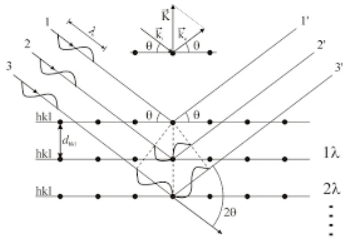
Reciprocal Lattice & Diffraction



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Outlines

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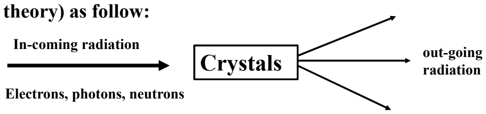
Introduction

In the past, because of the size and distance between atoms is on the order of 10^{-10} m, direct measurement of lattice is difficult, so indirect methods were developed to probe the structure of crystals. Diffraction is such a method that is widely used to probe crystal structure. The method can be illustrated (in the linear response theory) as follow:



Mathematically, we can view this diffraction process as an operation such as Fourier transform

$$n(\vec{k}) = \int n(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d\tau$$

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The incident radiation ($mc^2 = 511\ keV$ for electron)

1. Photons (x-ray)

$$E = hf = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E} = \frac{12400\ eV \cdot Å}{E(eV)}$$

Typical x-ray energy $\approx 10 \sim 100\ keV \Rightarrow \lambda = 1 \sim 0.1 Å$

2. Electrons

$$E = \frac{P^2}{2m} = \frac{h^2}{2m\lambda^2} \Rightarrow \lambda = \frac{hc}{\sqrt{2mc^2E}} = \frac{12.3}{\sqrt{E(eV)}} Å$$

For electron $E \approx 10 \sim 100\ eV$, implies $\lambda \approx 1 \sim 5$ Å

3. Neutrons (Neutron mass is 2000 times heavier than electron)

$$\lambda = \frac{0.28}{\sqrt{E(eV)}} Å \Rightarrow$$ For E $\approx 1 \sim 10\ eV$, $\lambda = 0.3 \sim 0.03$ Å

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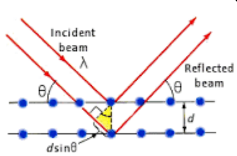
Bragg Law (x-ray)

$$2d\sin\theta = n\lambda \quad (1)$$

where d ------ lattice spacing
θ ------ incident angle
λ ------ wavelength of x-ray
n ------ integer



When the path difference is equal to $2d\sin\theta$, it leads to constructive interference.

Note: Each lattice plane reflects about $10^{-3} \sim 10^{-5}$ of the total incident radiation. Typical x-ray penetrates about a few thousand Å into a solid.

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Experimental diffraction methods

From Bragg law we can either fix the wavelength and measure the diffraction pattern as a function of angle, or we can fix the angle, and measure the diffraction pattern as a function of wavelength (energy).

Some useful x-ray techniques

1. Laue method (transmission)

Single crystal is used and continuous radiation is used. The method is widely used to identify the symmetry of crystals. The crystal selects the discrete values of λ for which the Bragg law is satisfied. The spots on the film come from the characteristic x-ray.

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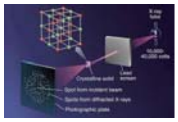
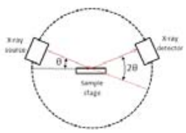
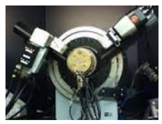


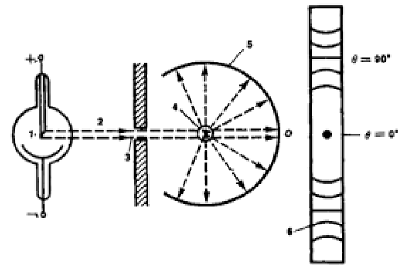
2. Rotating crystal method (also known as θ-2θ) (reflection)





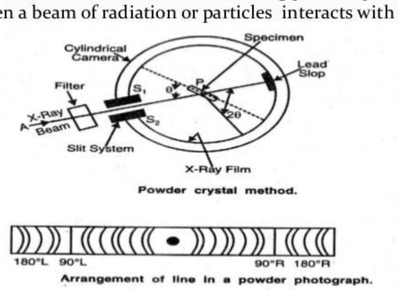
3. Powder method

Polycrystals or powder and monochromatic light are used. The radiation select the correct orientation for diffraction. Because of the rotation symmetry along the incident direction, rings are created.



X-ray powder diffractometer

A **diffractometer** is a measuring instrument for analyzing the structure of a material from the scattering pattern, produced when a beam of radiation or particles interacts with it.



Fourier Transform

Fourier transform is an integral transform of a time function into a frequency function:

$$g(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i\omega t}\, dt$$

The inverse transform is given by

$$f(t) = \int_{-\infty}^{\infty} g(\omega) e^{i\omega t} d\omega$$

This can be applied to 3D real space

$$g(\vec{k}) = \int_V f(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d^3 r$$

And the inverse transform is given by

$$f(\vec{r}) = \int_{k\ space} g(\vec{k})\, e^{i\vec{k}\cdot\vec{r}} d^3 k$$

Joseph Fourier, a French mathematician, in the early 19 century (1822), developed the basic concepts of this integral transformation that bears his name.

The basic concept of the Fourier transform is quite simple, namely, any time series function can be represented as an infinite summation of harmonic functions.

$$f(t) = \sum_{n=-\infty}^{\infty} c_n e^{i2\pi\left(\frac{n}{T}\right)t} \quad \text{and} \quad c_n = \frac{1}{T}\int_{-T/2}^{T/2} f(t)\, e^{-i2\pi\left(\frac{n}{T}\right)t} dt$$

Harmonic functions form a "complete set" of orthogonal functions which can represent any functions.

Scattering wave amplitude

We will use a few different approaches to demonstrate the physical meaning of the reciprocal lattice. In particular the scattering wave amplitude relates to the Fourier transform of the real space lattice structure.

One dimensional

Let $n(x)$ be the 1-D lattice location,

$$n(x) = \sum_{p=0}^{\infty} n_p e^{i\frac{2\pi p}{a}x} = \sum_k n_k e^{ikx} \qquad (5)$$

Here $k = \frac{2\pi p}{a}$. This expression satisfies the translational invariance of the lattice.

namely

$$n(x+a)=\sum_{p=0} n_p e^{i\frac{2\pi p}{a}(x+a)}=\sum_{p=0} n_p e^{i\frac{2\pi p}{a}x}\cdot e^{i2\pi p}$$
$$=\sum_{p=0} n_p e^{i\frac{2\pi p}{a}x}=n(x)$$

For 3-D system

$$n(\vec{r})=\sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \quad (9)$$

Later we shall show that $n_{\vec{G}}$ is related to the scattering amplitude.

$$\int_{cell} n(\vec{r})e^{-i\vec{G}\cdot\vec{r}}\,d^3r=\int_{cell}\sum_{\vec{G}'} n_{\vec{G}'}e^{i\vec{G}'\cdot\vec{r}}\cdot e^{-i\vec{G}\cdot\vec{r}}\,d^3r$$
$$=\int_{V_c}\delta(\vec{G}-\vec{G}')\cdot d^3r\cdot n_{\vec{G}'}=n_{\vec{G}}\cdot V_c$$

$$n_{\vec{G}}=\frac{1}{V_c}\int_{V_c} n(\vec{r})\cdot e^{-i\vec{G}\cdot\vec{r}}d^3r \quad (12)$$

This is the scattering amplitude, as we can see that it is also the Fourier transform of the real space lattice points.

Reciprocal lattice vectors and reciprocal space

For a given lattice, with $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ as its primitive vectors, then we define the following vectors,

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

as the primitive vectors of the reciprocal lattice.

For a vector in the reciprocal space, $\vec{G}$

$$\vec{G}=n_1\vec{b}_1+n_2\vec{b}_2+n_3\vec{b}_3 \quad (15)$$

where n_1, n_2, and n_3 are integers.

The $\vec{G}$ is the reciprocal lattice vector.

What is the physical meaning of $\vec{b}_n$?

From definition, $\vec{a}_2\times\vec{a}_3$ relates to a plane with its normal $\perp$ to $\vec{a}_2$ and $\vec{a}_3$, and $|\vec{a}_1\cdot\vec{a}_2\times\vec{a}_3|$ is just a volume, serving as a normalization factor.

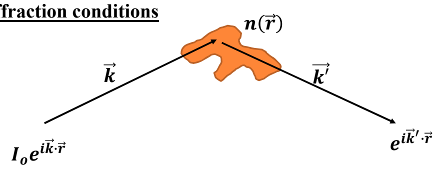
The ratio of the magnitudes of $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ is given by

$$\frac{1}{a_1}:\frac{1}{a_2}:\frac{1}{a_3}$$

$\vec{G}$ is a translational vector in reciprocal lattice. The reciprocal lattice points are defined by $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$.

The reciprocal lattice is the Fourier transform of the real crystal lattice. The X-ray scattering pattern is related to the reciprocal lattice.

Diffraction conditions



The amplitude F of the scattering wave is proportional to:

1. Number of scatteriers ------- $n(\vec{r})dV$
2. A phase factor ------ $e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$

$$F=\int n(\vec{r})\cdot e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}dV \quad (18)$$

Let $\Delta k=\vec{k}'-\vec{k}$

Eq. (9) on page 13

$$F=\int n(\vec{r})e^{-i\Delta\vec{k}\cdot\vec{r}}d^3r=\int\sum_{G} n_G e^{i\vec{G}\cdot\vec{r}}e^{-i\Delta\vec{k}\cdot\vec{r}}\,d^3r$$

$$F=\sum_{G} n_G\int e^{i(\vec{G}-\Delta\vec{k})\cdot\vec{r}}d^3r \quad (20)$$

If $\vec{G}\neq\Delta\vec{k}$, the integral is not defined or = 0, so when

$$\Delta\vec{k}=\vec{G} \quad (21)$$ Eq. (20) becomes $F=n_G V$

So this is the proof that the scattering amplitude F is proportional to the Fourier component n_G.

For elastic scattering, the energy is conserved, so the magnitude of the momentum is the same, even though they may have different direction. Start with

$$\vec{G} + \vec{k} = \vec{k}' \Rightarrow G^2 + 2\vec{k}\cdot\vec{G} + \vec{k}^2 = \vec{k'}^2$$

$$\Rightarrow \quad G^2 + 2\vec{G}\cdot\vec{k} = 0 \qquad (22)$$

Since $-\vec{G}$ is also a reciprocal lattice vector

$$G + 2\vec{k}\cdot\frac{-\vec{G}}{|G|} = 0$$

$$n\frac{2\pi}{d} = 2\cdot\frac{2\pi}{\lambda}\cdot sin\theta$$

$$\Rightarrow \quad 2dsin\theta = n\lambda \qquad (24)$$

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Laue equations

Another way to interpret the scattering condition $\Delta\vec{k} = \vec{G}$ was provided by von Laue who did the original x-ray works and was awarded Nobel prize in Physics in 1914.

If we take the scalar product of $\Delta\vec{k}$ and primitive translational vectors $\vec{a}_i$, we end up with

$$\vec{a}_1\cdot\Delta\vec{k} = 2\pi n_1\,; \quad \vec{a}_2\cdot\Delta\vec{k} = 2\pi n_2\,; \quad \vec{a}_3\cdot\Delta\vec{k} = 2\pi n_3 \qquad (25)$$

where n_1, n_2, and n_3 are integers.

Each equation above tells us that $\Delta\vec{k}$ has to lie on the surface of a cone about the directions $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$. In the x-ray scattering work, $\Delta\vec{k}$ must satisfy all three equations above.

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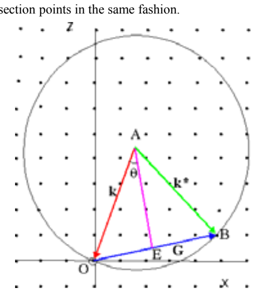
Ewald construction

1. Chose a point according to the orientation of the specimen with respect to the incident beam.
2. Draw a vector AO in the incident direction of length 2π/λ terminating at the origin.
3. Construct a circle of radius 2π/λ with center at A. Note whether this circle passes through any point of the reciprocal lattice; if it does:
4. Draw a vector AB to the point of the intersection.
5. Draw a vector OB to the point of the intersection.
6. Draw a line AE perpendicular to OB.
7. Complete the construction to all the intersection points in the same fashion.

Downloaded from http://www.chemistry.uoguelph.ca/educmat/chm729/recip/8ewald.htm



1. Since OB end at a point, $OB = \frac{2\pi}{d}n$.
2. $OA = \frac{2\pi}{\lambda}$, $OE = \frac{2\pi}{\lambda}sin\theta$, & $OB = 2OE$.
3. Combine above we obtain

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

$$n\lambda = 2dsin\theta$$

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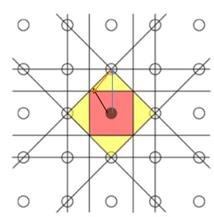
Brillouin Zones

A Brillouin zone is defined as the Wigner-Seitz cell in the reciprocal lattice. For example, the reciprocal lattice of a simple cubic system is given by

For a wavevector $\vec{k}$, if the tip of $\vec{k}$ is on the Brillouin zone boundary, then theis wavevector will be Bragg scattered.



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

$$\Rightarrow \quad \frac{2\pi}{\lambda}\cdot\frac{1}{2}\cdot\frac{2\pi}{d}\cdot sin\theta = \frac{1}{4}\left(\frac{2\pi}{d}\right)^2$$

$$\Rightarrow \quad 2dsin\theta = \lambda$$

Bragg condition for diffraction.

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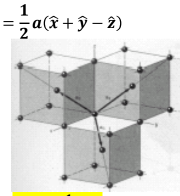
bcc lattice

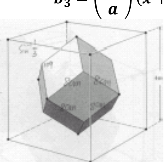
Primitive vectors of real space bcc lattice are:

$$\vec{a}_1 = \frac{1}{2}a(-\hat{x}+\hat{y}+\hat{z})$$
$$\vec{a}_2 = \frac{1}{2}a(\hat{x}-\hat{y}+\hat{z})$$
$$\vec{a}_3 = \frac{1}{2}a(\hat{x}+\hat{y}-\hat{z})$$

Reciprocal primitive vectors of bcc reciprocal space

$$\vec{b}_1 = \left(\frac{2\pi}{a}\right)(\hat{y}+\hat{z})$$
$$\vec{b}_2 = \left(\frac{2\pi}{a}\right)(\hat{z}+\hat{x})$$
$$\vec{b}_3 = \left(\frac{2\pi}{a}\right)(\hat{x}+\hat{y})$$





$$V_c = \frac{1}{2}a^3 \qquad V_k = 2\left(\frac{2\pi}{a}\right)^3$$

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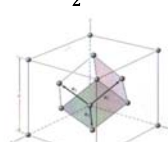
fcc lattice

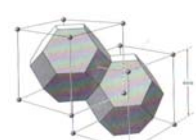
Primitive vectors of real space fcc lattice.

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z})$$
$$\vec{a}_2 = \frac{a}{2}(\hat{z}+\hat{x})$$
$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$$

Primitive vectors of fcc reciprocal lattice

$$\vec{b}_1 = \frac{2\pi}{a}(-\hat{x}+\hat{y}+\hat{z})$$
$$\vec{b}_1 = \frac{2\pi}{a}(\hat{x}-\hat{y}+\hat{z})$$
$$\vec{b}_3 = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z})$$





$$V = \frac{1}{4}a^3 \qquad V_k = 4\cdot\left(\frac{2\pi}{a}\right)^3$$

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Fourier analysis of the basis

When diffraction condition is satisfied ($\Delta\vec{k} = \vec{G}$), eq. (18) can be written as

$$F_G = N \int_{cell} n(\vec{r}) e^{-i\vec{G}\vec{r}}\, d^3r = NS_G \qquad (39)$$

The quantity S_G is called the **structure factor**.

It is useful to define the electron density $n(\vec{r})$ associated with individual atom in the cell, such that

$$n(\vec{r}) = \sum_{j=1}^{s} n_j(\vec{r} - \vec{r}_j) \qquad (40)$$

Where $\vec{r}_j$ is the vector to the center of j atom.

Substitute (40) into the definition of S_G

$$S_G = \int dV \sum_{j=1}^{s} n_j(\vec{r} - \vec{r}_j)\, e^{(-i\vec{G}\cdot\vec{r})}$$

Let $\vec{r} - \vec{r}_j = \vec{\rho}$, and $\vec{r} = \vec{\rho} + \vec{r}_j$ substitute in the above eq.

$$S_G = \sum_{j=1}^{s} e^{-i\vec{G}\cdot\vec{r}_j} \int dV n_j(\vec{\rho}) e^{-i\vec{G}\cdot\vec{\rho}}$$

Now we define the red integral above as **the atomic form factor, f_j** so

$$S_G = \sum_{j=1}^{s} f_j e^{-i\vec{G}\cdot\vec{r}_j} \qquad (43)$$

From definition of $\vec{G}$, we can write the structure factor as

$$S_G = \sum_{j=1}^{s} f_j exp[-i2\pi(n_1x_j + n_2y_j + n_3z_j)] \qquad (46)$$

If this is a pure element, all atoms are the same, then $f_j = f$, and can be moved out of the summation.

Structure factor of the bcc lattice

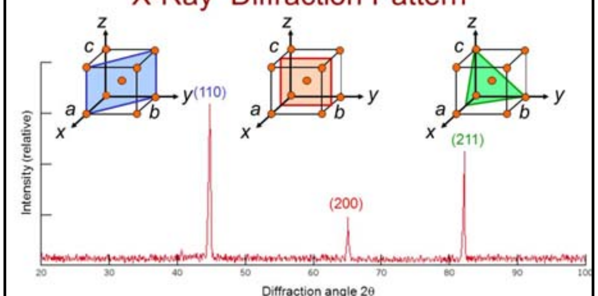
For bcc lattice, there are two atoms per conventional cell, the atoms are located at (0,0,0) and (½, ½, ½), so the structure factor.

$$S_G = f\left[1 + e^{-i\pi(n_1+n_2+n_3)}\right]$$

$n_1 + n_2 + n_3 = odd$ ⟹ $S_G = 0$

$n_1 + n_2 + n_3 = even$ ⟹ $S_G = 2f$

X-Ray Diffraction Pattern

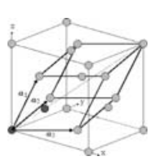


Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.20, Callister 5e.

Structure factor of the fcc lattice

There are 4 atoms per conventional cell at (0,0,0) (0,½,½), (½,0,½), and (½,½,0).

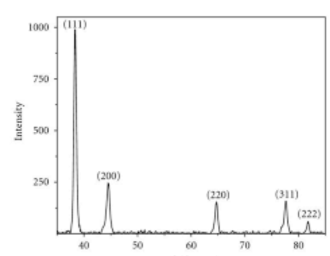


$$S_G = f\left[1 + e^{-i\pi(n_1+n_2)} + e^{-i\pi(n_2+n_3)} + e^{-i\pi(n_3+n_1)}\right]$$

n_1= even, n_2= even, n_3= even, ⟹ $S_G = 4f$

n_1= odd, n_2= odd, n_3= odd, ⟹ $S_G = 4f$

All other combinations ⟹ $S_G = 0$



X-ray diffraction pattern of Ag nanoparticles, indicating fcc structure.

/www.researchgate.net/publication/258387984_Green_Fabrication_of_Silver_Nanoparticles

Atomic form factor

The atomic form factor f_j defined on page 26 is given by

$$f_j = \int n_j(\vec{\rho})e^{-i\vec{G}\cdot\vec{\rho}}\,dV$$

The integration is over the volume of ONE atom only, and $\vec{\rho}$ is the vector from nucleus to the electron. The f_j is a measure of the scattering power of the jth atom in the unit cell. If we use spherical coordinates, $dV = r^2 dr sin\theta d\theta d\varphi$ and choose $\vec{G}$ in the z-direction:

$$f_j = 2\pi \iint r^2 sin\theta dr d\theta n_j e^{-iGrcos\theta}$$

$$= 4\pi \int r^2 n_j(r)\frac{sinGr}{Gr}dr$$

If all electrons are concentrated at $r = 0$, for example

$$n_j(r) = \frac{Z\delta(r)}{\frac{4\pi}{3}R^3} \quad \text{Then} \quad \lim_{r\to 0}\frac{sinGr}{Gr} = 1$$

$$f_j = 4\pi \int r^2 n_j(r)dr = Z$$

In general, $n_j(r)$ is a very difficult quantity to calculate. In most cases, the atomic Hartree-Foch approach is a very good approximation.