Basic principles of X-ray diffraction

Fundamentals of X-Ray diffraction:

X-rays
Crystals
X-rays interaction with matter
X-ray diffraction

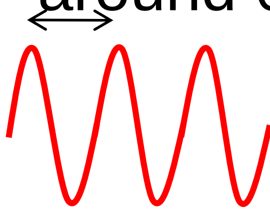
X-Rays and Crystals

- Why use X-Rays for crystal structure determination？

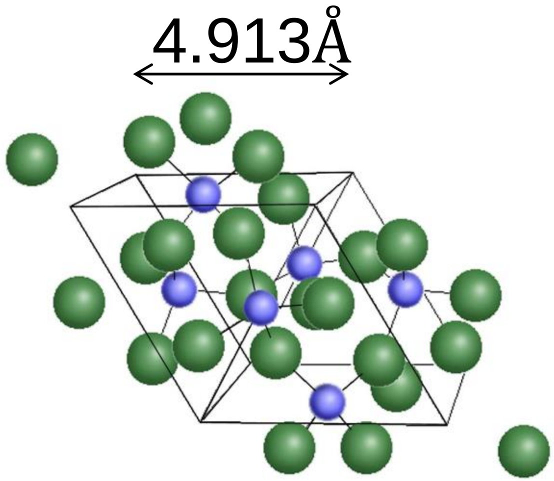
around several hundred nm

With the naked eye,
we can see colors and shapes of objects.

around 0.1nm（1Å）

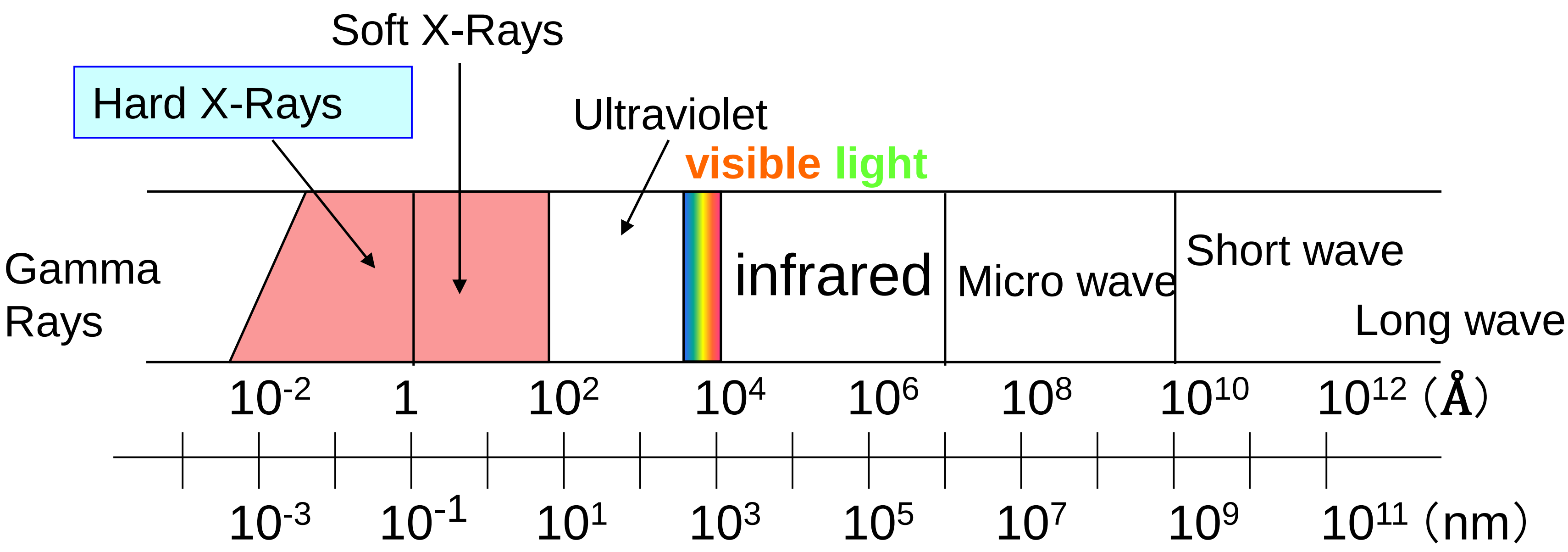


We can “see” atoms with X-rays.



What are X-rays?

- **X-rays are short wavelength electromagnetic waves**



Wilhelm Conrad Roentgen discovered X-Rays in 1895

Properties of X-rays

- X-Rays are a type of electromagnetic wave
  - γ-rays are generated by nuclear reactions
  - X-Rays are generated by energy transitions that happen when electrons hit a target
- An X-ray has a dual wave-particle character
  - As a wave motion: showing the diffraction phenomenon
  - As a particle: behaving as a particle that has an energy inversely proportional to its wavelength

$$E = 12.4 / \lambda$$

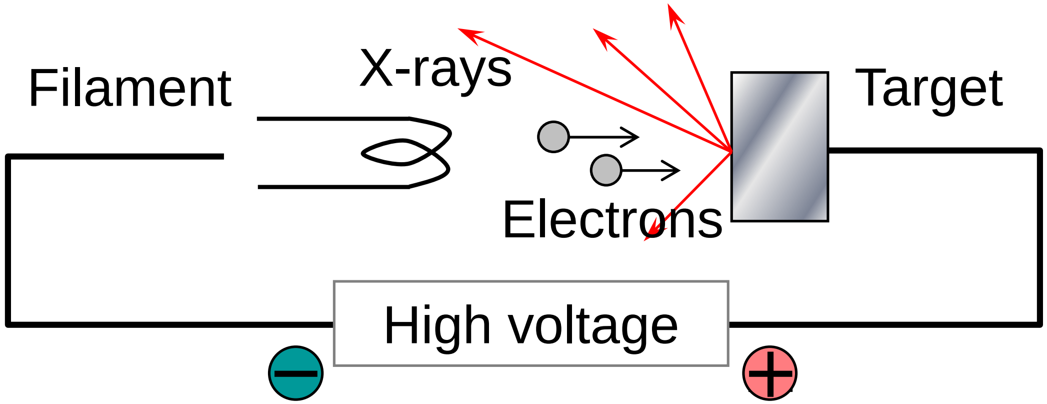
E : energy (keV)

λ : wavelength (Å)

Properties of X-rays

- Fluorescent behavior
  – Emitting visible light: scintillation counter (NaI)
- Ionization behavior
  – Generating positive and negative ions: proportional counter, position sensitive proportional counter (PSPC)
- The refractive index is nearly equal to 1
  – Not focused through a lens by refraction
  – Showing total reflection at very small incident angles
- High penetrating power
  – Passing through many materials due to high energy

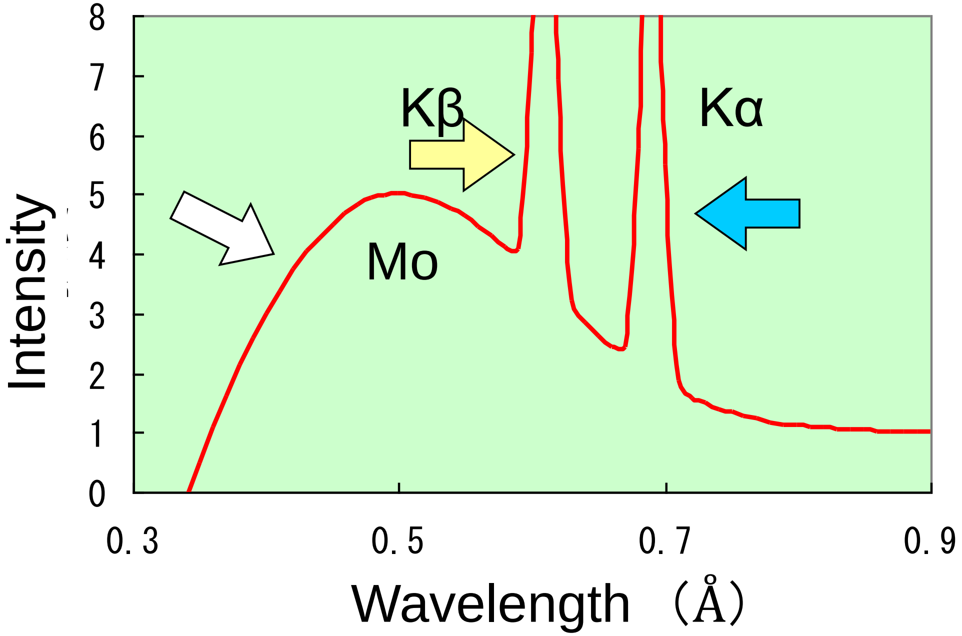
Generation of X-rays



- X-rays are generated when electrons extracted from the filament (Tungsten) and accelerated by high voltage bombard a target. Cu is commonly used for the target material.
- Almost all of the energy from the electrons is transformed into heat, and a small amount of the energy is converted into X-rays.

Generation efficiency $\varepsilon = 1.1 \times 10^{-9} ZV$ （Cu 0.1%）
Z：atomic number of a target material; V：applied voltage（V）

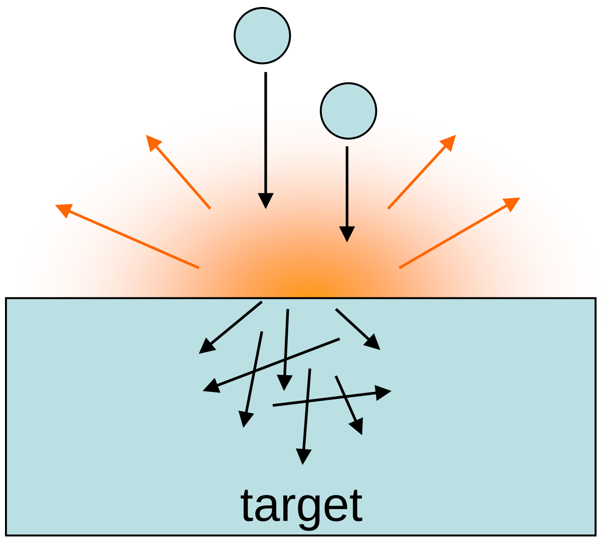
Characteristic X-rays & White X-rays

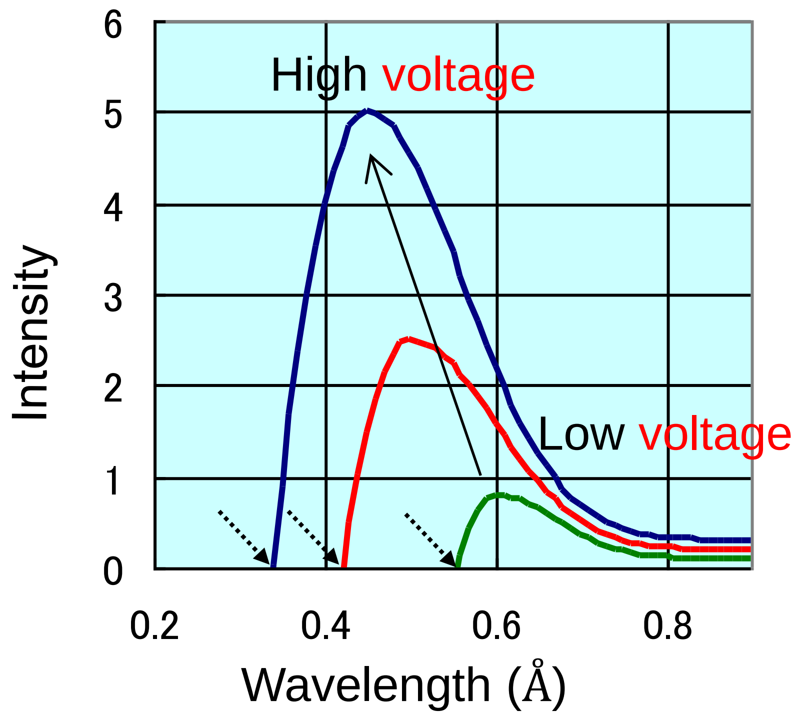


- White X-rays (Continuous X-rays, Bremsstrahlung X-rays)
- Characteristic X-rays (Kα and Kβ)

Principle of X-ray Generation

- White X-rays are emitted when the incident electron's speed is decelerated due to collision to the target





Properties of white X-rays

- As the voltage supplied to the target increases,
- the minimum wavelength decreases
- the larger integrated intensity is shown as a broad peak area
- the maximum peak position moves toward the shorter wavelength

Electron energy $E = V_e = hv$, $v = c / \lambda$

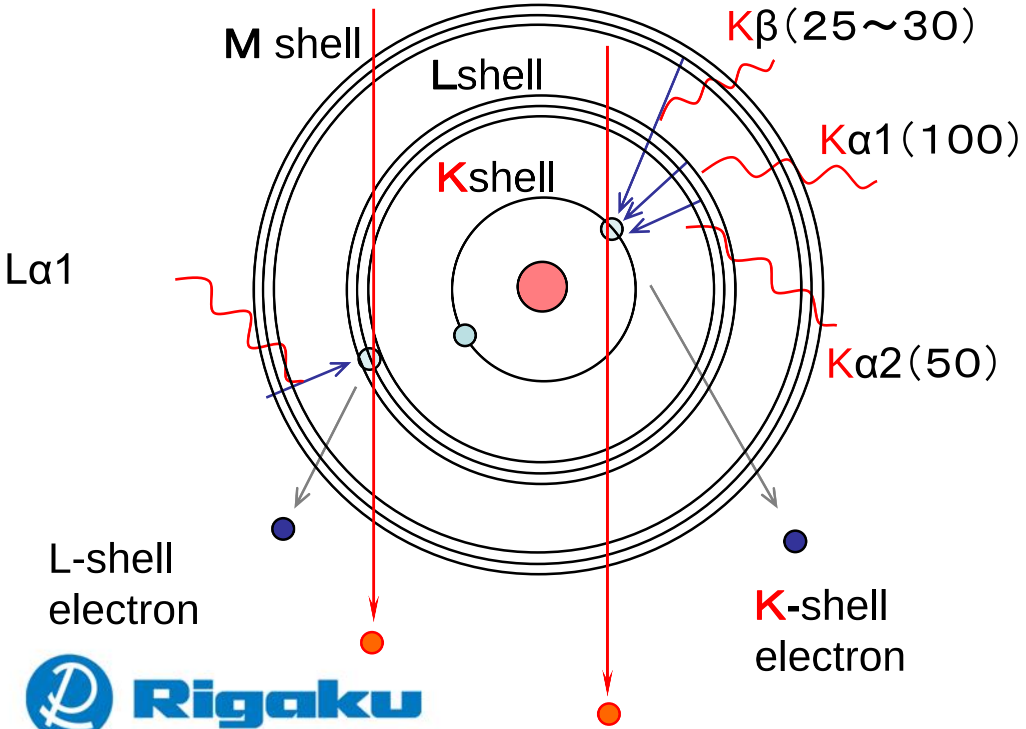
Minimum wavelength $\lambda_{min} = hc / V_e = 12.4 / V$

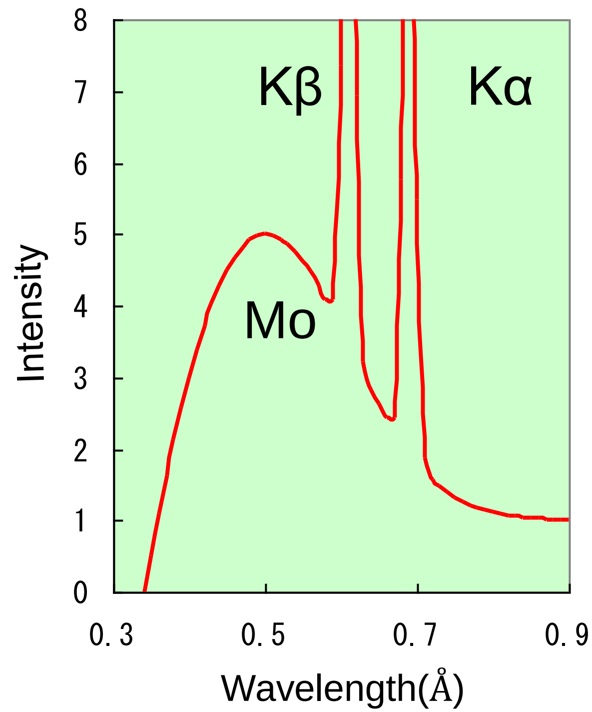
V : supplied voltage v : number of frequency

h : Plank's constant c : Velocity of light

Principle of characteristic X-ray Generation

- Characteristic X-rays are produced when an outer orbital electron falls into a vacancy in the K-shell created when high speed electrons eject an inner electron.





Intensity of characteristic X-rays and white X-rays

- Intensity of white X-rays

$$I \propto iV^2Z$$

- Intensity of characteristic X-rays

$$I \propto i(V-V_0)^n$$

The ratio between both intensities depends on the tube voltage.

I : Intensity
i : Tube current
V_0 : Excitation voltage
n : a coefficient dependent on the voltage
n=2 V is over 2～3 V_0
n=1 V is over $3V_0$

Z : Atomic number
V : Tube voltage

Set the X-ray tube voltage & current

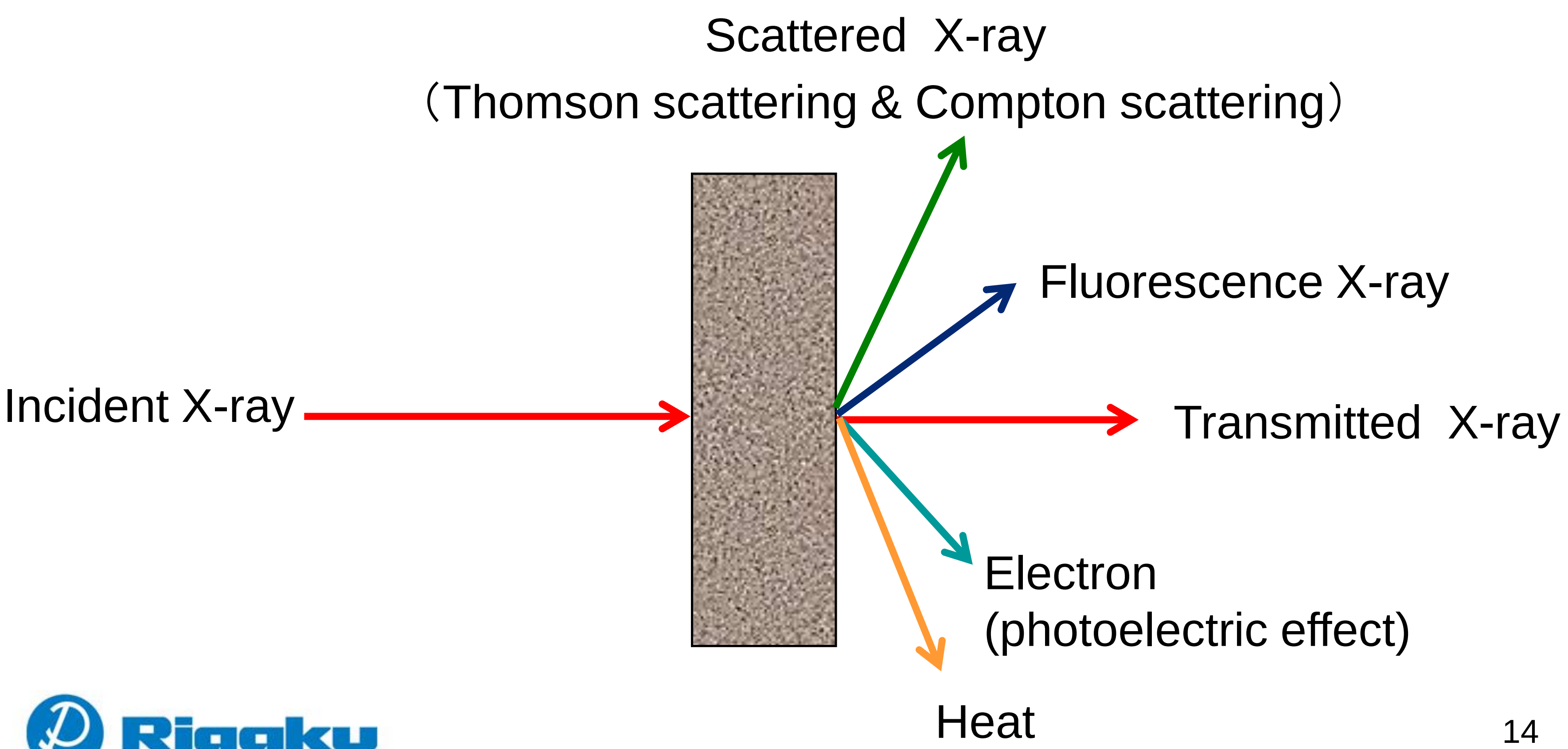
Proper tube voltage values to get maximum intensity & P/B ratio

X-ray tube	excitation voltage	proper voltage (kV)	
		max. intensity	max. P/B ratio
Mo	20.0	60	45～55
Cu	8.86	40～55	25～35
Co	7.71	35～50	25～35
Fe	7.10	35～45	25～35
Cr	5.98	30～40	20～30

The optimal tube voltage to get maximum intensity & P/B ratio is different for each X-ray tube

Interaction of X-rays with matter

- When X-rays encounter any form of matter, they are partly transmitted and partly absorbed.

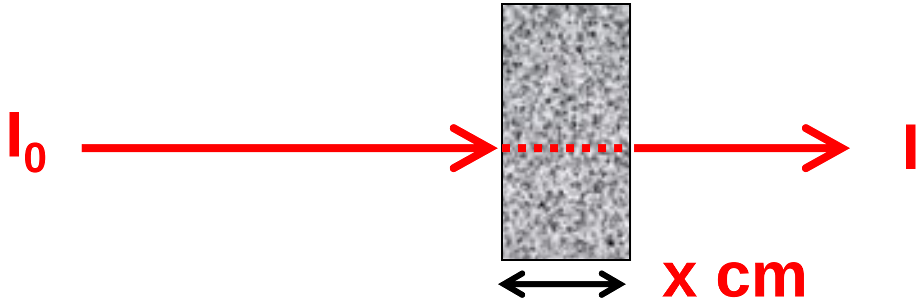


Absorption coefficient

- When X-rays pass through a sample with thickness of X cm, the intensity of the X-rays decrease from I_0 to I.

$$I = I_0 \exp^{(-\mu x)}$$

Beer-Lambert formula



μ : **Linear absorption coefficient** (cm^{-1})

μ/ρ : **Mass absorption coefficient** (cm^2/g)

ρ : **Density** (g/cm^3)

Mass absorption coefficient of compounds

- The Mass absorption coefficient of a compound, mixture or a liquid that consists of more than two elements can be calculated as

$$\mu/\rho = W_A(\mu/\rho)_A + W_B(\mu/\rho)_B + \cdots$$

W_A, $W_B \cdots$: A, B$\cdots$ weight percent of element

$(W_A + W_B + \cdots = 1)$

ex. :TiO_2 (CuKα)

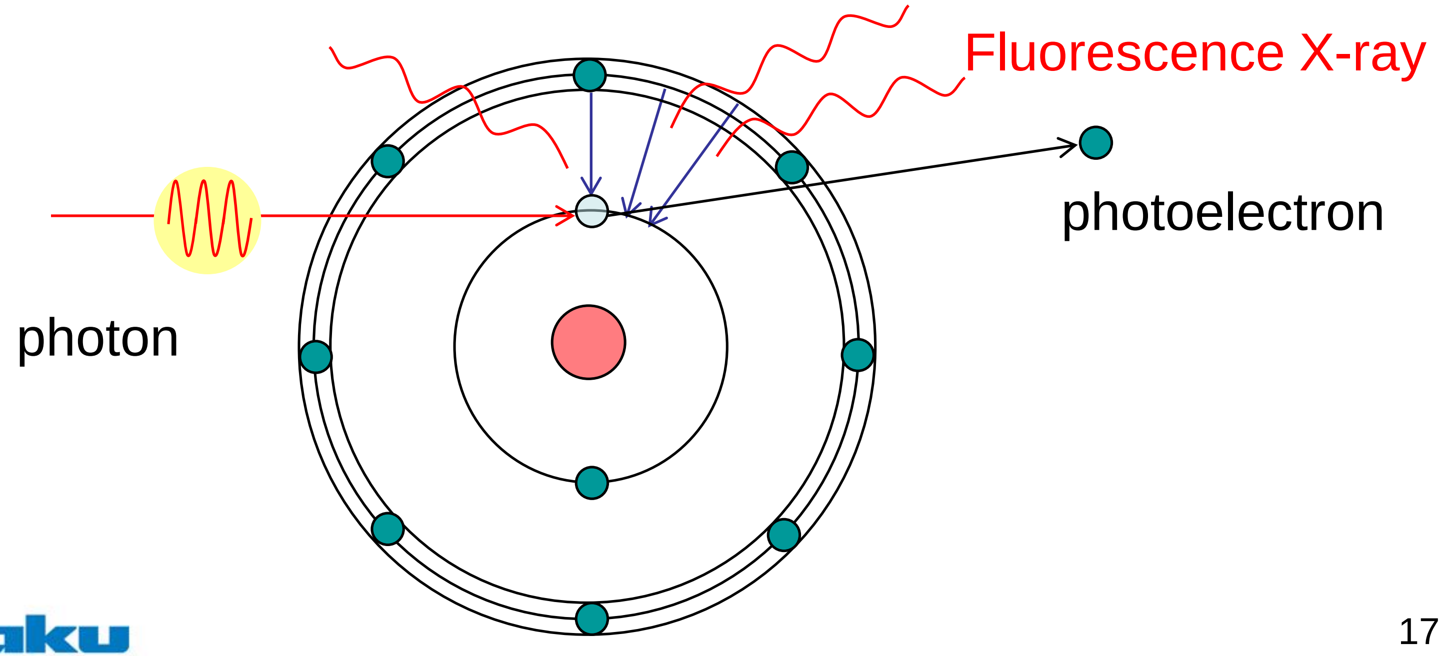
Ti : $\mu/\rho = 200$ atomic weight $= 47.9$

O : $\mu/\rho = 11.5$ atomic weight $= 16.0$

$$(\mu/\rho)_{TiO2} = \frac{47.9 \times 200}{47.9 + 16.0 \times 2} + \frac{16.0 \times 2 \times 11.5}{47.9 + 16.0 \times 2} = 124.5$$

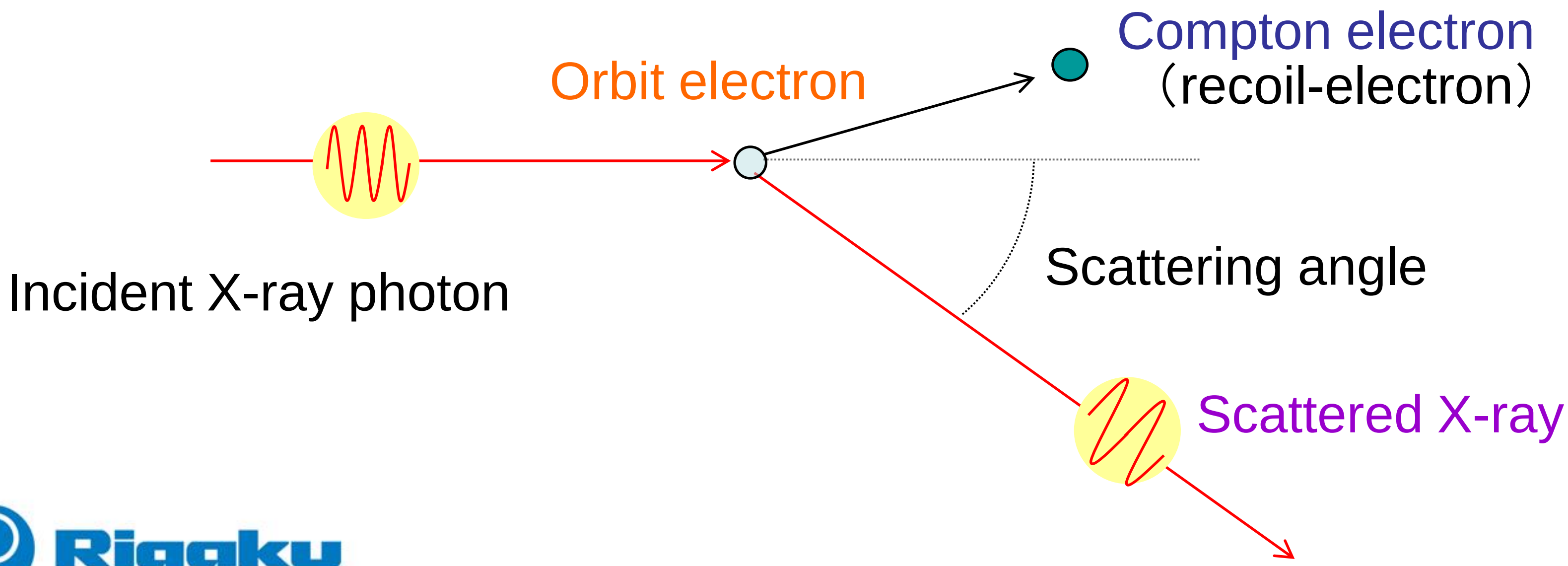
The photoelectric effect

- X-ray absorption can also occur when an X-ray photon ejects an inner electron.
- At the same time, a fluorescent X-ray is emitted when the electron of the outer orbit falls down to the vacancy of the inner orbit.



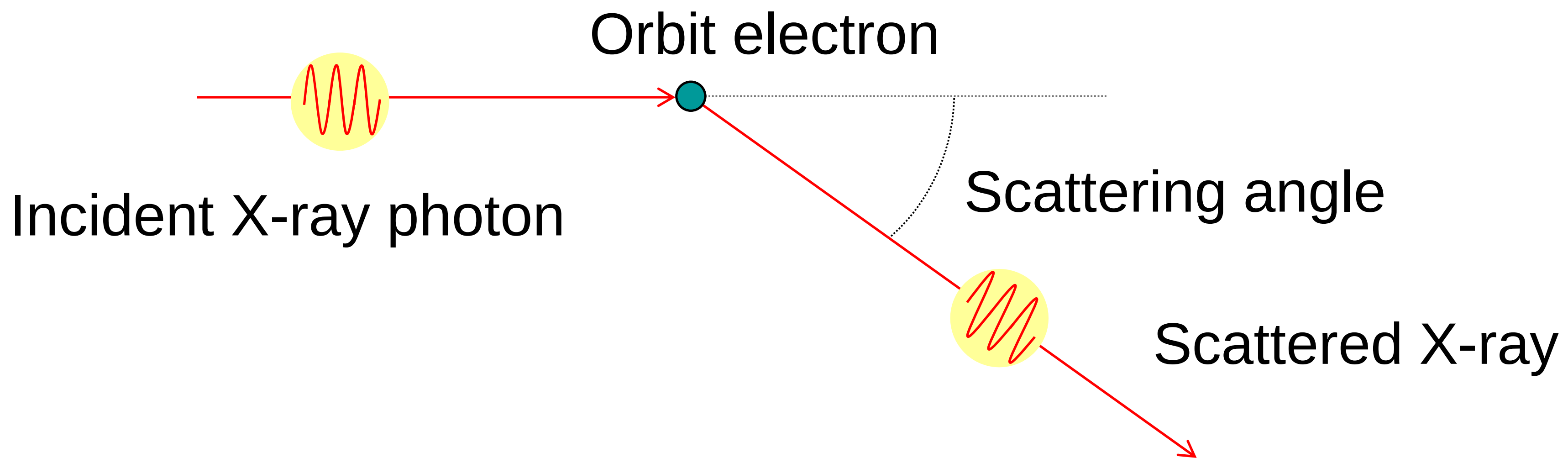
Compton scattering

- The X-ray photon shows inelastic collision with orbit electron and loses a part of its energy
- As the result of losing energy, the wavelength becomes longer and scatters relatively to the higher angle side.
- The Compton scattering contributes to the background in the measured data.



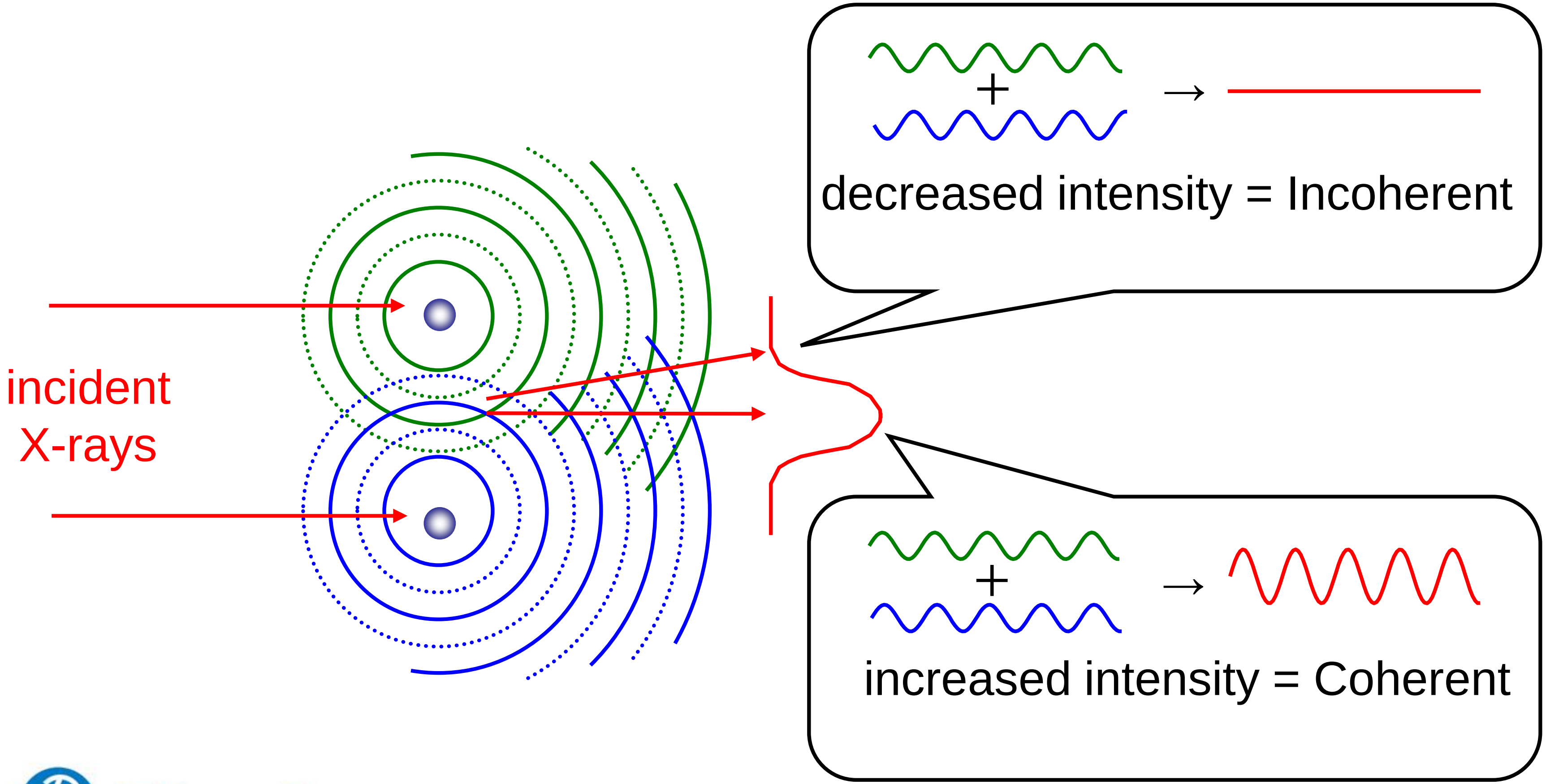
Thomson scattering

- The X-ray photon shows elastic collision: when the X-ray photon collides the orbit electron without losing any energy, it only changes the reflection direction with the same wavelength.
- This is called the diffraction phenomenon.



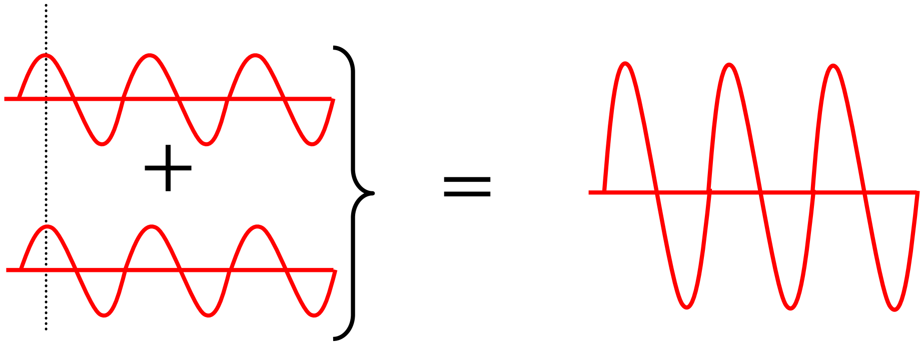
Interference from two point-like emitters

The interference takes place according to the way atoms are arranged

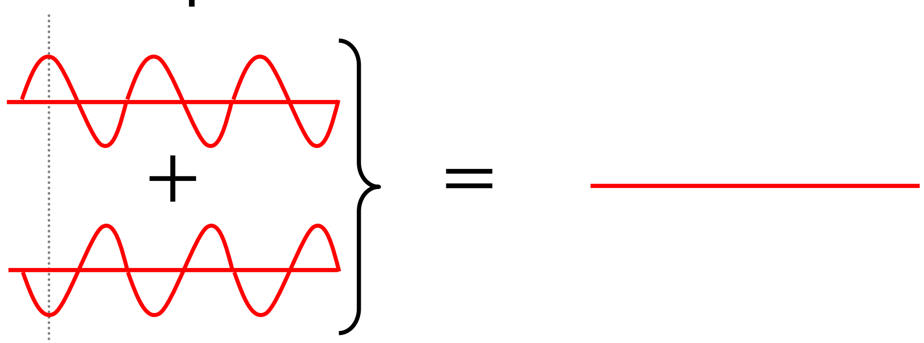


Interference

In phase ⇨ constructive

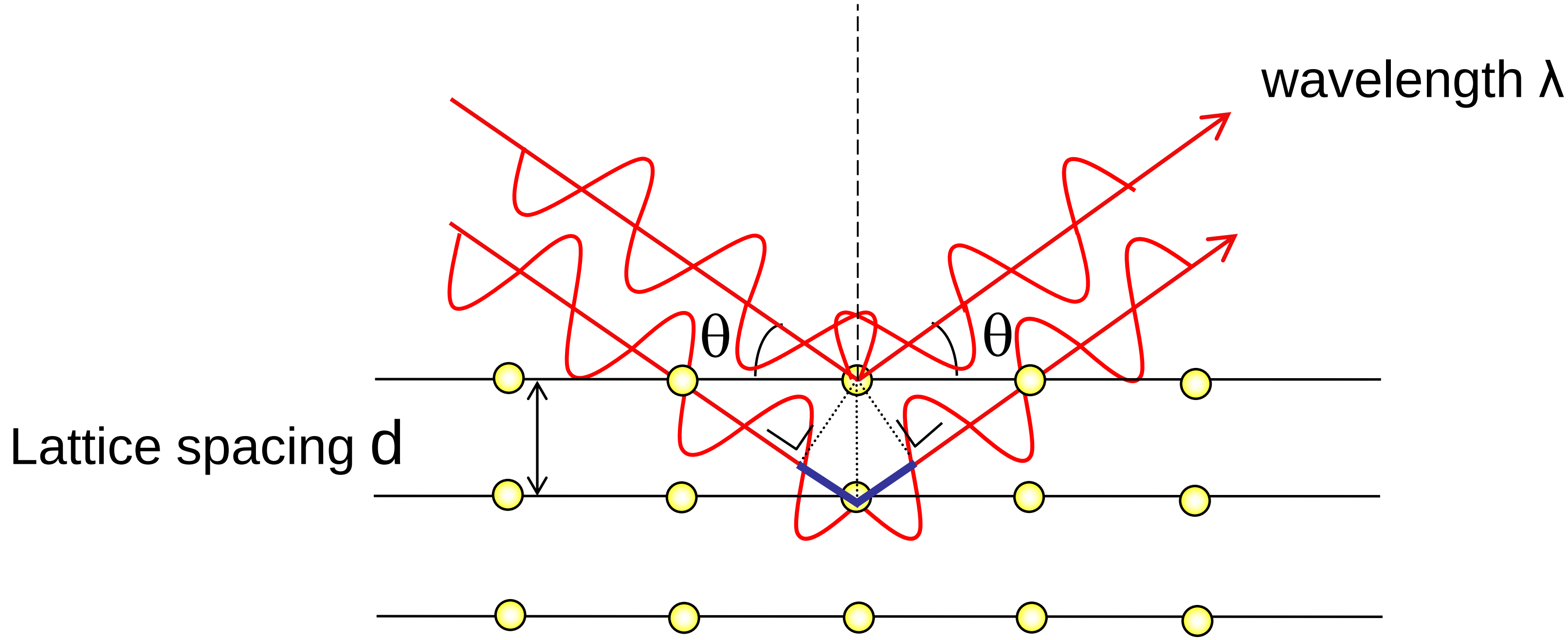


Out of phase ⇨ destructive



The Bragg Law

The Diffraction phenomenon

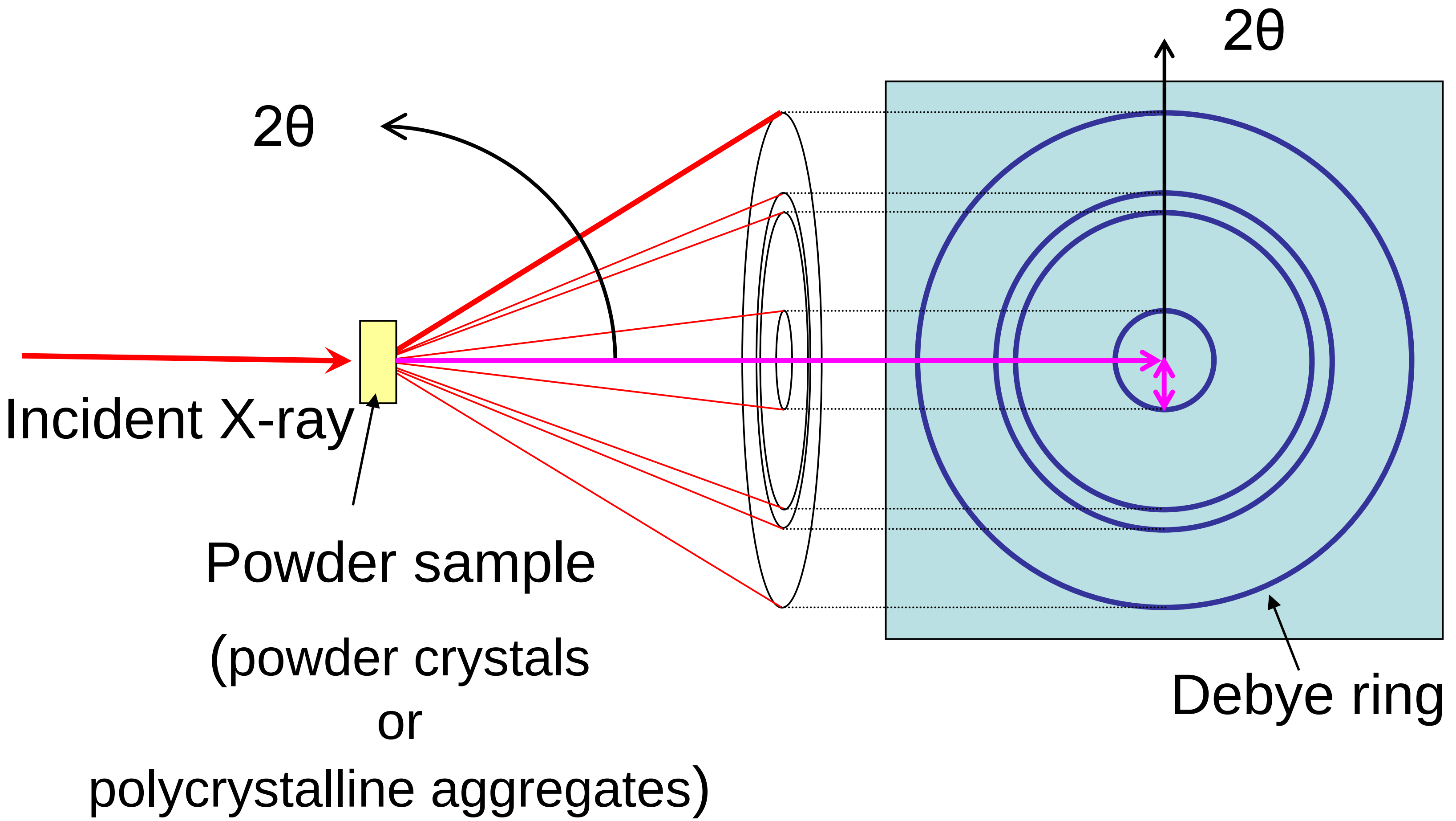


The Bragg Law: $2d \sin\theta = n\lambda$

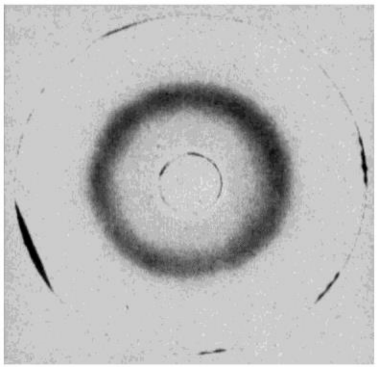
Fundamentals of X-ray diffraction:

XRD methods

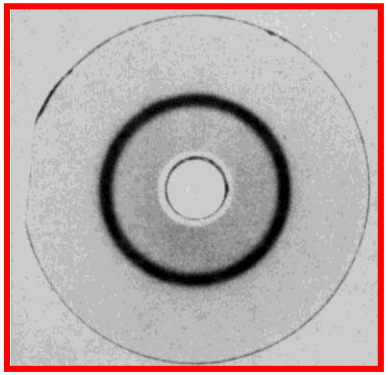
The principle of the X-ray Powder Diffraction



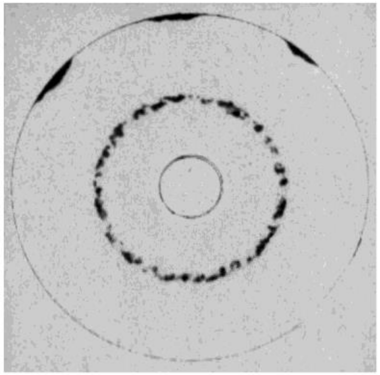
Crystallite size & Debye ring



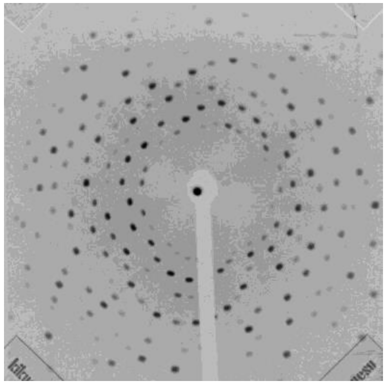
very small
Less than 0.1μm



small
～10μm

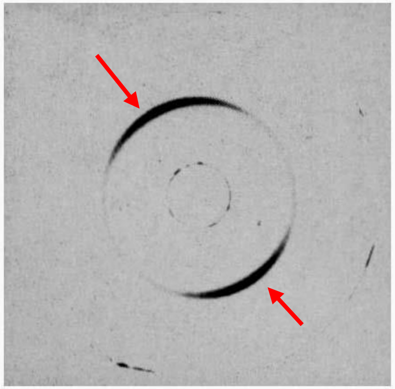


big
～50μm

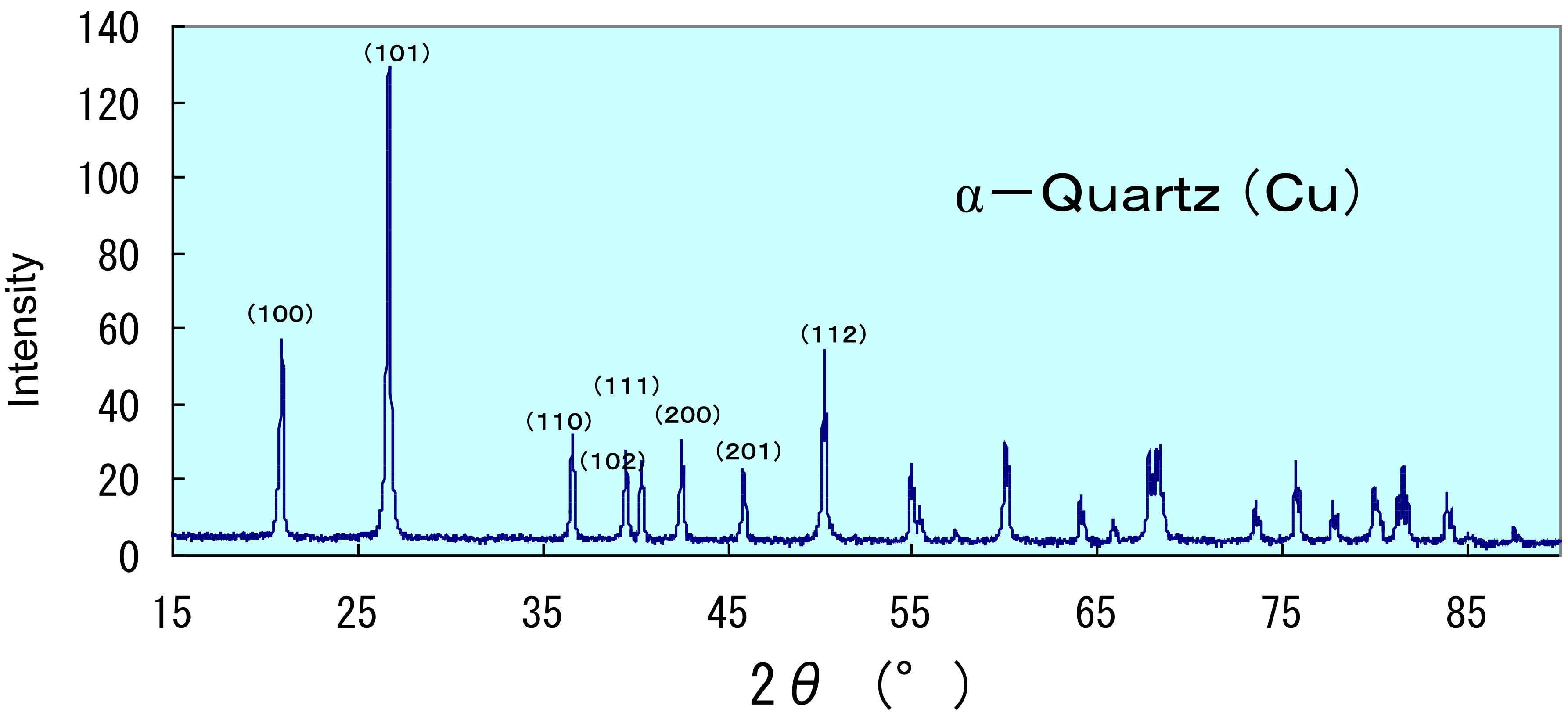


Single crystal

Preferred orientation



Measured data



Background in XRD patterns

The observed background has several sources

- Detector noise
- Natural background (cosmic rays)
- Air scattering
- Scattering from sample holder (e.g. from glass)
- X-ray fluorescence
- Inelastic scattering

The advantages of a powder diffraction method

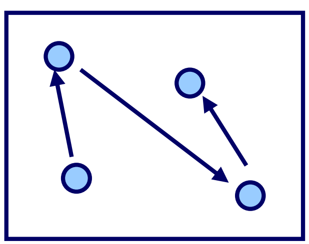
- The powder diffraction method can distinguish crystalline and amorphous phases.

Crystal

Diffraction peaks are detected

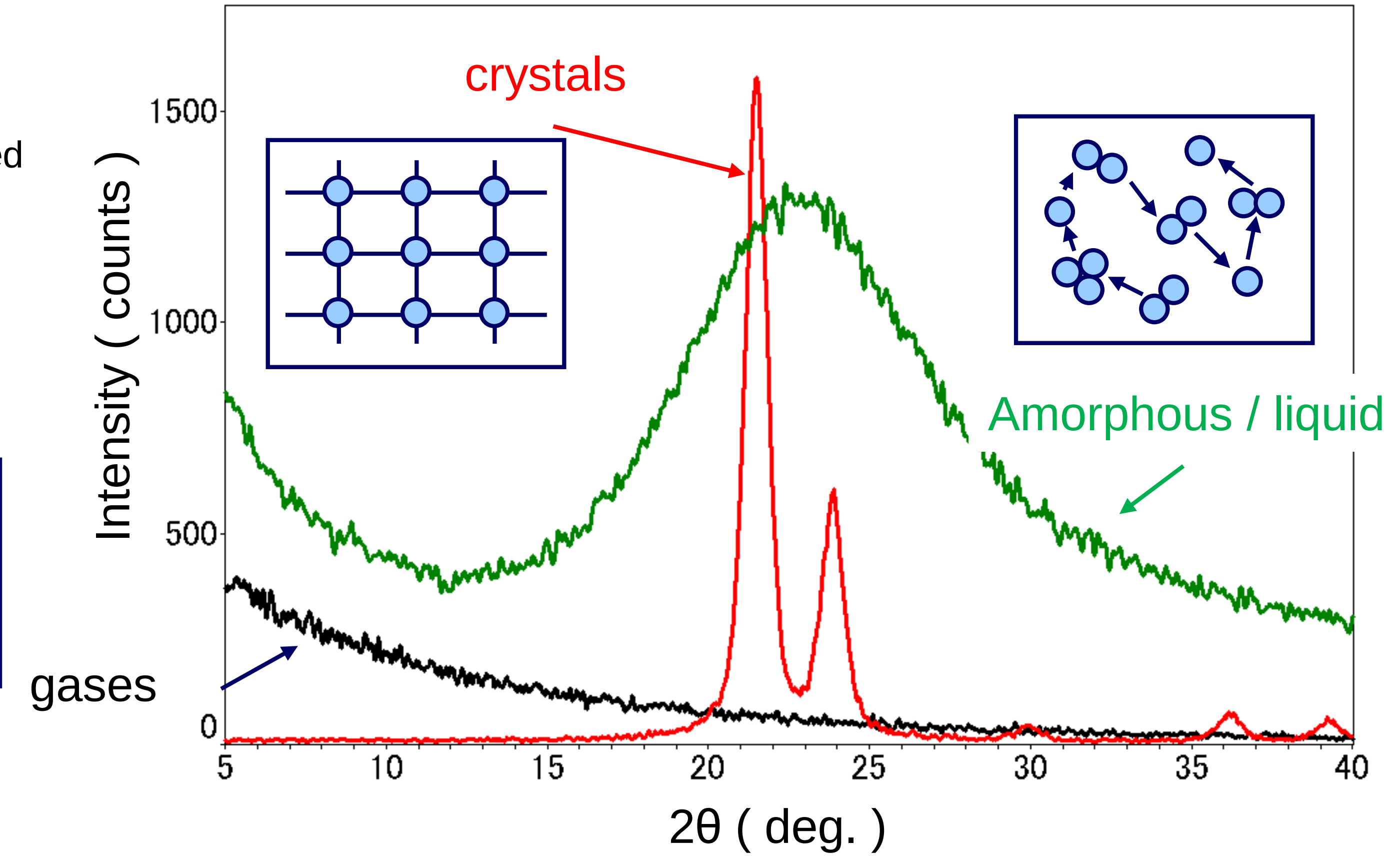
Amorphous / liquid

Halo pattern;
no orderly structure



Gases

Contributes only to background



Evaluation item in X-ray diffraction profile

- （more than 2θ=5deg）

Peak positions

d values : Phase Identification
Lattice constant
d shift : Residual stress
Solid solution

FWHM

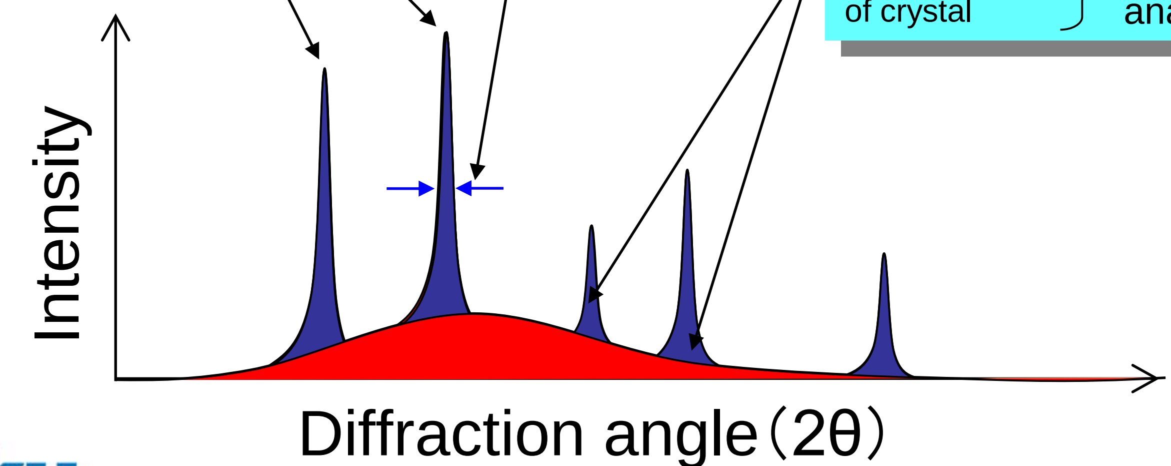
Crystal quality
Crystallite size
Lattice strain

Intensity vs. Orientation

Preferred orientation
Fiber structure
Pole figure

Integrated Int. of amorphous → Crystallinity

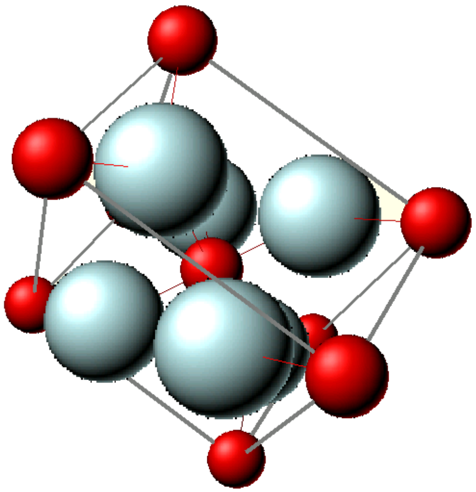
Integrated Int. of crystal → Quantitative analysis

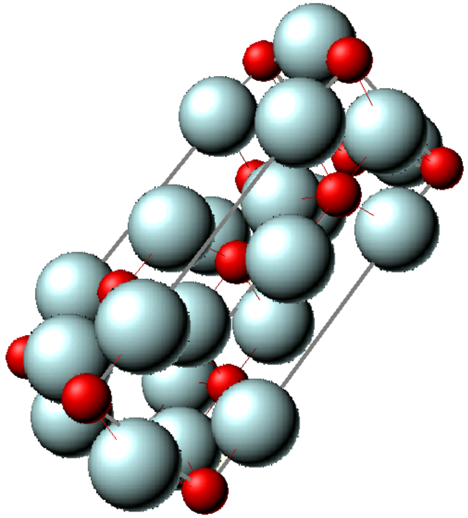


The advantages of a powder diffraction method

- The diffraction pattern indicates the crystal structure and is characteristic for a substance

Titanium oxide (TiO_2)： white powder





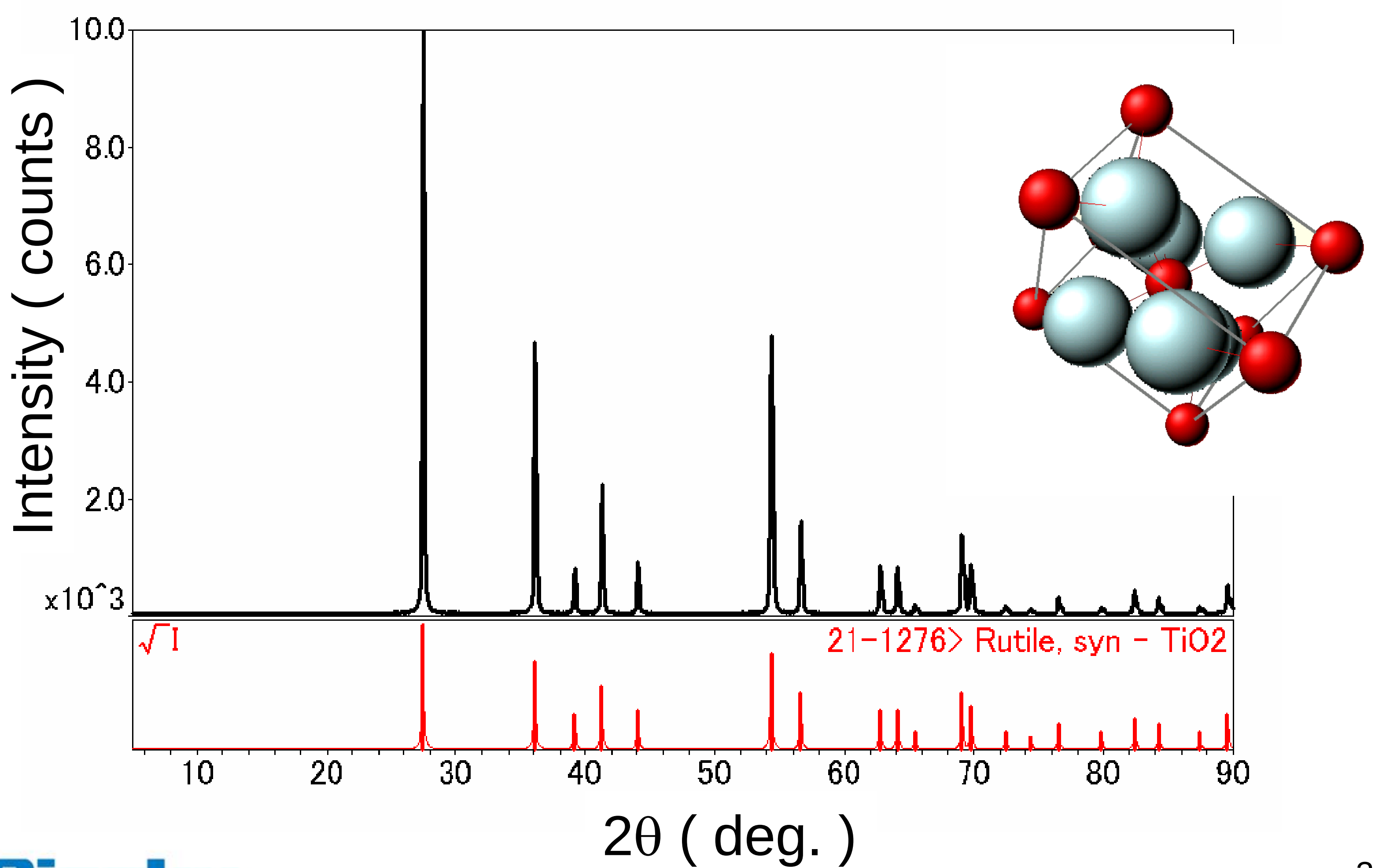
: Ti

: O

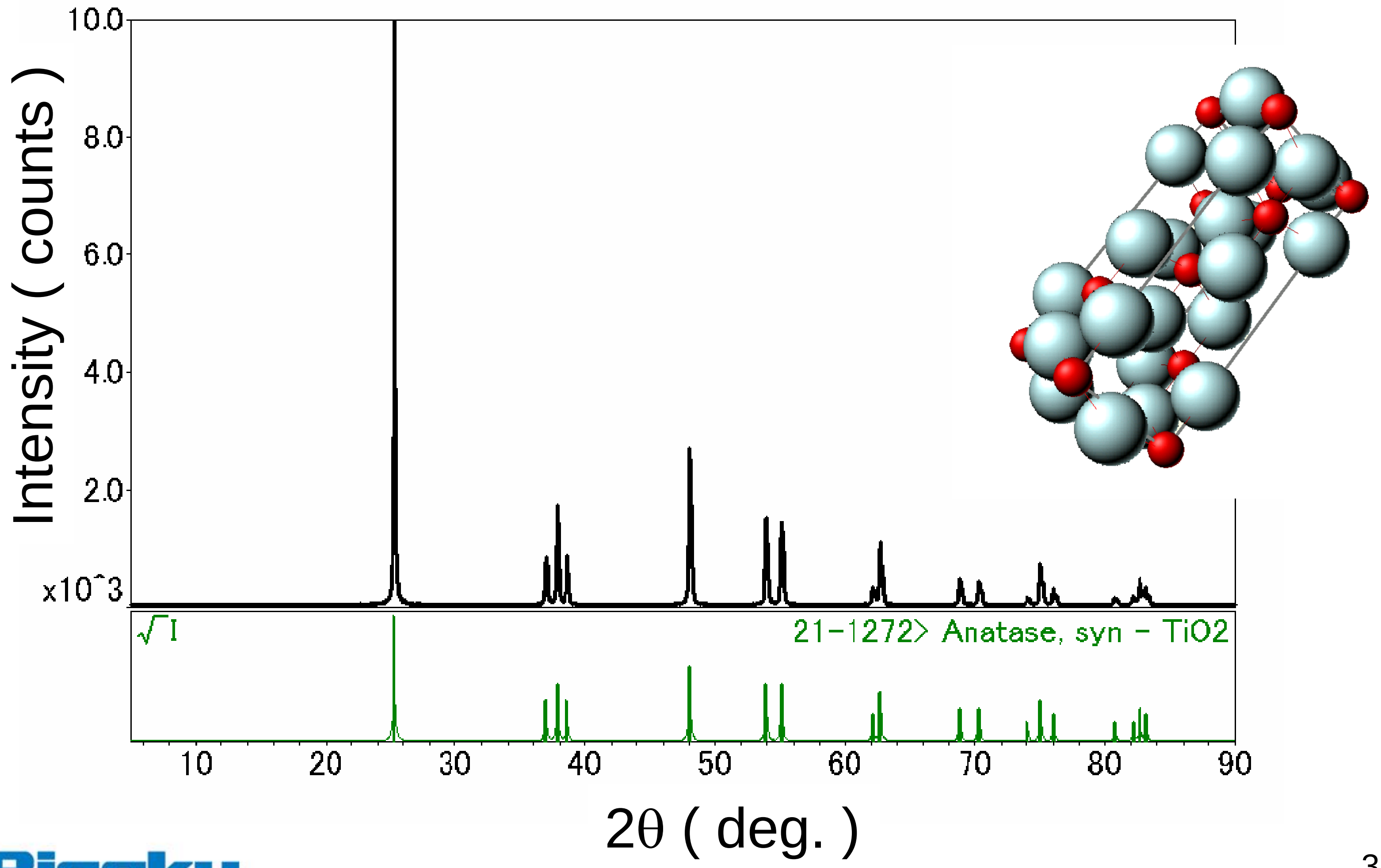
Rutile paint, ink

Anatase photocatalyst

The powder diffraction pattern of Rutile



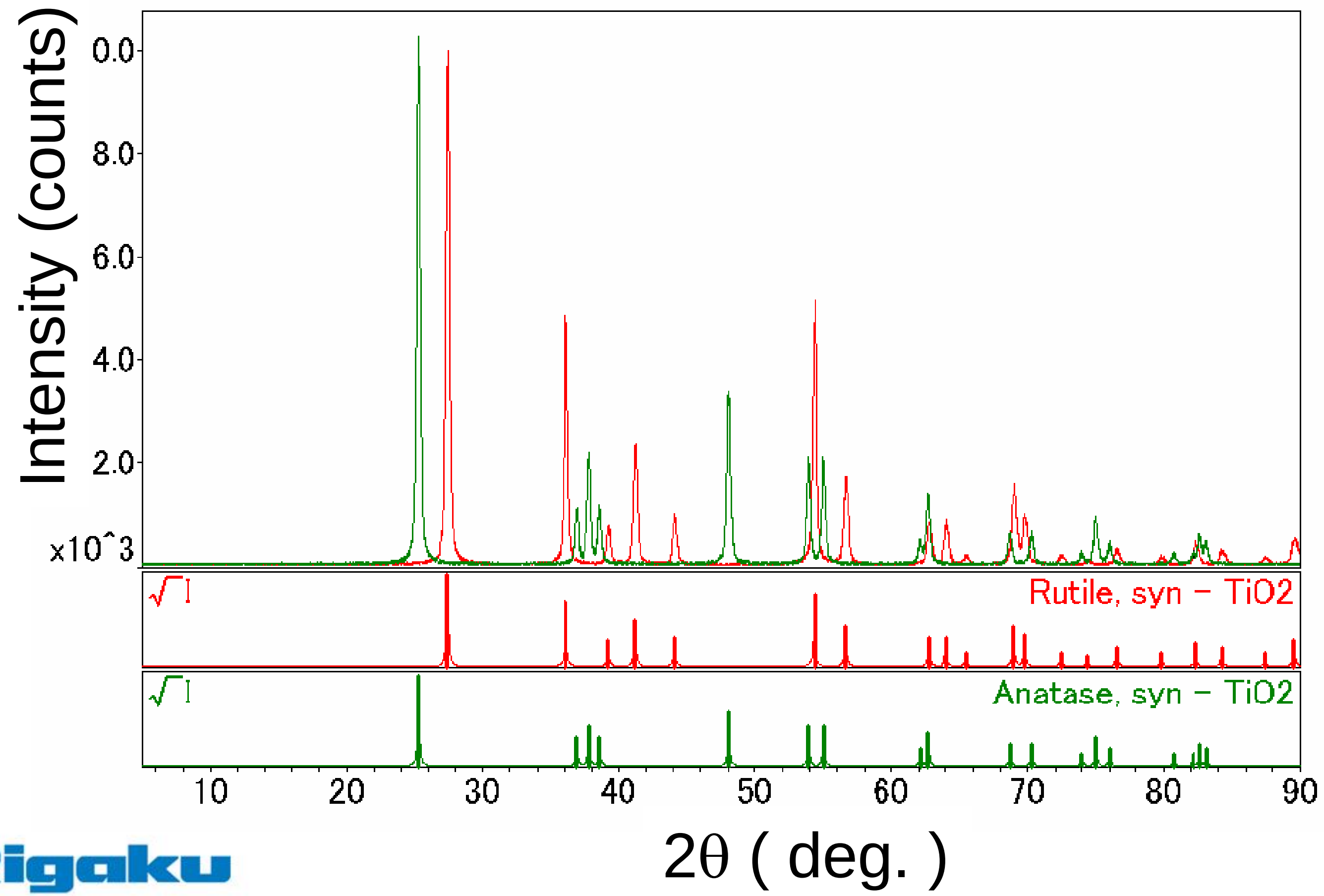
The powder diffraction pattern of Anatase



Rigaku

Powder diffraction pattern of a TiO_2-mixture

- The powder diffraction pattern is characteristic of the substance
- The diffraction pattern indicates the state of chemical combination



The advantages of a powder diffraction method

- A **crystal condition** of measured sample can be easily recognized
- The diffraction pattern indicates the crystal structure and is characteristic for a every substance
- Each substance in a mixture generates its diffraction pattern **independently**. This information can be used for both phase identification and phase quantification.

- The quantitative analysis of **polymorphism** (compounds with the same chemical composition but different crystal structures) is possible

(Example: α-Fe/γ-Fe (austenite), Quartz/Cristobalite/Tridymite…)