A bit of History

- William Roentgen discovered X-rays in 1895 and determined they had the following properties
  1. Travel in straight lines
  2. Are exponentially absorbed in matter with the exponent proportional to the mass of the absorbing material
  3. Darken photographic plates
  4. Make shadows of absorbing material on photosensitive paper
- Roentgen was awarded the Nobel Prize in 1901
- Debate over the wave vs. particle nature of X-rays led the development of relativity and quantum mechanics

Fig. 1.1. Röntgen’s experimental apparatus in 1895: B, Ruhmkorff induction coil; C, photographic plate; T, Hittorf-Crookes evacuated tube.
Max von Laue theorized that if X-rays were waves, the wavelengths must be extremely small (on the order of $10^{-10}$ meters).

If true, the regular structure of crystalline materials should be “viewable” using X-rays.

His experiment used an X-ray source directed into a lead box containing an oriented crystal with a photographic plate behind the box.

Von Laue’s results were published in 1912.
Bragg’s “Extensions” of Diffraction

- Lawrence Bragg and his father W.H. Bragg discovered that diffraction could be treated as reflection from evenly spaced planes if monochromatic x-radiation was used.

- Bragg’s Law: \( n\lambda = 2d \sin \theta \)
  - where \( n \) is an integer
  - \( \lambda \) is the wavelength of the X-radiation
  - \( d \) is the interplanar spacing in the crystalline material and
  - \( \theta \) is the diffraction angle

- The Bragg Law makes X-ray powder diffraction possible.
Notes on Units of Measure

- an angstrom (Å) is $10^{-10}$ meters
- a nanometer (nm) is $10^{-9}$ meters
- a micrometer (µm) or micron is $10^{-6}$ meters
- a millimeter (mm) is $10^{-3}$ meters

In X-ray crystallography, d-spacings and X-ray wavelengths are commonly given in angstroms
An ICDD Data “Card”

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**Radiation=** CuKα₁  
**λ**=1.540562  
**Calibration**=  
2θ=25.578-88.994  
Ref: Huang, T., Parrish, W., Masciocchi, N., Wang, P.  

**Rhombohedral - (Unknown), R-3c (167)**  
**Z**=6  
**mp**=  
**CELL:** 4.7587 × 4.7587 × 12.9929  
<90.0×90.0×120.0>  
**P:**=hR₁₀ (Al₂ O₃)  
**Density(c)**=3.987  
**Density(m)**=3.39A  
**Mwt**=101.96  
**Vol**=254.81  

**F(25)=357.4(0.0028,25/0)**

**Strong Lines:** 2.55/X 1.60/9 2.09/7 3.48/5 1.74/3 1.24/3 1.37/3 1.40/2 2.38/2 1.51/1
PDF#46-1212: QM=Star(S); d=Diffractometer; I=Diffractometer
Corundum, syn
Al2 O3
Radiation=CuKa1  Lambda=1.540562  Filter=
Calibration= 2T=25.578-88.994  I/Ic(RIR)=
Ref: Huang, T., Parrish, W., Masciocchi, N., Wang, P.
Rhombohedral - (Unknown), R-3c (167)  Z=6  mp=
CELL: 4.7587 x 4.7587 x 12.9929 <90.0 x 90.0 x 120.0>  P.S=hR10 (Al2 O3)
Density(c)=3.987  Density(m)=3.39A  Mwt=101.96  Vol=254.81  F(25)=357.4(.0028,25/0)

Strong Lines: 2.55/X 1.60/9 2.09/7 3.48/5 1.74/3 1.24/3 1.37/3 1.40/2 2.38/2 1.51/1
NOTE: The sample is an alumina plate as received from ICDD.
Unit cell computed from dobs.

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The Electromagnetic Spectrum

Cu-Kα
To get an accurate picture of the structure of a crystalline material requires X-radiation that is as close to monochromatic as possible.

The function of the x-ray tube and associated electronics is to produce a limited frequency range of high-intensity x-rays.

Filters, monochromators, specially tuned detectors and software are then used to further refine the frequency used in the analysis.
The X-ray Tube

- Schematic cross section of an X-ray tube as used in our lab
- The anode is a pure metal. Cu, Mo, Fe, Co and Cr are in common use in XRD applications. Cu is used on our Scintag system
- Cu, Co and Mo will be available on our new systems
- The tube is cooled by water and housed in a shielding aluminum tower
X-rays Tube Schematic
In most systems, the anode (at top in 8) is kept at ground

#2 (KV) and #7 (ma) are what are adjusted on the power supply with #1 and #5

In our lab, we only routinely adjust filament current (#5) from operating (35 ma) to “idle” (10 ma) levels
### Characteristics of Common Anode Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>At. #</th>
<th>$K_{\alpha_1}$ (Å)</th>
<th>$K_{\alpha_2}$ (Å)</th>
<th>Char Min (keV)</th>
<th>Opt kV</th>
<th>Advantages (Disadvantages)</th>
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<tr>
<td>Cr</td>
<td>24</td>
<td>2.290</td>
<td>2.294</td>
<td>5.98</td>
<td>40</td>
<td>High resolution for large d-spacings, particularly organics (High attenuation in air)</td>
</tr>
<tr>
<td>Fe</td>
<td>26</td>
<td>1.936</td>
<td>1.940</td>
<td>7.10</td>
<td>40</td>
<td>Most useful for Fe-rich materials where Fe fluorescence is a problem (Strongly fluoresces Cr in specimens)</td>
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<td>Co</td>
<td>27</td>
<td>1.789</td>
<td>1.793</td>
<td>7.71</td>
<td>40</td>
<td>Useful for Fe-rich materials where Fe fluorescence is a problem</td>
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<td>Cu</td>
<td>29</td>
<td>1.541</td>
<td>1.544</td>
<td>8.86</td>
<td>45</td>
<td>Best overall for most inorganic materials (Fluoresces Fe and Co $K_\alpha$ and these elements in specimens can be problematic)</td>
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<tr>
<td>Mo</td>
<td>42</td>
<td>0.709</td>
<td>0.714</td>
<td>20.00</td>
<td>80</td>
<td>Short wavelength good for small unit cells, particularly metal alloys (Poor resolution of large d-spacings; optimal kV exceeds capabilities of most HV power supplies.)</td>
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Generation of X-rays

- X-rays may be described as waves and particles, having both wavelength ($\lambda$) and energy ($E$).

- In the equations at left:
  - $E$ is the energy of the electron flux in KeV
  - $h$ is Planck’s constant ($4.135 \times 10^{-15}$ eVs)
  - $\nu$ is the frequency
  - $c$ is the speed of light ($3 \times 10^{18}$ Å/s)
  - $\lambda$ is the wavelength in Å

- Substituting (1) into (2) yields (3), the relationship between wavelength and energy.

- In (4) all constants are substituted.
Continuous Spectrum

- X-rays are produced whenever matter is irradiated with a beam of high-energy charged particles or photons.
- In an x-ray tube, the interactions are between the electrons and the target. Since energy must be conserved, the energy loss from the interaction results in the release of x-ray photons.
- The energy (wavelength) will be equal to the energy loss (Equation 4).
- This process generates a broad band of continuous radiation (a.k.a. bremsstrahlung or white radiation).
Continuous Spectrum

- The minimum wavelength (\( \lambda \) in angstroms) is dependent on the accelerating potential (\( \nu \) in KV) of the electrons, by the equation above.

\[
\lambda_{\text{min}} = \frac{hc}{V} = \frac{12.398}{V}
\]

- The continuum reaches a maximum intensity at a wavelength of about 1.5 to 2 times the \( \lambda_{\text{min}} \) as indicated by the shape of the curve.
Generating Characteristic Radiation

The photoelectric effect is responsible for generation of characteristic x-rays. Qualitatively here’s what is happening:

- An incoming high-energy photoelectron dislodge a k-shell electron in the target, leaving a vacancy in the shell.
- An outer shell electron then “jumps” to fill the vacancy.
- A characteristic x-ray (equivalent to the energy change in the “jump”) is generated.

L-shell to K-shell jump produces a $K\alpha$ x-ray

M-shell to K-shell jump produces a $K\beta$ x-ray
The Copper K Spectrum

- The diagram at left shows the 5 possible Cu K transitions.
- L to K "jumps:
  - $K\alpha_1$ (8.045 keV, 1.5406\AA)
  - $K\alpha_2$ (8.025 keV, 1.5444\AA)
- M to K
  - $K\beta_1$, $K\beta_3$ (8.903 keV, 1.3922\AA)
  - $K\beta_5$

Note: The energy of the $K\beta$ transitions is higher than that of the $K\alpha$ transitions, but because they are much less frequent, intensity is lower.
Continuous and Characteristic Spectrum

\[ \lambda_{\text{min}} = \frac{12.4}{V} \]

Continuous and characteristic radiation for copper.
### Characteristic Wavelength values (in Å) for Common Anode Materials

<table>
<thead>
<tr>
<th>Anode</th>
<th>$K_{\alpha_1}$ (100)</th>
<th>$K_{\alpha_2}$ (50)</th>
<th>$K_{\beta}$ (15)</th>
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<tr>
<td>Cu</td>
<td>1.54060</td>
<td>1.54439</td>
<td>1.39222</td>
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<tr>
<td>Cr</td>
<td>2.28970</td>
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<td>Fe</td>
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<td>Co</td>
<td>1.78897</td>
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<tr>
<td>Mo</td>
<td>0.70930</td>
<td>0.71359</td>
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* Relative intensities are shown in parentheses
Making Monochromatic X-rays

- X-rays coming out of the tube will include the continuum, and the characteristic $K\alpha_1$, $K\alpha_2$, and $K\beta$ radiations

- A variety of methods may be used to convert this radiation into something effectively monochromatic for diffraction analysis:
  - Use of a $\beta$ filter
  - Use of proportional detector and pulse height selection
  - Use of a Si(Li) solid-state detector
  - Use of a diffracted- or primary-beam monochromator
There are two types of absorption of x-rays.

- **Mass absorption** is linear and dependent on mass.
- **Photoelectric absorption** is based on quantum interactions and will increase up to a particular wavelength, then drop abruptly.

By careful selection of the correct absorber, photoelectric absorption can be used to select a “filter” to remove most β radiation while “passing” most α radiation.
### β Filters for Common Anodes

<table>
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<tr>
<th>Target</th>
<th>$K_\alpha$ (Å)</th>
<th>β-filter</th>
<th>Thickness (µm)</th>
<th>Density (g/cc)</th>
<th>% $K_\alpha$</th>
<th>% $K_\beta$</th>
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<td>Mo</td>
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<td>Zr</td>
<td>81</td>
<td>6.50</td>
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Note: Thickness is selected for max/min attenuation/transmission. Standard practice is to choose a filter thickness where the $\alpha : \beta$ is between 25:1 and 50:1.
Filtration of the Cu Spectrum by a Ni Filter

- The Ni absorption edge lies between the \( K\beta \) and \( K\alpha \) peaks.
- Note the jump in the continuum to the left of the \( K\beta \) peak from Cu self-absorption.
- Note that the Ni filter does little to remove the high-energy high-intensity portion of the continuum.

Filter Placement:
- In a diffractometer, the filter may be placed on the tube or detector side.
- In powder cameras (or systems with large 2D detectors), the filter will be between the tube and the camera (or specimen).

Discriminating with Detectors

- **Pulse-height Discrimination**
  - Detector electronics are set to limit the energy of x-rays seen by the detector to a threshold level
  - Effectively removes the most of the continuum and radiation produced by sample fluorescence
  - Particularly effective combined with a crystal monochromator

- **“Tunable” Detectors**
  - Modern solid state detectors, are capable of extremely good energy resolution
  - Can selectively “see” only $K\alpha$ or $K\beta$ energy
  - No other filtration is necessary, thus signal to noise ratios can be extremely high
  - Can negatively impact intensity of signal
Monochromators

- Following the Bragg law, each component wavelength of a polychromatic beam of radiation directed at a single crystal of known orientation and d-spacing will be diffracted at a discrete angle.

- Monochromators make use of this fact to selectively remove radiation outside of a tunable energy range, and pass only the radiation of interest.
  - A filter selectively attenuates K$\beta$ and has limited effect on other wavelengths of X-rays.
  - A monochromator selectively passes the desired wavelength and attenuates everything else.

- Monochromators may be placed anywhere in the diffractometer signal path.
Monochromator configurations: in each case $r_g$ is the radius of the goniometer circle and $r_m$ is the radius of the monochromator circle.
The pyrolitic graphite curved-crystal monochromator is the most widely used type in XRD laboratories.

- A planar crystal will diffract over a very small angular range and significantly reduce the intensity of the x-ray signal.
- Precisely “bent” and machined synthetic crystals allow a divergent x-ray beam to be focused effectively with minimal signal loss.
Graphite Monochromator on Scintag Diffractometer

Diffracted-beam parallel geometry
From left: Receiving scatter slit, soller slit assembly, receiving slit, monochromator (path bends) and scintillation detector
Summary

- A Ni filter will attenuate Cu Kβ radiation, but pass almost everything else (including high-energy portions of the background spectrum).

- A Si(Li) detector may be tuned to see only Kα radiation.

- A graphite (PG) monochromator will select Cu Kα, but the acceptance windows will also admit a few other wavelengths. A tungsten (W) Lα line may be present as anode contamination in an “aged” Cu x-ray tube.

- Compton scatter will always contribute something to the background.