

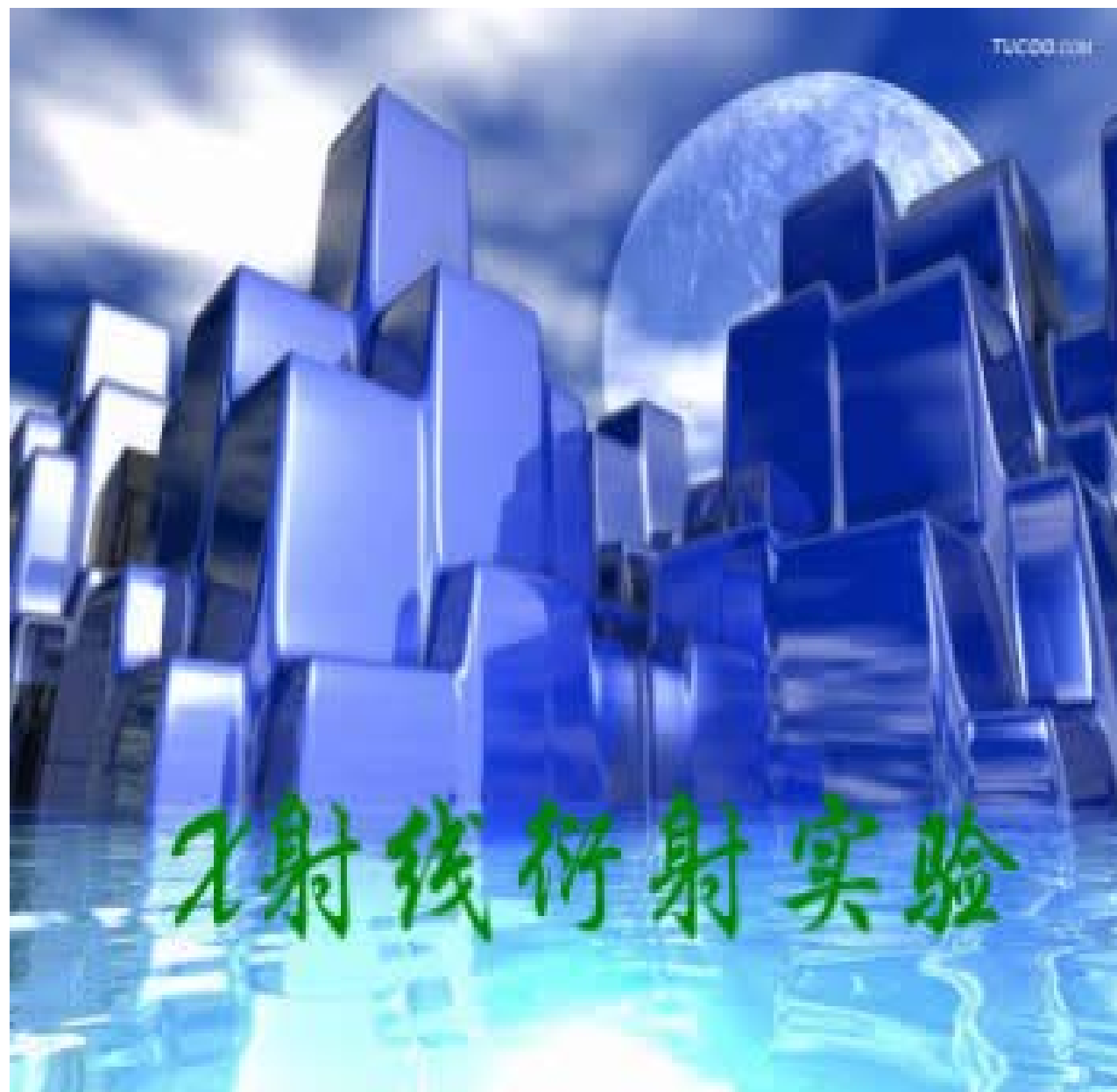
实验原理

仪器介绍

制备样品

开 机

样品扫描

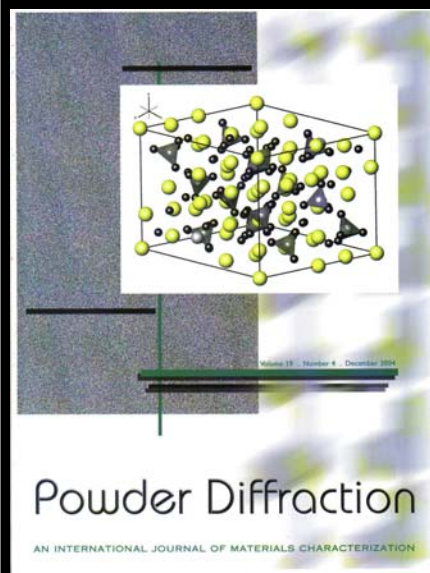
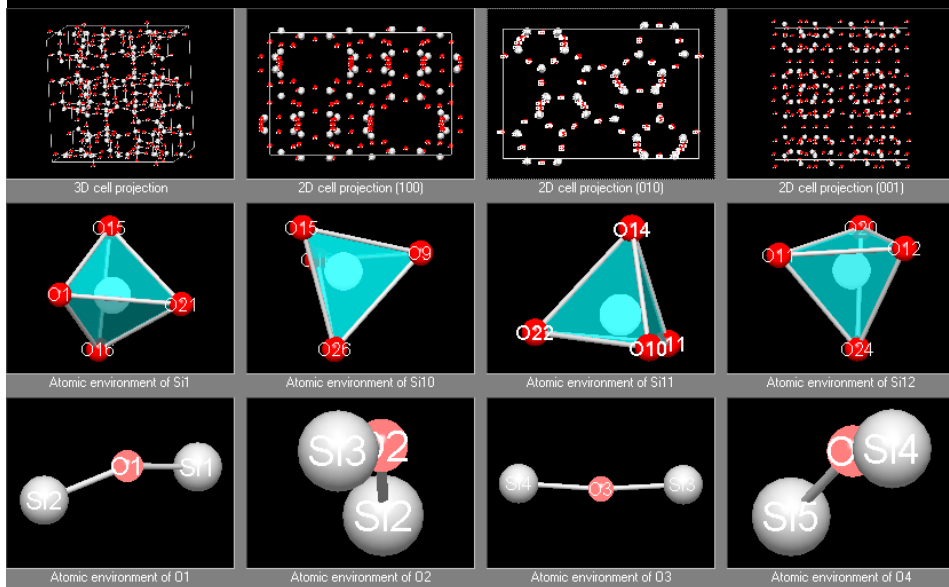
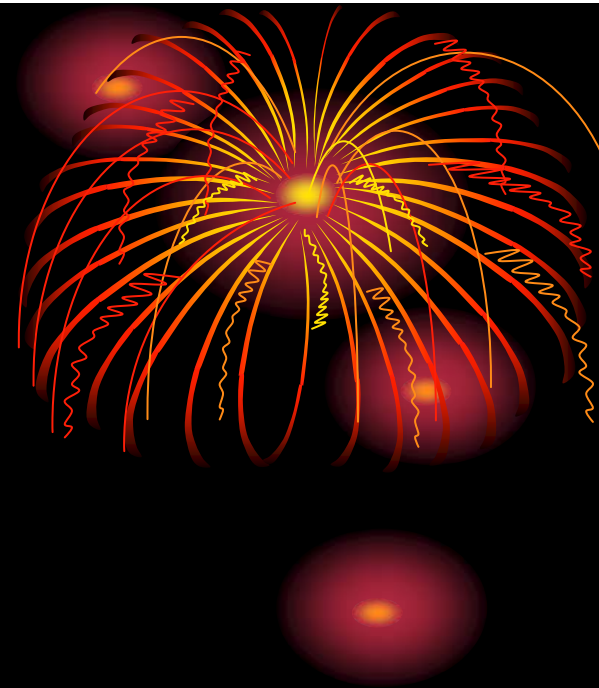


# 晶体基本概念

## 衍射原理

## 多晶衍射仪

## 应用

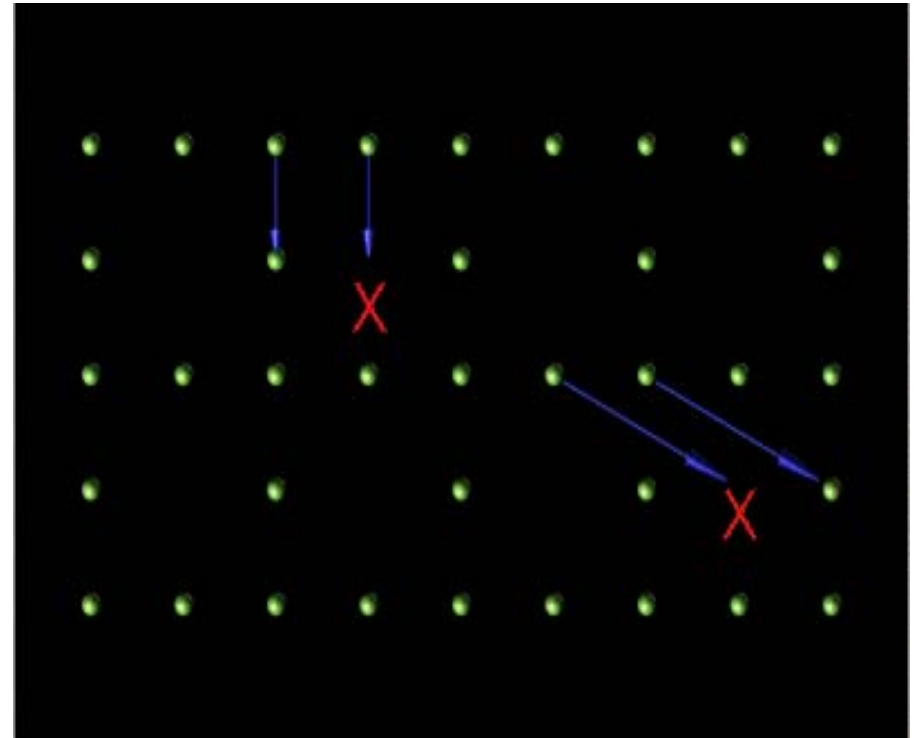
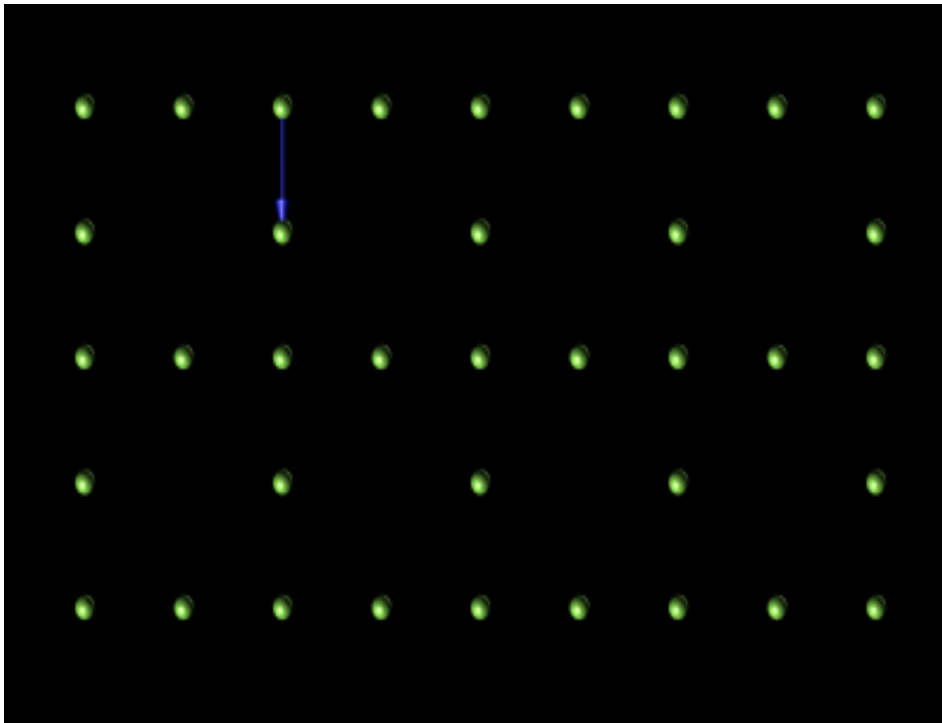


一. 晶体的基本概念:

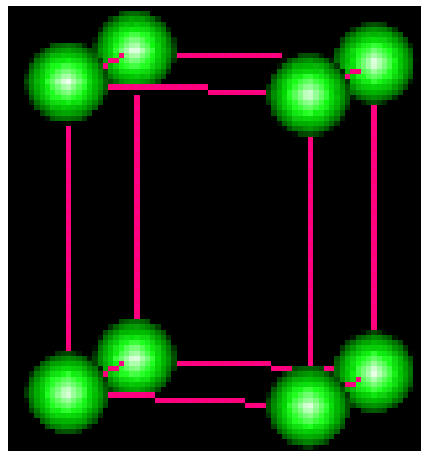
(1) 晶体的点阵, 晶胞和晶系

可以用下列的公式表示晶体结构与点阵的关系

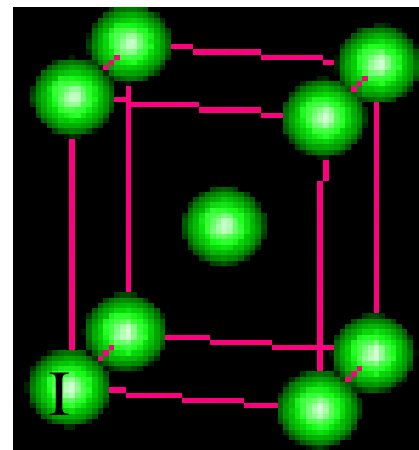
晶体结构 = 点阵 + 基元



P

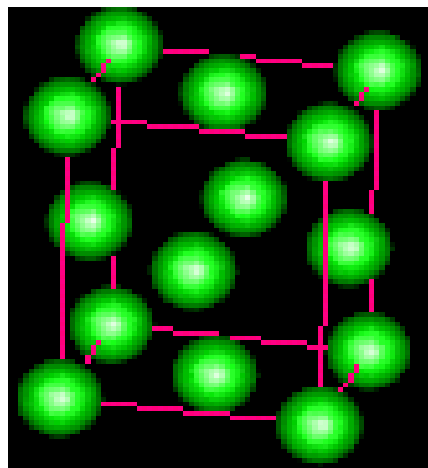


$(0,0,0)$



$(0,0,0)$

$(1/2,1/2,1/2)$



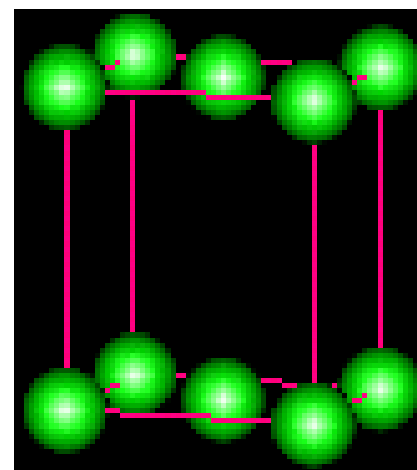
$(0,0,0)$

$(1/2,1/2,0)$

$(1/2,0,1/2)$

$(0,1/2,1/2)$

F

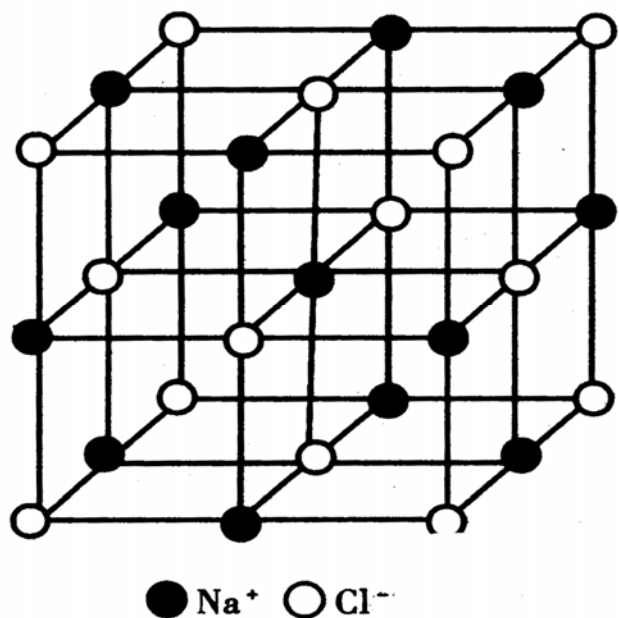


$(0,0,0)$

$(1/2,1/2,0)$

C

晶胞 = 点阵格子 + 结构基元



面心立方格子阵点坐标:

$(0,0,0)$ ,  $(1/2,1/2,0)$ ,  $(1/2,0,1/2)$ ,  
 $(0,1/2,1/2)$

Na:  $(0,0,0)$ ,  $(1/2,1/2,0)$













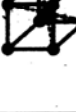

$(1/2,0,1/2)$ ,  $(0,1/2,1/2)$

Cl:  $(1/2,0,0)$ ,  $(0,1/2,0)$

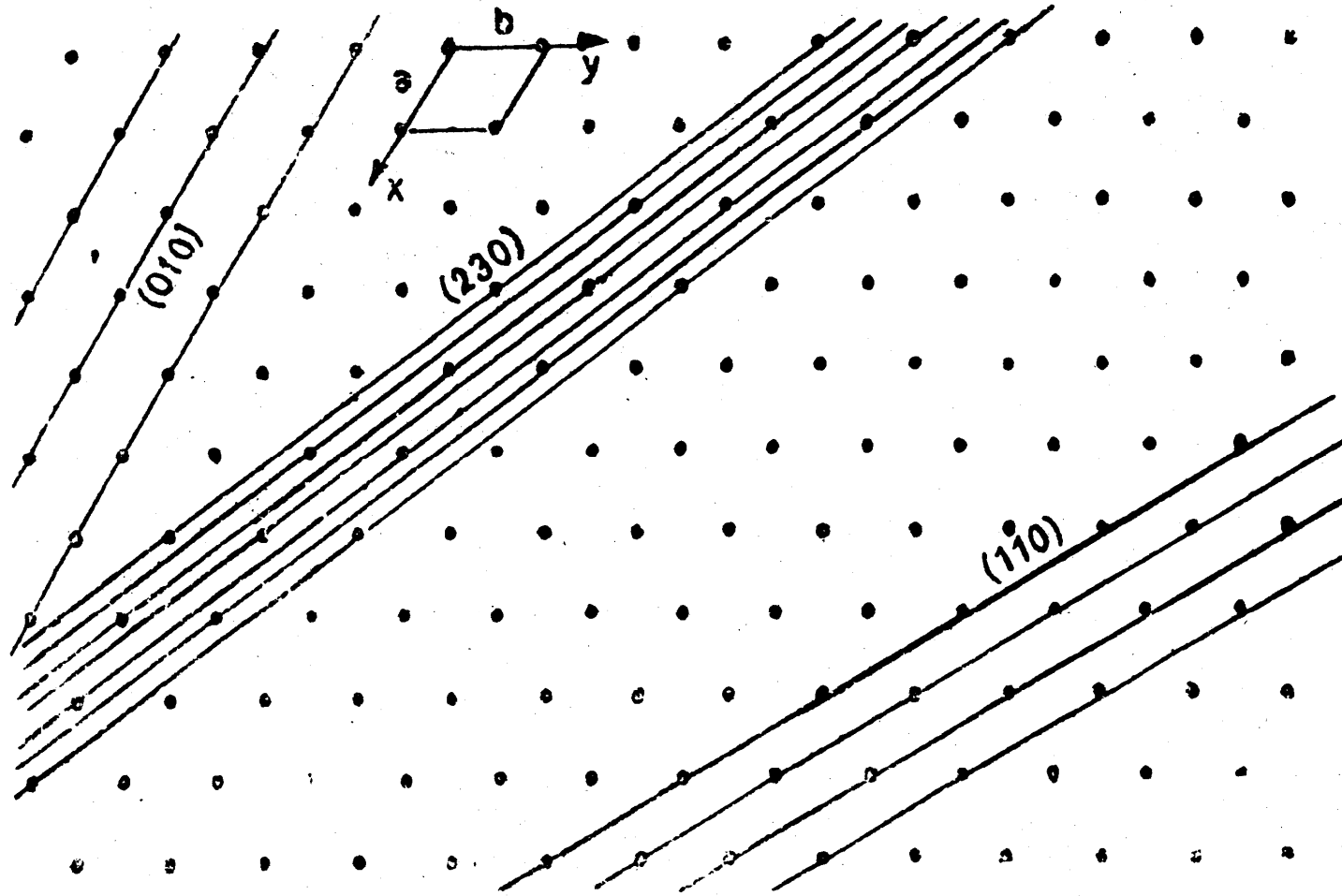
$(0,0,1/2)$ ,  $(1/2,1/2,1/2)$

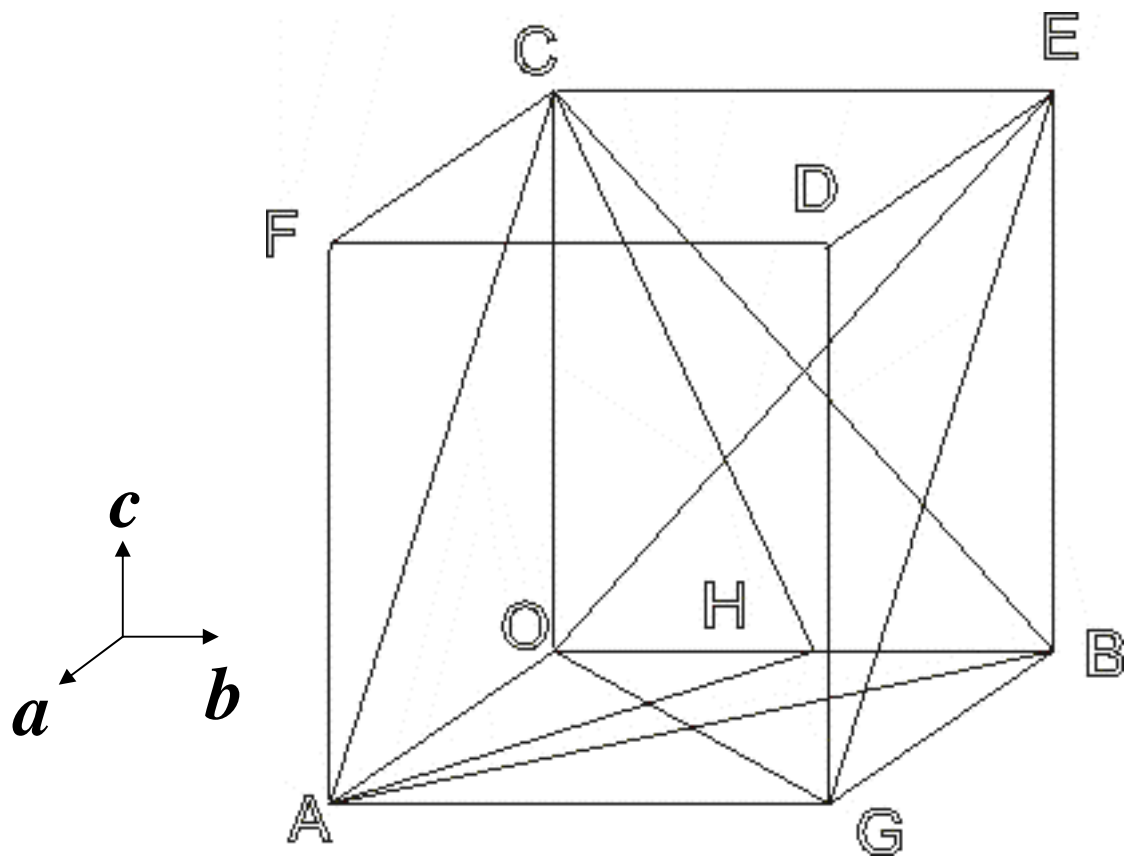
根据宏观  
对称性，有十  
四种空间格子，  
对应七种晶系

十四种空间格子

晶系	简单 <i>P</i>	底心 <i>C</i>	体心 <i>I</i>	面心 <i>F</i>
三斜				
单斜				
正交				
三方				
四方				
六方				
立方				

## 2) 晶面，晶面指数，面间距





- AGDF (100)
- BEDG (010)
- CEDF (001)
- ACEG (101)
- ABC (111)
- AHC (121)
- OEG ( $\bar{1}\bar{1}\bar{1}$ )

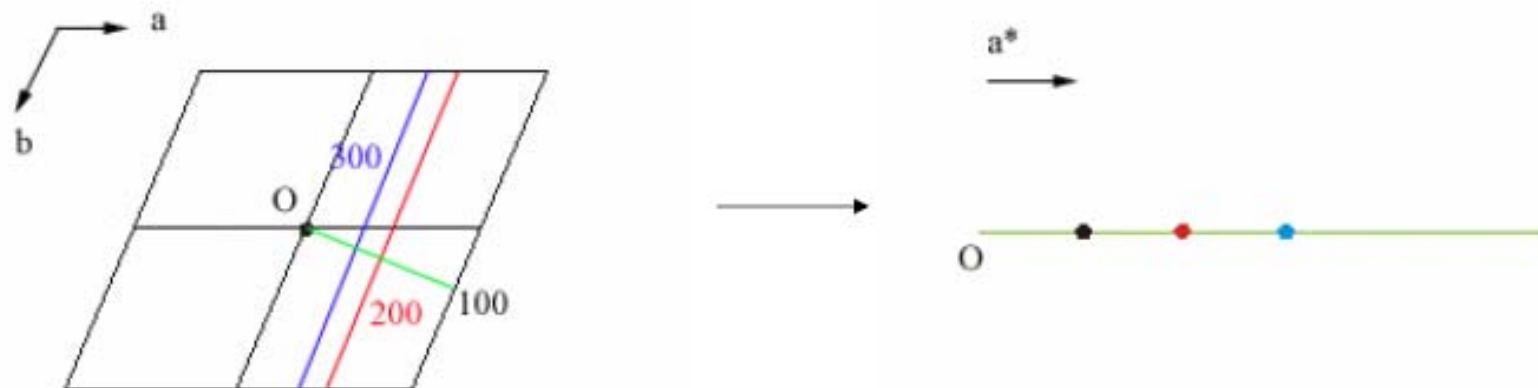
— — —

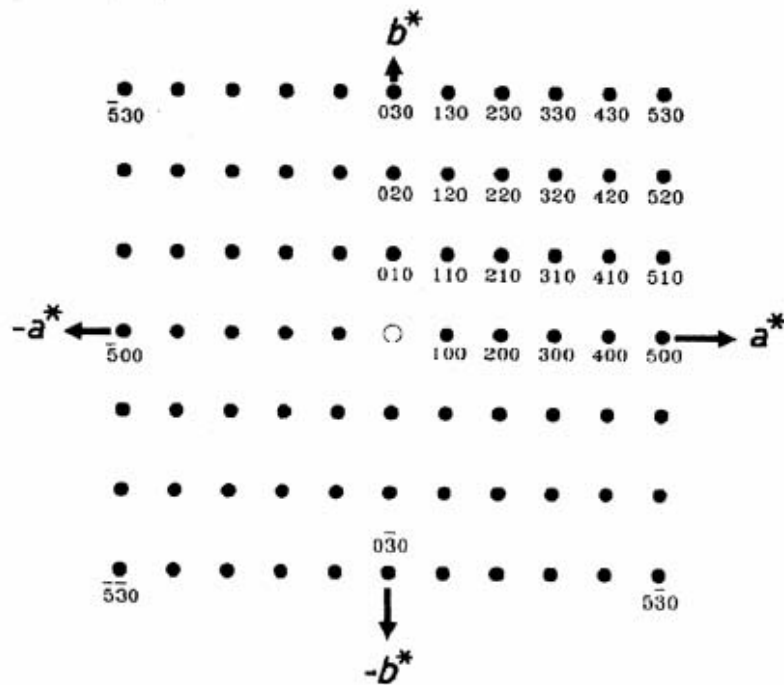
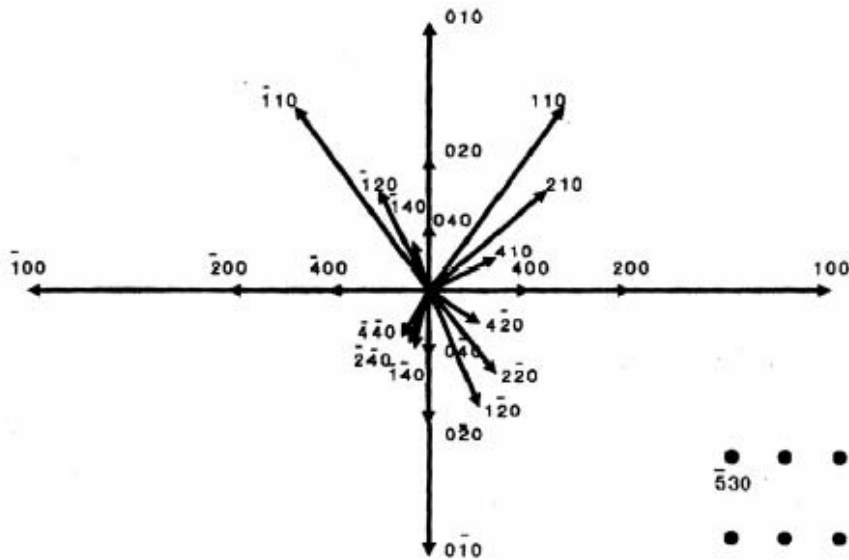


## 倒易点阵

在X射线衍射晶体学中，引入倒易点阵的概念，以描述晶体的衍射几何。晶体中的原子在三维空间周期性排列，这种点阵称为正点阵或真点阵。以长度倒数为量纲与正点阵按一定法则对应的虚拟点阵-----称倒易点阵

对于一族平行的点阵面(h00), 其面间距 $d \propto 1/h$ , 从点阵原点对(h00)面作法线, 从原点为起点截出法线的一段 $\sigma = 1/d$ 作为倒易矢量长度, 则 $\sigma \propto h$ , 取不同整数的h得到一直线倒易点阵。





(hk0) 面族的  
倒易点阵

对于(hkl)点阵面，从原点对点阵面作法线，得到的将是一空间倒易点阵。



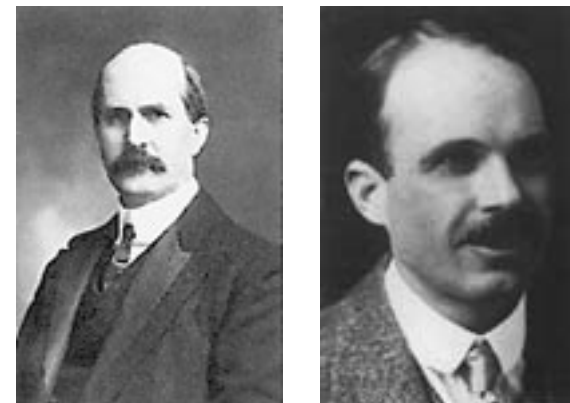
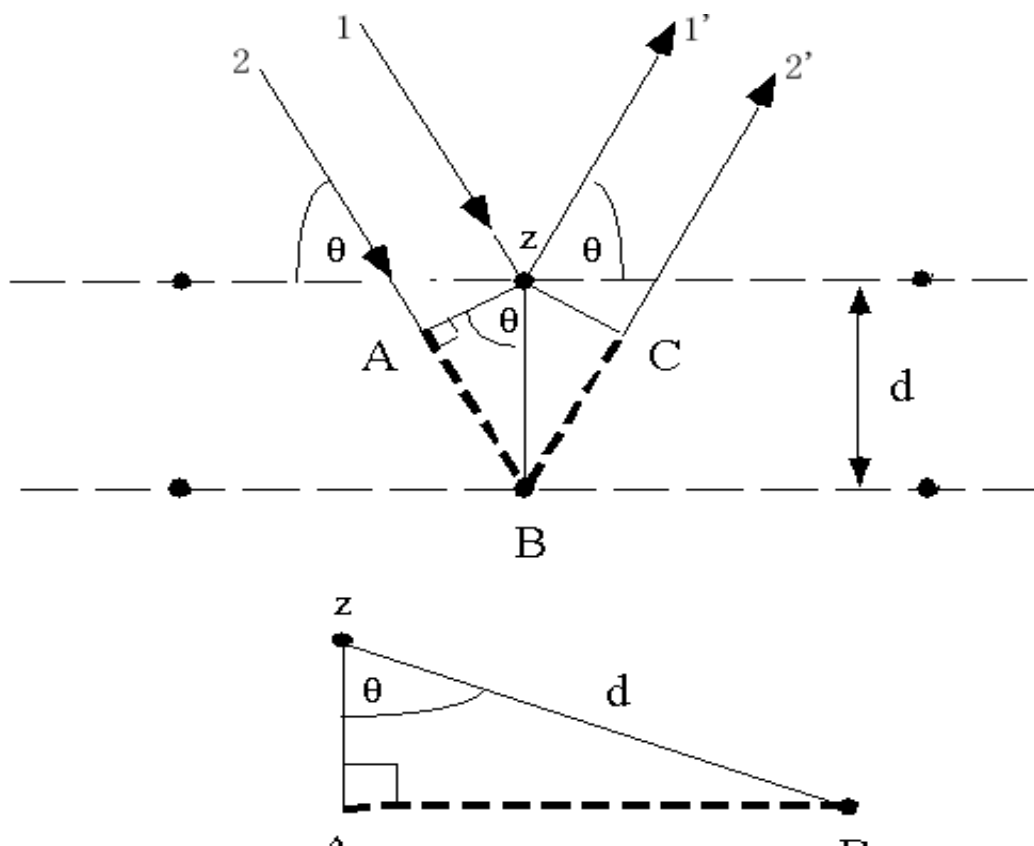
## 二. X射线衍射原理

X射线衍射花样有两方面信息：

衍射强度

衍射方向

### 1. Braag方程



满足衍射的条件为：

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

$d$ 为面间距， $\theta$ 为  
**Bragg角**。这即为  
**Bragg方程**。

## 2. Laue方程

一维点阵的情况:

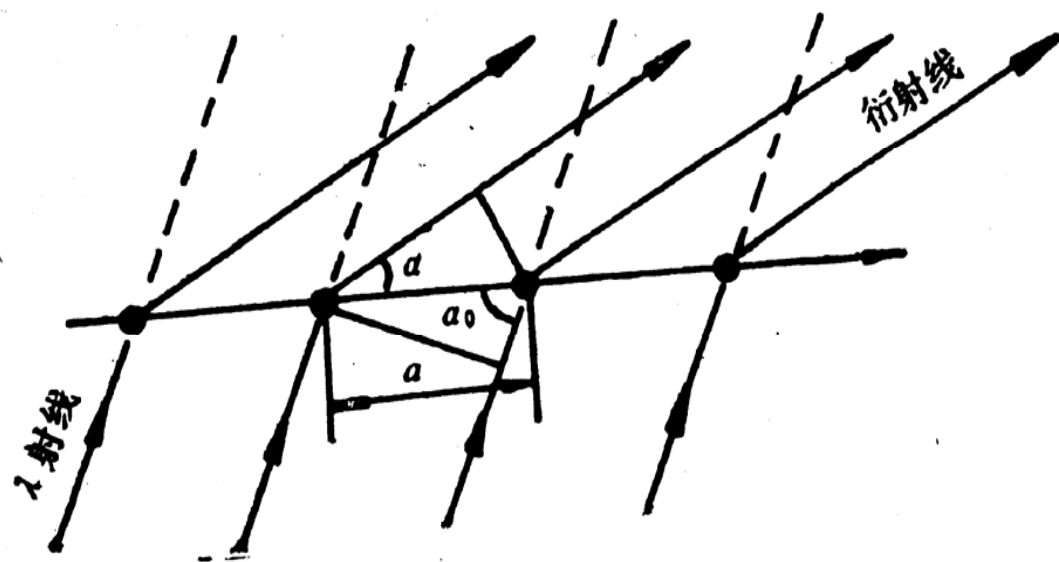
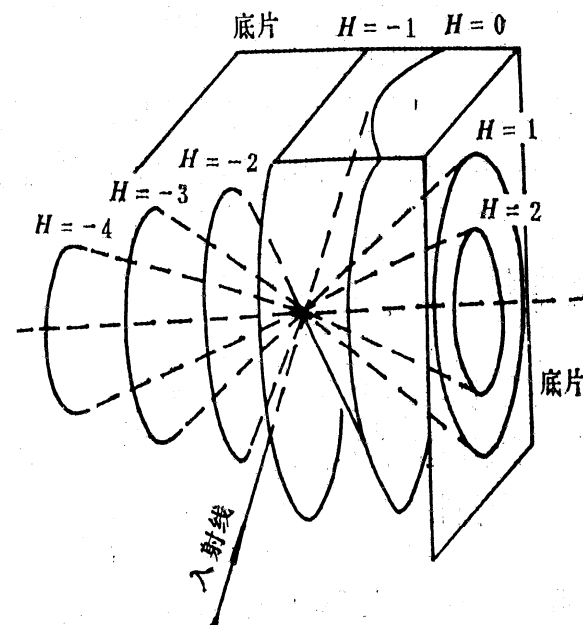


图 5.2 一维点阵(原子列)的衍射

$$a (\cos\alpha_0 - \cos\alpha) = H\lambda$$



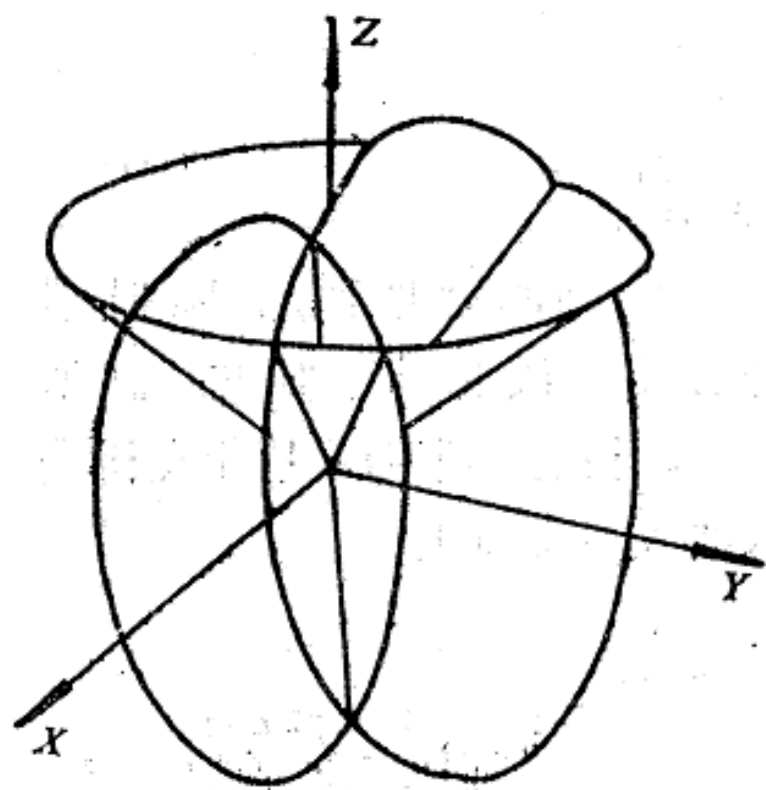
点阵衍射圆锥

对于三维情形，就可以得到晶体光栅的衍射条件：

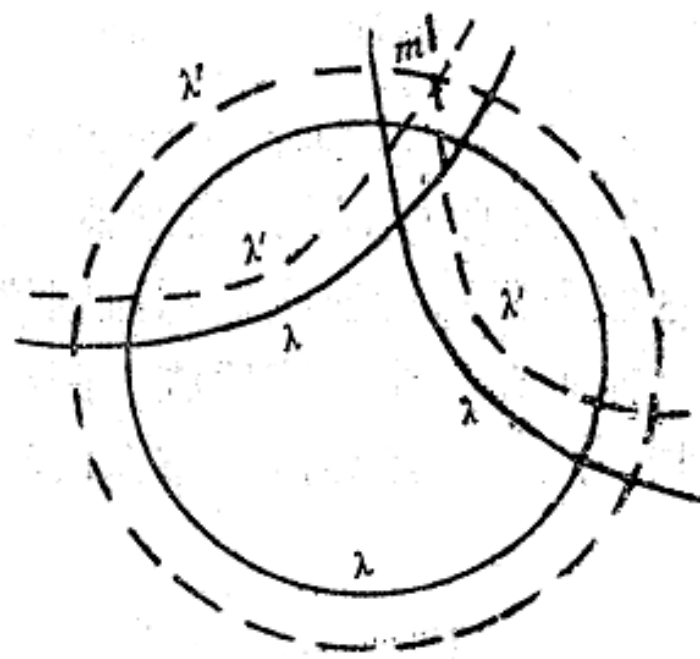
$$\left\{ \begin{array}{l} a (\cos\alpha_0 - \cos\alpha) = H\lambda \\ b (\cos\beta_0 - \cos\beta) = K\lambda \\ c (\cos\gamma_0 - \cos\gamma) = L\lambda \end{array} \right.$$

该方程组即为**Laue**方程。**H**，**K**，**L**称为衍射指数。

$\alpha, \beta, \gamma, \alpha_0, \beta_0, \gamma_0$ 分别为散射光和入射光与三个点阵轴矢的夹角。



(a)



(b)

三维衍射时三个衍射圆锥相交条件

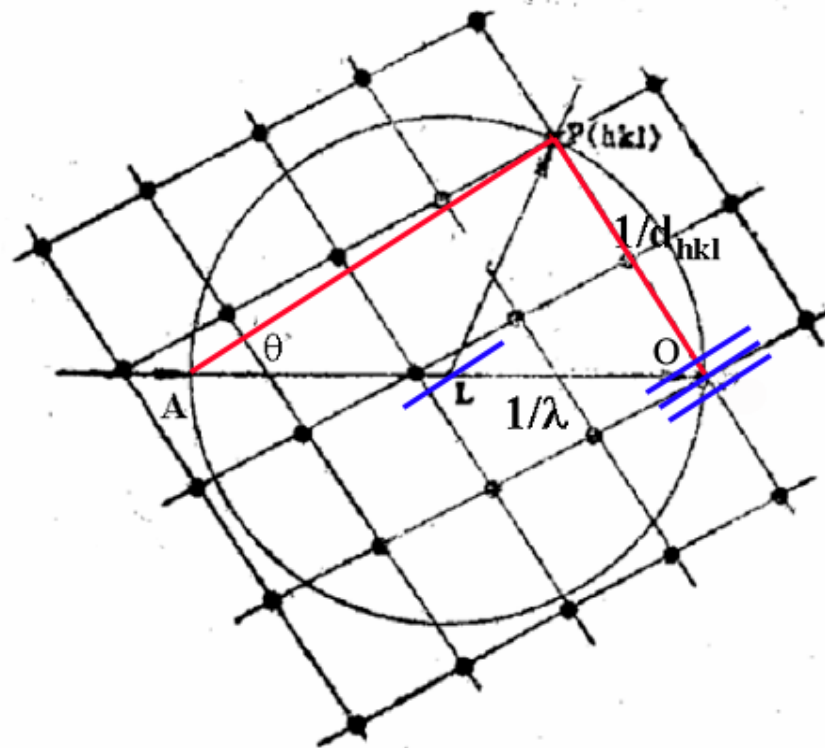
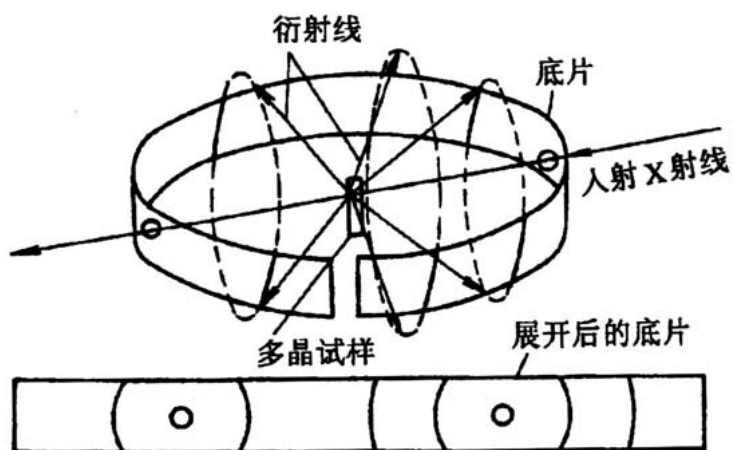
(a) 三个衍射圆锥无公共母线 (b) 连续 X 射线时, 三个衍射圆锥相交

## Ewald作图与衍射方法

Bragg方程:  $2d_{hkl}\sin\theta = \lambda$  可转变为:  $\sin\theta = (1/d_{hkl}) / (2/\lambda)$   
 即:  $2/\lambda$ ,  $1/d_{hkl}$  和  $\theta$  呈正弦关系。对于固定的  $\lambda$ , 改变  $\theta$ , 满足衍射条件的直角三角形的直角顶点将落在以  $2/\lambda$  为直径的球面上。Bragg方程:  $2d_{hkl}\sin\theta = \lambda$  可转变为:  $\sin\theta = (1/d_{hkl}) / (2/\lambda)$

表 7.0.1 三种实验方法比较

实验方法	X 射线	样品	照 相 法		衍射仪法
粉末法	单色	多晶体 或粉末	样品转动 (也可不转动)	德拜相机	粉末衍射 仪(二圆)
劳厄法	连续	单晶体	样品不动	劳厄相机	单晶或粉 末衍射仪
转晶法	单色	单晶体	样品转动 或摆动	转晶一回摆 相机	单晶衍射 仪(四圆)



### 3. X射线的衍射强度

$$I(hkl)=P.L.J.A.|F|^2.e^{-2M}$$

**P**偏振因子，**L**劳仑兹因子，**J**多重性因子，**A**吸收因子，**e<sup>-2M</sup>**温度因子，**F**结构因子。



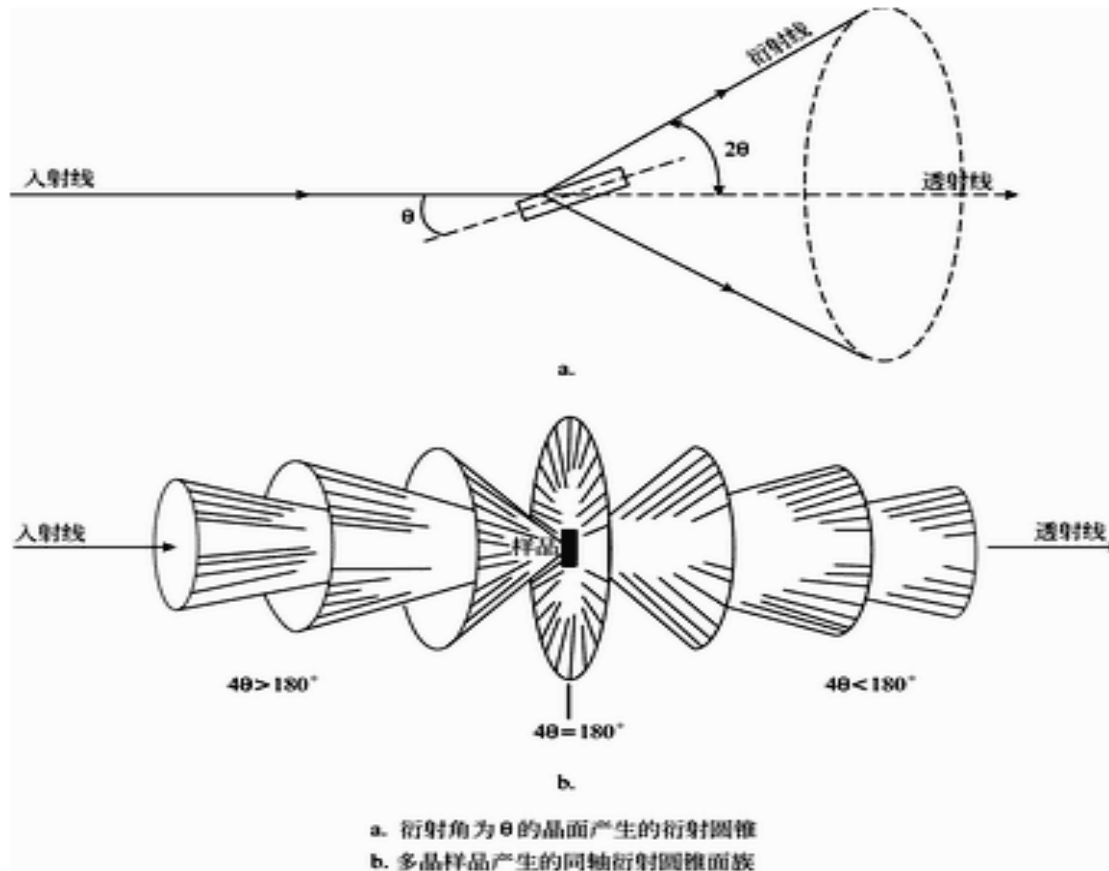


# 三. 多晶衍射仪

## (一) 两种衍射几何:

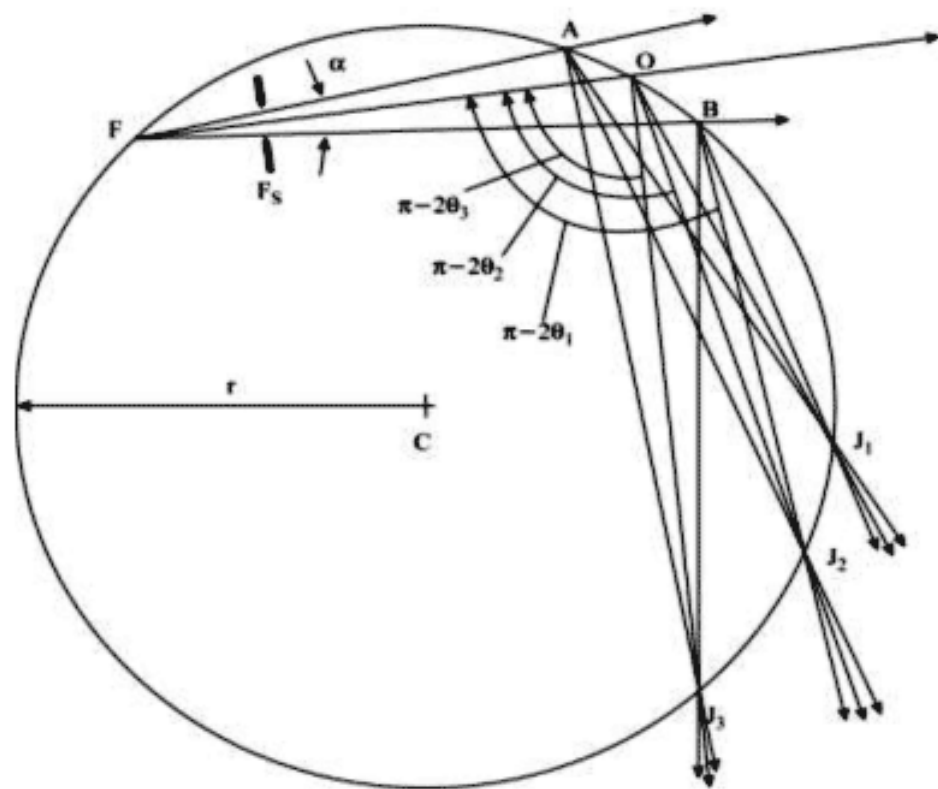
多晶衍射仪按仪器设计所采用的衍射几何来区分, 有两大类型:

平行光束型和聚焦光束型



平行光束型:

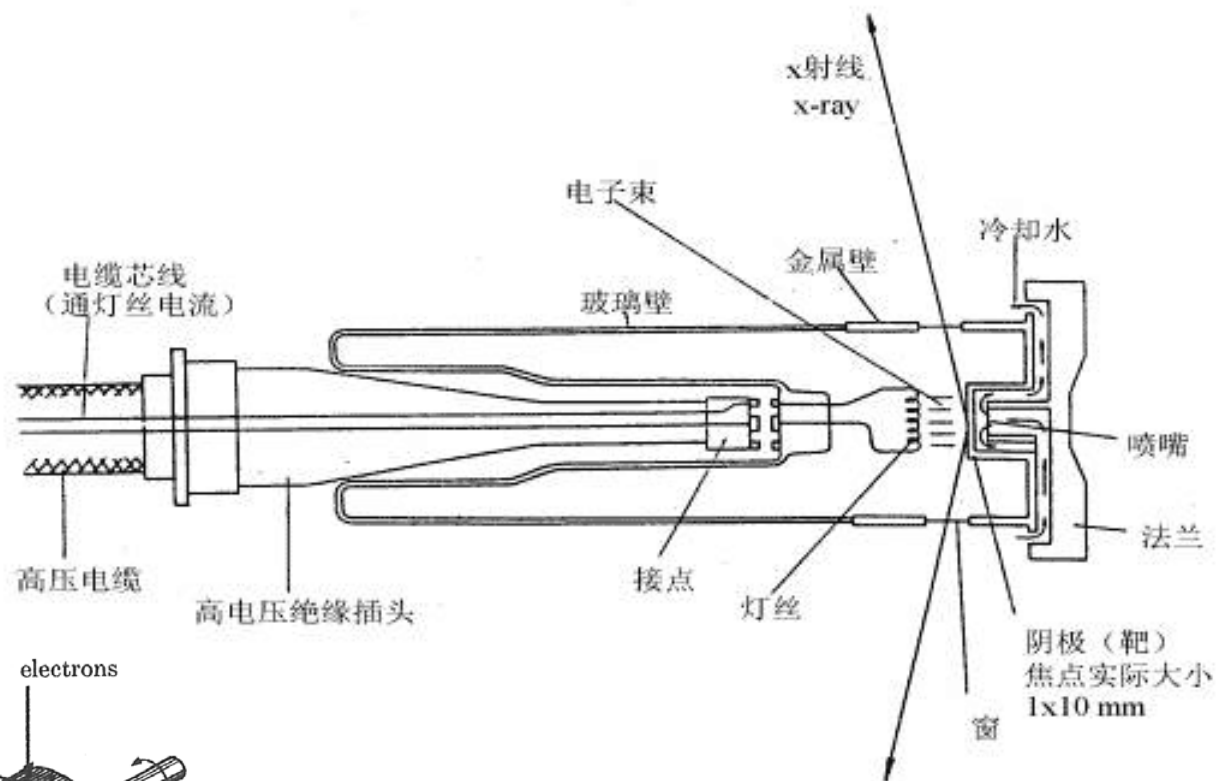
聚焦光束型：



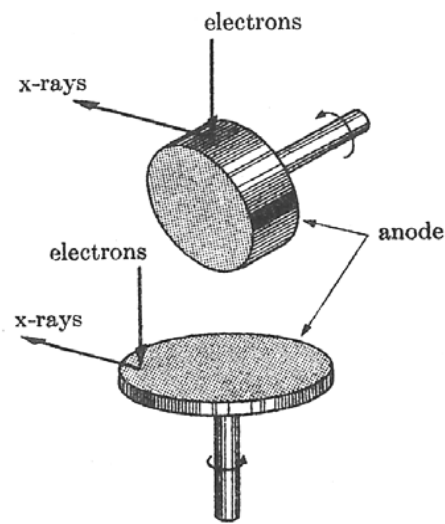
## (二) 粉末X射线衍射仪

### 一. X射线管:

#### (1). 密封式管

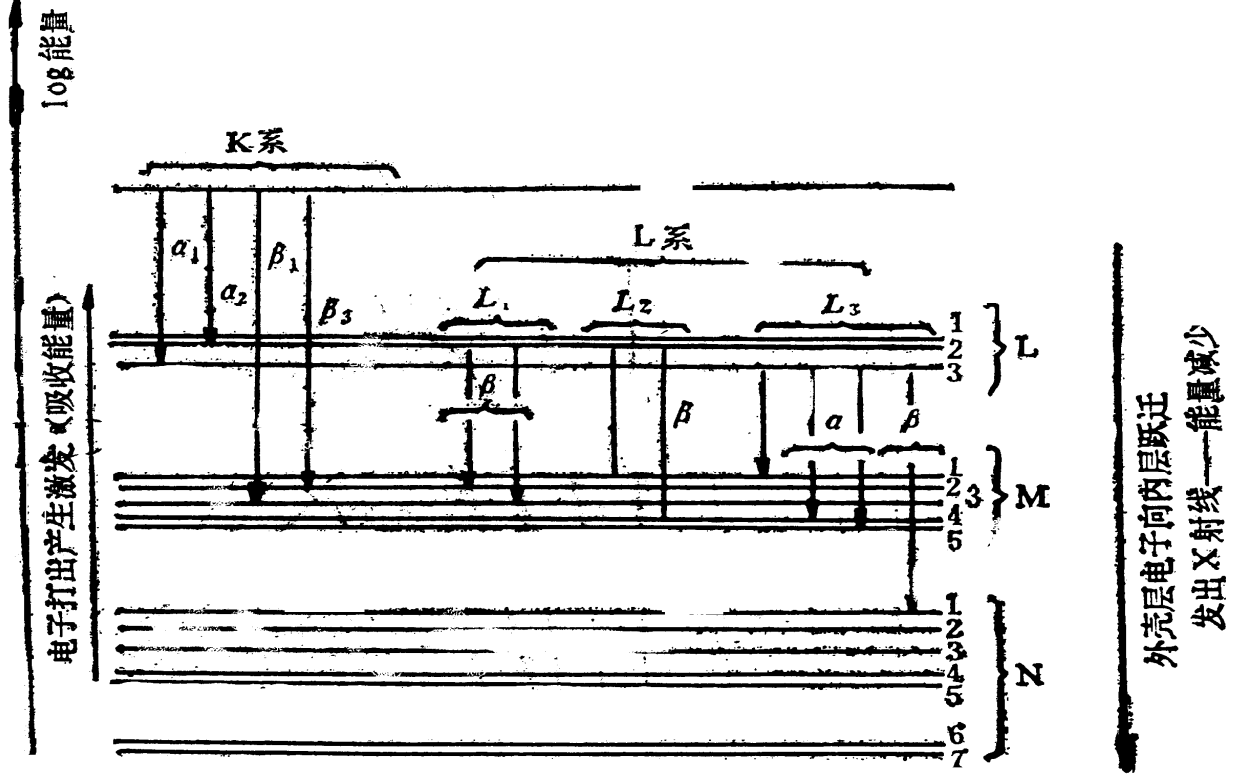


#### (2). 转靶式管



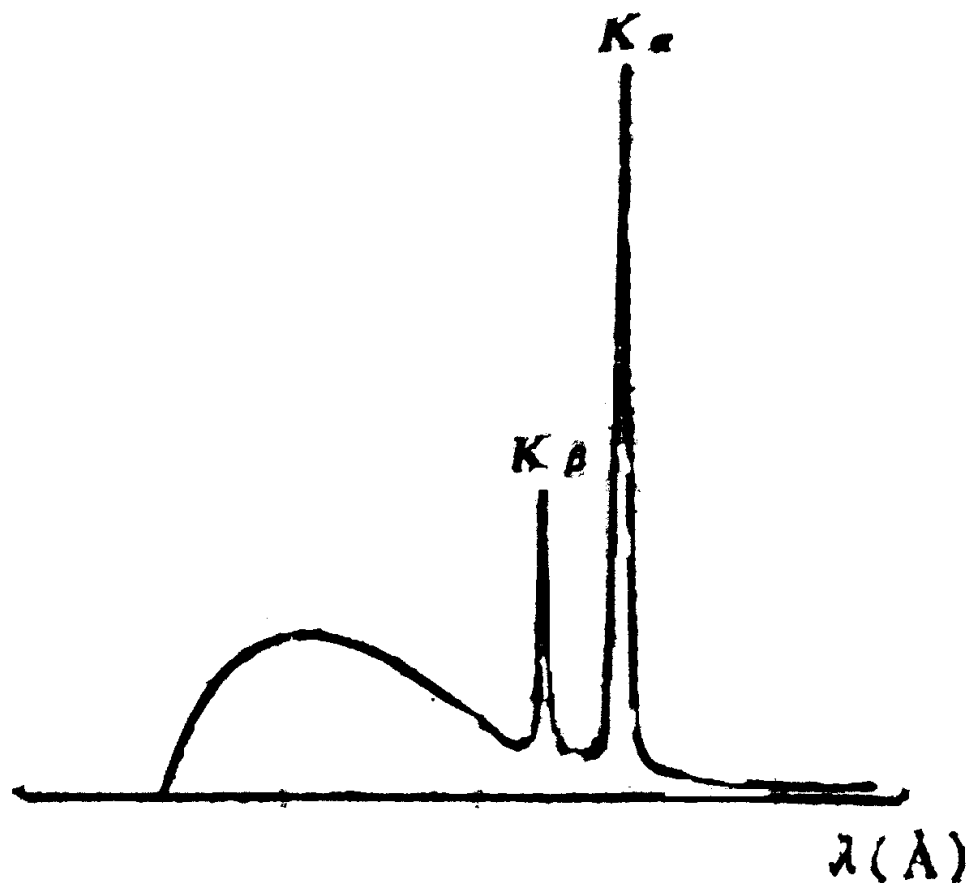
Schematic drawings of two types of rotating anode for high-power x-ray tubes.

# 特征X射线谱：

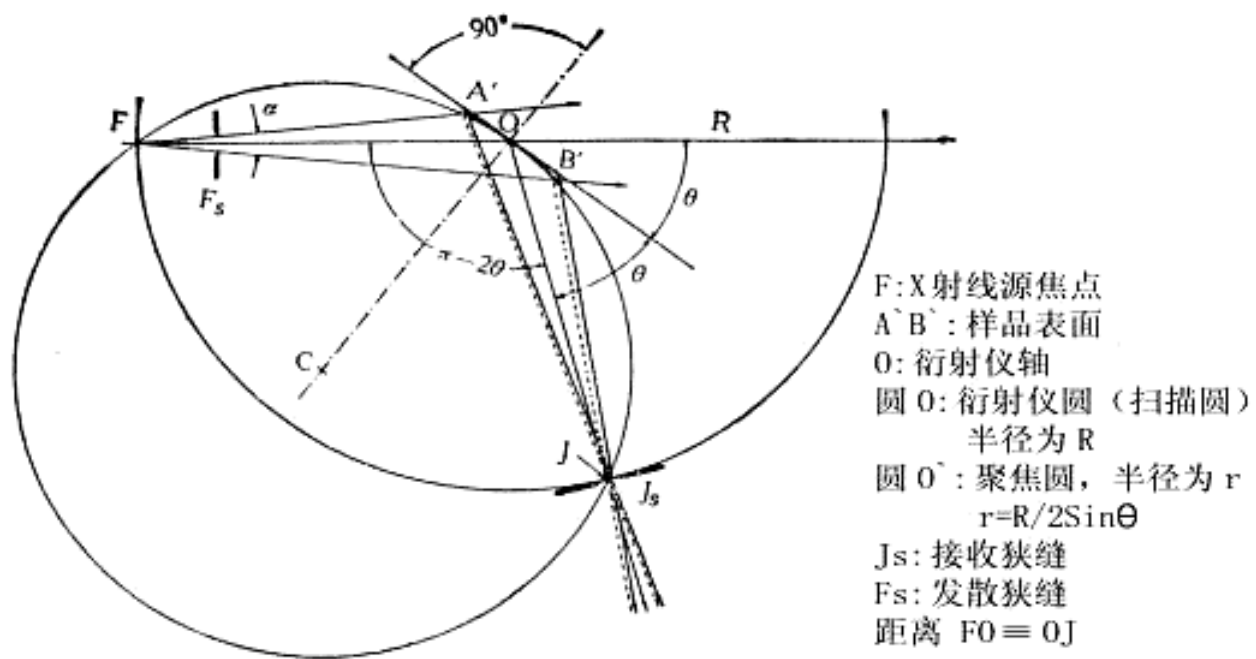


## 连续X射线谱：

当高能电子与靶上原子碰撞时，高能电子突然受阻产生负加速度。按照经典电磁辐射理论，作加速带电粒子辐射电磁波，从而产生连续X射线。

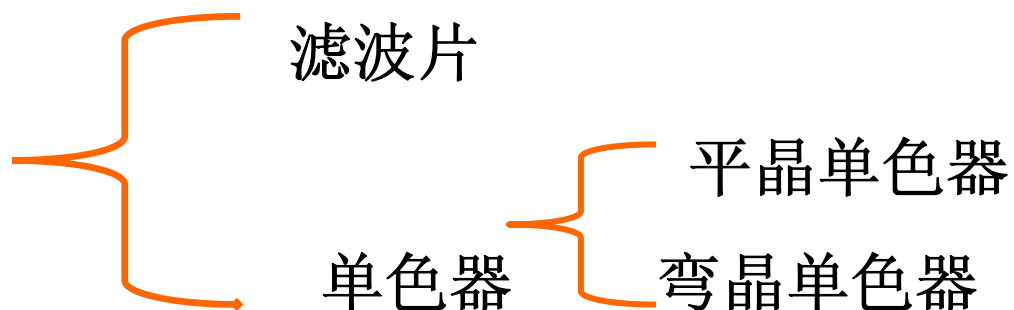


## 二. 测角系统:

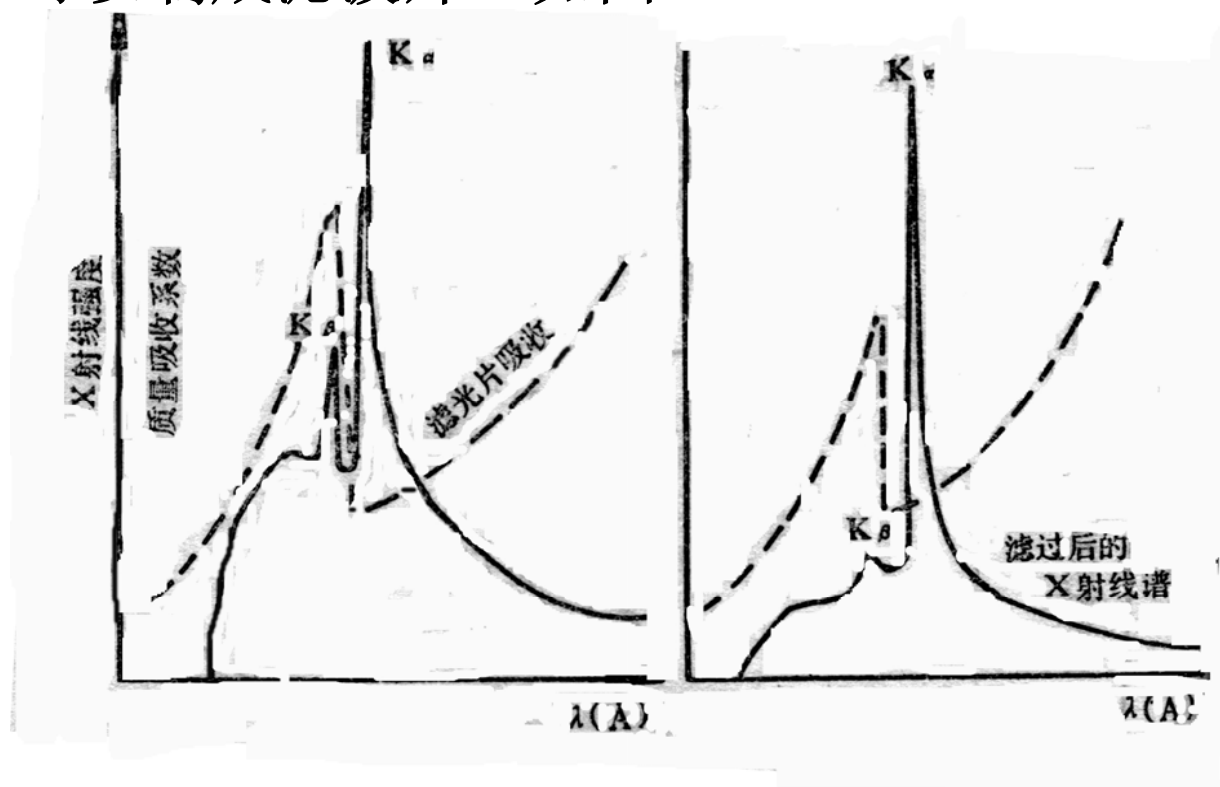


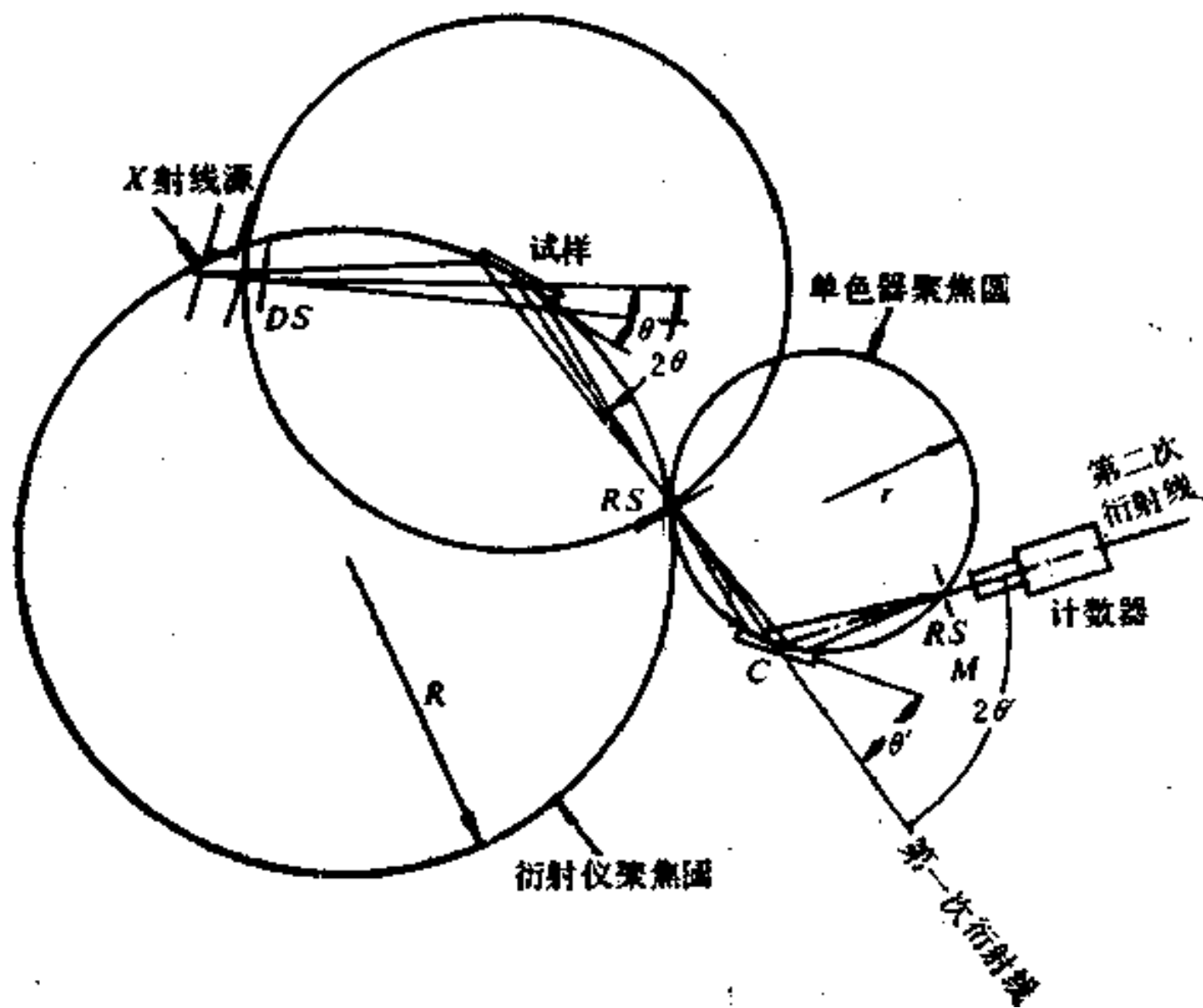
卧式测角仪  
立式测角仪

### 三 滤波装置:



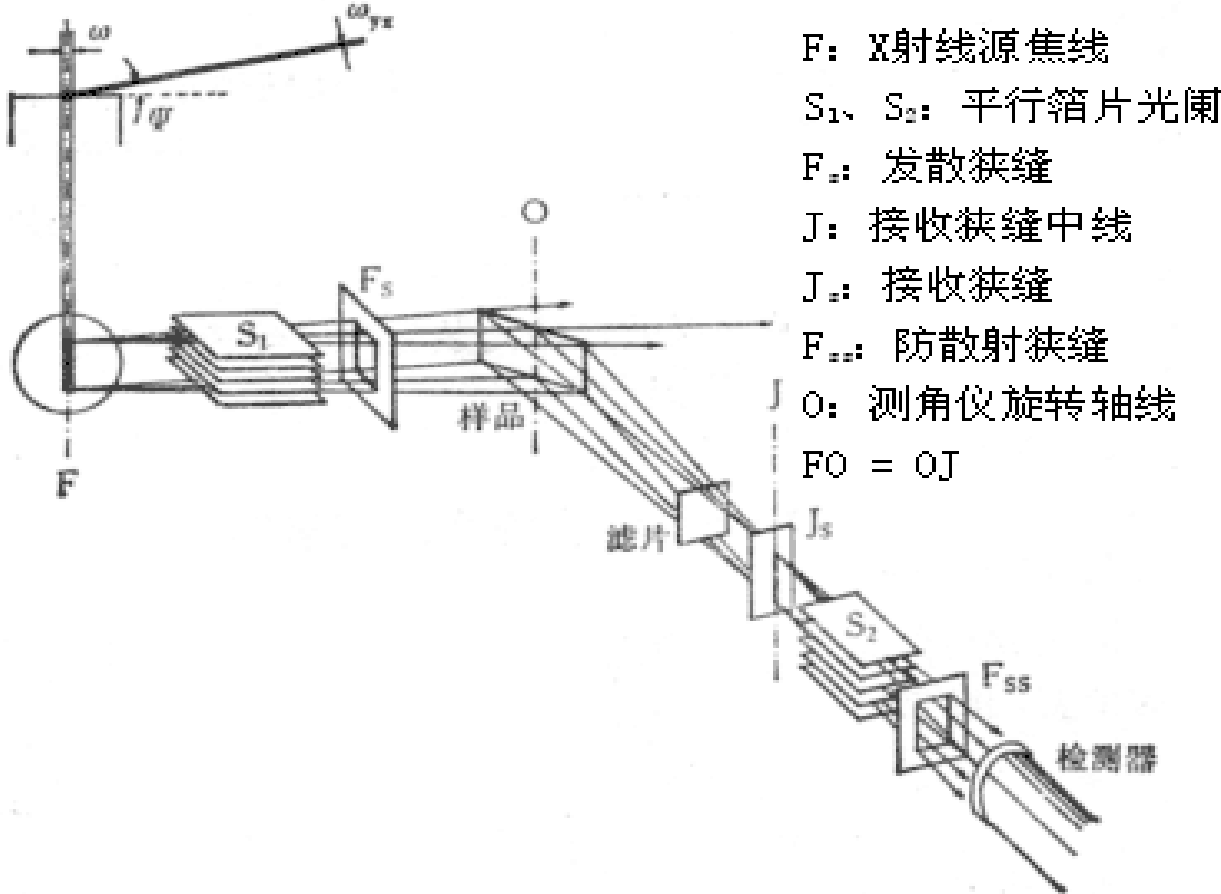
$K_{\beta}$  线的存在会给分析衍射花样带来困难, 需要滤掉 $K_{\beta}$ 。利用元素的吸收限, 可以制成滤波片。如图:







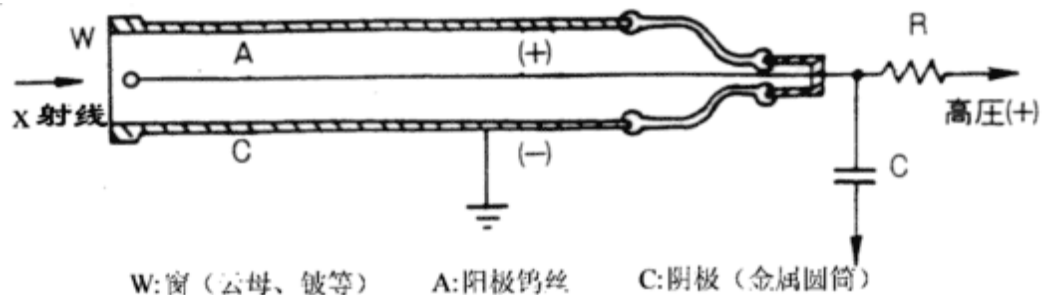
### 四.测角仪光路上狭缝系统:



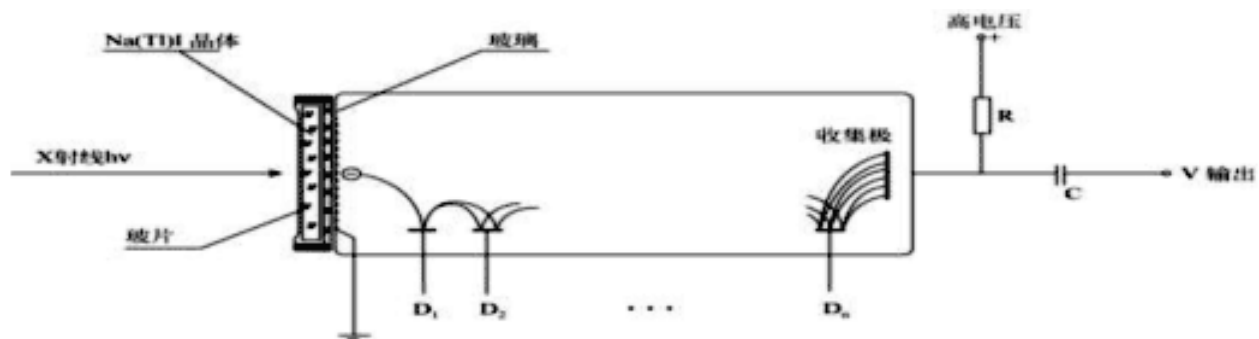
- F: X射线源焦线
- $S_1$ 、 $S_2$ : 平行箔片光阑
- $F_s$ : 发散狭缝
- J: 接收狭缝中线
- $J_s$ : 接收狭缝
- $F_{ss}$ : 防散射狭缝
- O: 测角仪旋转轴线
- $FO = OJ$

## 五 检测器

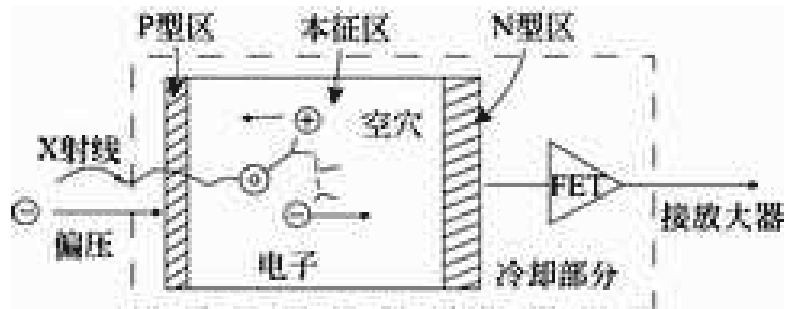
### (1) 正比计数管 (PC)



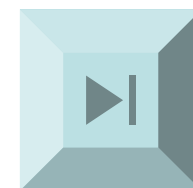
### (2) NaI(Tl)闪烁计数管(SC)



### (3) 固体检测器(SSD)



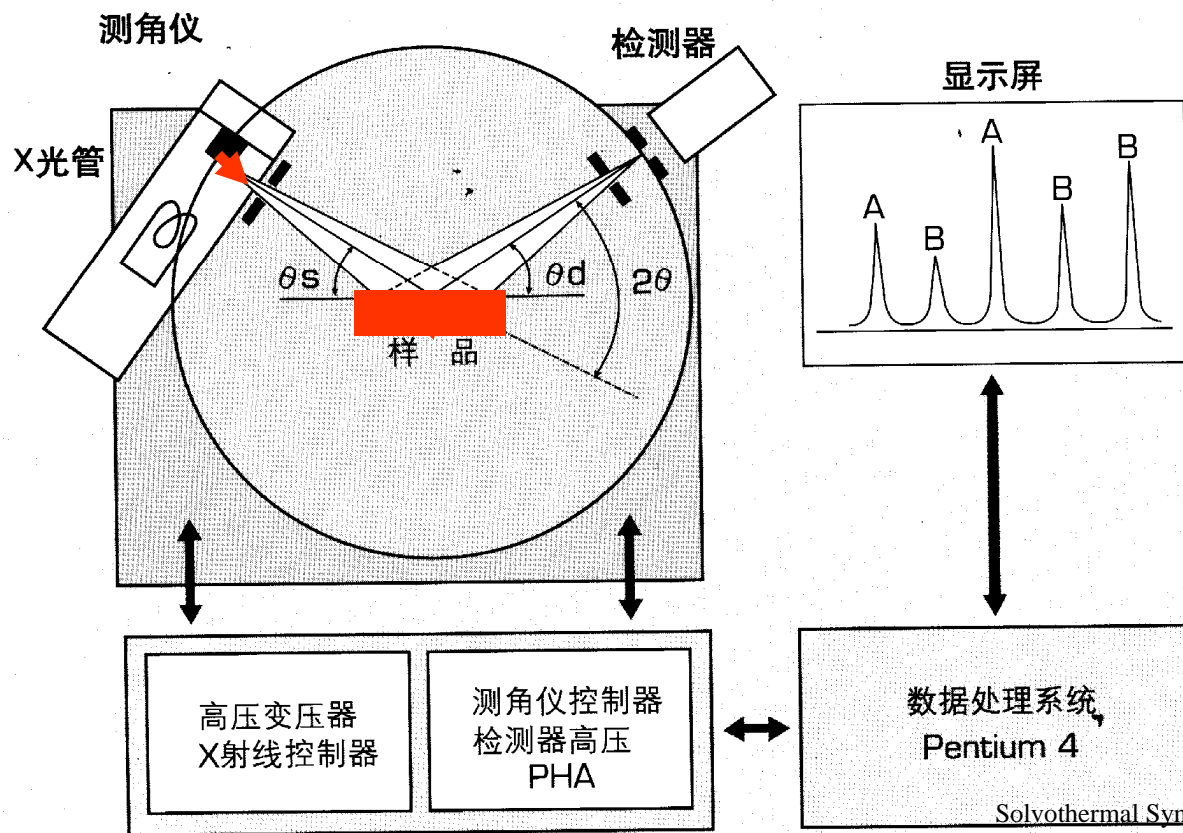
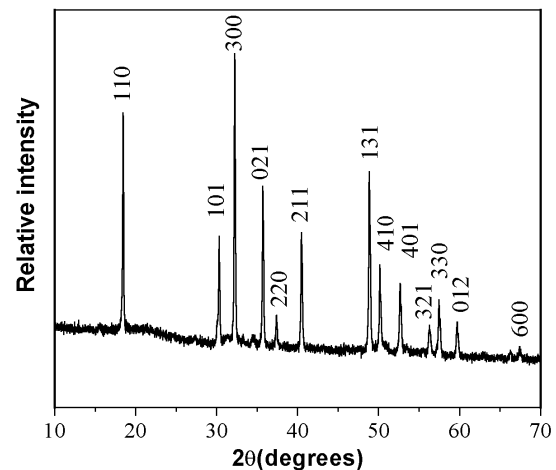
### (4) 超能探测器:

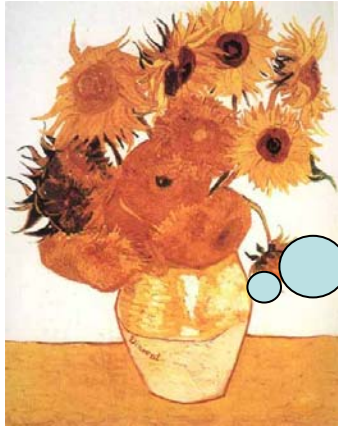


# X射线衍射的应用:

## 1. 物相定性分析

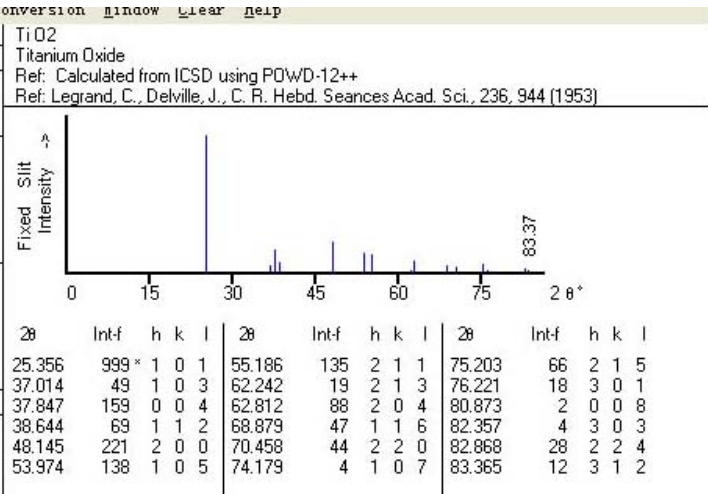
方向 (角度) ----- 方向



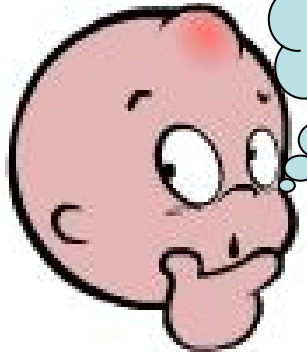


**TiO<sub>2</sub>**  
**金红石?**  
**锐钛矿?**

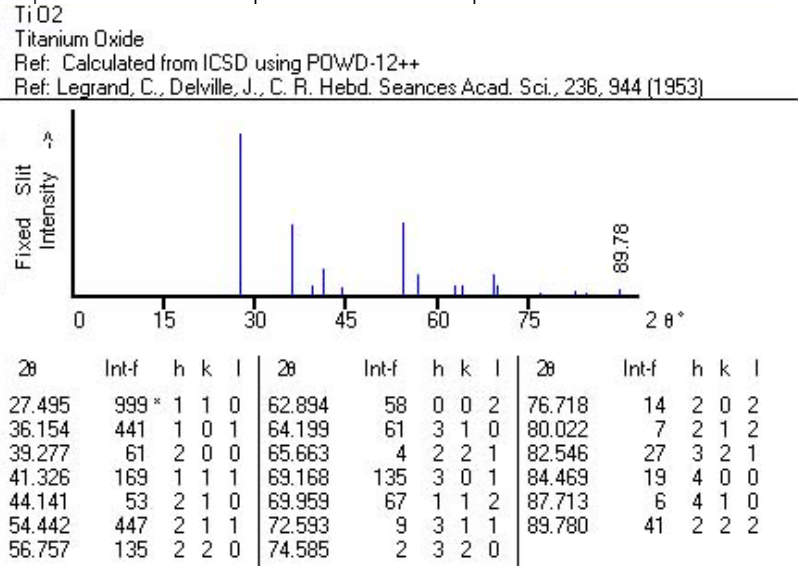
4921	Quality: C	
S Number:		
Molecular Weight:	79.90	
Volume[CD]:	135.54	
Dx:	3.915	
Dm:		
Sys: Tetragonal		
Lattice: Body-centered		
S.G.: I4 <sub>1</sub> /amd (141)		
Cell Parameters:		
3.777	b	c 9.501
	β	γ
I/cor: 5.04		
Rad: CuKα1		
Lambda: 1.54060		
Filter:		
d-sp: calculated		
ICSD #: 076173		
Mineral Name:		
Rutile, syn		

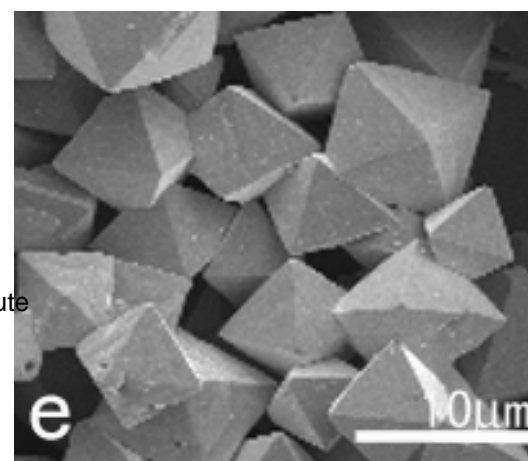
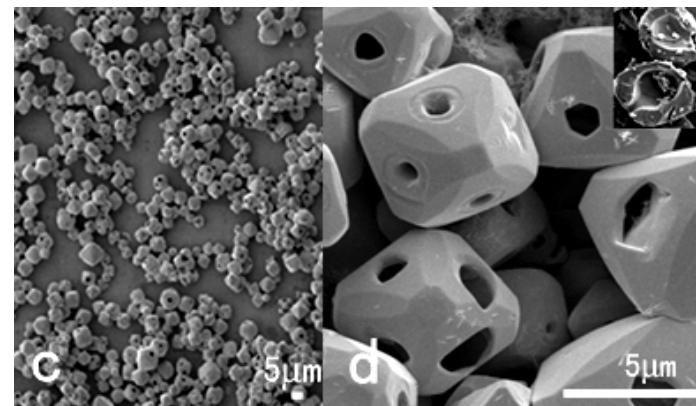
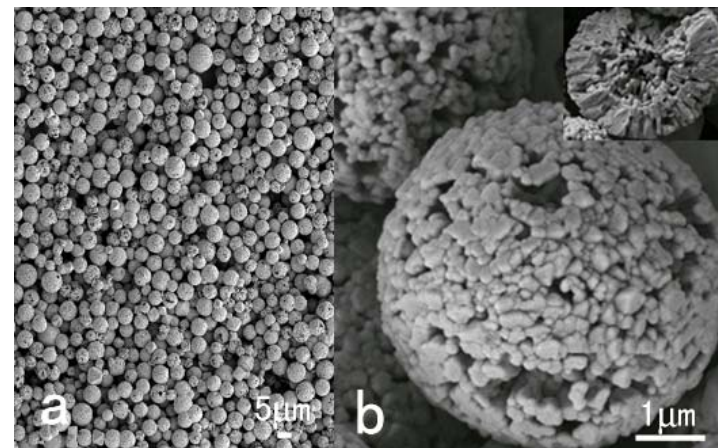
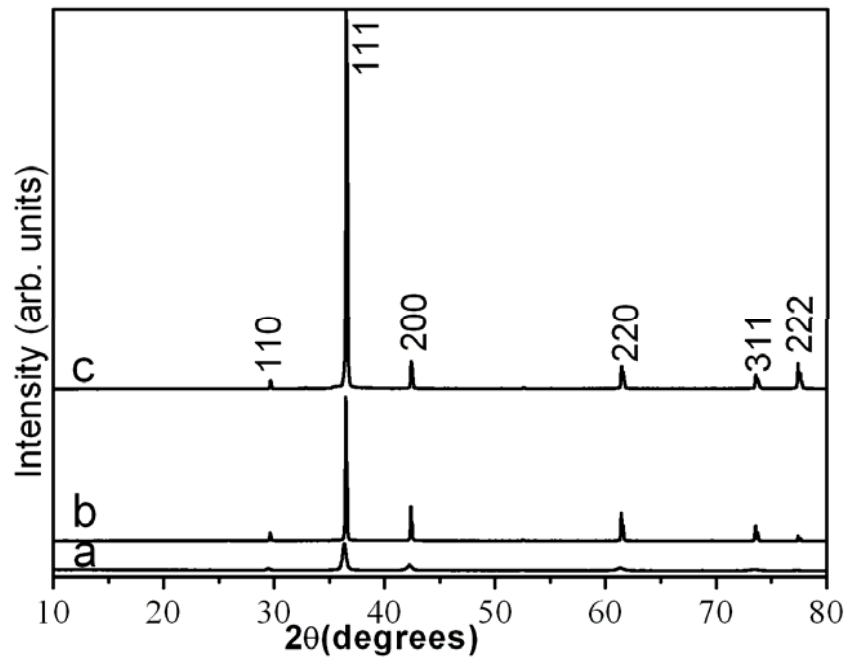


是真的，就发财了!



89-4920	Quality: C	
CAS Number:		
Molecular Weight:	79.90	
Volume[CD]:	62.05	
Dx:	4.276	
Dm:		
Sys: Tetragonal		
Lattice: Primitive		
S.G.: P4 <sub>2</sub> /mm (136)		
Cell Parameters:		
a 4.584	b	c 2.953
α	β	γ
I/cor: 3.49		
Rad: CuKα1		
Lambda: 1.54060		
Filter:		
d-sp: calculated		
ICSD #: 076172		
Mineral Name:		
Rutile, syn		





$$D_c = 0.89 \lambda / (B \cos \theta)$$

Controllable Synthesis of Cu<sub>2</sub>O Microcrystals via a Complexant-assisted Synthetic Route

Wanqun Zhang[a],[b], Kaibin Tang[a],[b], Shumei Dou[b] *Eu.J.I.C.*, 2009

## 2.物相定量分析

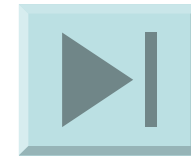
$$I = I_0 \cdot K \cdot |F|^2 \cdot V$$

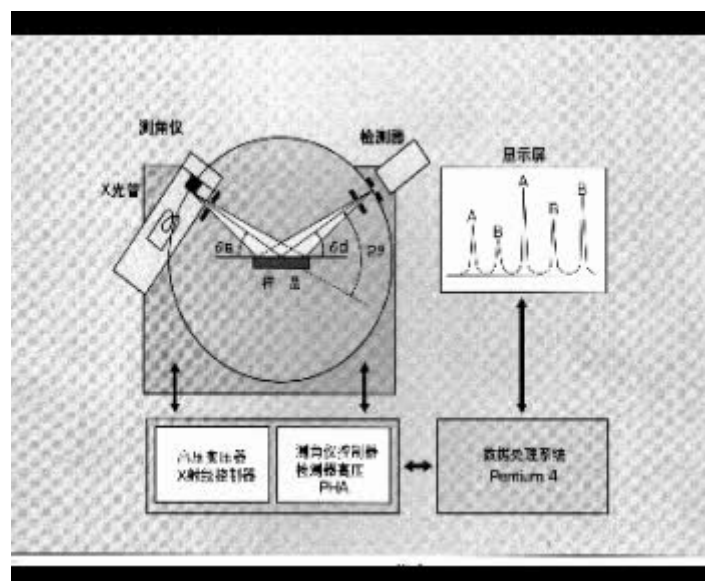
3.晶胞参数的精确测定

4. 结构精修

5.金属材料中宏观应力的测量

6 测定有关的晶体性质数据







# 样品制备



样品扫描