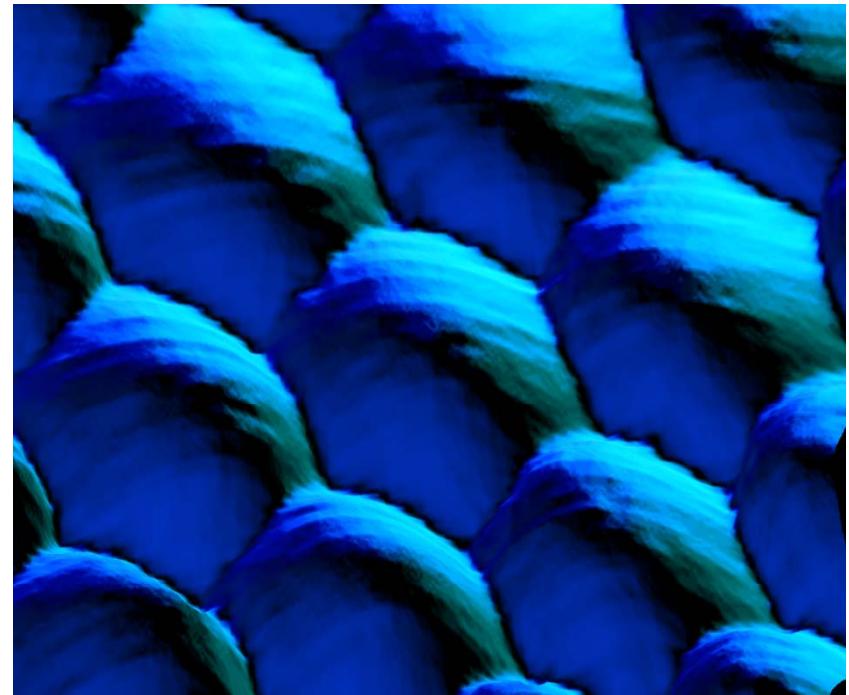
Sometimes Nature is the best artist and all we need to do is catch it in the act. Here we see the result of imperfect sample preparation: two point defects adorning the copper (111) surface. The point defects (possibly impurity atoms) scatter the surface state electrons resulting in circular standing wave patterns.

M.F. Crommie, C.P. Lutz, D.M. Eigler. **Imaging standing waves in a two-dimensional electron gas.** *Nature* 363, 524-527 (1993).

*Nickel (110)*



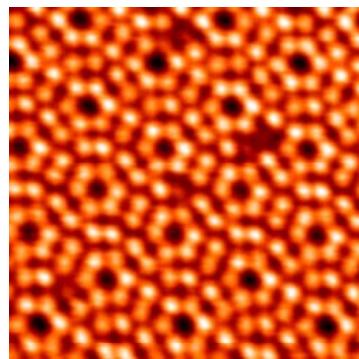
*Platinum (111)*



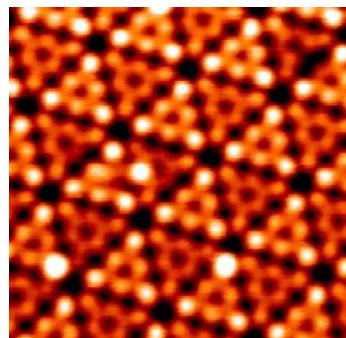
D.M. Eigler, IBM

# Complexity of STM images:

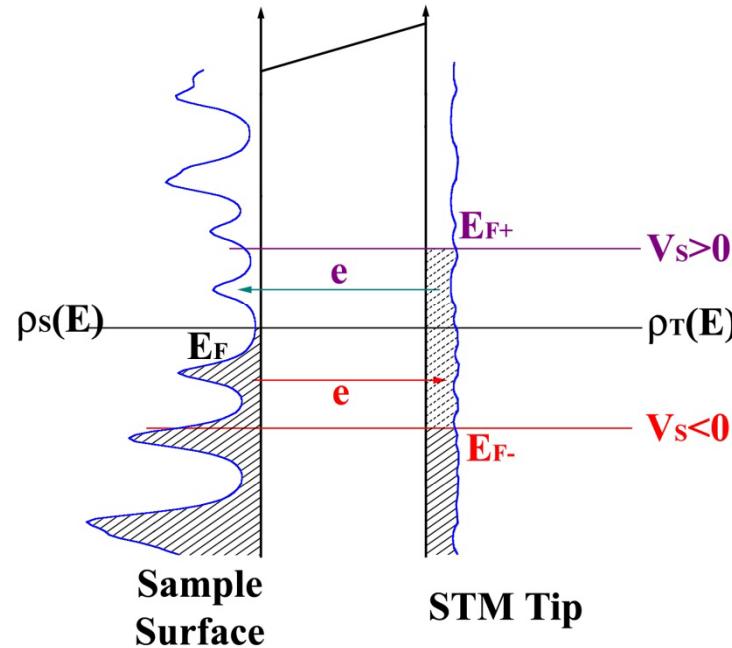
## 1. Bias voltage dependent



(a) Positive bias



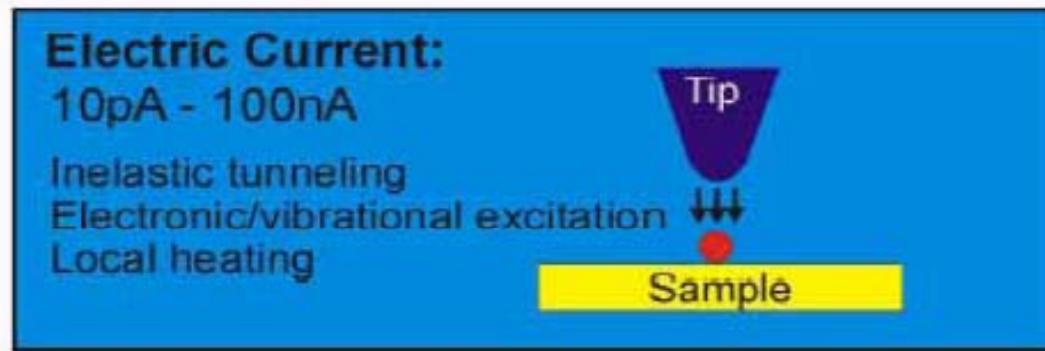
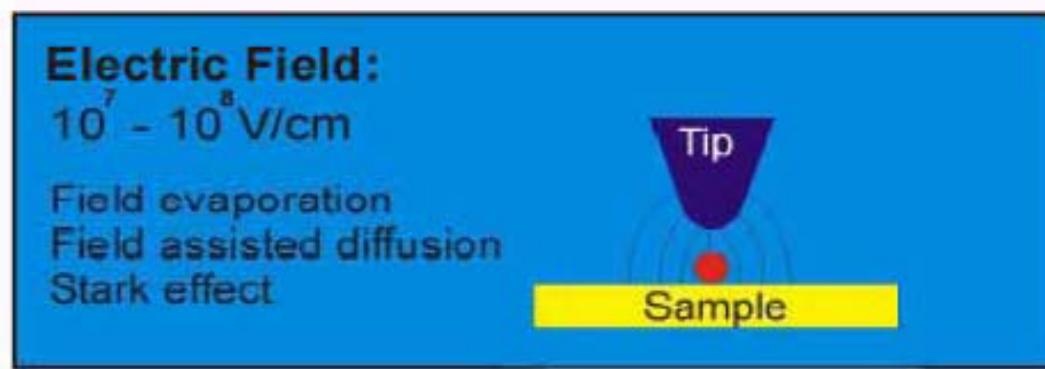
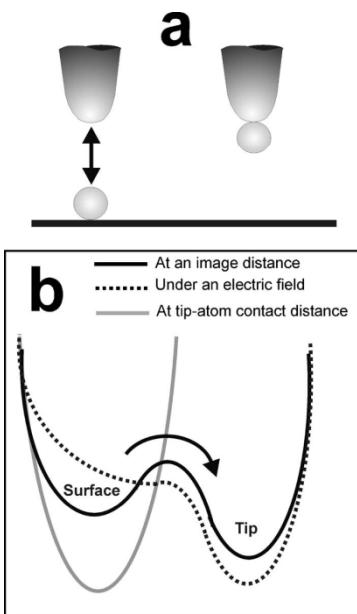
(b) Negative bias



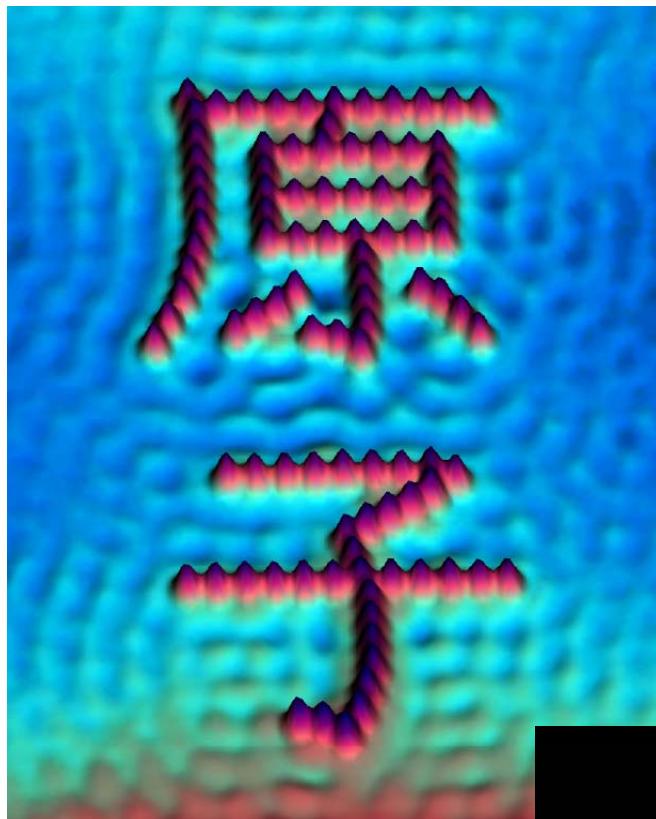
Si (111) 7x7 surface

# STM原子分子操纵

## Basic tip-sample interaction mechanisms for atomic scale modifications of surfaces

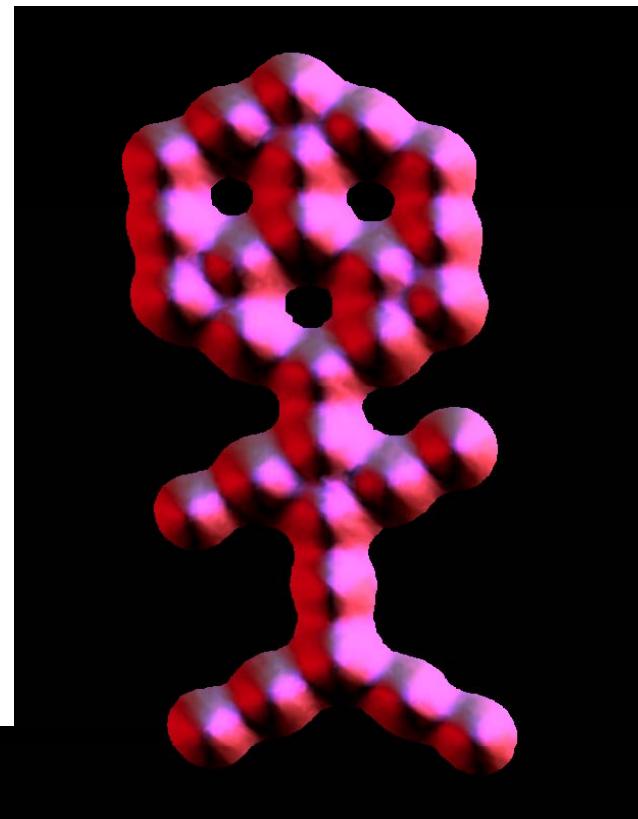
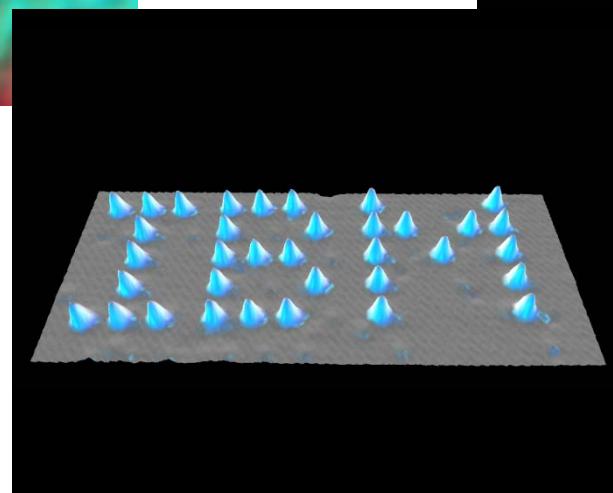


## Atomilism



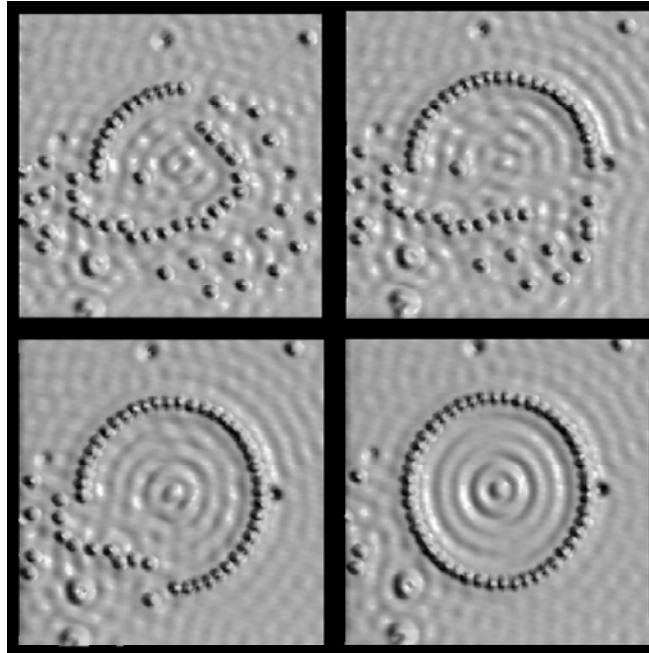
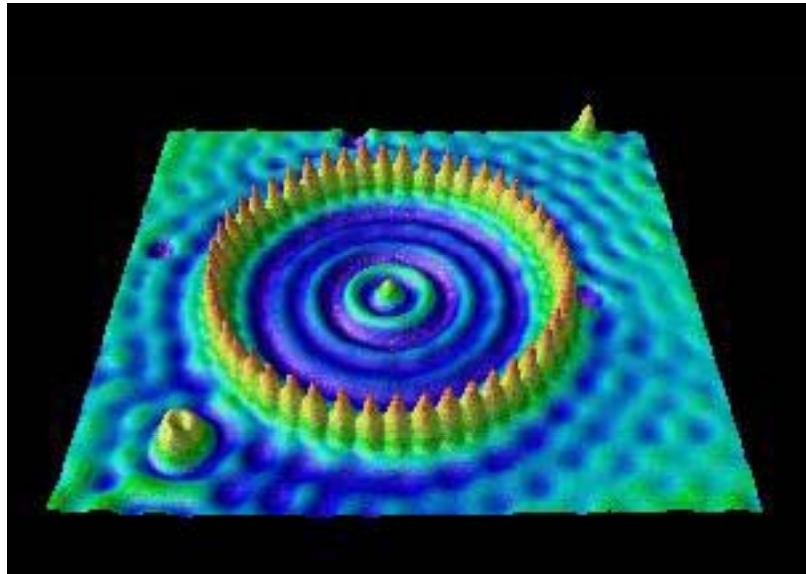
Iron on Copper (111)

Xenon on Nickel (110)



**Carbon Monoxide on Platinum (111)**  
D.M. Eigler, E.K. Schweizer.  
**Positioning single atoms with a scanning tunneling microscope.** *Nature* 344, 524-526 (1990).

## Quantum Corral (Iron on Copper (111))

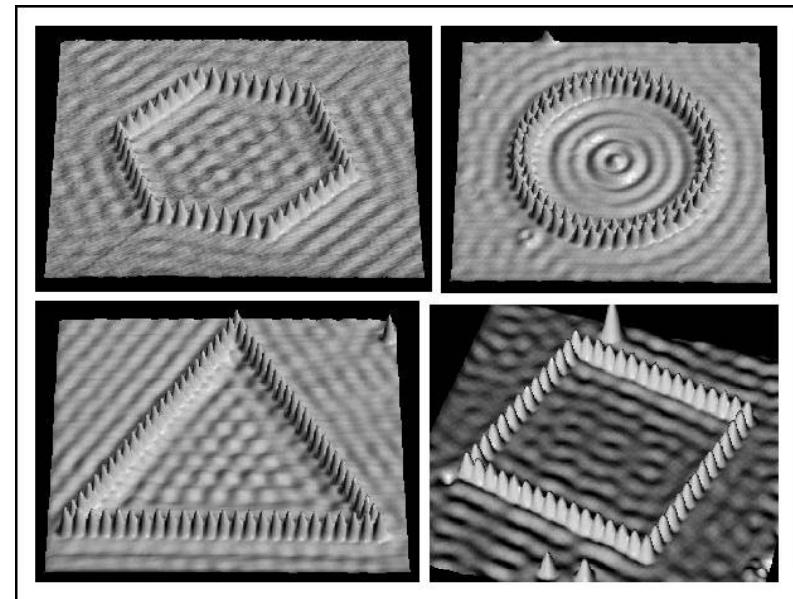
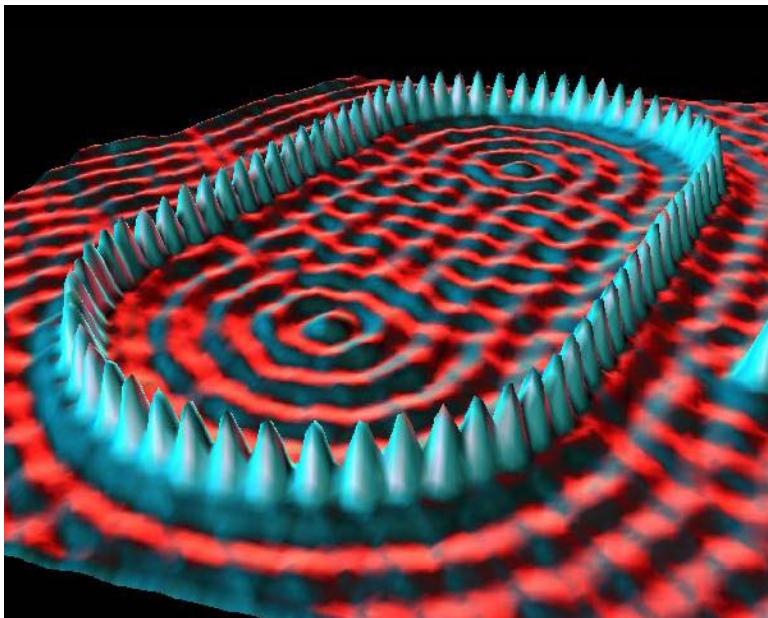


The discovery of the STM's ability to image variations in the density distribution of surface state electrons created in the artists a compulsion to have complete control of not only the atomic landscape, but the electronic landscape also. Here they have positioned 48 iron atoms into a circular ring in order to "corral" some surface state electrons and force them into "quantum" states of the circular structure. The ripples in the ring of atoms are the density distribution of a particular set of quantum states of the corral. The artists were delighted to discover that they could predict what goes on in the corral by solving the classic eigenvalue problem in quantum mechanics -- a particle in a hard-wall box.

M.F. Crommie, C.P. Lutz, D.M. Eigler. **Confinement of electrons to quantum corrals on a metal surface.** *Science* 262, 218-220 (1993).

# Stadium Corral

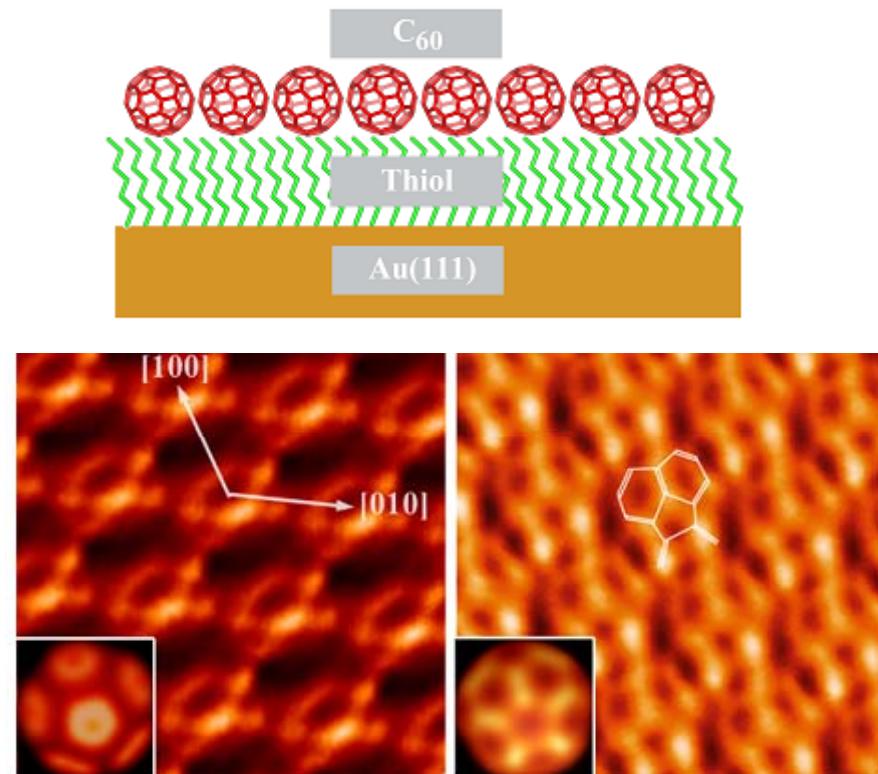
*(Iron on Copper (111) )*



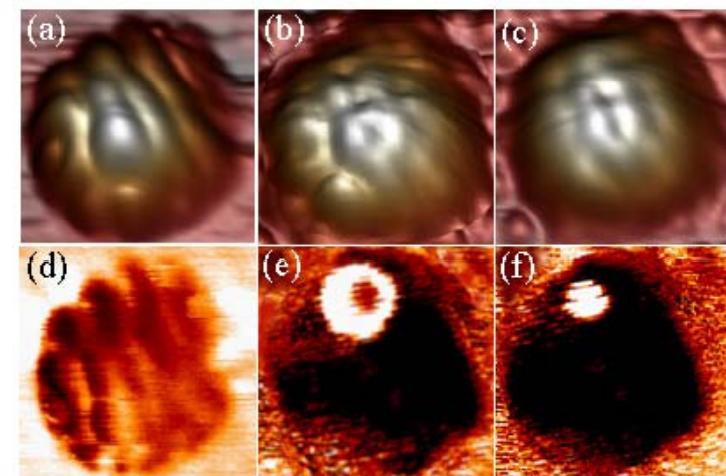
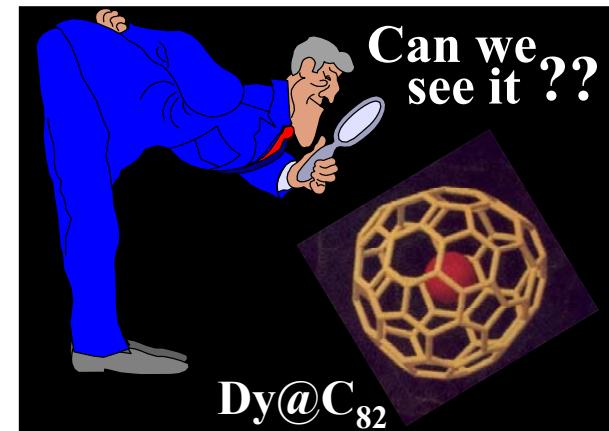
M.F. Crommie, C.P. Lutz, D.M. Eigler, E.J. Heller. **Waves on a metal surface and quantum corrals.** *Surface Review and Letters* 2 (1), 127-137 (1995).

# 我校的工作

## Example 1: High resolution STM image and dI/dV maps



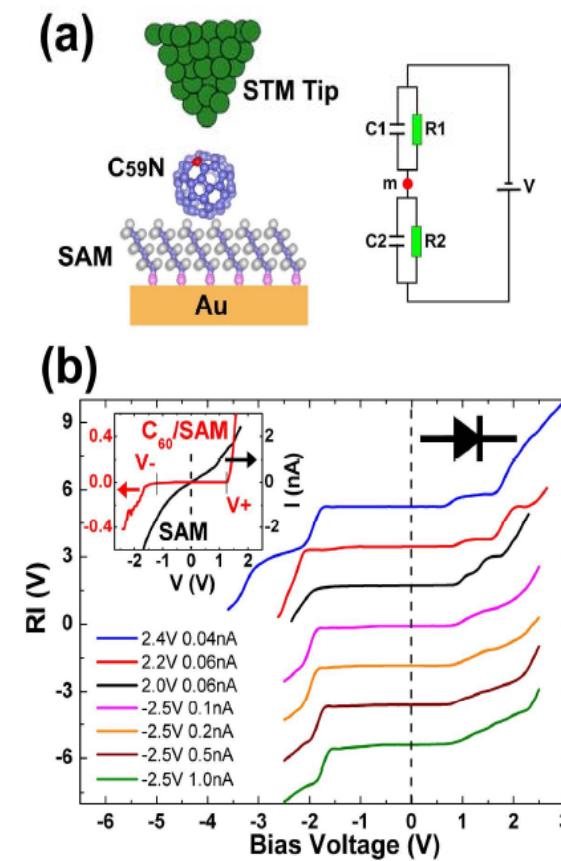
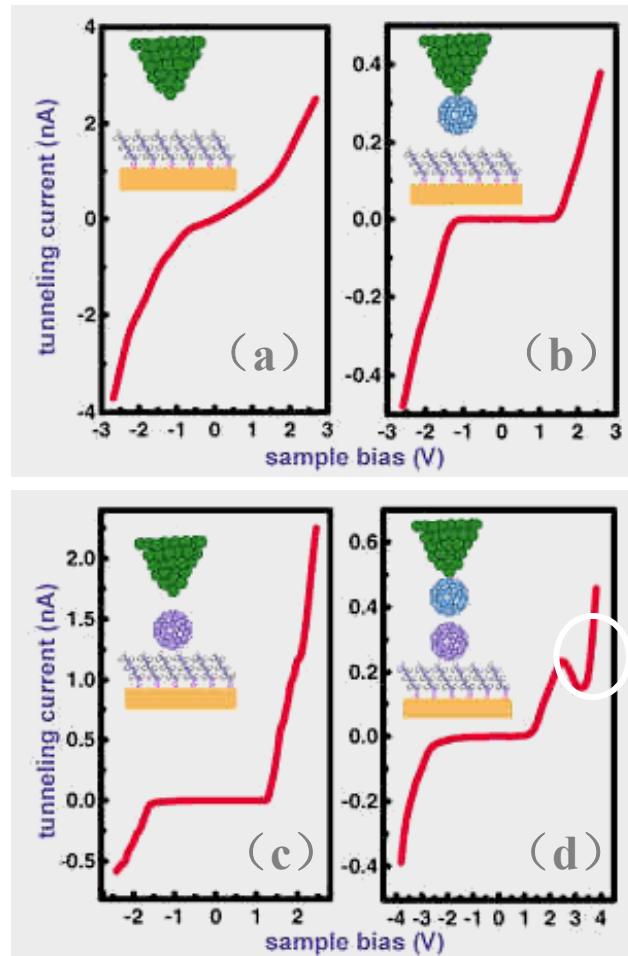
Nature 409, 6618(2001)



Phys.Rev.Lett. 91, 185504 (2003)



## Example 2: Quantum Electronic Features of Single-Molecule Device

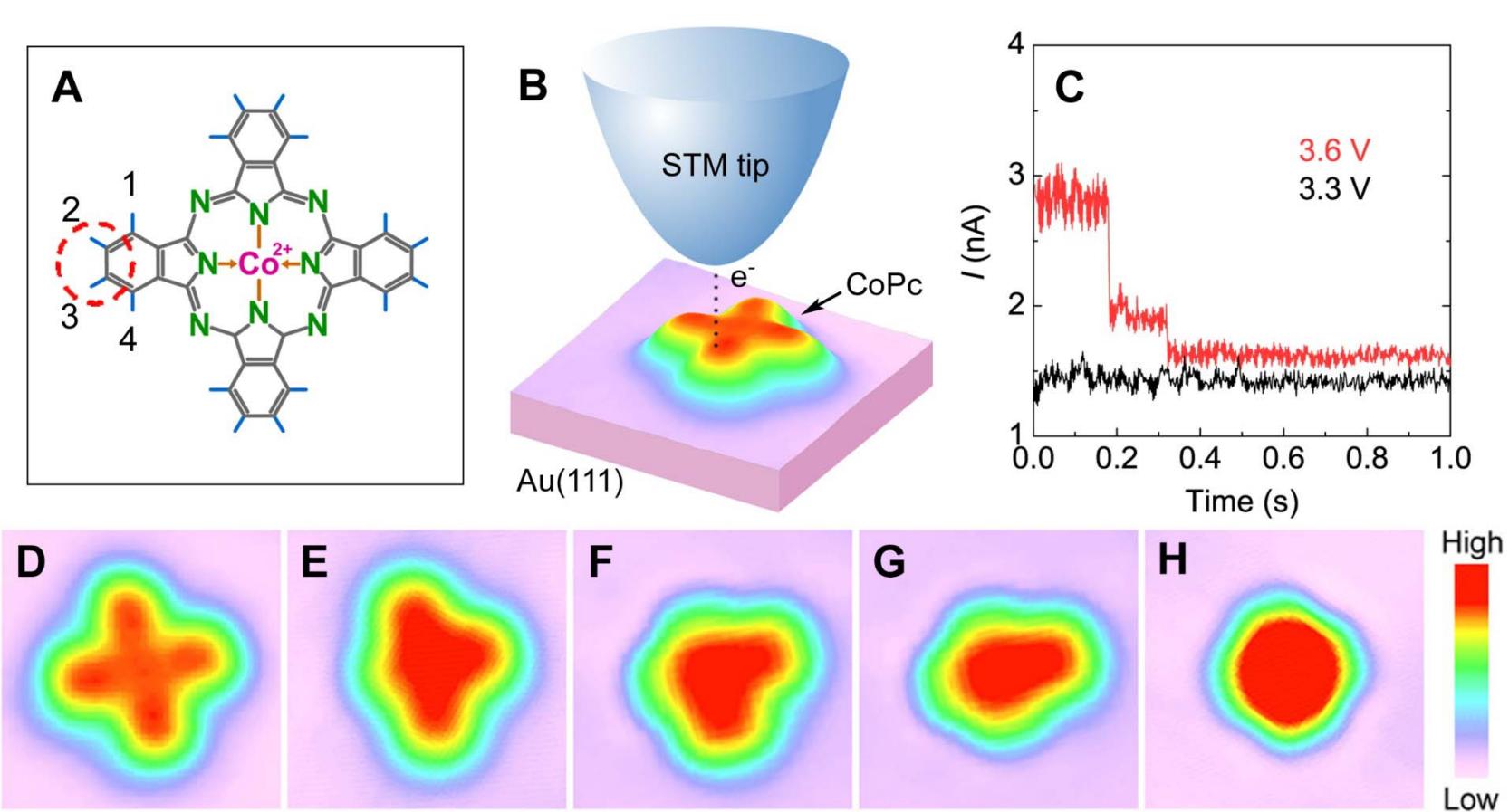


Phys.Rev.Lett. 95, 045502(2005)

Appl.Phys.Lett. 77, 3595(2000)

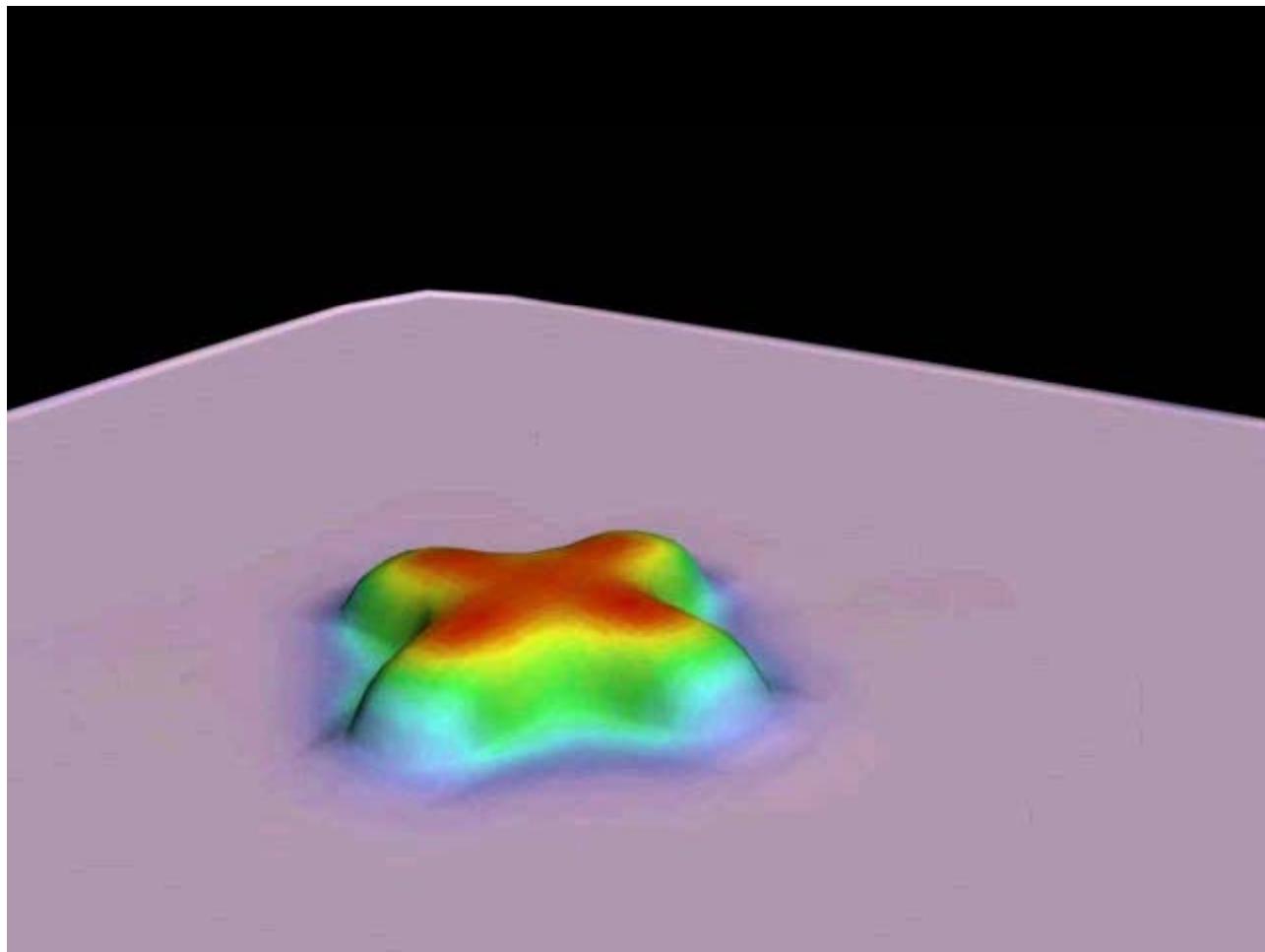


### Example 3: Manipulating magnetism in a single cobalt phthalocyanine molecule



Science 309, 1542(2005)

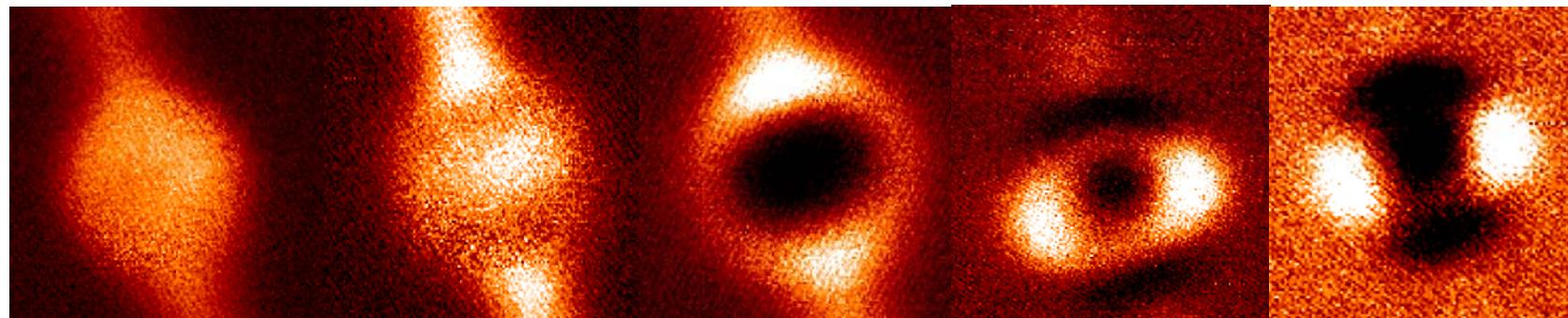
## 单分子手术控制分子的磁性



2005年中国十大科技进展

A. D. Zhao *et al.*, Science 309, 1542 (2005)

# STM measurements of SAMOs



3.98V

4.22V

4.6V

4.975V

5.01V

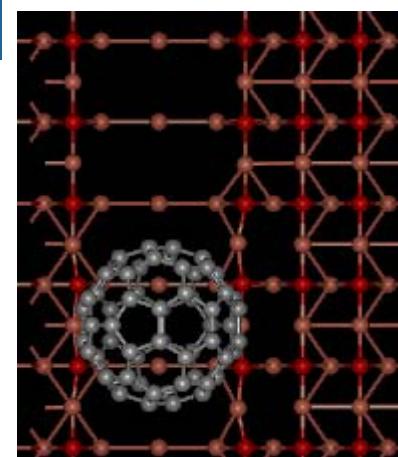
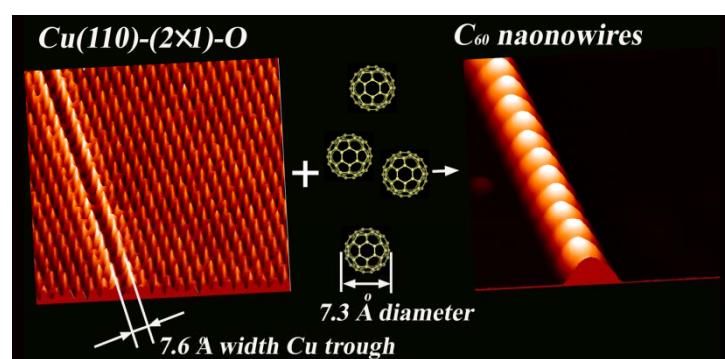
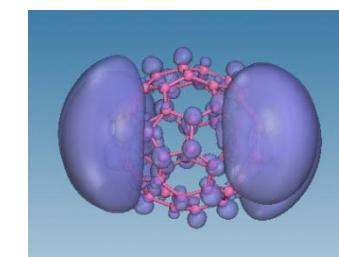
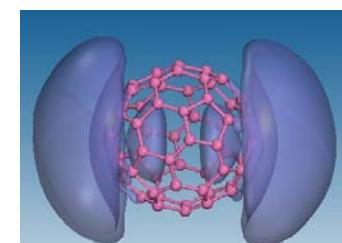
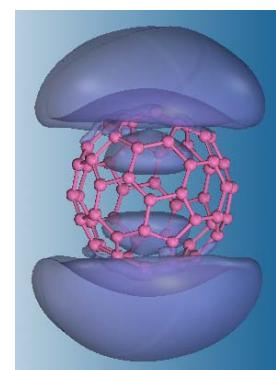
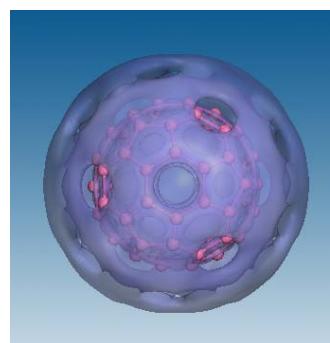
s

s+pz

px

py

d<sub>yz</sub>



Single C<sub>60</sub> on  
Cu(110)-(2×1)-O

M. Feng, J. Zhao, H. Petek  
Science 320, 359 (2008)

## 本章小结：

- 1、晶体学：**任何晶体可以用周期性布拉菲点阵加上一组基元来描述。所有可能的布拉菲点阵可以通过描述晶体宏观对称性的点群来分类。我们对元素晶体的结构，包括体心、面心、六方密堆、金刚石结构等做了讨论
- 2、倒易空间：**基于固体中波的共性，对晶体中的波函数做傅立叶变换至波矢空间（动量空间、倒易空间），倒出倒格子概念，其结构从几何角度来讲与正格子的布拉菲格子一一对应。布里渊区是倒易空间中一种特殊的原胞，它恰好是固体中各种准粒子能谱的表达空间
- 3、衍射学与显微学确定晶体结构：**讨论了Bragg, Laul基本衍射理论，晶体结构可以由倒易空间一系列衍射斑或衍射环决定。同时讨论了电子衍射、中子衍射。讨论了透射电镜与扫描隧道显微镜。

## 作业：

1、(Kittle 书2.5) 金刚石的几何结构因子。如果晶胞取惯用立方体晶胞，基元由8个原子组成。

- (a) 试求这个基元的几何结构因子
- (b) 求出几何结构因子的0点。

2、(Kittle 书2.6) 原子氢的原子散射因子。对于处于基态的氢原子，其电子数密度为 $n(r)=(\pi a_0^3)^{-1} \exp(-2r/a_0)$ , 式中 $a_0$ 是玻尔半径，试证明原子散射因子： $f_K=16/(4+K^2a_0^2)^2$