

EPSc 352: Lecture Overview for Part 5 X-Ray Crystallography

☞ X-Ray Crystallography

"The application of X-rays to the study of minerals has probably been the single most important technological advance in mineralogy." (Nesse, 2000, p. 160)

***** ESSENTIAL:** ☞ **Read textbook chapter 14, especially pp. 307-321.**

X-rays allow us to uncover the fundamental structure (atomic array) of crystalline solids.

One of several types of "energy-beam techniques" (e.g., Raman spectroscopy, infrared spectroscopy). Introduce radiation of known wavelength and intensity into sample, allow it to interact with sample, monitor the signal that arises. Knowledge of the nature of the interaction allows you to infer certain properties of the material.

Overview:

- Production of X-rays
- Absorption of X-rays
- Analytical applications

structural analysis: electromagnetic radiation interacts with atoms and cluster of atoms, allowing us to infer their spacings. **X-ray diffraction**

compositional analysis: X-ray wavelengths are characteristic of the elements that produce them. **Electron microprobe analysis**

⇒ **Introduction**

X-rays discovered accidentally in 1895 by Roentgen

By 1912, von Laue doing X-ray application to minerals

mid 19-teens: English physicists W.L. Bragg and W.H. Bragg opened doors to x-ray mineralogy

X-rays energy is part of electromagnetic spectrum (H.O. #43): 0.2 - 100 Å (visible light is several thousand Å).

X-rays are photons of high frequency and short wavelength

$e = hv = h(c/\lambda)$ Planck's Law

X-rays produced by certain types of electronic transitions in atoms (H.O. #43)

Transitions named according to (lowest) shell into which electron drops (K, L) and from/to which orbital ($K\alpha$, $K\alpha_1$, $K\alpha_2$, $K\beta$)

$K\alpha_1$ of each element/atom is a characteristic value. No overlaps of $K\alpha_1$'s.

TWO WAYS TO USE X-RAYS in MINERALOGY:

- 1) produce X-rays from a substance to determine its composition (electron microprobe)
- 2) use X-rays as a wave source to investigate structures of materials (X-ray diffraction)

⇒ Generate X-rays as a source for structural analysis

Select the λ needed for your “probe.” [Why use X-rays? Need something to probe structure on the atomic scale. So, need λ on order of Å. Fine-tune the λ selection based on the nature of the atomic spacing in the mineral.]

Heat (i.e., apply high voltage) tungsten filament (the cathode, -) until electrons stream off.

Accelerate and focus electrons by applying high voltage (10s of thousands of volts) to an anode (+), typically made of Cu.

Cathode's electrons create vacancies in anode (Cu) plate. Then X-rays characteristic of the element Cu are produced. Choose target metal according to λ requirement.

Production of X-ray spectrum (H.O. #43).

Incorporation into an instrument:

X-ray generator

various targets (λ choices)

try to get monochromatic radiation, by using filters or a monochromator

⇒ X-ray Diffraction

Periodic arrangement of atoms in a crystal causes specific interactions with X-rays/radiation

Atoms can be thought of as scattering incoming X-ray photons OR X-ray waves can be considered to vibrate the target electrons with the same frequency as incoming waves.

In any event, new waves (X-rays) are produced, which interact with each other

usually interference is destructive

but, along certain directions in crystal, all interacting waves are in phase and interfere constructively: said to diffract

Look at difference in path length between two closely-spaced rays as they enter mineral, interact, and exit. Can specify path-length difference necessary for constructive interference:

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

n = an integer λ = wavelength of incoming X-ray

d = spacing between atomic planes in one direction

θ = angle of incidence of X-ray on the atomic plane

NOTE: These are X-ray diffractions, not reflections. Why is “reflection” inappropriate here?

⇒ X-ray Diffraction Analysis Techniques

Typically powder diffraction – small, randomly oriented grains

At any given 2Θ orientation, there are many grains lined up so that one of their planes meets the Bragg condition and will diffract.

Derive a list of d-spacings: $d(100)$ $d(110)$ $d(111)$ OR $d_{(100)}$ $d_{(110)}$ $d_{(111)}$

Determination of over-all symmetry of a crystal and its unit-cell dimensions many require more sophisticated (e.g., single-crystal) X-ray techniques.

Glass and other amorphous materials do not yield peaks, but only broad humps in the XRD pattern. Why?

⇒ Related Techniques: Ex., Electron Microprobe Analysis

(See H.O. from Nesse; reserve reading e-mailed to you before visits to labs)

Heated filament directs electrons onto anode target, which is the sample to be analyzed.

X-rays produced in and detected from sample – indicates what atoms present and their proportions. **λ = identifies atom** **intensity = indicates “amount” present**

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

Before the intensity-detector, use a crystal with **known d-spacings**. Rotate the sample to a **known Θ** . Thus, **λ is the unknown**. When you calculate λ , you determine the element (atoms) present in the sample.