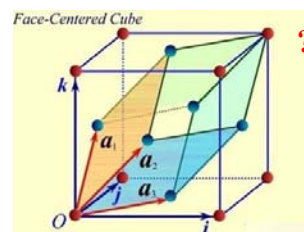
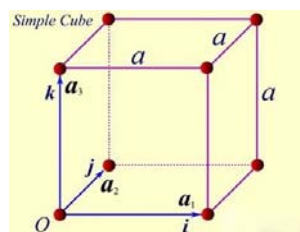


第二讲 晶体结构及研究方法

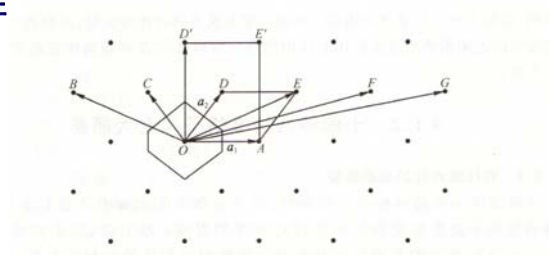
— 晶体衍射和倒格子

晶胞

原(晶)胞-涉及周期性(与对称性)的最小单元

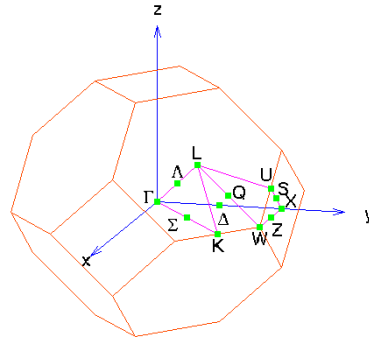
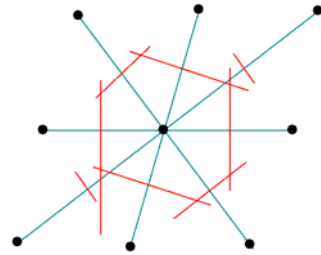


晶胞-兼顾晶体对称性



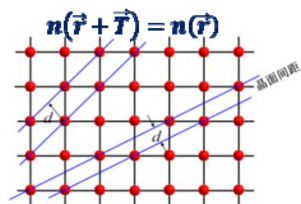
Wigner Seitz 原胞

只包含一个格点



以某一格点为中心，作它与最近邻、次近邻等格点的垂直平分面，由这些面所围成的封闭多面体。

晶体的周期性点阵

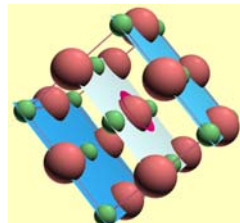


晶面指数 (*hkl*)

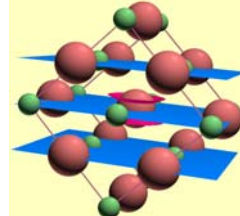
晶面间距、原子点阵

.....

The (200) planes of atoms in NaCl



The (220) planes of atoms in NaCl



Crystalline: macroszie microsize nanosize

X-ray diffraction electron diffraction neutron diffraction

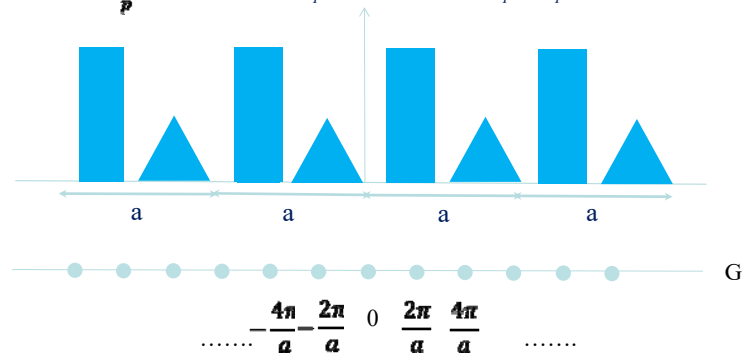
Amorphous: EXAFS (disorder)

傅里叶分析 $n(\vec{r}) = n(\vec{T} + \vec{r})$ 晶体 \rightarrow 晶格周期性的物理量

$$n(x) = n_0 + \sum_{p>0} [C \cos(2\pi p x/a) + S \sin(2\pi p x/a)]$$

$$n(x) = \sum_p n_p e^{i2\pi p x/a}$$

p 取所有整数, 正、负和零
 n_p 复数, 且满足 $n_p = n_{-p}^*$



$$n(x) = \sum_p n_p e^{i2\pi p x/a} \longrightarrow n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}$$

一组矢量 \mathbf{G} 满足 $n(\vec{r} + \vec{T}) = n(\vec{r})$

定义倒易点阵

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

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

以 $\vec{b}_1, \vec{b}_2, \vec{b}_3$ 为基矢构成一个倒格子

倒格子矢量 $\vec{G}_{n_1 n_2 n_3} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$

$$\text{性质 } \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij} \quad i, j=1, 2, 3$$

晶体点阵一组 a_1, a_2, a_3 可导出 一组倒易点阵;
 b_1, b_2, b_3 是 a_1, a_2, a_3 倒易点阵的初级基矢;
 每个矢量与晶体点阵的两个矢量轴正交;
 每个晶体结构都有两个点阵, 晶体点阵和倒易点阵;

倒易点阵 \leftrightarrow 晶体点阵的 Fourier 变换;

正格子的量纲是长度 l , 称作坐标空间;

倒格子的量纲是长度的倒数 l^{-1} , 称作波矢空间;

正点阵取 \AA , 倒易点阵 \AA^{-1}

晶体的显微图像是真实晶体结构在坐标空间的映像;
 晶体的衍射图像则是晶体倒易点阵的映像.

倒易点阵与原子点阵间的关系

1) 正格子原胞体积反比于倒格子原胞体积

$$\Omega^* = \bar{b}_1 \cdot (\bar{b}_2 \times \bar{b}_3) \quad \bar{A} \times \bar{B} \times \bar{C} = (\bar{A} \cdot \bar{C})\bar{B} - (\bar{A} \cdot \bar{B})\bar{C}$$

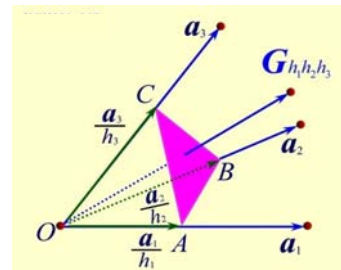
$$\Omega^* = \frac{(2\pi)^3}{\Omega^2} (\bar{a}_2 \times \bar{a}_3) \cdot \bar{a}_1 \quad \Omega^* = \frac{(2\pi)^3}{\Omega}$$

2) 正格子中(一簇)晶面 $(h_1 \ h_2 \ h_3)$ 和 $\bar{G}_{h_1 h_2 h_3}$ 正交

$$\bar{a}_i \cdot \bar{b}_j = 2\pi \delta_{ij}$$

$$\bar{G}_{h_1 h_2 h_3} = h_1 \bar{b}_1 + h_2 \bar{b}_2 + h_3 \bar{b}_3$$

$\bar{G}_{h_1 h_2 h_3}$ 与晶面族正交



3) 倒格子矢量 $\vec{G}_{h_1 h_2 h_3}$ 为晶面 $(h_1 h_2 h_3)$ 的法线方向

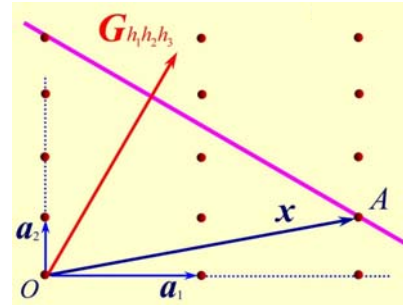
晶面方程 $(h_1 \vec{b}_1 + h_2 \vec{b}_2 + h_3 \vec{b}_3) \cdot \vec{x} = 2\pi n$

各晶面到原点的距离

$$\frac{2\pi |n|}{|h_1 \vec{b}_1 + h_2 \vec{b}_2 + h_3 \vec{b}_3|}$$

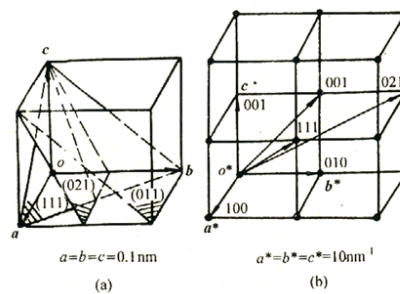
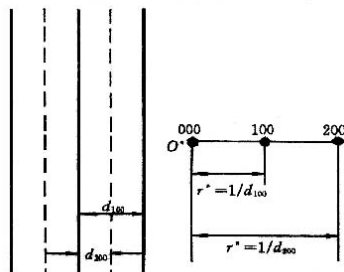
面间距 $d = \frac{2\pi}{|h_1 \vec{b}_1 + h_2 \vec{b}_2 + h_3 \vec{b}_3|}$

$$d = 2\pi / |\vec{G}_{h_1 h_2 h_3}|$$



倒易点阵的一个基矢与正点阵晶格中的一族晶面对应，它的方向是该族晶面的法线方向、大小是该族晶面间距倒数的 2π 倍；

倒易点阵基矢对应一个阵点，晶体点阵中的晶面取向和晶面间距在倒易点阵里可用一个点阵矢量(或阵点)表达。



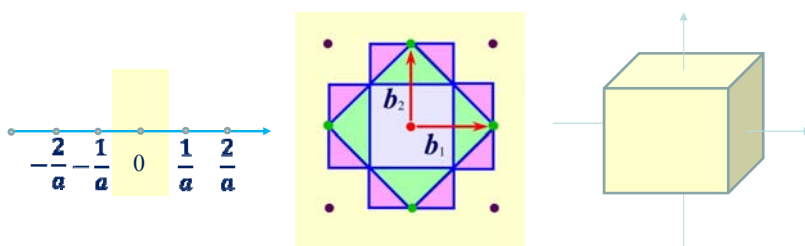
布里渊区

布里渊区为倒易点阵中的维格纳-塞茨晶胞

布里渊区边界方程

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

$$\vec{k} \cdot \left(\frac{1}{2}\vec{G}\right) = \left(\frac{1}{2}G\right)^2$$



布里渊区的特点

- 每个布里渊区只包含一个倒格点
- 每个布里渊区有相同的体积
- 布里渊区的体积应等于倒格点初级点阵的体积

第一布里渊区

- 倒易点阵的中央晶胞为第一布里渊区

原点出发紧邻倒易矢量中垂面所围城的、完全封闭的最小体积

几种晶格倒易点阵及布里渊区

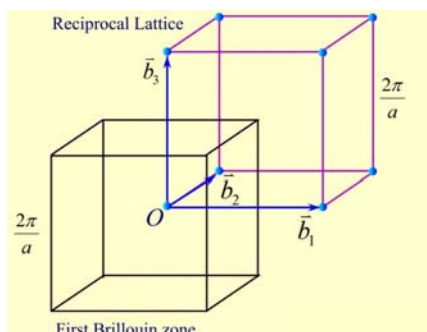
1) 简单立方晶格

正格子基矢

$$\vec{a}_1 = a\vec{i}, \vec{a}_2 = a\vec{j}, \vec{a}_3 = a\vec{k}$$

倒格子基矢

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



第一布里渊区为原点和6个近邻格点的垂直平分面围成的立方体，简单立方晶格

2) 体心立方晶格

正格子基矢

$$\vec{a}_1 = \frac{a}{2}(-\vec{i} + \vec{j} + \vec{k}), \vec{a}_2 = \frac{a}{2}(\vec{i} - \vec{j} + \vec{k})$$

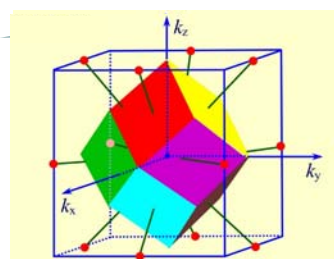
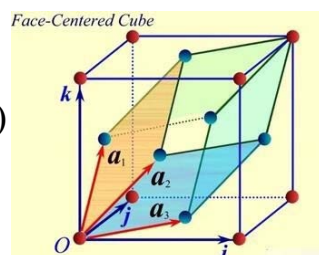
$$\vec{a}_3 = \frac{a}{2}(\vec{i} + \vec{j} - \vec{k})$$

倒格子基矢

$$\vec{b}_1 = \frac{2\pi}{a}(\vec{j} + \vec{k}), \vec{b}_2 = \frac{2\pi}{a}(\vec{i} + \vec{k})$$

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

边长为 $4\pi/a$ 的面心立方晶格



3) 面心立方晶格

正格子基矢

$$\bar{a}_1 = \frac{a}{2}(\bar{j} + \bar{k}) \quad \bar{a}_2 = \frac{a}{2}(\bar{k} + \bar{i})$$

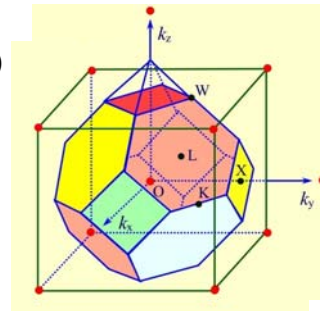
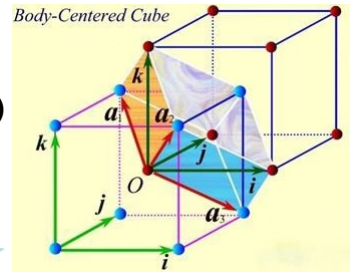
$$\bar{a}_3 = \frac{a}{2}(\bar{i} + \bar{j})$$

倒格子基矢

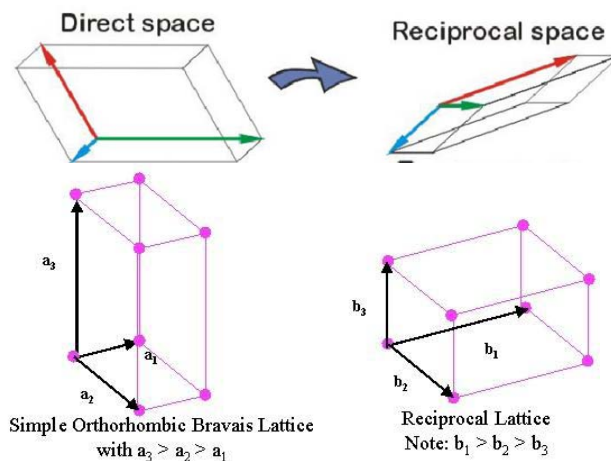
$$\bar{b}_1 = \frac{2\pi}{a}(-\bar{i} + \bar{j} + \bar{k}) \quad \bar{b}_2 = \frac{2\pi}{a}(\bar{i} - \bar{j} + \bar{k})$$

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

边长为 $4\pi/a$ 的体心立方晶格



三维晶格的倒易点阵



正点阵有心点阵→倒易点阵有心点阵，类型可能不同

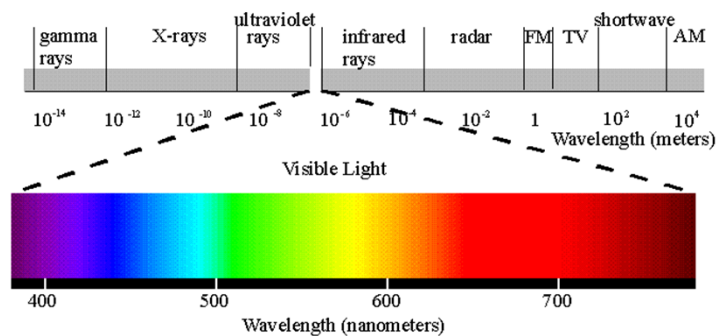
体心立方点阵的倒格子为面心立方点阵

X-ray Crystallography

X-rays were discovered in 1895 by the German physicist Wilhelm Conrad Röntgen

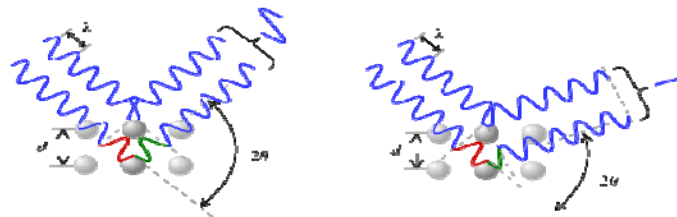
X ray, invisible, highly penetrating electromagnetic radiation of much shorter wavelength (higher frequency).

The wavelength range for X rays is from about 10^{-8} m to about 10^{-11} m, the corresponding frequency range is from about 3×10^{16} Hz to about 3×10^{19} Hz.



晶体中的衍射现象

晶体中不同位置的原子向外辐射的电磁波相互干涉→某些方向上散射波互相叠加或相互抵消，而产生衍射线。



晶体的衍射花样反映出晶体内部原子分布的规律

Nobel物理学奖:

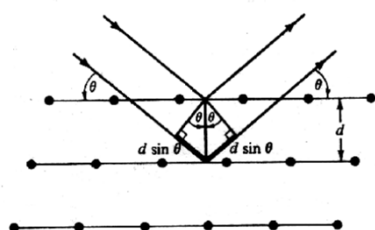
1914 Laue; 1915 Bragg父子; 1937 Davisson;

1986 Binnig和 Rohrer; 1994 Brockhouse和Shull;

2011 Dan Shechtman

<https://en.wikipedia.org>

**晶体衍射的几何理论：
发生衍射的条件的Bragg解释**



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



William Henry Bragg



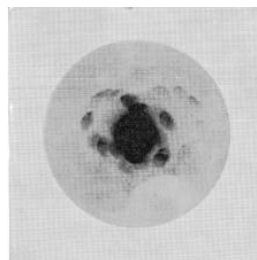
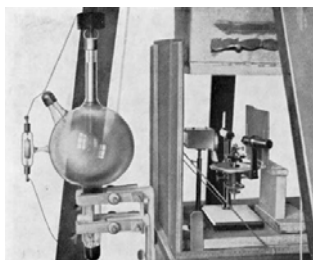
William Lawrence Bragg

特定的入射方向发生衍射

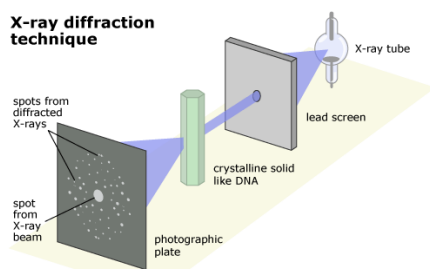
Bragg 衍射：格点处散射波的相长干涉

散射振幅：每个晶胞中电子的空间分布散射强度的叠加

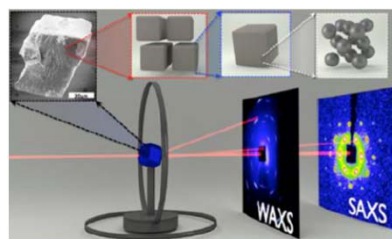
The first X-ray diffraction from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



X-ray diffraction technique



<http://www.scienceiscool.org/solids/intro.html>



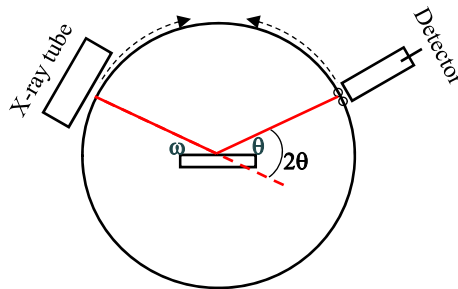
An Obtuse Rhombohedral Superlattice Assembled by Pt Nanocubes

DOI: 10.1021/acs.nanolett.5b02879

20世纪基于X-Ray及相关发现

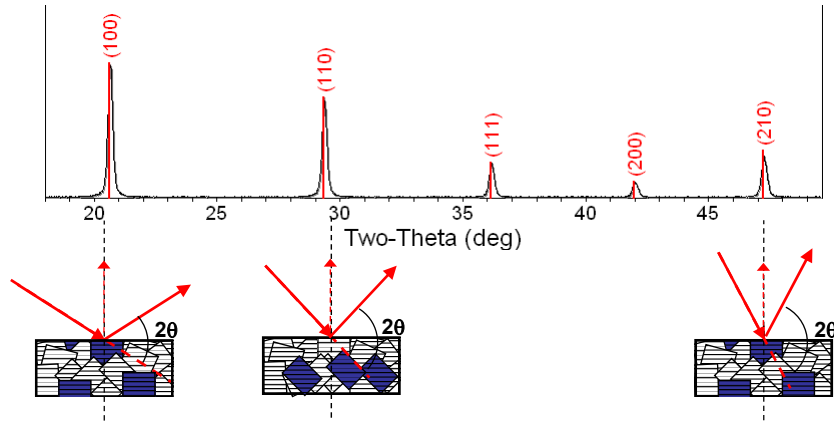
1901: WILHELM RÖNTGEN	X射线的发现
1914: MAX VON LAUE	晶体的X射线衍射
1915: SIR WILLIAM HENRY BRAGG and SIR WILLIAM LAWRENCE BRAGG	晶体结构的X射线分析
1917: CHARLES BARKLA	元素的特征X射线谱
1924: KARL MANNE SIEGBAHN	
1927: ARTHUR COMPTON	康普顿效应
1981: KAI SIEGBAHN	化学分析电子能谱
1936: PETER DEBYE	液体和气体中X射线和电子衍射
1962: MAX PERUTZ and SIR JOHN KENDREW	肌红蛋白和血红蛋白晶体结构的测定
1964: DOROTHY HODGKIN	青霉素和维生素B等晶体结构的测定
1976: WILLIAM LIPSCOMB	硼氢化物的结构和键
1985: HERBERT HAUPTMAN and JEROME KARLE	晶体学中的直接法解相角
1988: JOHANN DEISENHOFER, ROBERT HUBER	绿色红假单胞菌光合作用 反应中心膜蛋白的晶
1997、2002、2003、2006	

Powder diffractometers- Bragg-Brentano geometry



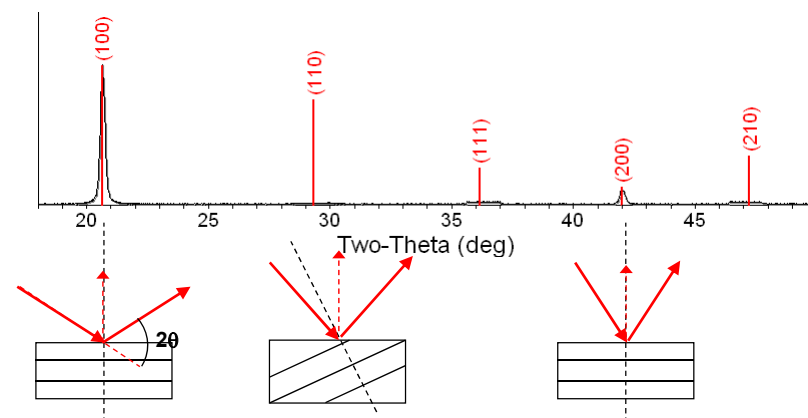
- The incident angle, ω , is defined between the X-ray source and the sample.
- The diffracted angle, 2θ , is defined between the incident beam and the detector angle.
- The incident angle ω is always $\frac{1}{2}$ of the detector angle 2θ .
- In a $\theta : 2\theta$ instrument (e.g. Rigaku RU300), the tube is fixed, the sample rotates at $\theta^\circ / \text{min}$ and the detector rotates at $2\theta^\circ / \text{min}$.

A polycrystalline sample, all possible diffraction peaks should be observed.



For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).

A single crystal specimen would produce only one family of peaks in the diffraction pattern.

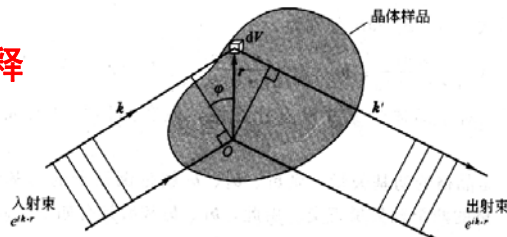


At 20.6° , Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

The (110) planes would diffract at 29.3° ; however, they are not properly aligned to produce a diffraction peak, only background is observed.

The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is $\frac{1}{2} d_{100}$, they appear at 42° .

衍射条件的Laue 解释



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

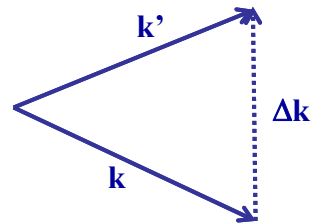
一组倒格矢G 决定了可能的X 射线衍射方向

弹性散射：光子能量守恒

散射前后波矢大小相等

$$\Delta \vec{k} = \vec{G} \quad (\vec{k} + \vec{G})^2 = k^2$$

衍射条件 $2\vec{k} \cdot \vec{G} = G^2$



Ewald construction

Reciprocal space: sphere radius $1/\lambda$ represents possible scattering wave vectors intersecting reciprocal space

Electron diffraction: radius of sphere very large compared to reciprocal lattice
 \Rightarrow sphere circumference almost flat

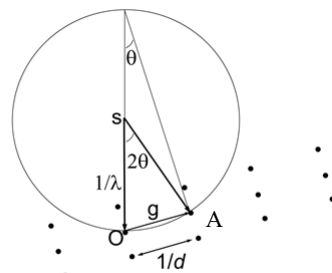
$$2 \sin \theta = OA \cdot \lambda$$

Bragg's law $2d \sin \theta = \lambda$

If $AO = 1/d$, AO is normal to planes

O is origin then A is a reciprocal lattice point

Ewald球上的点满足Bragg 衍射条件



七种晶系的晶面间距 d_{hkl}

$$d_{hkl}$$

$$d_{hkl} = \frac{2\pi}{|\mathbf{G}|}$$

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

System	d_{hkl}
Cubic	$\left[\frac{1}{a^2}(h^2 + k^2 + l^2) \right]^{-1/2}$
Tetragonal	$\left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right]^{-1/2}$
Orthorhombic	$\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right]^{-1/2}$
Hexagonal	$\left\{ \begin{array}{l} \left[\frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2} \right]^{-1/2} \quad \text{hexagonal indexing} \\ \left[\frac{1}{a^2} \frac{(h^2 + k^2 + l^2)\sin^2 \alpha + 2(hk + kl + lh)(\cos^2 \alpha - \cos \alpha)}{1 - 2\cos^3 \alpha + 3\cos^2 \alpha} \right]^{-1/2} \quad \text{rhombohedral indexing} \end{array} \right.$
Monoclinic	$\left[\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} + \frac{k^2}{b^2} \right]^{-1/2}$
Triclinic	$\left[\frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} \sin^2 \beta + \frac{l^2}{c^2} \sin^2 \gamma + \frac{2hk}{ab} (\cos \alpha \cos \beta - \cos \gamma) + \frac{2kl}{bc} (\cos \beta \cos \gamma - \cos \alpha) + \frac{2lh}{ca} (\cos \gamma \cos \alpha - \cos \beta) \right]^{-1/2}$

衍射花样和晶体结构的关系

在一定波长下，衍射方向是晶面间距的函数

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

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

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

六方晶系: $\sin^2 \theta = \frac{\lambda^2}{4} \left(\frac{4}{3} \frac{H^2 + HK + K^2}{a^2} + \frac{L^2}{c^2} \right)$

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，但无法反映晶胞内原子的品种、数量及位置的分布。

衍射花样的强度及分布

- 单个电子对X射线的散射能力;

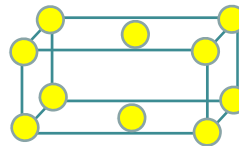
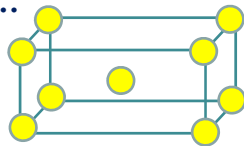
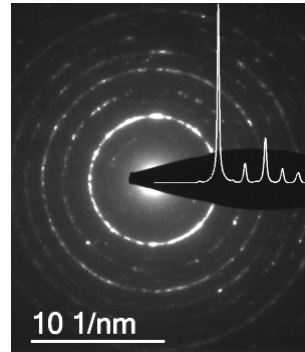
$$I = I_0 \frac{K}{r^2} \left(\frac{1 + \cos^2 2\theta}{2} \right)$$

- 单个原子对X射线的散射与散射角度、X射线波长有关;

- 晶胞对X射线的散射;
原子散射因子 f ;
原子在晶胞中的占位-结构因子 F ;

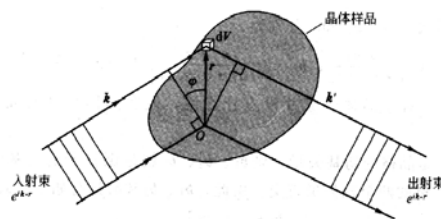
- 吸收因子;

- 温度...



晶体的结构因子

仅与原子种类及其在晶胞中的位置有关



$$F_G = N \int dV_n(\vec{r}) \exp(-i\Delta\vec{k} \cdot \vec{r}) = NS_G$$

$$S_G = \sum_j f_i \exp(-i\vec{G} \cdot \vec{r}_j)$$

$$S_G = \sum_j f_j \exp(-i\vec{G} \cdot \vec{r}_j)$$

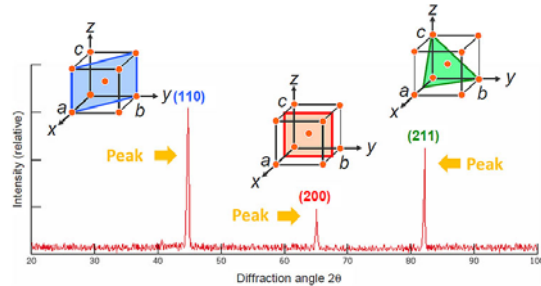
体心立方结构→ (0, 0, 0) 、 (½, ½, ½) 两种原子

$$S(v_1 v_2 v_3) = f [1 + \exp[-i\pi(v_1 + v_2 + v_3)]] \begin{cases} S=0 \\ S=2f \end{cases}$$

$h+k+l$ 为奇数时, $S=0$, (100)、(300)、(221) 等衍射不出现;

$h+k+l$ 为偶数时, $S=2f$, (200)、(110)、(222) 等衍射出现。

BCC-Fe XRD pattern



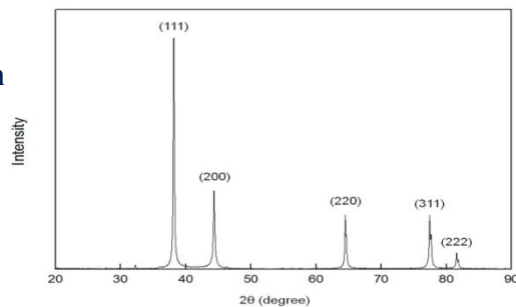
面心立方结构→ (0, 0, 0) 、 (0, ½, ½)、 (½, 0, ½)和(½, ½, 0)

$$S(v_1 v_2 v_3) = f [1 + \exp[-i\pi(v_2 + v_3)] + \exp[-i\pi(v_1 + v_3)] + \exp[-i\pi(v_1 + v_2)]]$$

hkl 全为偶数或奇数时, $S=4f$, 衍射出现;

hkl 为奇偶数混杂时, $S=0$, 不能产生衍射。

FCC-Ag XRD pattern



复杂晶胞的结构因子

$$S_G = \sum_j f_j \exp(-i\vec{G} \cdot \vec{r}_j)$$

NaCl结构

Na (0, 0, 0)、(0, 1/2, 1/2)、(1/2, 0, 1/2) 和 (1/2, 1/2, 0)

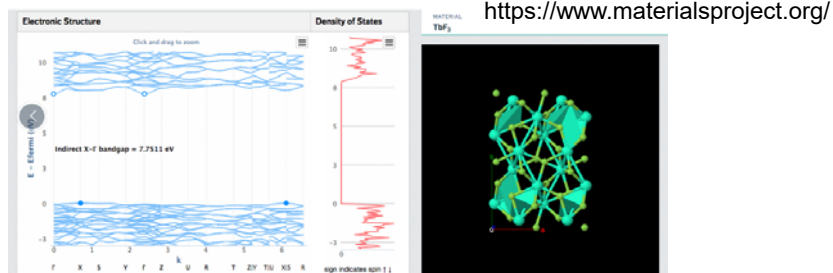
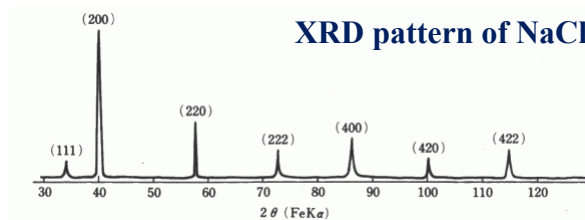
Cl (1/2, 1/2, 1/2)、(1, 1, 1/2)、(1, 1/2, 1) 和 (1/2, 1, 1), 可等效为

Cl (1/2, 1/2, 1/2)、(0, 0, 1/2)、(0, 1/2, 0) 和 (1/2, 0, 0)

分别计算 S_{Na} 、 S_{Cl} 后,

$$S(v_1 v_2 v_3) = (f_{Na} + f_{Cl} \exp^{-\pi i(v_1 + v_2 + v_3)}) [1 + e^{-\pi i(v_1 + v_2)} + e^{-\pi i(v_1 + v_3)} + \exp^{-\pi i(v_2 + v_3)}]$$

hkl 为偶数时, $S=4(f_{Cl}+f_{Na})$; hkl 为奇数时, $S=4(f_{Cl}f_{Na})$;
 hkl 为奇偶数混杂时, $S=0$, 不产生衍射。



You can use XRD to determine

- Crystal structure
By Rietveld refinement of the entire diffraction pattern
- Phase composition of a sample
Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
Index peak positions
Lattice parameters can vary as a function of composition, and therefore give you information about, alloying, doping, solid solutions, strains, etc.
- Crystallite Size and Microstrain
Indicated by peak broadening
Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width
- Residual Strain (macrostrain)
- Epitaxy/Texture/Orientation

未知物结构的确定

立方结构为例: $(1/d)^2$ 正比于 $h^2+k^2+l^2$

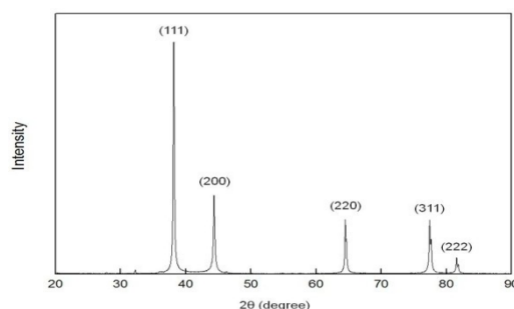
$h^2+k^2+l^2$	1	2	3	4	5	6	8	9	10	11	12	13	14	16	17	18	19	20
hkl	100	110	111	200	210	211	220	300, 221	310	311	222	320	321	400	410, 322	411, 330	331	420
Simple Cubic																		
BCC																		
FCC																		
Diamond Cubic																		

1:2:3:4:5:6:8

1:2:3:4:5:5:7

3:4:8:12:16:19:20

3:8:16:19



$$(1/d_1)^2 : (1/d_2)^2 : (1/d_3)^2 = 3 : 4 : 8$$

衍射峰的宽化

仪器的影响： 光源的波长不是单一值；
样品表面与旋转轴没有完全重合；

样品的影响： 微晶效应；
微观应变； $B(2\theta) = 4\varepsilon \frac{\sin\theta}{\cos\theta}$

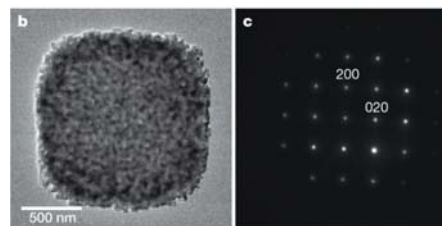
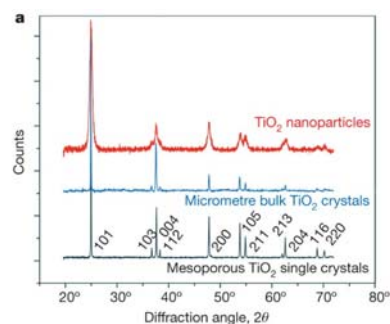
Scherrer公式（1918）

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

L 为晶粒尺寸；K为形状因子0.94

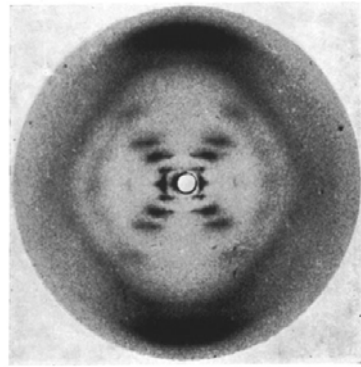
晶粒尺寸越小，衍射峰的半高宽越大；
高指数晶面 ($\cos\theta$ 越小)，衍射峰的半高宽越大

X-ray and electron diffraction of mesoporous TiO_2 crystals

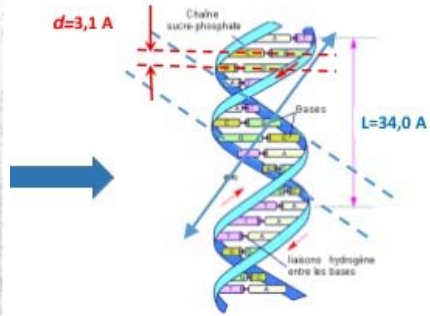


EJW Crossland *et al. Nature* **2013**, 495, 215-219

Analysis of XRD patterns and determination of relevant structural parameters

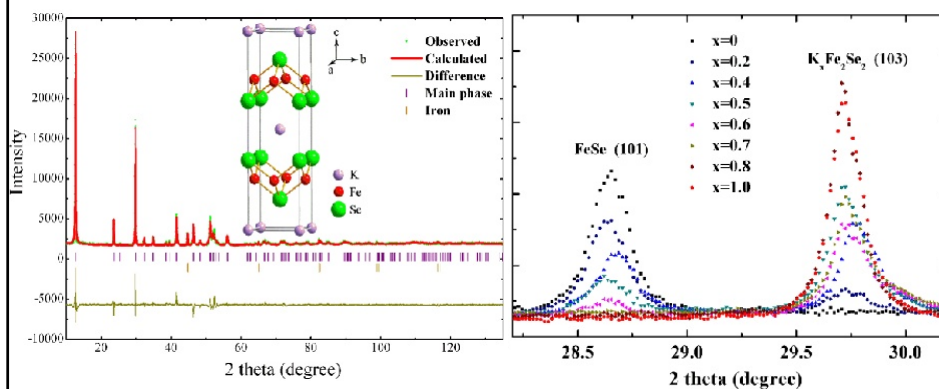


X-ray diffraction pattern of DNA



Structure model derived from XRD patterns

X射线衍射图谱

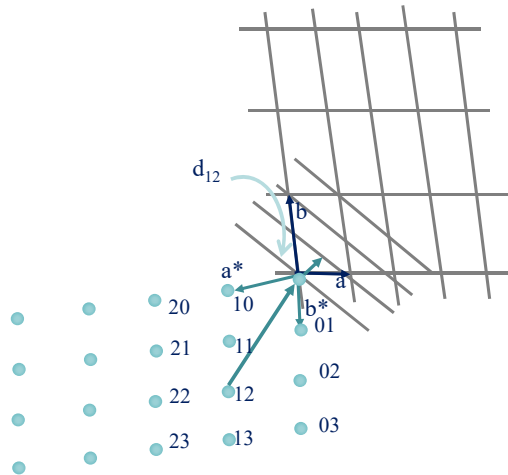


具有层状结构的新铁硒超导体 KFe_2Se_2

Phys. Rev. B, **2010**, 82, 182520 (R)

每个晶体结构联系实空间、倒易空间两个格子:

实空间:各种电子显微镜, STM, AFM 研究表面



倒易空间:

X射线衍射 $\varepsilon = h\nu = hc/\lambda$ $\lambda(\text{\AA}) = 12.4/\varepsilon(\text{keV})$

穿透深度大, 对轻原子灵敏度低

$\text{CuK}\alpha = 1.5418 \text{\AA}$

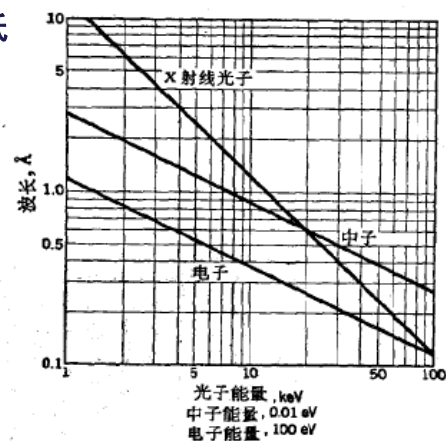
电子衍射 $\varepsilon = h^2/2m\lambda^2$

$\lambda(\text{\AA}) = 12.4/[\varepsilon(\text{eV})]^{1/2}$

中子衍射 $\varepsilon = h^2/2M_n\lambda^2$

$\lambda(\text{\AA}) = 0.28/[\varepsilon(\text{eV})]^{1/2}$

与原子核短程作用, 对原子序数不灵敏, 有磁矩



电子衍射

$$r = L \tan 2\theta$$

电子入射波长约为 10^{-2} nm，而一般晶体的面间距 d 大约为 10^{-1} nm，具备一定强度的衍射线所对应的 θ 均很小。

$\tan 2\theta \approx \sin 2\theta \approx 2\theta$ ，且因 $2d \sin \theta = n\lambda$ ， $2 \sin \theta = (1/d)/(1/\lambda) = \lambda/d$

所以

$$rd = L\lambda$$

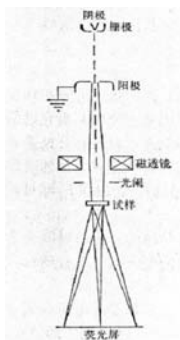


图 4-9 电子衍射仪示意图

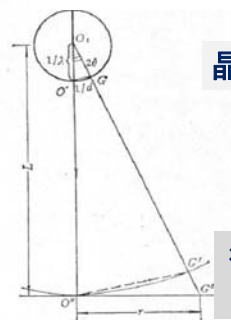
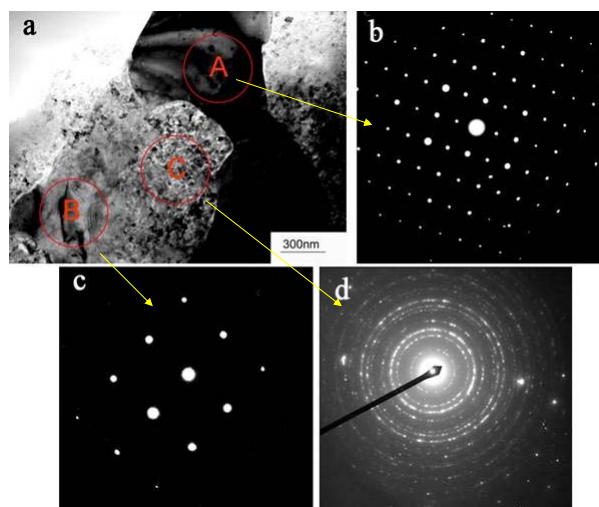


图 4-10 电子衍射的几何关系
(注意：此图中反射球大小与 L 不成比例)

晶体某晶面的间距 d

衍射图上衍射斑点
到原点的距离 r

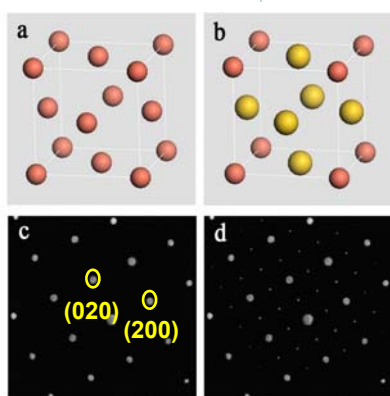
选区电子衍射 不同组成、结构物质



电子衍射：合金的无序和有序

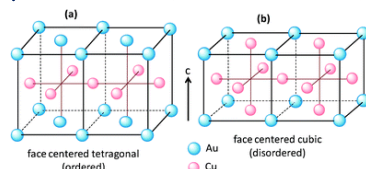
超点阵结构

Au_3Cu 晶体从无序相向有序相转变后，产生有序的方向**平移周期性变化**



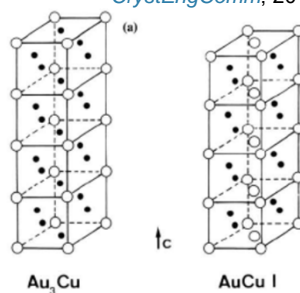
无序

有序



(a) Ordered (fct) and (b) disordered (fcc) Au–Cu alloy

CrystEngComm, 2014, **16**, 56-63

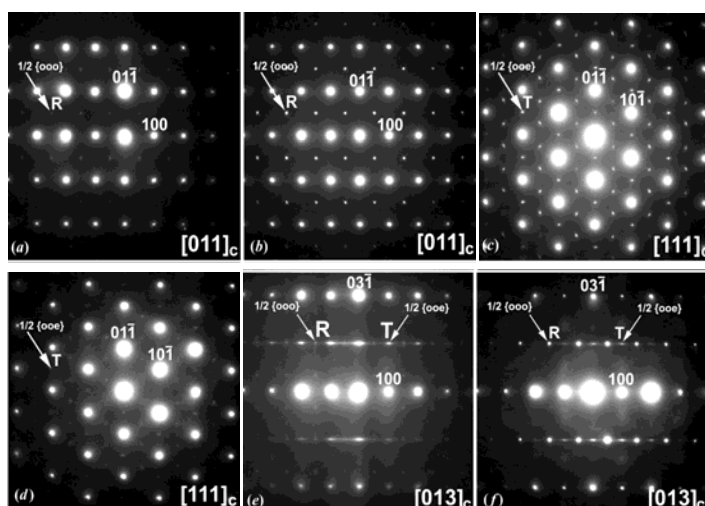


Au_3Cu

AuCu I

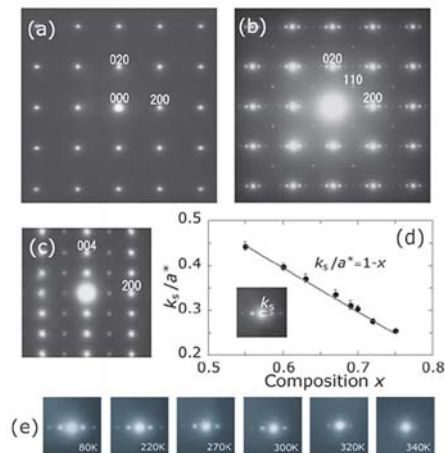
<http://jdr.sagepub.com/content/65/9/1179.full.pdf>

Selected-area electron diffraction (SAED) patterns of the $[011]_c$, $[111]_c$ and $[013]_c$ zone axes. Arrows indicate the $1/2\{000\}$ and $1/2\{00e\}$ superstructure reflections, where R means rhombohedral and T for tetragonal.



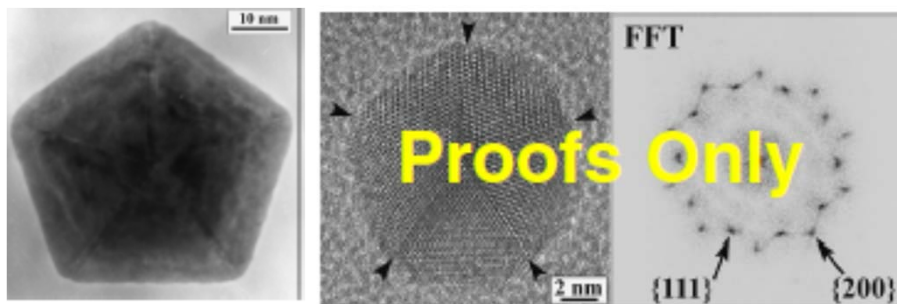
JAC
JOURNAL OF
APPLIED
CRYSTALLOGRAPHY

Schmitt *et al* J. Appl. Cryst. 43 (4) 2010, 805–810

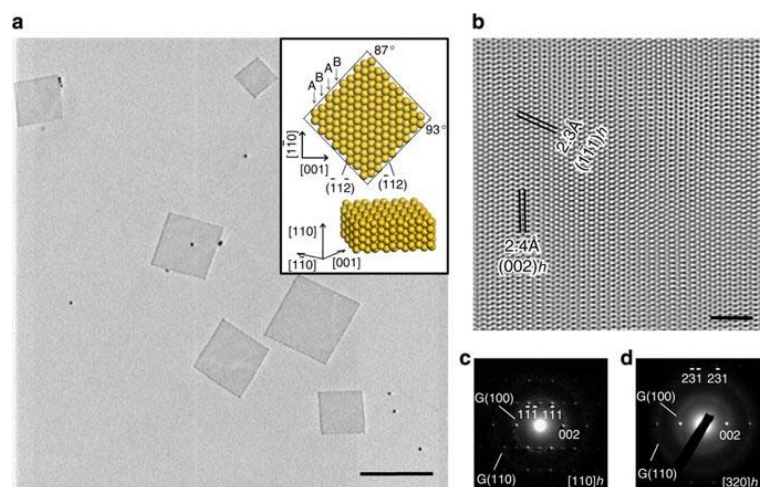


Electron diffraction patterns of $\text{Nd}_{1-x}\text{Ca}_{1+x}\text{MnO}_4$ ($x=0.69$) (a) at 340K ($>T_{\text{CO}}$) along [001], (b) at 80K ($<T_{\text{CO}}$) along [001], and (c) 80K ($<T_{\text{CO}}$) along [010]. The $hk0$ (h, k : odd number) reflections are fundamental ones of the low-temperature *Pccn* structure. (d) The relationship between the propagation vector of the superstructure k_s and the composition x . (e) Temperature dependence of the superlattice reflection intensity for $x=2/3$.

<http://www.nims.go.jp>



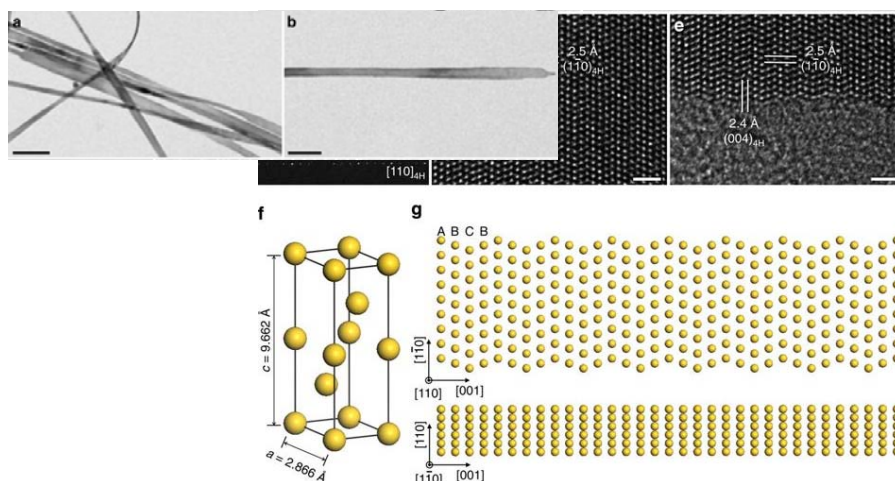
Decahedral particle of Rh in 5-fold orientation grown by vapor deposition on NaCl.



2.4-nm thick Au plates on a GO surface (scale bar, 500 nm). *Inset*: crystallographic models for a typical Au plate with its basal plane along the $[110]_h$ zone axis, showing ABAB stacking along the $[001]_h$ direction.

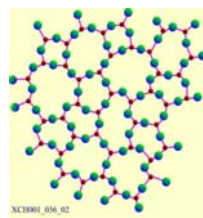
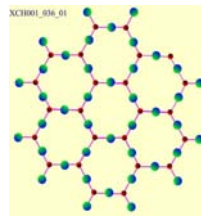
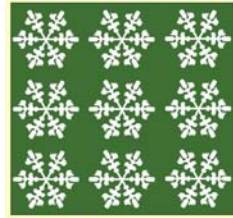
Nat. Commun. 2, 292 (2011)

Schematic illustration of a unit cell of 4H Au. *Nature Communications* 6, 7684 (2015)

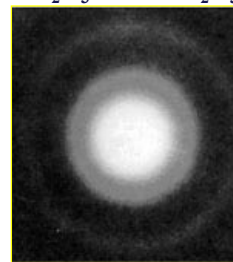
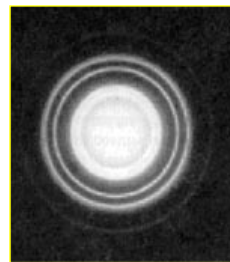


Crystallographic models illustrating the top view (top panel) and side view (bottom panel) of a typical 4H Au NRB. The close-packed planes along the $[001]_{4H}$ direction show a characteristic stacking sequence of 'ABCB'.

晶体和非晶



Be₂O₃晶体与Be₂O₃玻璃

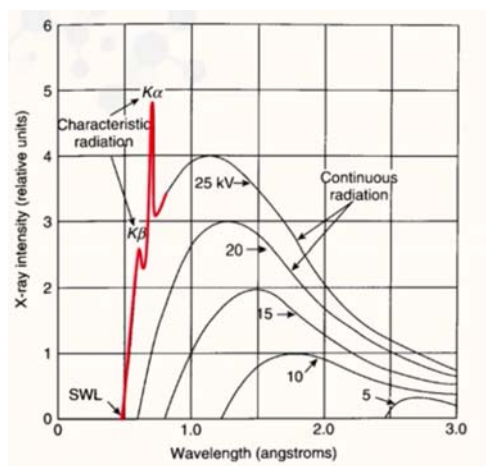


有序度 → 降低

X-ray

特征谱

连续谱



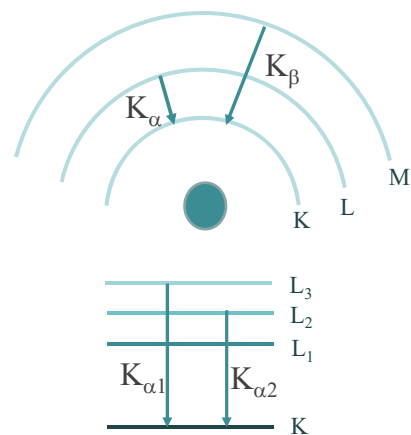
$$E = \hbar\omega = hc / \lambda$$

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

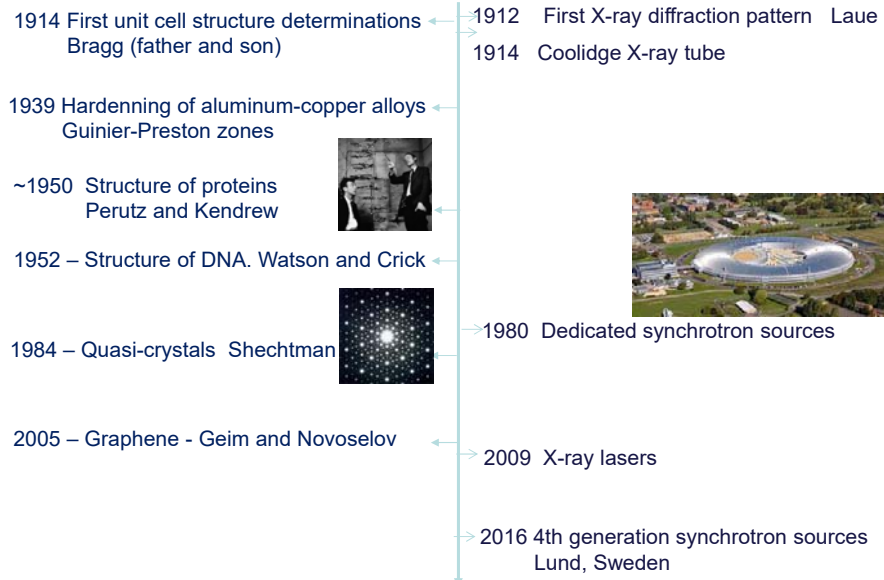
$$= 4.136 \times 10^{-15} \text{ eV}$$

$$\text{For } \lambda = 1 \text{ \AA},$$

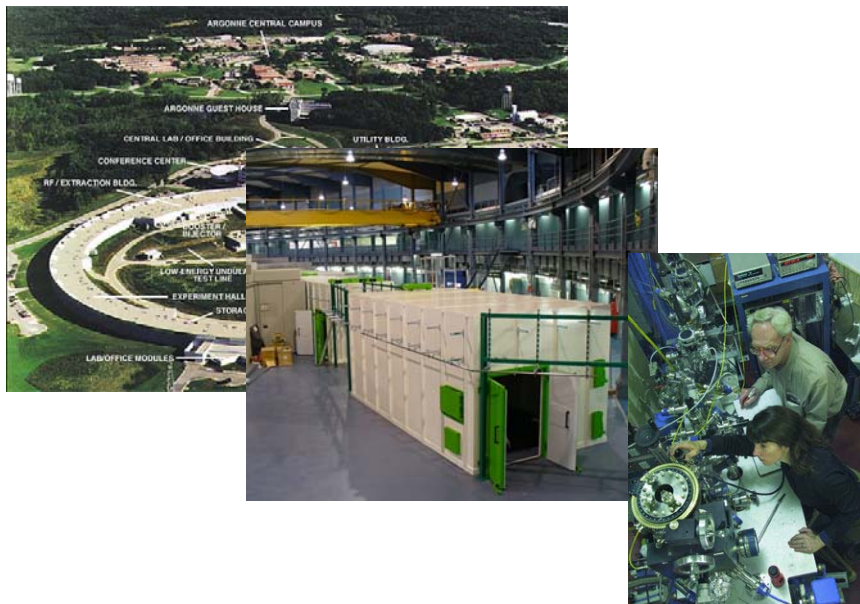
$$E \sim 10^4 \text{ eV}$$



One hundred years of Crystallography



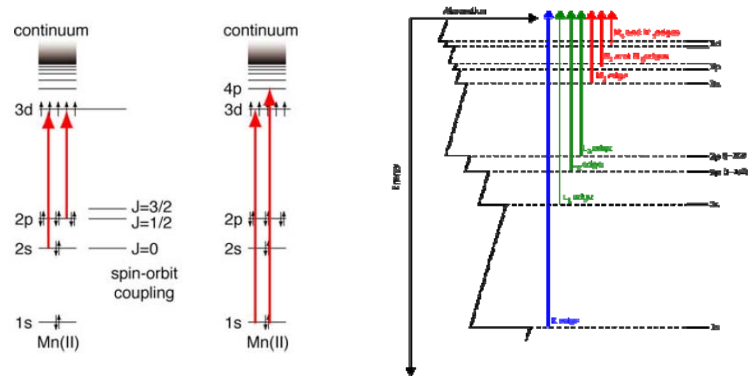
X射线吸收精细结构



X射线精细吸收结构(EXAFS) X射线吸收边

当原子被X射线照射时，遵循光电效应的基本原理；

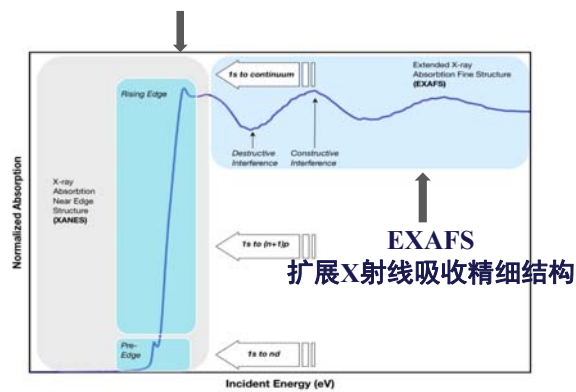
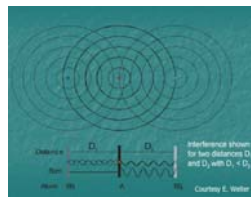
当入射X射线光子达到一定能量后，X射线吸收会突然增加，内层电子被激发到最低未占据轨道直至被电离，这一段能量范围这就是X射线吸收边。



J. Yano, et al. Photosynth. Rev. 2009, 102, 241

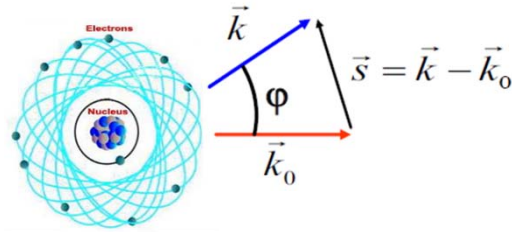
近邻结构信息，如近邻原子的键角、电子态/价态等；

XANES X射线吸收近边结构



小范围原子簇结构信息，包括近邻原子配位数、原子间距等；

原子的散射因子



散射振幅:
$$E(\vec{s}) = \int_{V_a} \rho(\vec{r}) e^{i\vec{s} \cdot \vec{r}} f_e E_0 dV$$

原子散射因子:
$$f(\vec{s}) = \int_{V_a} \rho(\vec{r}) e^{i\vec{s} \cdot \vec{r}} dV$$

EXAFS谱图的解析

$$\chi(k) = -\sum_i s_0^2 \frac{N_i}{k r_i^2} |f_i(k, \pi)| \sin(2k r_i + 2\delta_i + \varphi_i) e^{-2\sigma_i^2 k^2} e^{-\frac{2r_i}{\lambda}}$$

N_i

临近原子*i*的数目

r_i

临近原子*i*

$f_i(k, \pi)$

背散射振幅

δ_i, φ_i

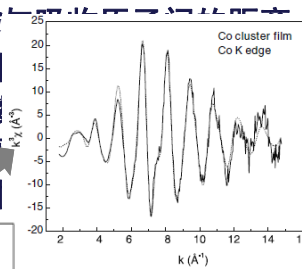
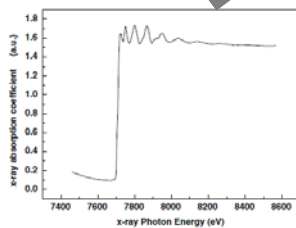
电子波函数

σ_i

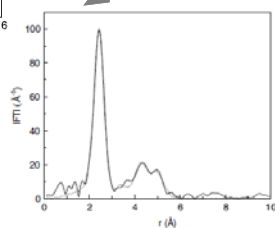
原子间距

λ

电子的弹性

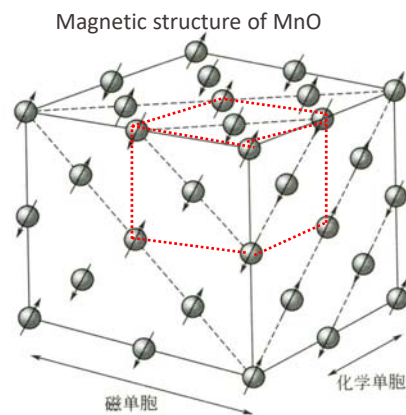
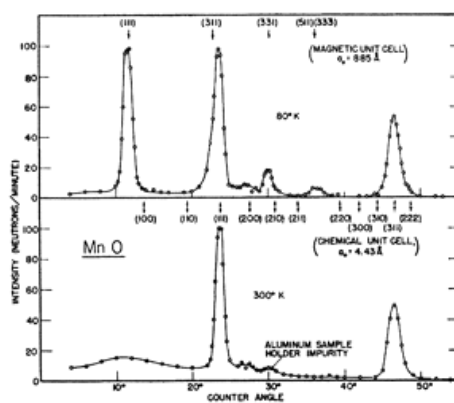


原子上的相位移动



S. H. Baker, *et al. J. Phys. Condense. Matter* **2009**, 21, 183002

- 利用EXAFS，可以直接获得：
 - 配位原子与中心原子间的距离；
- 通过拟合，可以估计：
 - 配位原子的种类；
 - 中心原子的配位数；
 - 原子间距的分布状况。
- 对通过傅立叶变换后得到的EXAFS图谱，可认为其描述特定元素的一个原子周围出现其他原子的概率密度函数。



Comparison of the neutron diffraction pattern of MnO above and below its Néel temperature of 120 K (Shull et al. 1951b). Diffuse scattering around the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ position of the room temperature nuclear structure becomes a coherent magnetic superlattice peak at low temperature. The low-temperature diffraction pattern can be indexed on a cubic unit cell that is double the size of the nuclear unit cell.



Thanks for your attention !