

Structural analysis

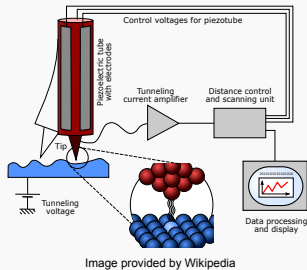
- Reciprocal lattice

- Diffraction theory

- X-ray scattering: Experimental methods

How to analyze the atomic arrangement in crystals?

Atomic resolution imaging



Scattering methods

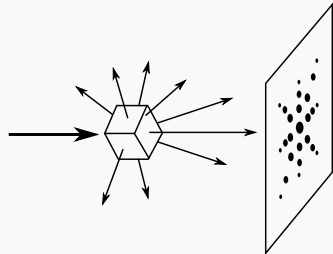


Image provided by Wikipedia

Structural analysis

- Reciprocal lattice

- Diffraction theory

- X-ray scattering: Experimental methods

Definition of the reciprocal lattice

- Consider a Bravais lattice with lattice vectors $\mathbf{R} = \sum_i u_i \mathbf{a}_i$. In the following, we will call this lattice the direct lattice.
- The corresponding reciprocal lattice is defined by the set of all vectors $\mathbf{G}$, for which the relation

$$\mathbf{G} \cdot \mathbf{R} = m2\pi; m \in \mathbb{Z}$$

holds for any lattice vector $\mathbf{R}$.

- We can write any lattice vector of the reciprocal lattice as

$$\mathbf{G} = \sum_j v_j \mathbf{b}_j,$$

where the primitive translation vectors $\mathbf{b}_j$ of the reciprocal lattice satisfy the condition

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

- The reciprocal lattice of the reciprocal lattice is the direct lattice.
- The first Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice.

Primitive translation vectors of the reciprocal lattice

- 1D lattice:

$$b = \frac{2\pi}{a}.$$

- 2D lattice:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{Q}\mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{Q}\mathbf{a}_2},$$
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{Q}\mathbf{a}_1}{\mathbf{a}_2 \cdot \mathbf{Q}\mathbf{a}_1}.$$

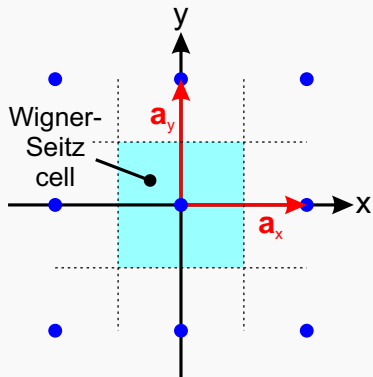
Here, $\mathbf{Q}$ is an anti-clockwise rotation by 90° .

- 3D lattice:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},$$
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},$$
$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.$$

Example: 2D square lattice

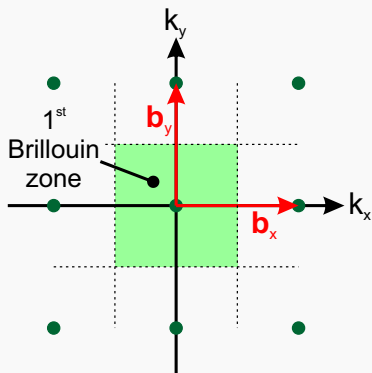
Real space



$$\mathbf{a}_x = (a, 0)$$

$$\mathbf{a}_y = (0, a)$$

Reciprocal space

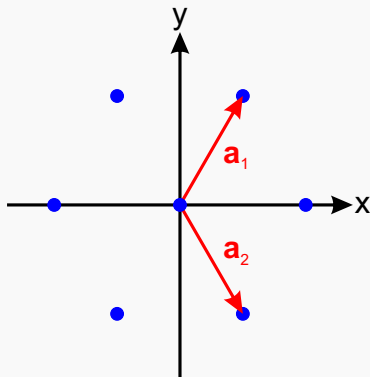


$$\mathbf{b}_x = \left(\frac{2\pi}{a}, 0 \right)$$

$$\mathbf{b}_y = \left(0, \frac{2\pi}{a} \right)$$

Example: 2D triangular lattice

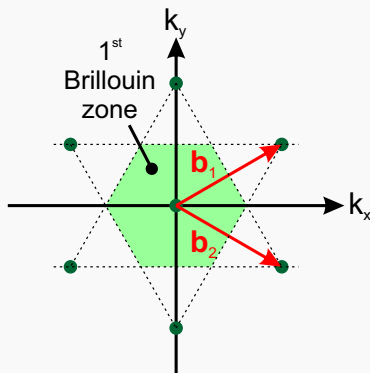
Real space



$$\mathbf{a}_1 = \frac{a}{2}(\mathbf{e}_x + \mathbf{e}_y\sqrt{3})$$

$$\mathbf{a}_2 = \frac{a}{2}(\mathbf{e}_x - \mathbf{e}_y\sqrt{3})$$

Reciprocal space



$$\mathbf{b}_1 = \frac{2\pi}{a}(\mathbf{e}_x + \mathbf{e}_y/\sqrt{3})$$

$$\mathbf{b}_2 = \frac{2\pi}{a}(\mathbf{e}_x - \mathbf{e}_y/\sqrt{3})$$

Reciprocal lattice and Miller indices

- The reciprocal lattice vector $\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is normal to the lattice plane with Miller indices (hkl) .

Proof: Exercise.

- The separation d_{hkl} between two adjacent lattice planes of this family is given by

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

Proof: Exercise.

Why do we need another lattice?

- Consider a periodic function $\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R})$ that is invariant under translation by any lattice vector $\mathbf{R}$.
- The Fourier expansion of $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}},$$

with the expansion coefficients

$$\rho_{\mathbf{G}} = \frac{1}{V_u} \int_{V_u} \rho(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} dV.$$

The sum runs over all reciprocal lattice vectors $\mathbf{G}$. The domain of integration is the primitive unit cell of the direct lattice and V_u is its volume.

Proof: Exercise.

Structural analysis

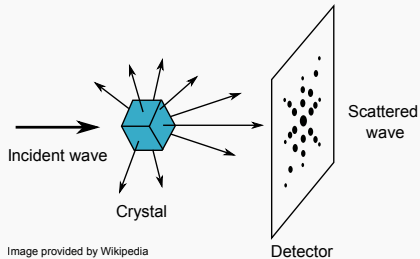
Reciprocal lattice

Diffraction theory

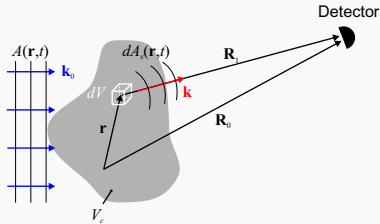
X-ray scattering: Experimental methods

Diffraction theory

- In the following, we discuss diffraction of a wave by a crystal.
- Our goal is to infer the arrangement of atoms in the crystal from the diffraction pattern.
- Originally, this theory was developed to explain x-ray diffraction patterns from crystals. Since the theory is not specific to the nature of the wave, it can be also applied to neutron- or electron-scattering.



Wave scattering by a crystal (1)

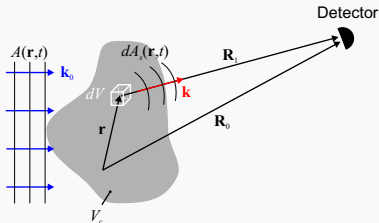


- Consider a plane wave with frequency ω_0 , wave vector $\mathbf{k}_0$, and amplitude A_0 impinging on a crystal:

$$A(\mathbf{r}, t) = A_0 e^{i(\mathbf{k}_0 \cdot \mathbf{r} - \omega_0 t)}.$$

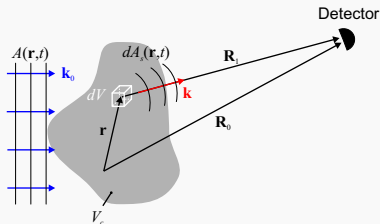
- The incident wave interacts with the atoms of the crystal and creates secondary, spherical waves.
- The field of the latter will vary as $e^{i\mathbf{k} \cdot \mathbf{R}}/|\mathbf{R}|$, where $|\mathbf{R}|$ is the distance from the scattering center.

Wave scattering by a crystal (2)



- The distribution of scattering centers in the crystal is characterized by a function $\rho(\mathbf{r})$ that depends both on the material and the nature of the incident wave.
- For example, x-rays are scattered for the most part from the electrons in the crystal while neutrons predominately interact with the atomic nuclei.
- We consider only elastic scattering and assume that the scattered waves do not undergo a second scattering event in the crystal.

Wave scattering by a crystal (3)



- The total scattered field at the detector results from the coherent superposition of the scattered waves emitted from all scattering centers. The contribution dA_s of a small volume dV around the point $\mathbf{r}$ is given by

$$\begin{aligned} dA_s(\mathbf{R}_0, t) &= \rho(\mathbf{r}) A(\mathbf{r}, t) \frac{e^{i\mathbf{k} \cdot \mathbf{R}_1}}{|\mathbf{R}_1|} dV \\ &= \rho(\mathbf{r}) A_0 e^{i(\mathbf{k}_0 \cdot \mathbf{r} - \omega_0 t)} \frac{e^{i\mathbf{k} \cdot \mathbf{R}_1}}{|\mathbf{R}_1|} dV. \end{aligned}$$

Wave scattering by a crystal (4)

- Integration over the volume of the crystal V_c yields the total scattered field:

$$A_s(\mathbf{R}_0, t) = \frac{A_0 e^{i(\mathbf{k} \cdot \mathbf{R}_0 - \omega_0 t)}}{|\mathbf{R}_0|} \int_{V_c} \rho(\mathbf{r}) e^{i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}} dV.$$

- The spatial arrangement of the atoms is encoded in the so-called scattering amplitude:

$$A(\mathbf{K}) = \int_{V_c} \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} dV.$$

Here, we have introduced the scattering vector

$$\mathbf{K} = \mathbf{k} - \mathbf{k}_0.$$

- The detector signal is proportional to the intensity of the scattered wave:

$$I(\mathbf{K}) \propto |A(\mathbf{K})|^2 = \left| \int_{V_c} \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} dV \right|^2.$$

Wave scattering by a crystal (5)

- For a crystal, the distribution of scattering centers $\rho(\mathbf{r})$ is a periodic function and can be expanded in a Fourier-series. The intensity of the scattered wave can thus be written as

$$I(\mathbf{K}) \propto |A(\mathbf{K})|^2 = \left| \sum_{\mathbf{G}} \rho_{\mathbf{G}} \int_{V_c} e^{i(\mathbf{G}-\mathbf{K}) \cdot \mathbf{r}} dV \right|^2.$$

- For sufficiently large volumes, the integral is a representation of the δ -function:

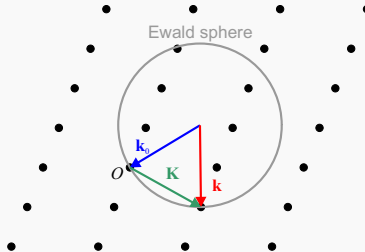
$$\int_{V_c} e^{i(\mathbf{G}-\mathbf{K}) \cdot \mathbf{r}} dV \simeq \begin{cases} V_c & \text{for } \mathbf{G} = \mathbf{K} \\ 0 & \text{for } \mathbf{G} \neq \mathbf{K} \end{cases}$$

- Hence, we can only observe a signal at the detector if the diffraction condition

$$\mathbf{G} = \mathbf{K}$$

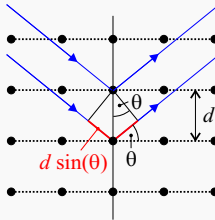
is fulfilled. In this case, the scattered waves from different unit cells are in phase and interfere constructively. Otherwise, destructive interference results in a negligible signal at the detector.

Ewald construction



- The Ewald construction is an elegant geometrical approach to find solutions of the diffraction condition:
 - Fix the tip of the incident wave vector $\mathbf{k}_0$ at the origin of the reciprocal lattice.
 - Draw a sphere (in 2D a circle) with radius $|\mathbf{k}_0|$ about the tail of $\mathbf{k}_0$. This sphere is usually referred to as the Ewald sphere.
 - The diffraction condition is fulfilled if a reciprocal lattice point $\mathbf{G}$ lies on the the Ewald sphere. The wave vector of the diffracted wave $\mathbf{k}$ is constructed by connecting the tail of $\mathbf{k}_0$ with the lattice point $\mathbf{G}$.

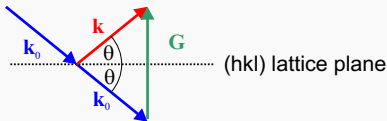
Bragg's law



- An intuitive explanation for the diffraction pattern produced a crystal was introduced by William Lawrence Bragg. He assumed, that a crystal is composed of parallel planes of atoms and that the incident wave is specularly reflected from these planes.
- A diffraction peak occurs if the reflected waves interfere constructively, i.e., the path difference is an integer multiple n of the wavelength λ . This condition leads to Bragg's law:

$$2d \sin(\theta) = n\lambda.$$

Bragg's law and the diffraction condition (1)



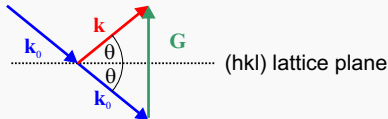
- The diffraction condition requires that the three vectors $\mathbf{k}_0$, $\mathbf{k}$, $\mathbf{G}$ can be arranged in a triangle.
- Inspection of the figure above shows that

$$\sin(\theta) = \frac{1}{2} \frac{\lambda}{2\pi} |\mathbf{G}|.$$

Here, we have used that

$$|\mathbf{k}_0| = |\mathbf{k}| = \frac{2\pi}{\lambda}.$$

Bragg's law and the diffraction condition (2)



- The reciprocal lattice vector $\mathbf{G}$ can always be written as

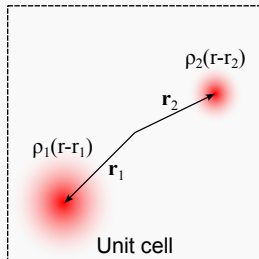
$$\mathbf{G} = n\mathbf{G}_{hkl},$$

where $\mathbf{G}_{hkl}$ is the shortest reciprocal lattice vector parallel to $\mathbf{G}$ and n is an integer.

- $\mathbf{G}_{hkl}$ is normal to the family of lattice planes characterized by the Miller indices (hkl) (see last section). Next, we identify Bragg's planes of atoms with this family of lattice planes and obtain together with $d_{hkl} = 2\pi/|\mathbf{G}_{hkl}|$ again Bragg's law

$$2d_{hkl} \sin(\theta) = n\lambda.$$

Structure factor of the basis and atomic form factor (1)



- We have shown that the reciprocal lattice of a given crystal determines the directions of the diffracted signals.
- The intensities of these signals are proportional to $|\rho_{\mathbf{G}}|^2$ and hence depend on the spatial distribution of scattering centers $\rho(\mathbf{r})$ in the unit cell.
- For further analysis, we start with the expansion coefficient

$$\rho_{\mathbf{G}} = \frac{1}{V_u} \int_{V_u} \rho(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} dV.$$

Structure factor of the basis and atomic form factor (2)

- Next, we write the distribution function $\rho(\mathbf{r})$ as the sum of the distribution functions $\rho_j(\mathbf{r} - \mathbf{r}_j)$ of the atoms contained in the unit cell:

$$\rho(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j).$$

Here, $\mathbf{r}_j$ is the vector to the center of the j -th atom.

- With this, we can express the expansion coefficient as

$$\begin{aligned}\rho_{\mathbf{G}} &= \frac{1}{V_u} \int_{V_u} \rho(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} dV = \frac{1}{V_u} \sum_j e^{-i\mathbf{G} \cdot \mathbf{r}_j} \int_{V_j} \rho_j(\mathbf{r}') e^{-i\mathbf{G} \cdot \mathbf{r}'} dV' \\ &= \frac{1}{V_u} \sum_j f_j(\mathbf{G}) e^{-i\mathbf{G} \cdot \mathbf{r}_j},\end{aligned}$$

where $\mathbf{r}' = \mathbf{r} - \mathbf{r}_j$.

- The function $f_j(\mathbf{G}) = \int_{V_j} \rho_j(\mathbf{r}') e^{-i\mathbf{G} \cdot \mathbf{r}'} dV'$ characterizes the scattering power of the j -th atom and is called the atomic form factor of this atom.

Structure factor of the basis and atomic form factor (3)

- Next, we define the structure factor of the basis by

$$S_{\mathbf{G}} = \rho_{\mathbf{G}} V_u = \sum_j f_j(\mathbf{G}) e^{-i\mathbf{G} \cdot \mathbf{r}_j}.$$

- For further analysis, it is useful to express the position vector of the atom j in terms of the translation vectors of the lattice:

$$\mathbf{r}_j = u_j \mathbf{a}_1 + v_j \mathbf{a}_2 + w_j \mathbf{a}_3.$$

Note that u_j , v_j , and w_j are no integers.

- With $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, we obtain

$$S_{\mathbf{G}} = \sum_j f_j(\mathbf{G}) e^{-2\pi i(hu_j + kv_j + lw_j)}.$$

Example: Structure factor of the bcc lattice

- A bcc lattice can be regarded as a simple cubic lattice with a unit cell containing two atoms located at $\mathbf{r}_1 = \mathbf{0}$ and $\mathbf{r}_2 = \frac{a}{2}(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y + \hat{\mathbf{e}}_z)$, respectively.
- The corresponding structure factor is given by

$$\begin{aligned} S_{\mathbf{G}} &= f(\mathbf{G}) \left[1 + e^{-i\pi(h+k+l)} \right] \\ &= \begin{cases} 2f(\mathbf{G}) & \text{for } h+k+l \text{ even} \\ 0 & \text{for } h+k+l \text{ odd} \end{cases} \end{aligned}$$

- Since the structure factor vanishes for odd $h+k+l$, there is, e.g., no Bragg reflex from the (100)-plane of a bcc crystal.

Structural analysis

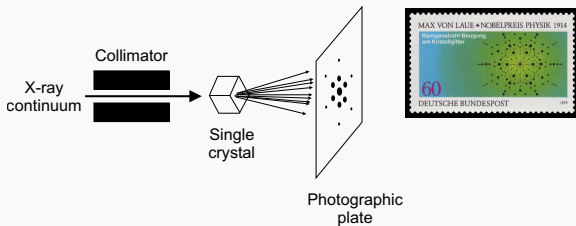
Reciprocal lattice

Diffraction theory

X-ray scattering: Experimental methods

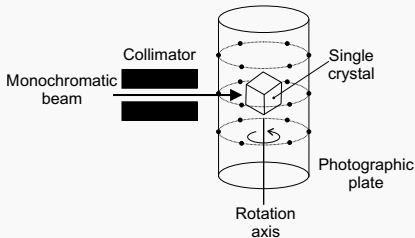
Laue method

- The Laue method uses a collimated x-ray beam with a continuous spectrum to illuminate a single crystal of fixed orientation.
- A Bragg peak can be observed with the detector if the diffraction condition is fulfilled by a wavelength component of the incident spectrum.
- If the incident beam is parallel to a symmetry axis of the crystal, the Laue diffraction pattern has the same symmetry. Hence, the Laue method is often used to determine the orientation of single crystals whose structure is known.



Rotating crystal method

- A single crystal is illuminated with a monochromatic x-ray beam. The crystal is oriented with one crystal axis perpendicular to the beam and rotated around this axis. As the crystal rotates, the reciprocal lattice also rotates by the same amount around this axis. Hence, the reciprocal lattice points move on circles around the axis and a Bragg reflex occurs whenever a circle intersects the Ewald sphere. The diffracted beams are recorded with a cylindrical photographic plate.
- The rotating crystal method can be used to determine the crystal structure of unknown materials.



Powder diffraction or Debye-Scherrer method

- Powder diffraction uses samples which contains many randomly oriented crystallites. As the sample is illuminated with a monochromatic x-ray beam, one will always find crystallites with proper orientation to satisfy the Bragg condition for a given family of lattice planes. The corresponding diffracted beams all lie on a cone with full opening angle 4θ (proof: exercise) around the incident beam direction.
- Powder diffraction allows for rapid analysis of multi-component mixtures without the need for extensive sample preparation.

