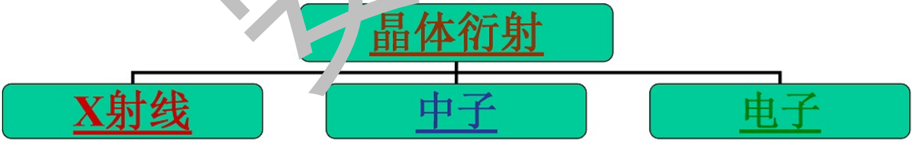
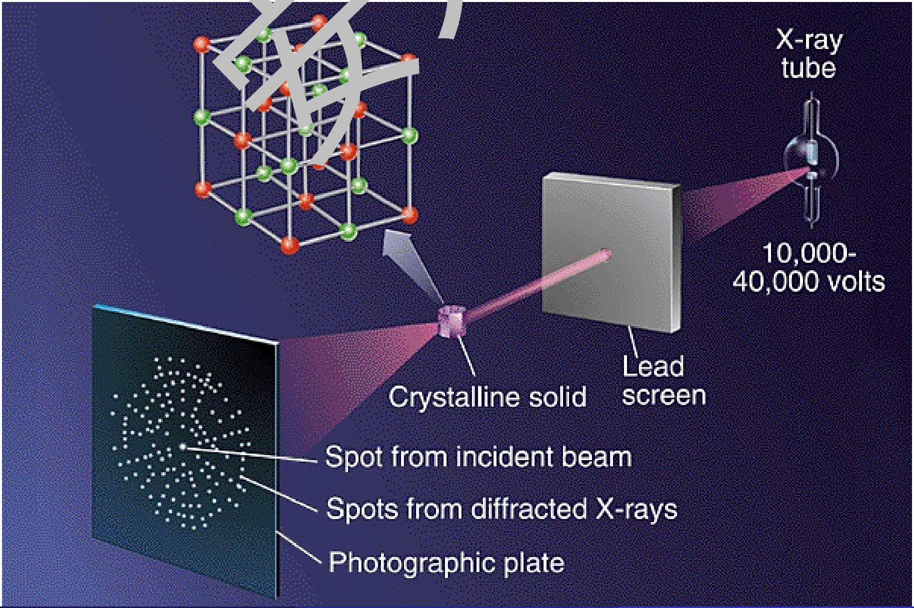
§1-4 晶体衍射和倒格子

晶体衍射



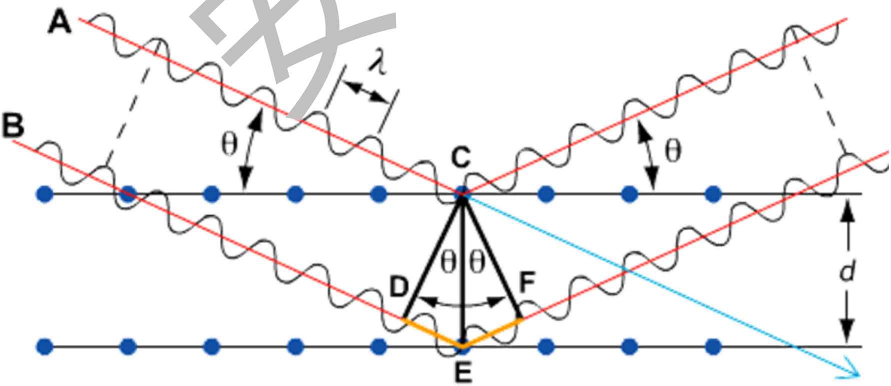
X射线和晶体的相互作用，是由于原子中电子的散射；
中子主要是受原子核的散射，轻的原子，例如氢、碳对于中子的散射也很强，所以常用来决定H、C在晶体中的位置。此外，中子还具有磁矩，尤其适合研究磁性物质的结构；
电子波和晶格的作用是由于晶格的电场，即电子波不仅受到电子的散射，并且也受到原子核的散射，所以散射很大，透射力很弱。电子束衍射主要用在薄膜研究上。

晶体衍射



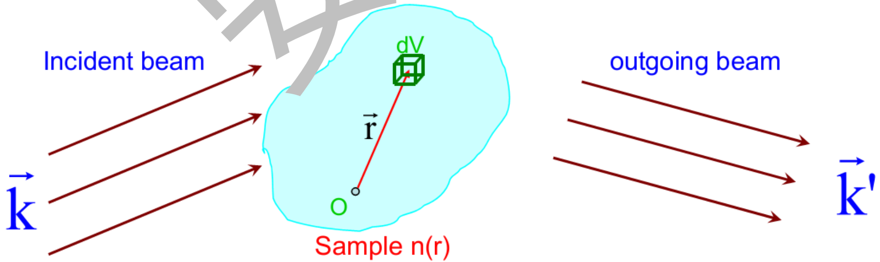
X-ray tube
10,000-40,000 volts
Lead screen
Crystalline solid
Spot from incident beam
Spots from diffracted X-rays
Photographic plate

布拉格（Bragg）反射条件



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

成立条件:$\lambda \leq 2d$

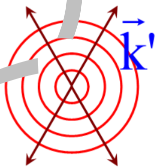


$n(\vec{r}) \equiv$ 电子密度

入射平面波

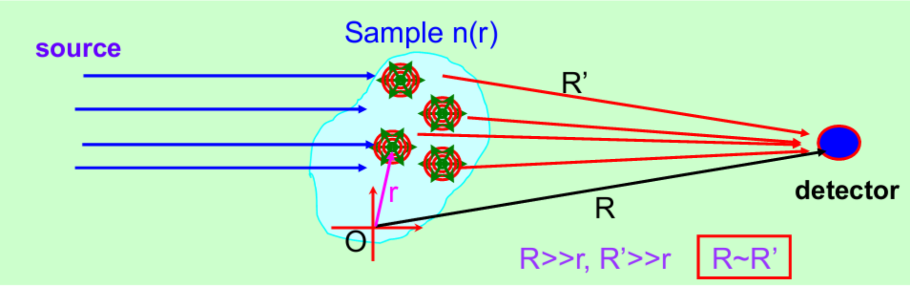
$$E_i = E_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

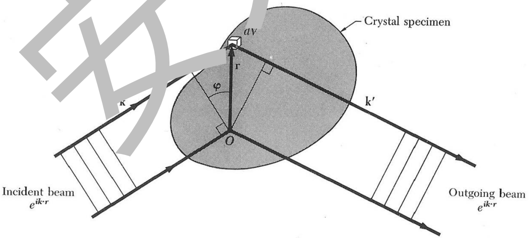
电磁波的散射



球面波：

$$E_s^r(R') \propto n(\vec{r})E_0 \frac{e^{i(\vec{k'}\cdot\vec{R'}-\omega' t)}}{R'}$$





相移因子：$\Delta\varphi = \vec{k}\cdot\vec{r} + (-\vec{k'}\cdot\vec{r}) = -(\vec{k'}-\vec{k})\cdot\vec{r} \equiv -\Delta\vec{k}\cdot\vec{r} = -\Delta\vec{k}\cdot(\vec{R'}-\vec{R})$

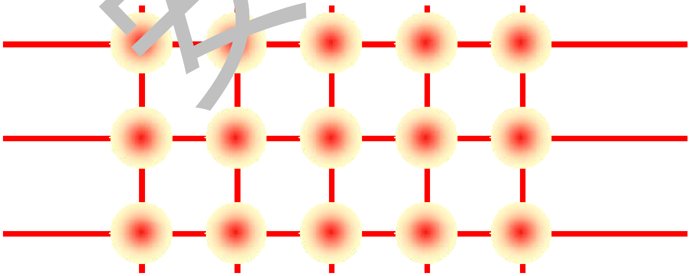
对于弹性散射$|\vec{k'}| = |\vec{k}|$

$$E_s^r(R') \propto n(\vec{r})E_0\frac{e^{i(\vec{k'}\cdot\vec{R'}-\omega' t)}}{R'} \propto n(\vec{r})\exp(-i\Delta\vec{k}\cdot\vec{r})E_0\frac{\exp i(\vec{k}\cdot\vec{R}-\omega t)}{R}$$

总散射振幅

$$E_s(\vec{R}) \propto E_0\frac{\exp i(\vec{k}\cdot\vec{R}-\omega t)}{R}\int_{crystal} n(\vec{r})\exp(-i\Delta\vec{k}\cdot\vec{r})\,dV$$

晶体中的电子密度



由于晶体的周期性，$n(\vec{r}) = n(\vec{r} + \mathbf{R})$，其中，$\mathbf{R} = l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3$
将$n(\vec{r})$做傅里叶展开

$$n(\vec{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp\left(i\mathbf{G} \cdot \vec{r}\right)$$

对于晶体中的物理量，例如静电势能、电子密度等，均存在晶体的周期性，即

$$V(\vec{r}) = V(\vec{r} + \mathbf{R})$$

$$V(\vec{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp\left(i\mathbf{G} \cdot \vec{r}\right)$$

其中

$$V_{\mathbf{G}} = V_c^{-1} \int_{\text{原胞}} dV\, V(\vec{r}) \exp(-i\mathbf{G} \cdot \vec{r})$$

$$V(\vec{r} + \mathbf{R}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp\left[i\mathbf{G} \cdot (\vec{r} + \mathbf{R})\right] = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp\left(i\mathbf{G} \cdot \vec{r}\right) \exp\left(i\mathbf{G} \cdot \mathbf{R}\right) = V(\vec{r})$$

则$\exp\left(i\mathbf{G} \cdot \mathbf{R}\right) = 1$，即$\mathbf{G} \cdot \mathbf{R} = 2n\pi$，对于一定的晶体结构**R**，一系列**G**就构成了对应于**R**的倒格子空间，称**R**构成正格子空间。**R**称为正格子矢量，**G**称为倒格子矢量。

倒格矢的选取

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot[\vec{a}_2\times\vec{a}_3]};\ \vec{b}_2 = 2\pi\frac{\vec{a}_3\times\vec{a}_1}{\vec{a}_1\cdot[\vec{a}_2\times\vec{a}_3]};\ \vec{b}_3 = 2\pi\frac{\vec{a}_1\times\vec{a}_2}{\vec{a}_1\cdot[\vec{a}_2\times\vec{a}_3]}$$

请证明：

$$\vec{b}_i\cdot\vec{a}_j = 2\pi\delta_{ij}, \qquad \delta_{ij} = \begin{cases} 1 & i=j \\ 0 & i\neq j \end{cases}$$

$$\mathbf{G} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3, \qquad (n_{i=1,2,3}\text{为整数})$$

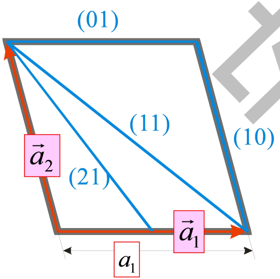
倒格子也是布拉伐格子。

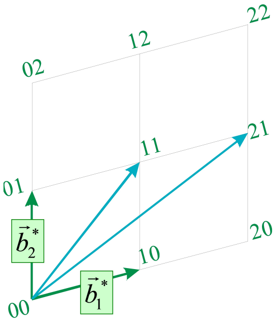
$$\exp(i\mathbf{G}\cdot\mathbf{R}) = \exp\left[i(n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3)\cdot(l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3)\right]$$

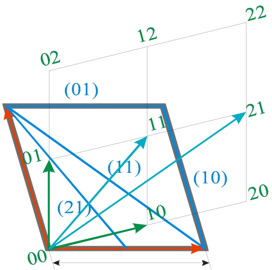
$$= \exp\left[i2\pi(n_1l_1 + n_2l_2 + n_3l_3)\right] = 1$$

倒格子基矢的量纲为[长度]$^{-1}$,为波矢的量纲。倒格子空间也可称为动量空间、傅里叶空间。

倒格矢的选取


(01)
(11)
(10)
(21)
$\vec{a}_2$
$\vec{a}_1$
a_1


22
12
02
21
11
01
20
10
00
$\vec{b}_2^*$
$\vec{b}_1^*$


22
12
02
(01)
21
11
01
(11)
(10)
(21)
20
10
00

1、倒格子原胞体积反比于正格子原胞体积

$$\Omega^* = \vec{b}_1 \cdot [\vec{b}_2 \times \vec{b}_3] = \frac{(2\pi)^3}{\Omega^3}[\vec{a}_2 \times \vec{a}_3] \cdot [\vec{a}_3 \times \vec{a}_1] \times [\vec{a}_1 \times \vec{a}_2]$$

应用$\vec{A} \times (\vec{B} \times \vec{C}) = (\vec{A} \cdot \vec{C})\vec{B} - (\vec{A} \cdot \vec{B})\vec{C}$

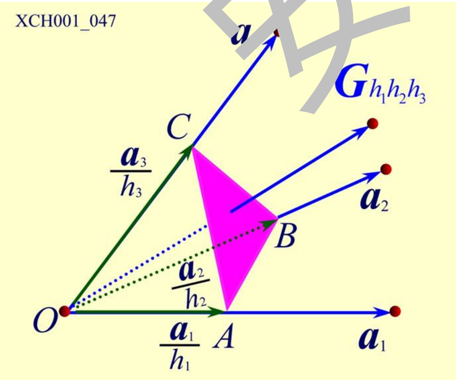
$$[\vec{a}_3 \times \vec{a}_1] \times [\vec{a}_1 \times \vec{a}_2] = \{[\vec{a}_3 \times \vec{a}_1] \cdot \vec{a}_2\}\vec{a}_1 - \{[\vec{a}_3 \times \vec{a}_1] \cdot \vec{a}_1\}\vec{a}_2 = \Omega\vec{a}_1 - 0\vec{a}_2$$

$$\therefore \Omega^* = \frac{(2\pi)^3}{\Omega^3}[\vec{a}_2 \times \vec{a}_3] \cdot \Omega\vec{a}_1 = \frac{(2\pi)^3}{\Omega}$$

一般的

$$\Omega^* = \frac{(2\pi)^d}{a^d}$$

2、$\mathbf{G}_{h_1h_2h_3} \perp (h_1h_2h_3)$



$$\vec{CA} = \vec{OA} - \vec{OC} = \frac{\vec{a}_1}{h_1} - \frac{\vec{a}_3}{h_3}$$

$$\vec{CB} = \vec{OB} - \vec{OC} = \frac{\vec{a}_2}{h_2} - \frac{\vec{a}_3}{h_3}$$

$$\therefore \mathbf{G}_{h_1h_2h_3} \cdot \vec{CA}$$

$$= (h_1\vec{b}_1 + h_2\vec{b}_2 + h_3\vec{b}_3) \cdot (\frac{\vec{a}_1}{h_1} - \frac{\vec{a}_3}{h_3})$$

$$= \frac{h_1\vec{b}_1 \cdot \vec{a}_1}{h_1} - \frac{h_3\vec{b}_3 \cdot \vec{a}_3}{h_3} = 0$$

同理，$\mathbf{G}_{h_1h_2h_3} \cdot \vec{CB} = 0$，因此$\mathbf{G}_{h_1h_2h_3} \perp (h_1h_2h_3)$。

倒格子与正格子间的关系

3、$(h_1h_2h_3)$面间距$d = \frac{2\pi}{|\mathbf{G}_{h_1h_2h_3}|}$

晶面方程$\mathbf{G}\cdot(\vec{x}-\mathbf{R}) = 0$

$$\Rightarrow \mathbf{G}\cdot\vec{x} = \mathbf{G}\cdot\mathbf{R} = 2\pi n$$

$$\Rightarrow |\mathbf{G}||\vec{x}|\cos\theta = 2\pi n$$

$$\Rightarrow |\vec{x}|\cos\theta = \frac{2\pi n}{|\mathbf{G}|}$$

$$\Rightarrow d = \frac{2\pi}{|\mathbf{G}|} = \frac{2\pi}{|h_1\vec{b}_1 + h_2\vec{b}_2 + h_3\vec{b}_3|}$$

$$E_s(\vec{R}) \propto E_0 \frac{\exp i(\vec{k}\cdot\vec{R} - \omega t)}{R} \int n(\vec{r}) \exp\left(-i\Delta\vec{k}\cdot\vec{r}\right) dV \equiv E_i \cdot F$$

$$n(\vec{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp\left(i\mathbf{G}\cdot\vec{r}\right)$$

$$\Rightarrow F = \sum_{\mathbf{G}} n_{\mathbf{G}} \int \exp\left[i(\mathbf{G} - \Delta\vec{k})\cdot\vec{r}\right] dV$$

$$\therefore F = \begin{cases} V n_{\mathbf{G}} & \mathbf{G} = \Delta\vec{k} \\ \sim 0 & \mathbf{G} \neq \Delta\vec{k} \end{cases}$$

即，$\mathbf{G} = \Delta\vec{k}$时才有衍射x射线出射。

衍射条件：$\Delta\vec{k} = \mathbf{G}$，也即$\vec{k}' = \vec{k} + \mathbf{G}$

对于弹性散射，光子能量$\hbar\omega$散射前后不变，则$\omega' = ck' = \omega = ck$，因此散射前后$k' = k$，波矢只改变方向。

$$\vec{k}' = \vec{k} + \mathbf{G} \Rightarrow (\vec{k} + \mathbf{G})^2 = k^2 \Rightarrow 2\vec{k} \cdot \mathbf{G} + G^2 = 0$$

$\mathbf{G}$是倒格子矢量，则$-\mathbf{G}$也是倒格子矢量，将$-\mathbf{G}$代入上式可得

$$2\vec{k} \cdot \mathbf{G} = G^2$$

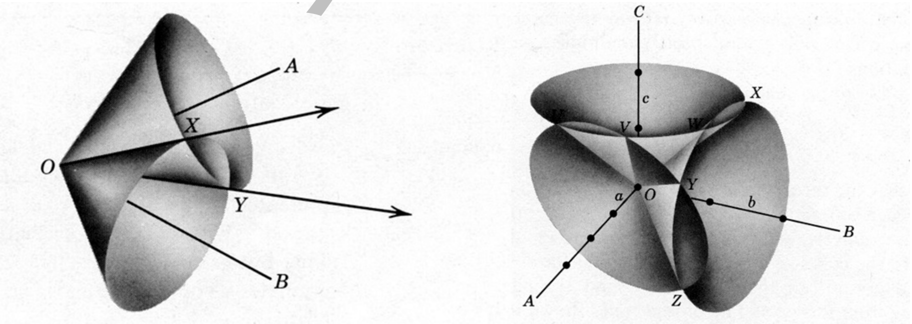
与布拉格定律的关系：

$$2kG\cos\varphi = G^2 \Rightarrow 2k\cos\varphi = G$$

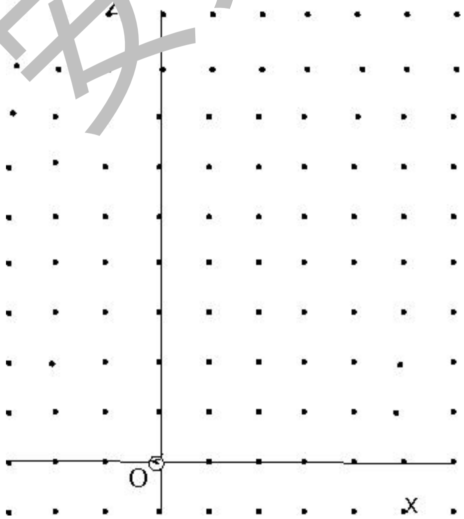
其中φ为$\vec{k}$与$\mathbf{G}$的夹角，因此$\cos\varphi = \sin\theta$，θ为$\vec{k}$与晶面$(h_1h_2h_3)$的夹角。
而$G = nG_{h_1h_2h_3} = n\frac{2\pi}{d}$，

$$\therefore 2\left(\frac{2\pi}{\lambda}\right)\sin\theta = n\frac{2\pi}{d} \Rightarrow 2d\sin\theta = n\lambda$$

$$\vec{a}_i \cdot \Delta\vec{k} = \vec{a}_i \cdot \mathbf{G} = 2\pi h_i, \qquad i = 1, 2, 3$$



埃瓦尔德（Ewald）反射球



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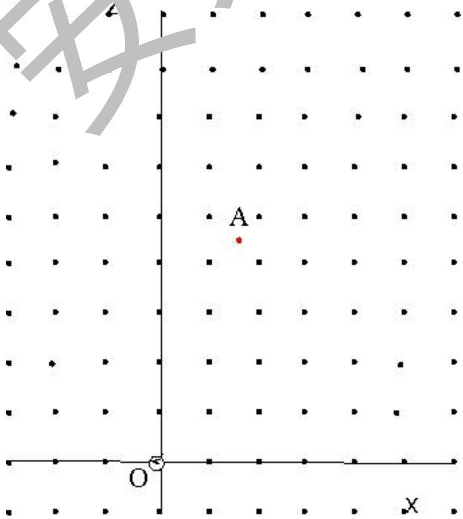

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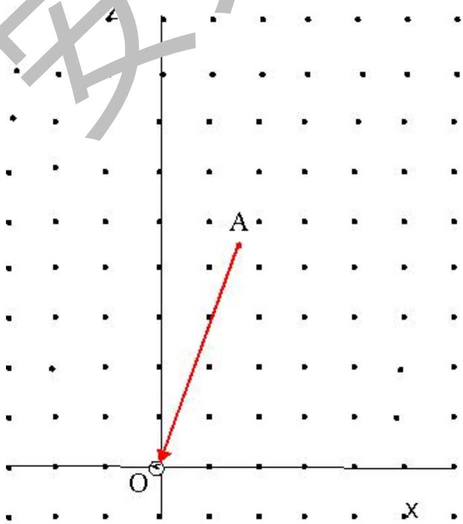

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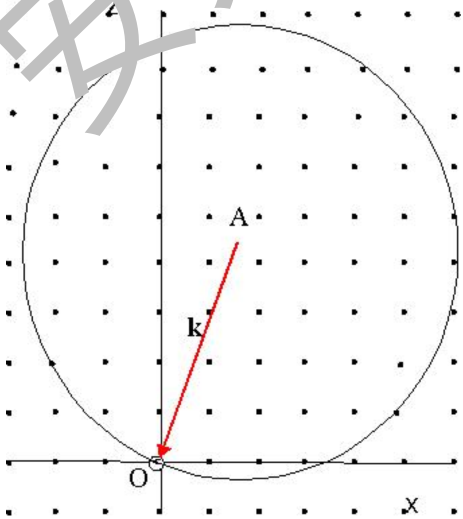

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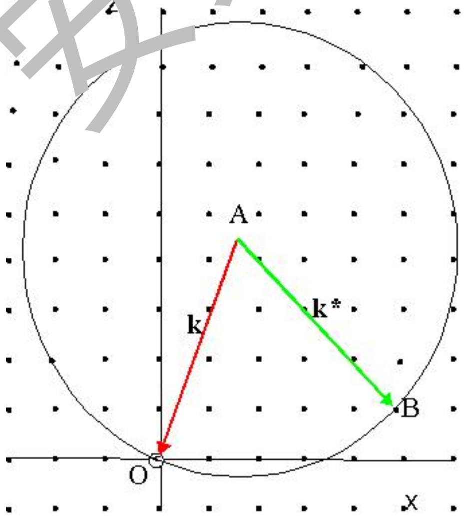

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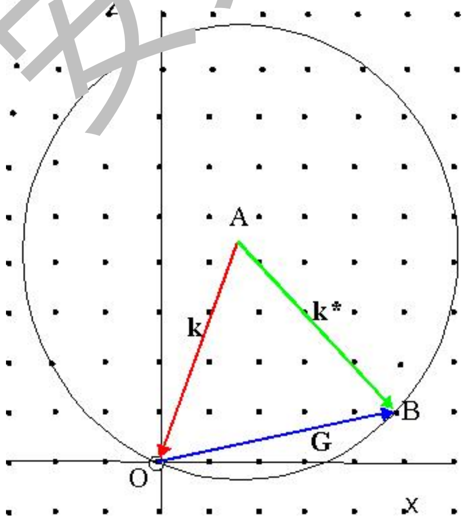
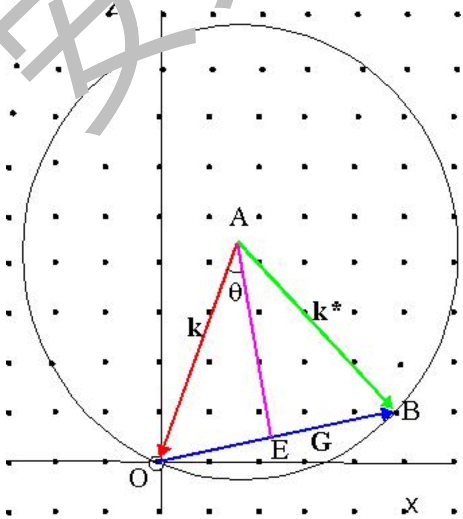
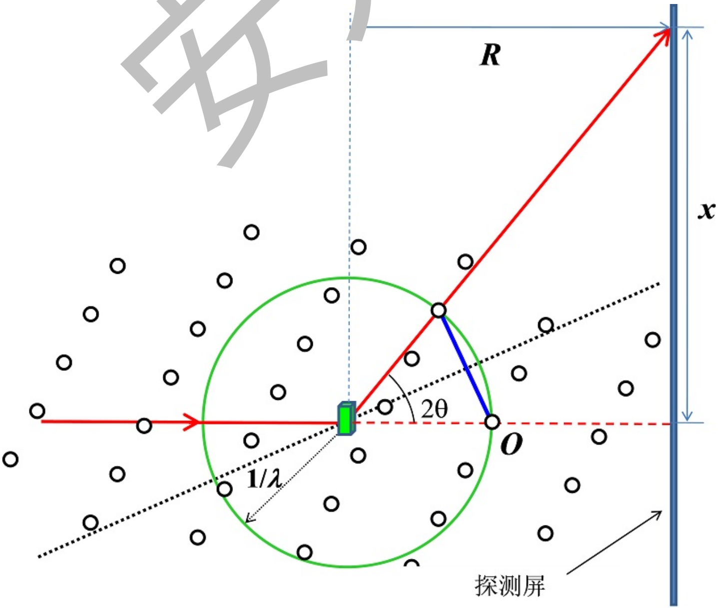
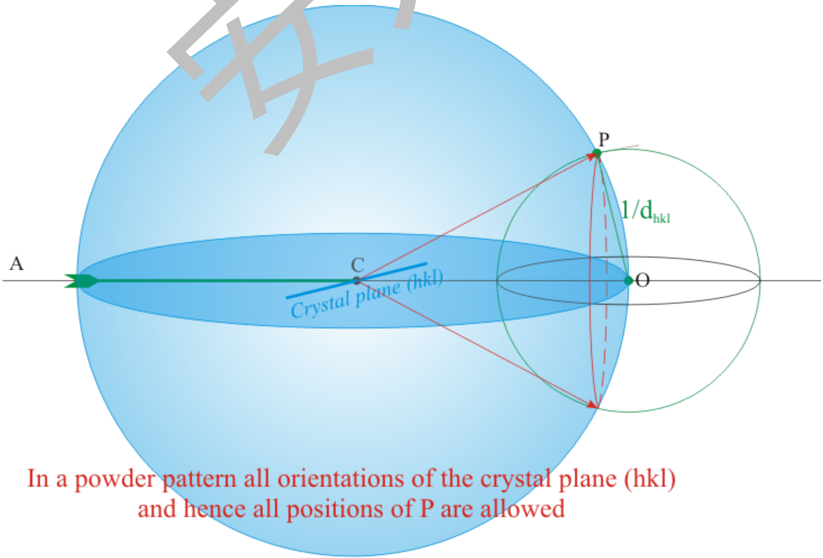


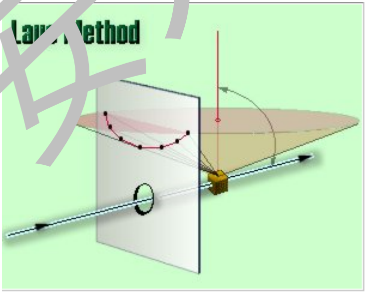

A
θ
k
k*
B
E
G
O
X

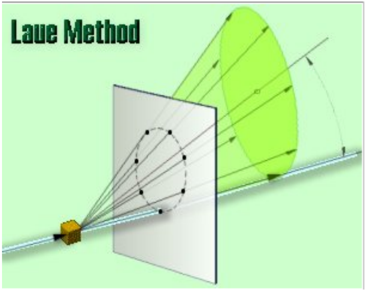
埃瓦尔德（Ewald）反射球




P
$1/d_{hkl}$
A
C
O
Crystal plane (hkl)
In a powder pattern all orientations of the crystal plane (hkl) and hence all positions of P are allowed

埃瓦尔德（Ewald）反射球





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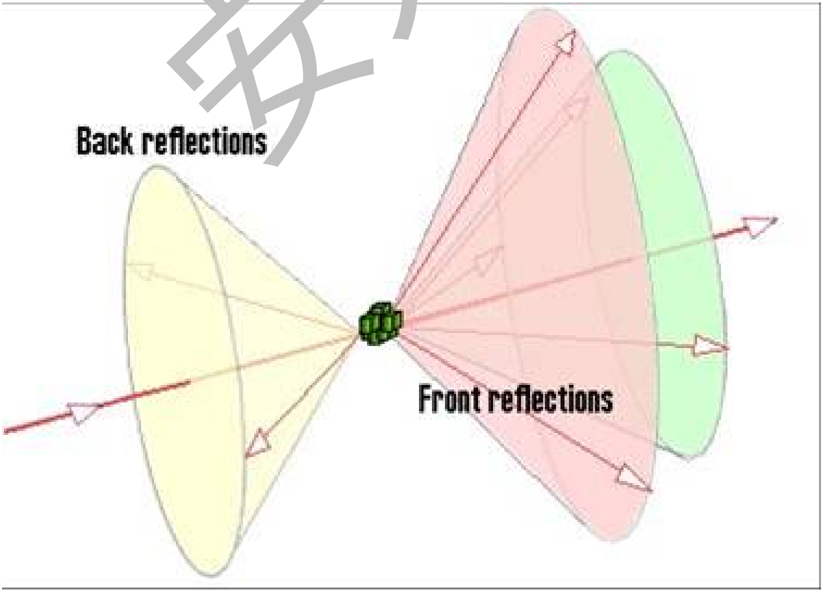

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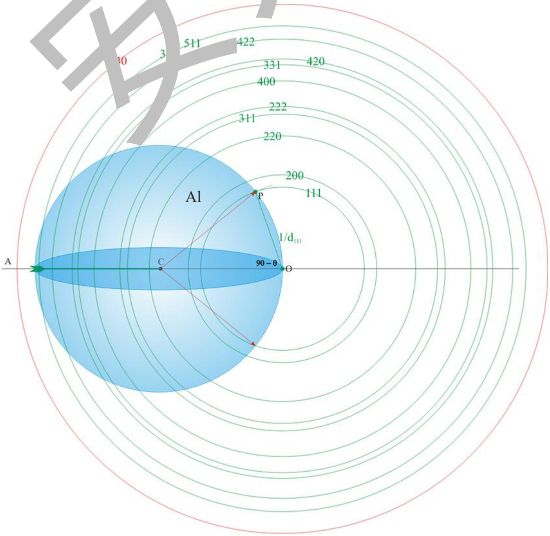

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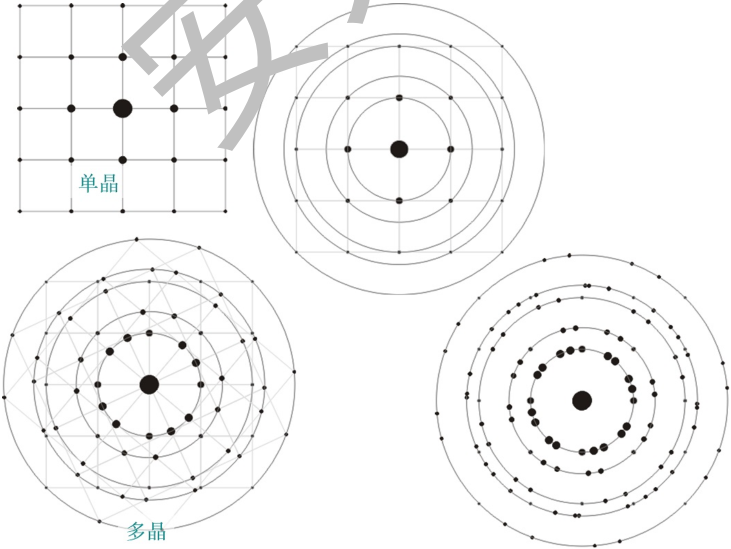
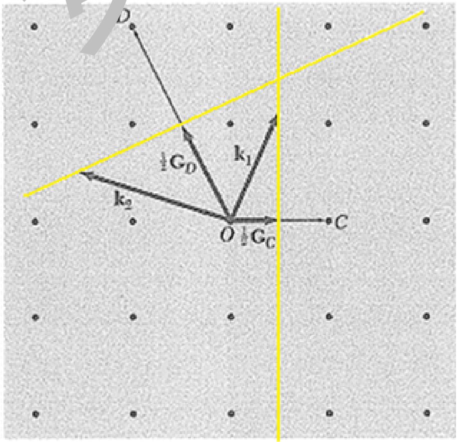


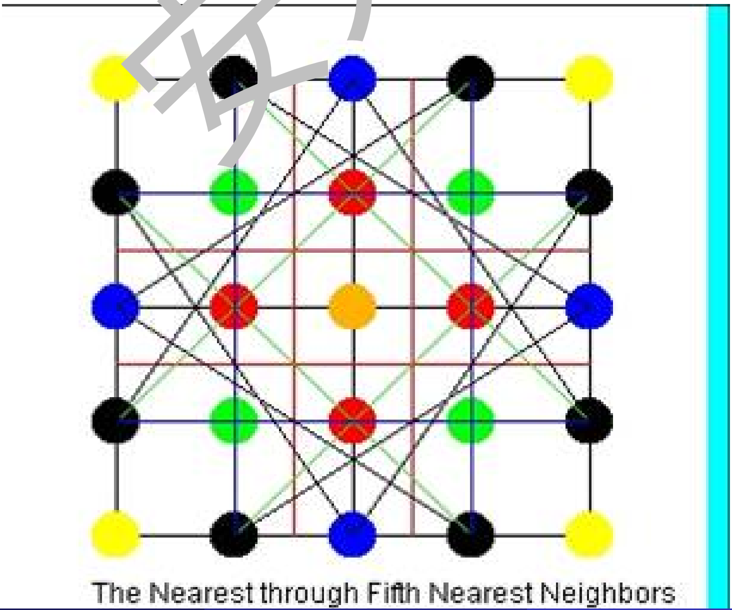
布里渊区（Brilloum Zone）

衍射条件 $2\vec{k}\cdot\mathbf{G} = G^2 \Rightarrow \vec{k}\cdot\frac{1}{2}\mathbf{G} = \left(\frac{G}{2}\right)^2 \Rightarrow k\cos\theta = \frac{G}{2}$

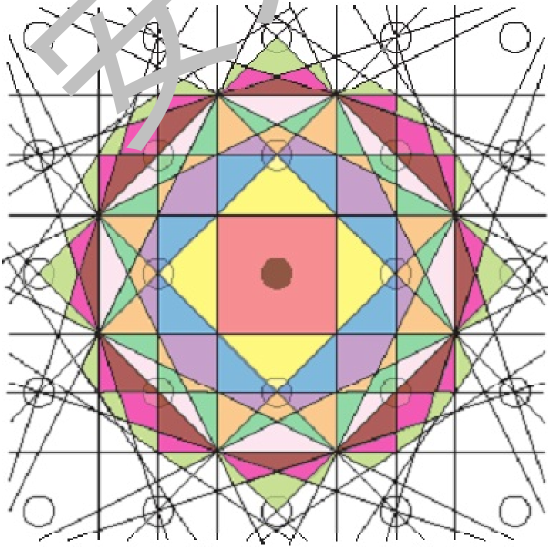


中垂面（图中黄色线）称为布拉格面

布里渊区（Brilloum Zone）



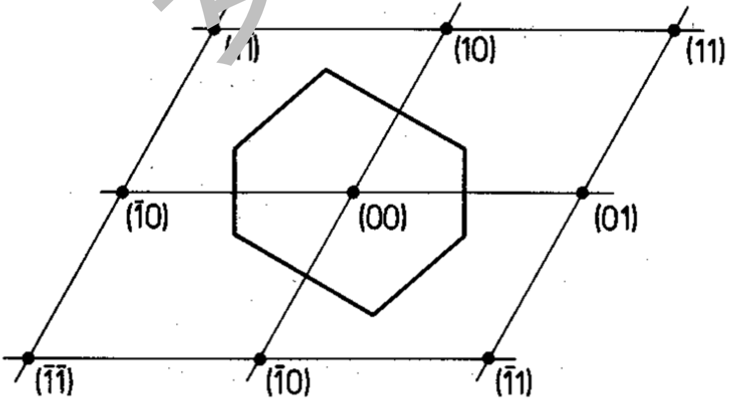
布里渊区（Brilloum Zone）

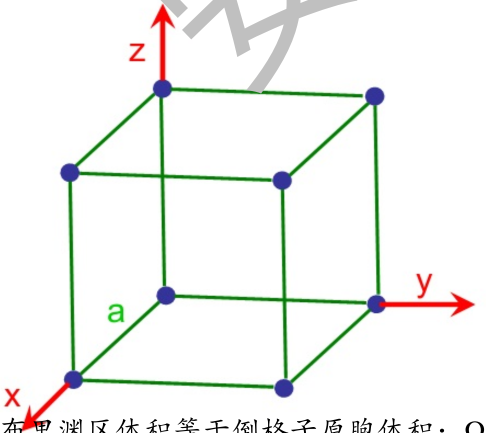


等价条件

- Bragg law $n\lambda = 2d \sin\theta$
- Diffraction condition $G^2 = 2\vec{k}\cdot\vec{G}$ $(\Delta\vec{k} = \vec{k}' - \vec{k} = \vec{G})$
- Laue equations $\vec{a}_i \bullet \overrightarrow{\Delta k} = 2\pi\ v_i$
- Brillouin zone $k\cos\theta = \dfrac{G}{2}$ (k on BZ boundary)

倒格子空间的维格纳-塞茨原胞称为第一布里渊区或本征布里渊区。





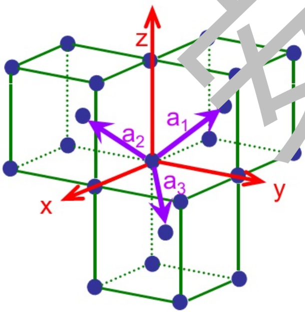
正格子基矢：$\vec{a}_1 = a\vec{i}$; $\vec{a}_2 = a\vec{j}$; $\vec{a}_3 = a\vec{k}$,
原胞体积为$\Omega = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3$
倒格子基矢：

$$\vec{b}_1 = \frac{2\pi}{a}\vec{i};\ \vec{b}_2 = \frac{2\pi}{a}\vec{j};\ \vec{b}_3 = \frac{2\pi}{a}\vec{k}$$

可见倒格子是简立方结构，倒格子的维格纳-赛茨原胞即简立方的第一布里渊区为简立方。

第一布里渊区体积等于倒格子原胞体积：$\Omega^* = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \left(\frac{2\pi}{a}\right)^3$

体心立方（BCC）的第一布里渊区



正格子基矢：

$$\vec{a}_1 = \frac{a}{2}(\vec{j} + \vec{k} - \vec{i})$$

$$\vec{a}_2 = \frac{a}{2}(\vec{k} + \vec{i} - \vec{j})$$

$$\vec{a}_3 = \frac{a}{2}(\vec{i} + \vec{j} - \vec{k})$$

原胞体积为$\Omega = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3/2$

倒格子基矢：

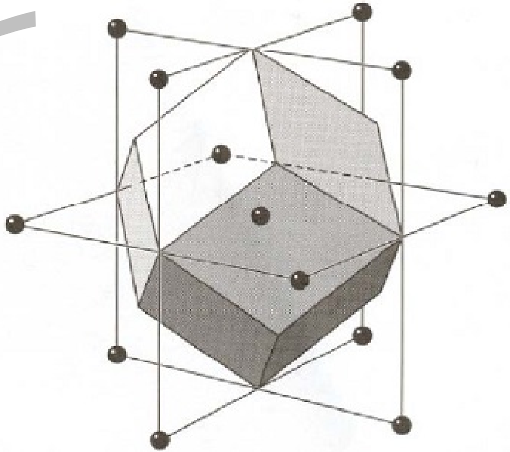
$$\vec{b}_1 = \frac{2\pi}{a}(\vec{j} + \vec{k})$$

$$\vec{b}_2 = \frac{2\pi}{a}(\vec{k} + \vec{i})$$

$$\vec{b}_3 = \frac{2\pi}{a}(\vec{i} + \vec{j})$$

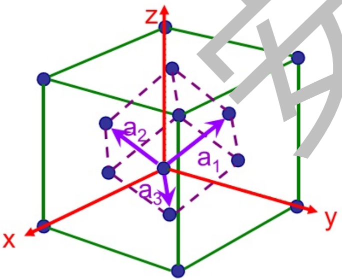
倒格子是面心立方结构，倒格子原胞体积：$\Omega^* = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{\Omega}$

体心立方（BCC）的第一布里渊区



第一布里渊区：正十二面体

面心立方（FCC）的第一布里渊区



正格子基矢：

$$\vec{a}_1 = \frac{a}{2}(\vec{j} + \vec{k})$$

$$\vec{a}_2 = \frac{a}{2}(\vec{k} + \vec{i})$$

$$\vec{a}_3 = \frac{a}{2}(\vec{i} + \vec{j})$$

原胞体积为$\Omega = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3/4$

倒格子基矢：

$$\vec{b}_1 = \frac{2\pi}{a}(\vec{j} + \vec{k} - \vec{i})$$

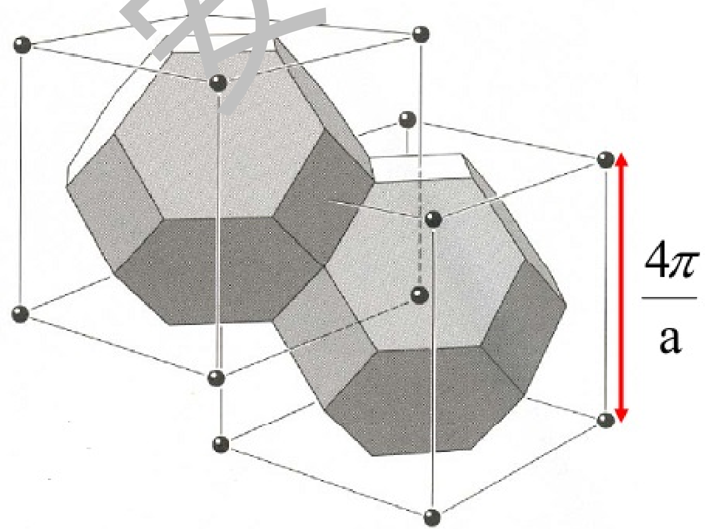
$$\vec{b}_2 = \frac{2\pi}{a}(\vec{k} + \vec{i} - \vec{j})$$

$$\vec{b}_3 = \frac{2\pi}{a}(\vec{i} + \vec{j} - \vec{k})$$

倒格子是体心立方结构，倒格子原胞体积：$\Omega^* = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{\Omega}$

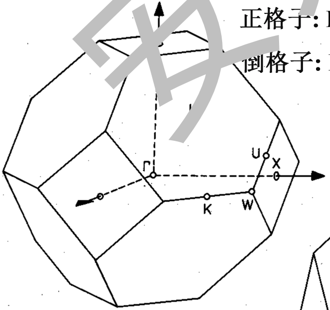
面心立方（FCC）的第一布里渊区

第一布里渊区：截角八面体



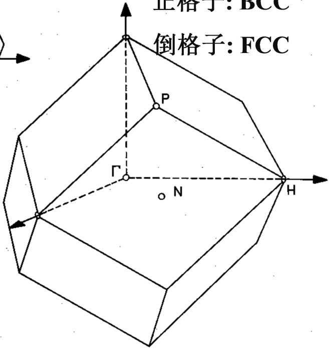
正格子: FCC

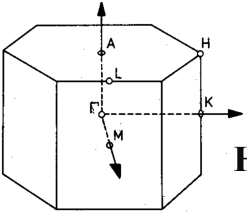
倒格子: BCC



正格子: BCC

倒格子: FCC

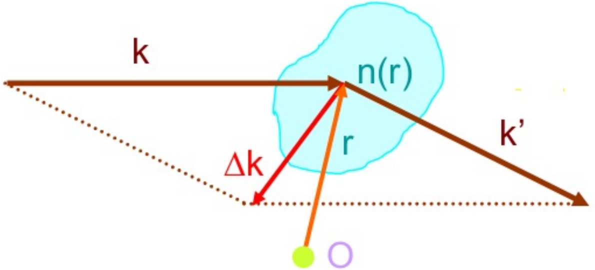




HCP

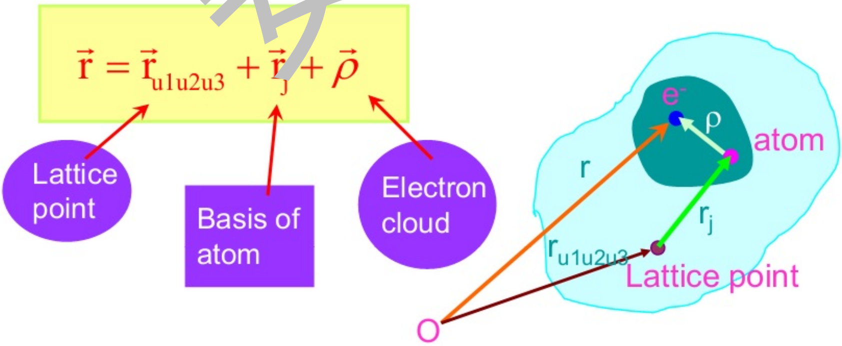
散射振幅

$$E_s(\vec{R}) \propto E_0 \frac{\exp(i\vec{k}\cdot\vec{R}-\omega t)}{R} \int n(\vec{r}) \exp(-i\Delta\vec{k}\cdot\vec{r})\, dV \equiv E_i \cdot F$$



衍射条件：$\Delta\vec{k} = \mathbf{G}$。

单胞的结构因子



为了将单个原子的电子密度做球对称近似，采用单胞进行研究。

单胞的结构因子

$$F = \int d^3\vec{r}\, n(\vec{r}) \exp\left(-i\Delta\vec{k}\cdot\vec{r}\right)$$

$$= \sum_{u_1u_2u_3}\sum_j \int d^3\vec{\rho}\, n_j(\vec{\rho}) \exp\left[-i\Delta\vec{k}\cdot\vec{r}_{u_1u_2u_3}\right] \exp\left[-i\Delta\vec{k}\cdot\vec{r}_j\right] \exp\left[-i\Delta\vec{k}\cdot\vec{\rho}\right]$$

$$\Delta\vec{k} = \mathbf{G} \Rightarrow \exp\left(-i\Delta\vec{k}\cdot\vec{r}_{u_1u_2u_3}\right) = 1$$

$$\therefore F = N\sum_j \exp\left[-i\mathbf{G}\cdot\vec{r}_j\right] \underbrace{\int d^3\vec{\rho}\, n_j(\vec{\rho}) \exp[-i\mathbf{G}\cdot\vec{\rho}]}_{f_j\ \text{原子形状因子}}$$

$$= \underbrace{N\sum_j f_j \exp[-i\mathbf{G}\cdot\vec{r}_j]}_{f_s\text{单胞结构因子}}$$

$$\Rightarrow F = Nf_s$$

单胞的结构因子

$$f_s = \sum_j^s f_j \exp[-i\mathbf{G}\cdot\vec{r}_j]$$

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

注意，$\vec{a}_i$为单胞基矢，当然，**G**也就是单胞对应的倒格子矢量。

$$\mathbf{G}\cdot\vec{r}_j = (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3)\cdot(x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3) = 2\pi(hx_j + ky_j + lz_j)$$

$$\therefore f_s = \sum_j^s f_j \exp[-i2\pi(hx_j + ky_j + lz_j)] \equiv F_{hkl}$$

$$I_{hkl} \propto |F_{hkl}|^2$$

$$\mathbf{G} \leftarrow \text{单胞密勒指数}(hkl)$$

简单例子：简立方，$x_1 = y_1 = z_1 = 0 \Rightarrow F_{hkl} = f$，及任意$(hkl)$均有可能出现x射线衍射峰。

体心立方的结构因子

$$x_1 = y_1 = z_1 = 0; \qquad x_2 = y_2 = z_2 = \frac{1}{2}$$

对于简单晶格，f_j相同，则

$$F_{hkl} = f\{1 + \exp[-i\pi(h+k+l)]\}$$

$$\therefore F_{hkl} = \begin{cases} 0 & h+k+l = \text{奇数} \\ 2f & h+k+l = \text{偶数} \end{cases}$$

不会出现(100), (300), (111), (221)谱线，可以出现(200), (110), (222)谱线。

$$x_1 = y_1 = z_1 = 0; \qquad x_2 = y_2 = \frac{1}{2}, z_2 = 0;$$

$$x_3 = z_3 = \frac{1}{2}, y_3 = 0; \qquad z_4 = y_4 = \frac{1}{2}, x_4 = 0$$

对于简单晶格，f_j相同，则

$$F_{hkl} = f\{1 + \exp[-i\pi(h+k)] + \exp[-i\pi(h+l)] + \exp[-i\pi(l+k)]\}$$

$$\therefore F_{hkl} = \begin{cases} 4f & h,k,l\text{均为奇数或均为偶数} \\ 0 & h,k,l\text{奇偶混杂} \end{cases}$$

不会出现(120), (121), (100), (110)谱线，可以出现(200), (111), (222)谱线。

金刚石结构的结构因子

$$x_1 = y_1 = z_1 = 0; \qquad x_2 = y_2 = \frac{1}{2}, z_2 = 0;$$

$$x_3 = z_3 = \frac{1}{2}, y_3 = 0; \qquad z_4 = y_4 = \frac{1}{2}, x_4 = 0$$

$$x_5 = y_5 = z_5 = \frac{1}{4}; \qquad x_6 = y_6 = \frac{3}{4}, z_6 = \frac{1}{4};$$

$$x_7 = z_7 = \frac{3}{4}, y_7 = \frac{1}{4}; \qquad z_8 = y_8 = \frac{3}{4}, x_8 = \frac{1}{4};$$

$$F_{hkl} = f\{1+\exp[-i\pi(h+k)]+\exp[-i\pi(h+l)]+\exp[-i\pi(l+k)]\}\{1+\exp[-i\pi\frac{1}{2}(h+k+l)]\}$$

$I_{hkl} \propto |F_{hkl}|^2 \neq 0$的条件：1、$h, k, l$均为奇数；或2、$h, k, l$均为偶数且$\frac{1}{2}(h+k+l)$也是偶数。

$I_{hkl} \neq 0$的条件

SC	所有的h, k, l
BCC	$h + k + l =$偶数
FCC	h, k, l为全奇或全偶
金刚石结构	h, k, l均为奇数；或h, k, l均为偶数且$\frac{1}{2}(h + k + l)$也是偶数。