x-ray diffraction

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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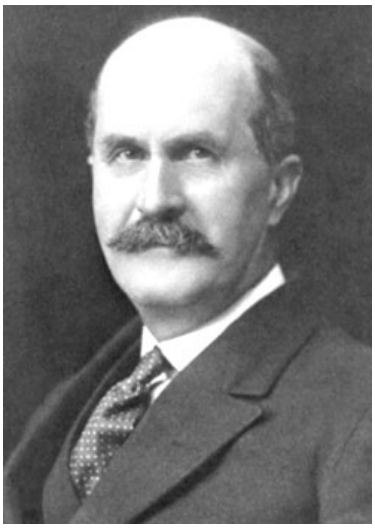
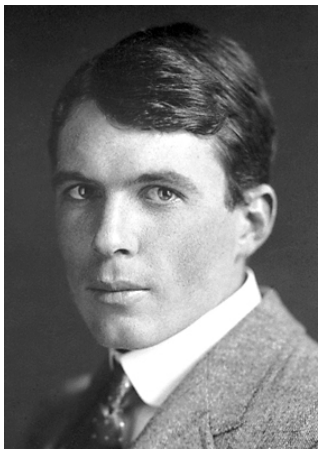
Sir William Henry Bragg OM, KBE, PRS[1] (2 July 1862 – 10 March 1942) was a British physicist, chemist, mathematician and active sportsman who uniquely shared a Nobel Prize with his son William Lawrence Bragg - the 1915 Nobel Prize in Physics. The mineral Braggite is named after him and his son.



http://en.wikipedia.org/wiki/William_Henry_Bragg

Sir **William Lawrence Bragg** CH OBE MC FRS (31 March 1890 – 1 July 1971) was an Australian-born British physicist and X-ray crystallographer, discoverer (1912) of the Bragg law of X-ray diffraction, which is basic for the determination of crystal structure. He was joint winner (with his father, Sir William Bragg) of the Nobel Prize for Physics in 1915.



http://en.wikipedia.org/wiki/William_Lawrence_Bragg

1. x-ray source

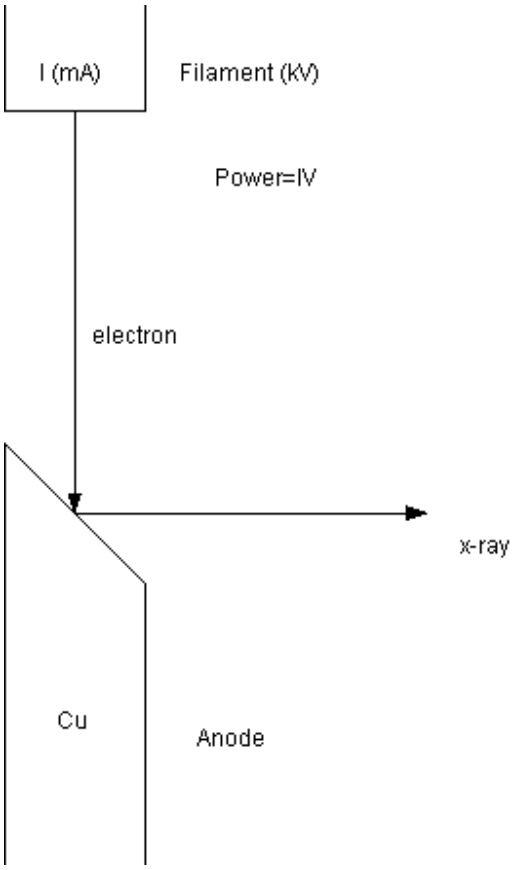


Fig. Schematic diagram for the generation of x-rays. Metal target (Cu or Mo) is bombarded by accelerating electrons. The power of the system is given by $P = I$(mA) V(keV), where I is the current of cathode and V is the voltage between the anode and cathode. Typically, we have $I = 30$ mA and $V = 50$ kV: $P = 1.5$ kW.

We use two kinds of targets to generate x-rays: Cu and Mo.
The wavelength of $CuK_{\alpha 1}$, $CuK_{\alpha 2}$ and CuK_{β} lines are given by

$$\lambda_{K\alpha 1} = 1.540562 \text{ Å}. \quad \lambda_{K\alpha 2} = 1.544390 \text{ Å}, \ \lambda_{K\beta} = 1.392218 \text{ Å}.$$

The intensity ratio of $CuK_{\alpha 1}$ and $CuK_{\alpha 2}$ lines is 2:1.

The weighed average wavelength $\lambda_{K\alpha}$ is calculated as

$$\lambda_{K\alpha} = \frac{2\lambda_{K\alpha 1} + \lambda_{K\alpha 2}}{3} = 1.54184 \text{ Å}.$$

((Note)) The wavelength of MoKα is $\lambda_{K\alpha}$ = 0.71073 Å. Figure shows the intensity versus wavelength distribution for x rays from a Mo target. The penetration depth of MoK_α line is much longer than that of CuK_α l,ine.

$\lambda_{K\alpha 1}$ = 0.709300 Å. $\lambda_{K\alpha 2}$ = 0.713590 Å, $\lambda_{K\beta}$ = 0.632 Å

$$\lambda_{K\alpha} = \frac{2\lambda_{K\alpha 1} + \lambda_{K\alpha 2}}{3} = 0.71073 \text{ Å}.$$

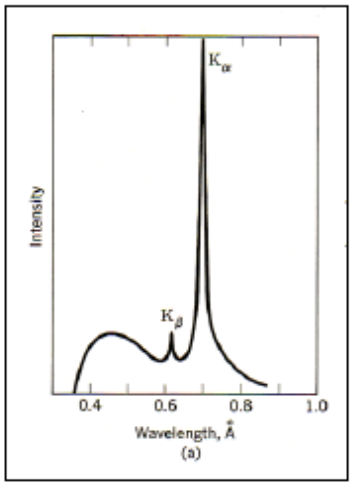


Fig. Intensitry vs wavelength distribution for x-rays from a Mo target bombarded by 30 keV electrons from C. Kittel, Introduction to Solid State Physics.

2. Principle of x-ray diffraction

x-ray (photon) behaves like both wave and particle. In a crystal, atoms are periodically located on the lattice. Each atom has a nucleus and electrons surrounding the nucleus. The electric field of the incident photon accelerates electrons. The electrons oscillate around a equilibrium position with the period of the incident photon. The nucleus does not oscillate because of the heavy mass.

Classical electrodynamics tells us that an accelerating charge radiates an electromagnetic field.

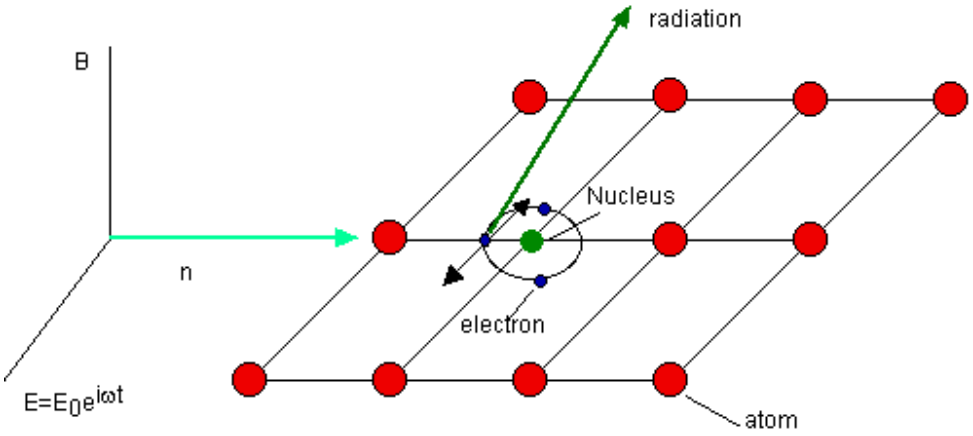


Fig. Schematic diagram for the interaction between an electromagnetic wave (x-ray) and electrons surrounding nucleus. The oscillatory electric field ($E = E_0 e^{i\omega t}$) of x-ray photon gives rise to the harmonic oscillation of the electrons along the electric field.

The instantaneous electromagnetic energy (radiation) flow is given by the pointing vector

$$\mathbf{S} \approx \frac{\dot{v}^2 \sin^2 \theta}{R^2}\mathbf{n}$$

The direction of the velocity **v** (the direction of the oscillation) is along the x direction. The direction of the photon radiation is in the (x, y) plane.

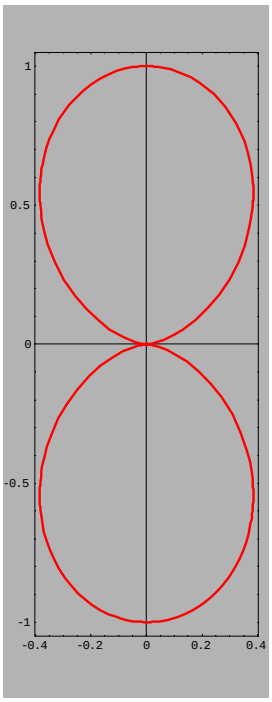


Fig.4 The distribution of instantaneous radiation energy due to the oscillation of electrons along the *x* direction. Thye Mathematica 5.2 (PolarPlot) is used.

3. Experimental configuration of x-ray scattering

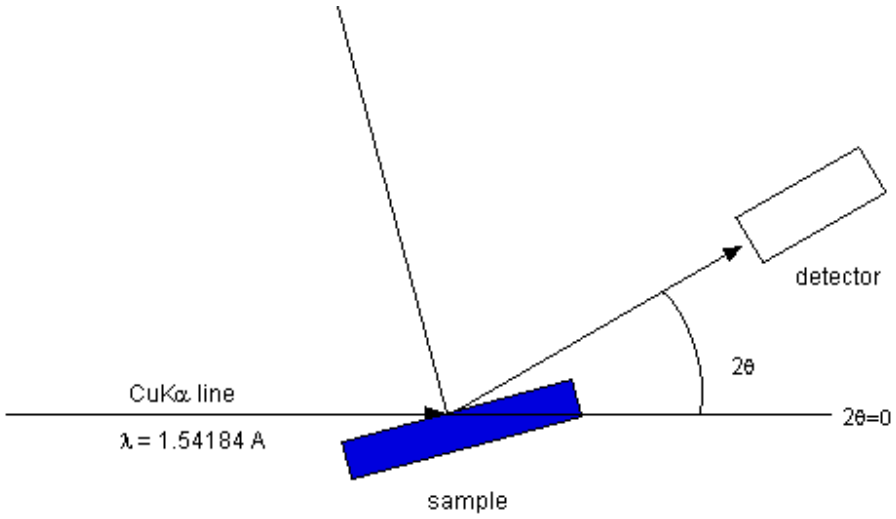


Fig. Example for the geometry of Ω (= θ)– 2θ scan for the (00*L*) x-ray diffraction. The Cu target is used. The direction of the incident x-ray is $2\theta = 0$. The angle between the detector and the direction of the incident x-ray is 2θ. W is the rotation angle of the sample.

4. Bragg condition

4.1. Bragg law

The incident x-rays are reflected specularly from parallel planes of atoms in the crystal.
(a) The angle of incoming x-rays is equal to the angle of outgoing x-rays.
(b) The energy of x-rays is conserved on reflection (elastic scattering).

The path difference for x-rays reflected from adjacent planes is equal to $\Delta d = 2d \sin\theta$. The corresponding phase difference is

$$\Delta\phi = \mathrm{k}\Delta d = (2\pi/\lambda)2d \sin\theta .$$

where k is the wave number ($k = 2\pi/\lambda$) and λ is the wave length.

Constructive interference of the radiation from successive planes occurs when $\Delta\phi = 2n\pi$, where n is an integer (Bragg's law).

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

The Bragg reflection can occur only for $\lambda \leq 2d$.

The Bragg law is a consequence of the periodicity of the lattice. The Bragg law does not refer to the composition of the basis of atoms associated with every lattice point. The composition of the bases determines the relative intensity of the various orders of diffraction.

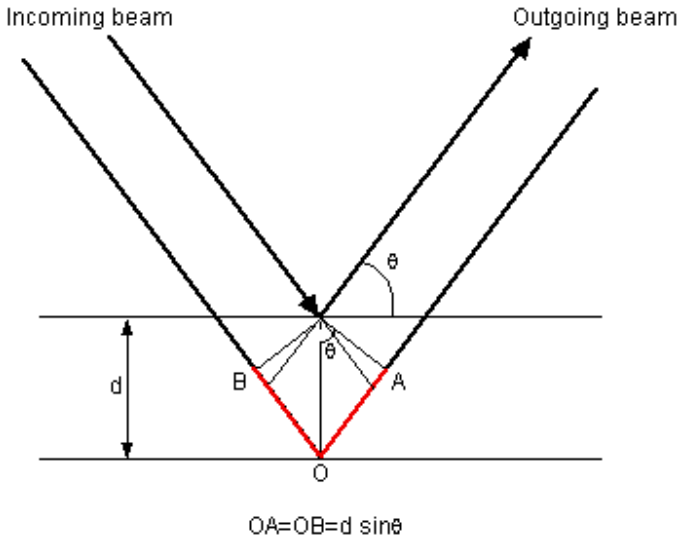


Fig.8 Geometry of the scattering of x-rays from planar arrays. The path difference between two rays reflected by planar arrays is $2d \sin\theta$.

4.2 Concept of Ewald sphere: introduction of reciprocal lattice

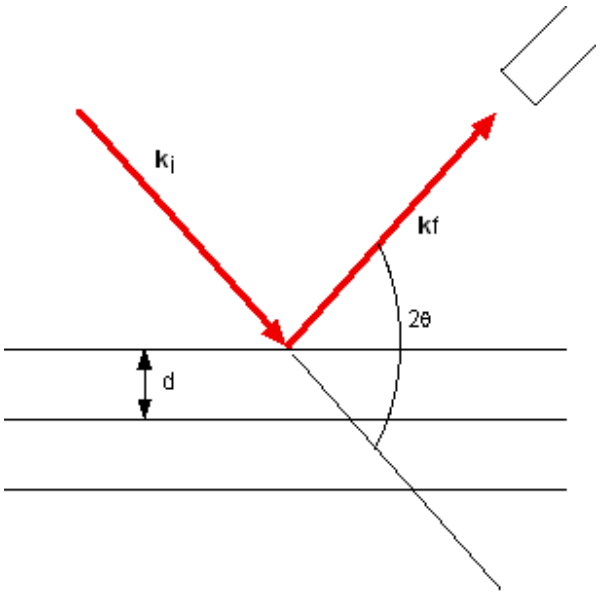


Fig. The geometry of the scattered x-ray beam. The incident x-ray has the wavevector k_i (= $\boldsymbol{k}$), while the outgoing x-ray has the wavevector $\boldsymbol{k}_f$ (= $\boldsymbol{k}$'). $|\mathbf{k}_i| = |\mathbf{k}_f| = 2\pi/\lambda$, where λ is the wavelength of x-ray.

Bragg law:

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

$\boldsymbol{k}_i$: incident wavevector.
$\boldsymbol{k}_f$ is the outgoing wavevector.

$$|\mathbf{k}_i| = |\mathbf{k}_f| = \frac{2\pi}{\lambda}$$

$\boldsymbol{Q}$ is the scattering vector:

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f, \quad \text{or} \qquad \mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$$

((**Ewald's sphere**))

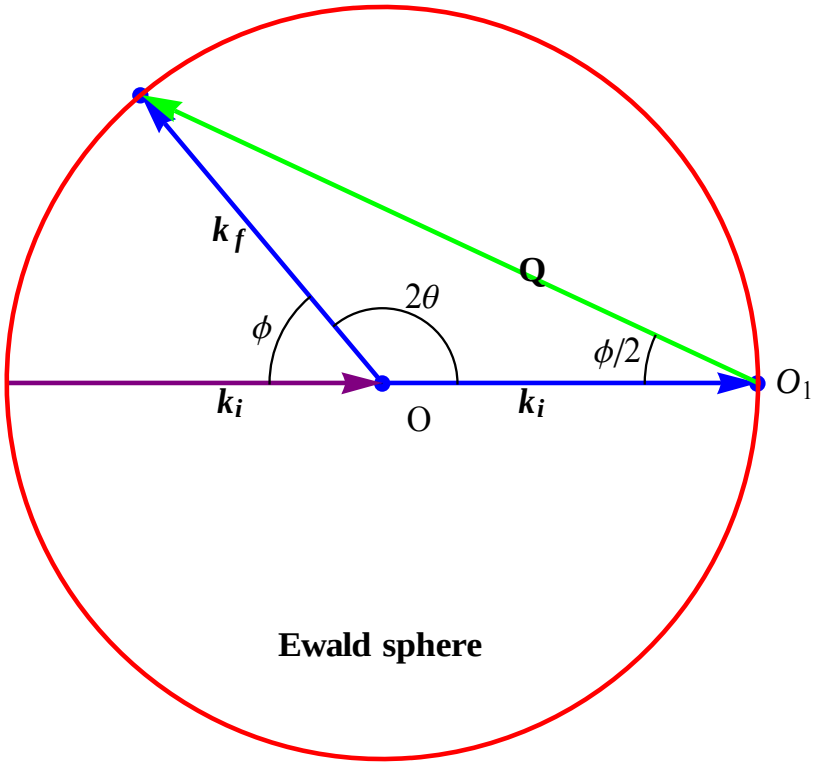


Fig. The geometry of Fig.10 using a circle with a radius k (= $2\pi/\lambda$). The scattering vector $\boldsymbol{Q}$ is defined by $\boldsymbol{Q} = \boldsymbol{k}_f - \boldsymbol{k}_i$.

This is a part of the Ewald sphere. The detail of the Ewald sphere will be discussed later.

In the above configuration, $\boldsymbol{Q}$ is perpendicular to the surface of the system

$$|\mathbf{Q}| = 2|\mathbf{k}_i|\sin\theta = \frac{4\pi}{\lambda}\sin\theta = \frac{4\pi}{\lambda}\frac{n\lambda}{2d} = \frac{2\pi}{d}n \quad \text{(Bragg condition)}$$

which coincides with the reciprocal lattice point. In other words, the Bragg reflections occur, when $\boldsymbol{Q}$ is equal to the reciprocal lattice vectors.

5. Ewald sphere and scattering

The reciprocal lattice will be discussed in the crystal structure and x-ray scattering.

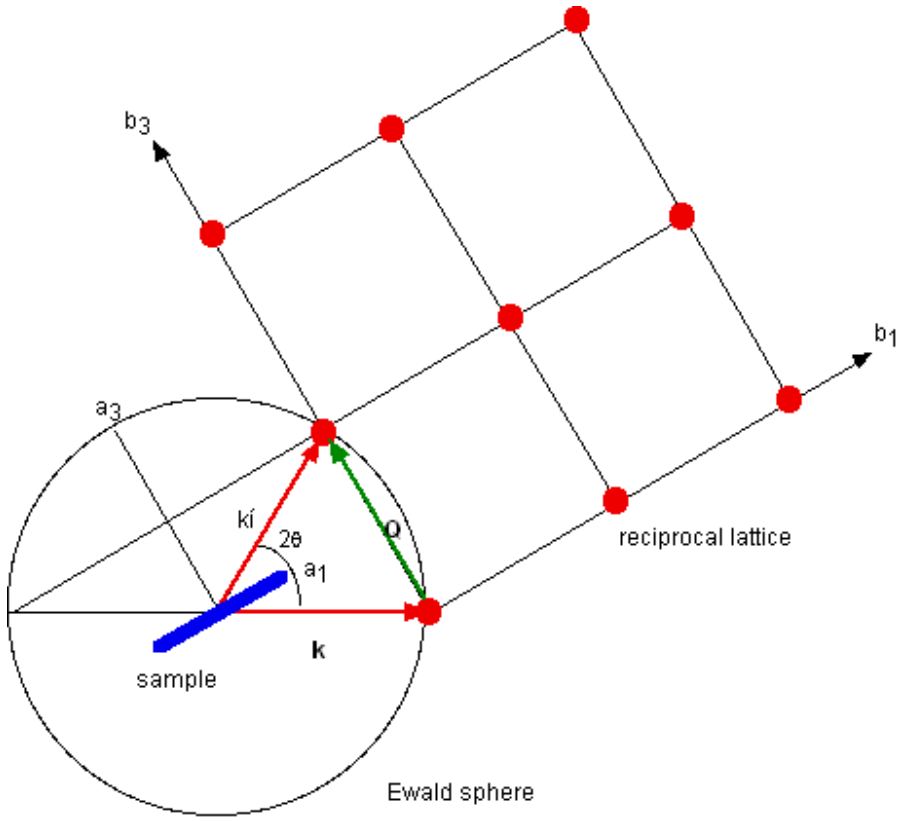


Fig. Ewald sphere. The origin of the reciprocal lattice is located at the end of the wavevector ***k*** of the incident beam.

We draw a sphere of radius $k=2\pi/\lambda$ about the starting point of ***k***. The origin of the reciprocal lattice plane corresponding to the real space of the sample is at the end point of ***k***. A diffracted beam will be formed if this sphere intersects any other point in the reciprocal lattice. The Ewald sphere intercepts a point connected with the end of ***k*** by a reciprocal lattice vector ***G***. This construction is due to Paul Peter Ewald.

Paul Peter Ewald: He was born in Berlin Germany on January 23, 1888. He was a U.S. (German-born) crystallographer and physicist. He was a pioneer of the x-ray diffraction methods. He was also the eponym of Ewald construction and the Ewald sphere. He was a Professor of Physics Department, Brooklyn Polytechnic Institute (1949 – 1959), New York. He was the father-in-law of Prof. Hans Bethe (the late). He died at Ithaca, New York on August 22, 1985. He was awarded the Max Planck medal in 1978.

6. (00l) scattering

Ewald sphere-1 (θ-2θ scan)

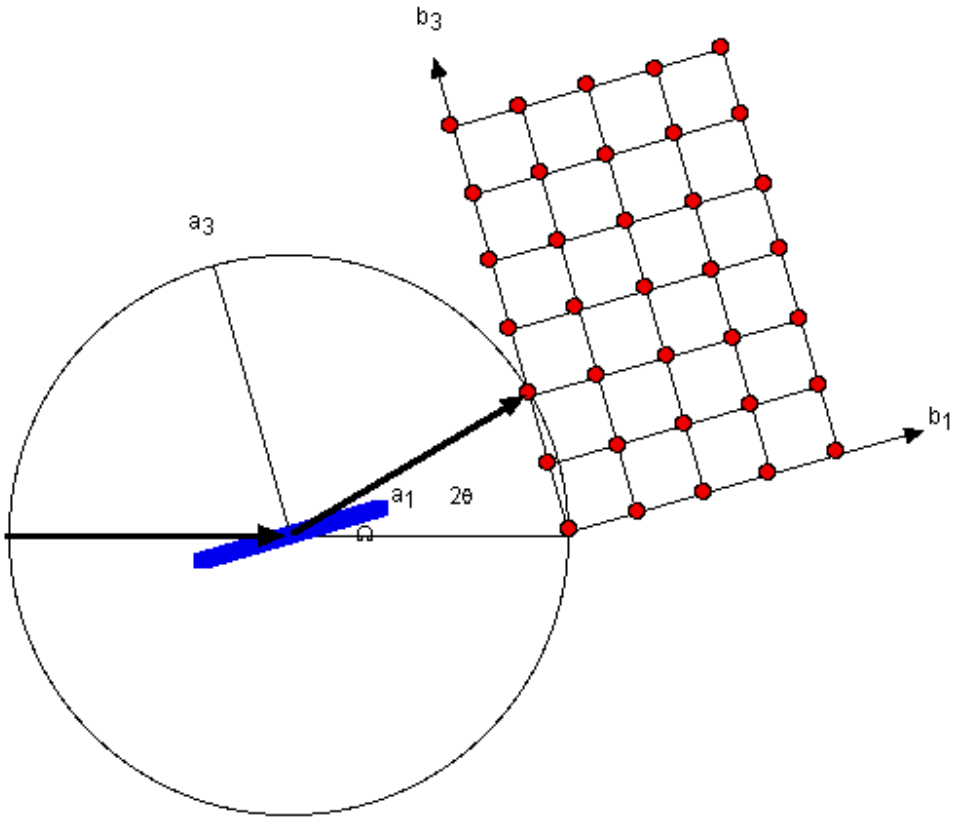


Fig.

Ewald sphere-2 (θ-2θ scan)

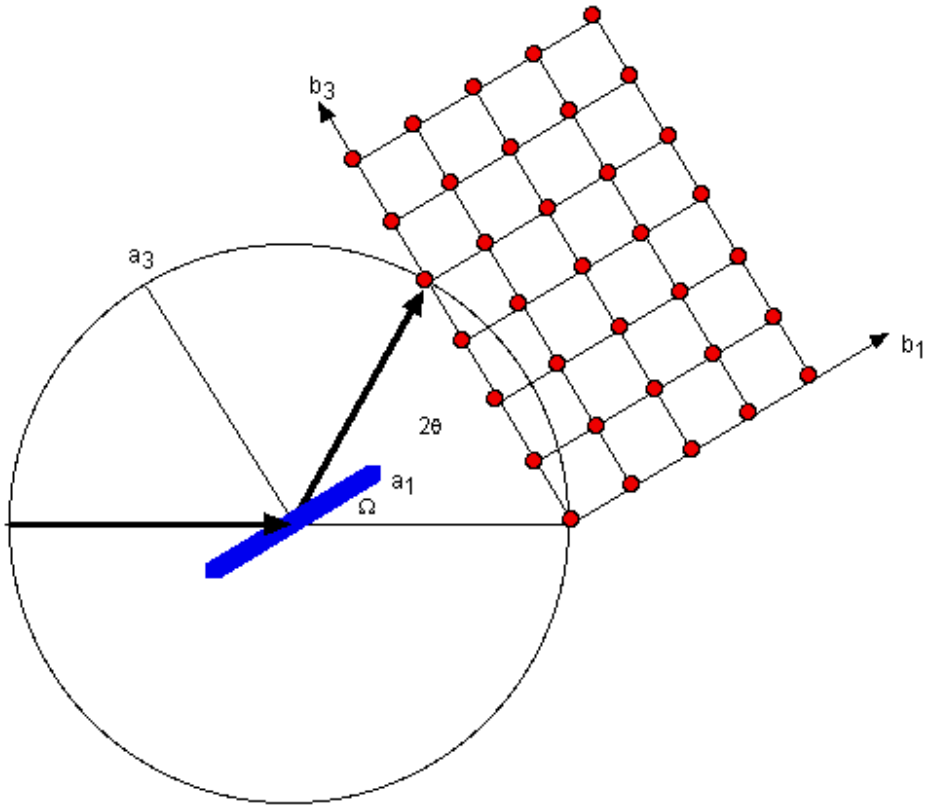


Fig.

Ewald sphere-3 (θ-2θ scan)

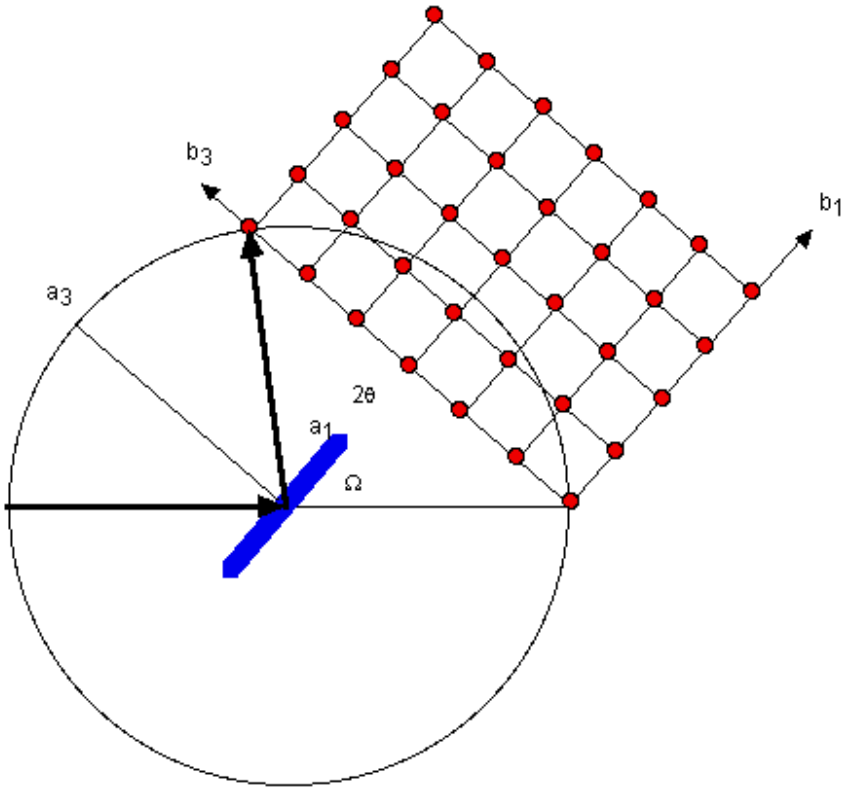


Fig. Examples for the Ewald construction for the (00*L*) x-ray diffraction. $\Omega (= \theta) - 2\theta$ scan.

7. Crystal structure of NaCl

The structure of NaCl:

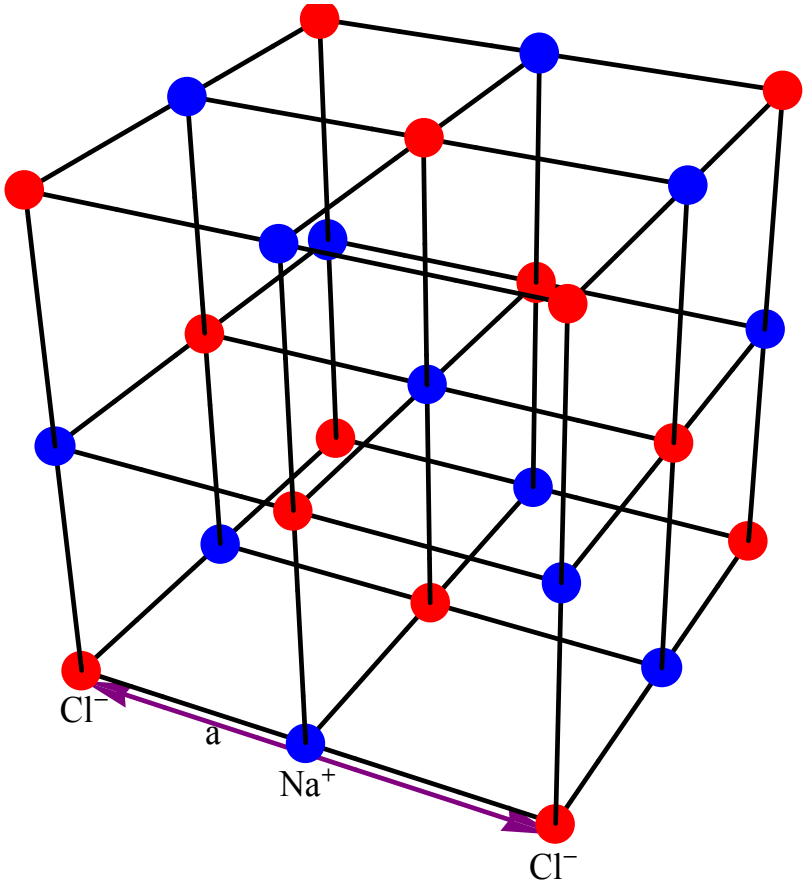


Fig. Crystal structure of NaCl. Na^+ (blue points). Cl^- (red points). The lattice constant *a* between the next nearest Cl^- ions is $a = 5.63$ Å.

((**Primitive cell**))

The primitive cell is the fcc (face centered cubic), where one Na^+ ion and one Cl^- ion are included. Na+ and Cl- are alternatively arranged at the lattice points of a SC (simple cubic). Each ion is surrounded by 6 nearest neighbors of the opposite charge.

((**Conventional cell**))

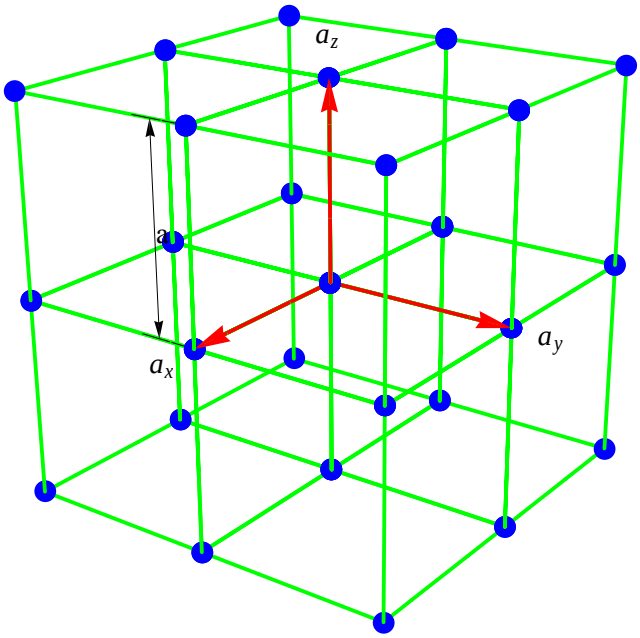
The conventional cell is the sc (simple cubic) with the lattice constant a = 5.63 Å, where 4 Na^+ ions and 4 Cl^- ions are included.

$$Cl^-: \quad 1 + 6 \times \frac{1}{2} = 4$$

$$Na^+: \quad 12 \times \frac{1}{4} + 1 = 4$$

The lattice constant *a* between Cl^- ions is equal to $a = 5.63$ Å.

8. Simple cubic(sc) structure:



Structure of simple cubic (sc) lattice,

$$\mathbf{a}_x = a(1,0,0), \qquad \mathbf{a}_y = a(0,1,0), \qquad \mathbf{a}_z = a(0,0,1)$$

$$\mathbf{a}_x \cdot (\mathbf{a}_y \times \mathbf{a}_z) = a^3$$

The reciprocal lattice vectors;

$$\mathbf{b}_x = \frac{2\pi(\mathbf{a}_y \times \mathbf{a}_z)}{\mathbf{a}_x \cdot (\mathbf{a}_y \times \mathbf{a}_z)} = \frac{2\pi}{a}(1,0,0)$$

$$\mathbf{b}_y = \frac{2\pi(\mathbf{a}_z \times \mathbf{a}_x)}{\mathbf{a}_x \cdot (\mathbf{a}_y \times \mathbf{a}_z)} = \frac{2\pi}{a}(0,1,0)$$

$$\mathbf{b}_z = \frac{2\pi(\mathbf{a}_x \times \mathbf{a}_y)}{\mathbf{a}_x \cdot (\mathbf{a}_y \times \mathbf{a}_z)} = \frac{2\pi}{a}(0,1,0)$$

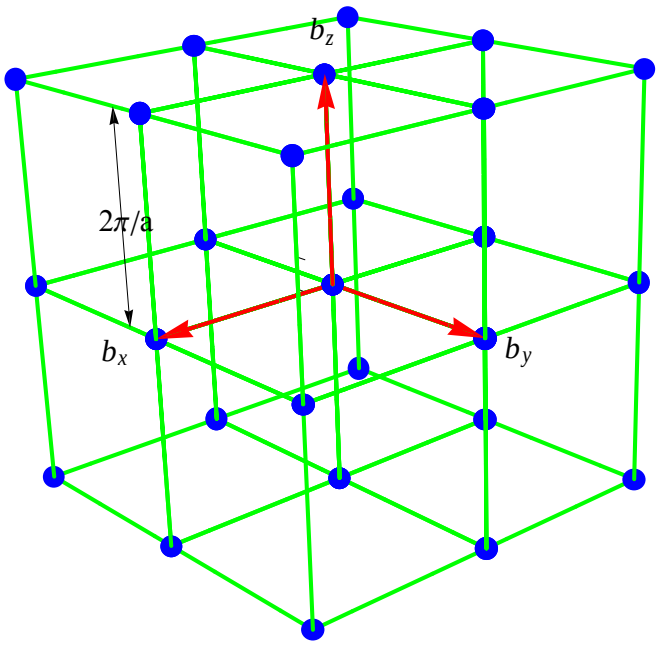


Fig. Reciprocal lattice points of scc. The vectors $\boldsymbol{b}_x$, $\boldsymbol{b}_y$, and $\boldsymbol{b}_z$ are the reciprocal lattice vectors.

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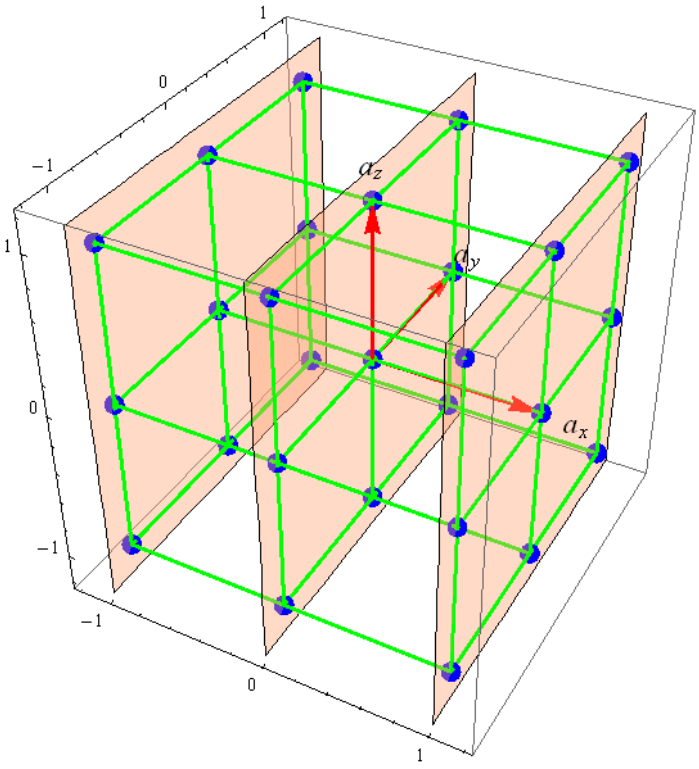
9. Typical planes for sc (simple cubic)

(a) (100) plane

The distance between the adjacent cubic (110) plane is

$$d(100) = a$$

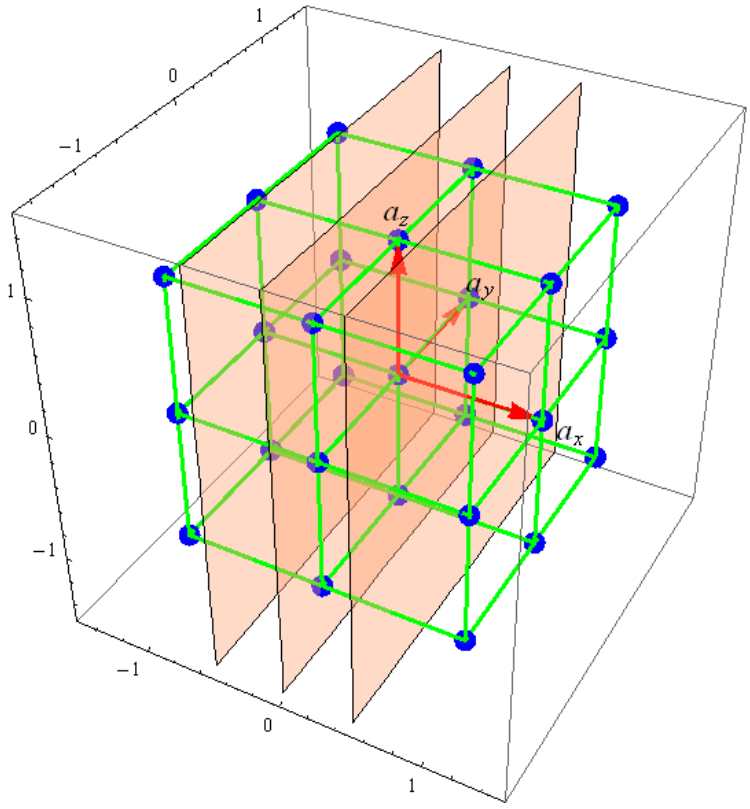


(100) plane

(b) (200) plane

The distance between the adjacent cubic (200) plane is given by

$$d(200) = \frac{a}{2}$$

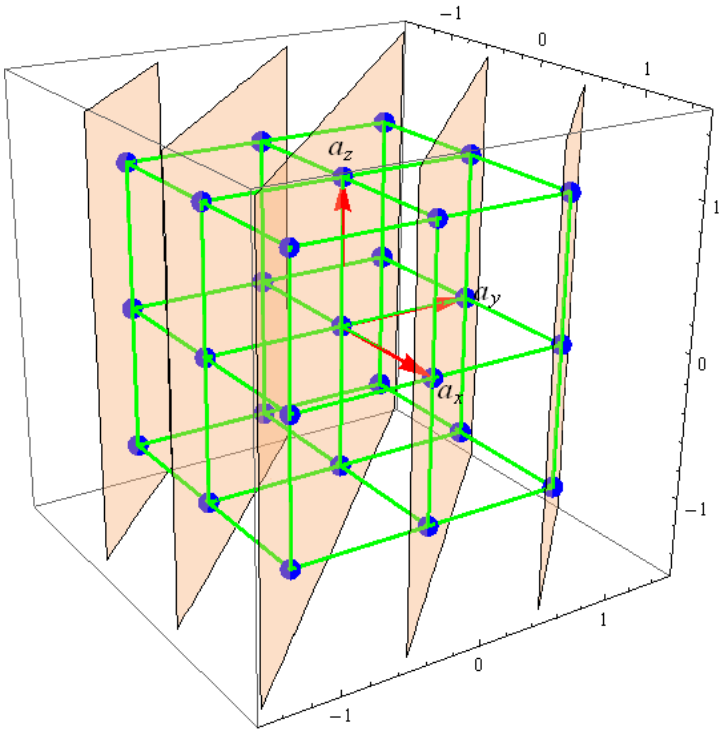


(200) plane

(c) (110) plane

The distance between the adjacent cubic (110) plane is

$$d(110) = \frac{a}{\sqrt{2}}$$

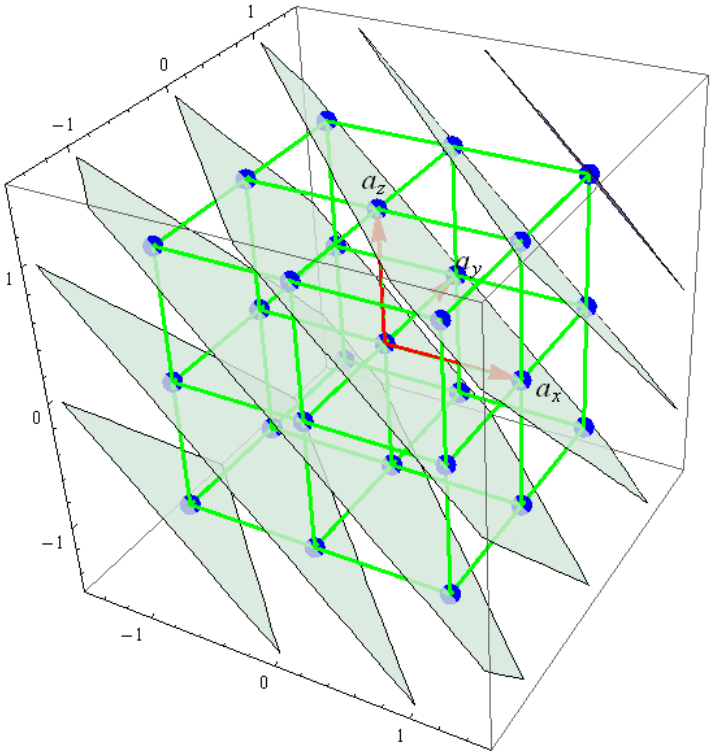


(110) plane

(d) (111) plane;

The distance between the adjacent cubic (111) plane is given by

$$d(111) = \frac{a}{\sqrt{3}}$$



(111) plane

10. x-ray diffraction pattern of NaCl

The wavelength of CuKa is λ = 1.54184 Å. A typicalx-ray powder diffraction is shown bellow, where the Miller indices for th planes are those for the conventional primitive cell (simple cubic, lattice constant a = 5.63 Å). The Bragg peaks appear at the (*h*, *k*, *l*) Miller indices with all even indeces or all odd indices. The strongest peak appears at the (200) Miller indices.

From the Bragg condition that

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

with

$$d = \frac{a}{2},$$

the angle of 2θ can be evaluated as

$$2\frac{a}{2}\sin\theta = \lambda$$

or

$2\theta = 31.79°$

((**x-ray diffraction of NaCl powder**))