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X-ray Crystallography

Department of Chemistry & Biochemistry

cora.lind@utoledo.edu

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- What?
  - Determination of the atomic structure of crystalline solids
  - Location and type of atoms, bond distances/local environment
  - Absolute structure
- Why?
  - Materials' properties(a)0.7 (-0 0 18 92.7 24T Tw 1222 rg/TT2 32 0 Td[oote

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- X-rays were discovered by Wilhelm Conrad Röntgen in 1895
  - “Interested in the effects of ultra-violet radiation, he covered a cathode-ray dis Tw [v3/34a (i)0. [r).7 C0s t7 (u)b (y)1.e7 ( )-6.w (ti)0.7 (th)2

- The first crystal structure ever solved was NaCl
- Clearly showed equally spaced sodium and chlorine atoms and thus proved the concept of ions and ionic bonding!
  - First proof that not all materials are made up of molecules!
  - Admittedly, not everybody was happy to accept this…
  - Armstrong, H. Nature, 1927, 120, 478-478

- This presentation used to have a slide that listed many Nobel Prizes – but even with a very small font size, there was not enough space!
- Check out https://www.iucr.org/people/nobel-prize for a comprehensive list of Nobel prizes in this field!
- Over 30 Nobel prizes – 9 of them were awarded since I started teaching at UToledo!

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- Historic definition before the advent of crystallography
  - A solid with well-defined faces
- Crystallographic definition
  - A material with a regularly repeating structural motif
- The strict definition is more vague
  - Any material that gives a diffraction pattern with sharp peaks

- The repeating structural motif in a crystal is referred to as a unit cell
  - Only the size and contents of one unit cell are necessary to describe the entire crystal
- Remember to use a right-handed axis system!

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

- First event: Nucleation
    - Depends strongly on availability of nucleation sites (container surfaces, impurities etc.)
- Growth of the nuclei
    - Usually not isotropic, high-energy faces grow fastest
    - Relative growth rates of faces can be influenced by additives to the solution
- Size distribution of crystals depends on relative nucleation and growth rates
    - High nucleation rates and low growth rates result in many small crystals

- Choice of method depends on material
  - Optimization for each problem
- Growth from solution
  - “Normal” solvents like water, organic solvents
  - Molten solids (NaCl, PbO, metals…)
  - Ideally, the solvent should dissolve the reactants and product(s)
  - Recent development esp. for proteins: Growth in zero gravity
- Growth from the vapor phase
  - Not very common

- Can be used for some sublimable materials
  - Menthol
- Can also be used for materials that can be transported by the addition of a transporting agent
  - $ZnS_{(solid)} + I_{2(gas)} \longrightarrow ZnI_{2(gas)} + 1/8\ S_{8(gas)}$
  - T-dependent equilibrium
  - Also used in "halogen lamps": WX_6 will transport tungsten back to the filament!

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- Strict definition of a flux: A liquid reaction medium that dissolves the reactants and products, but does not participate in the reaction
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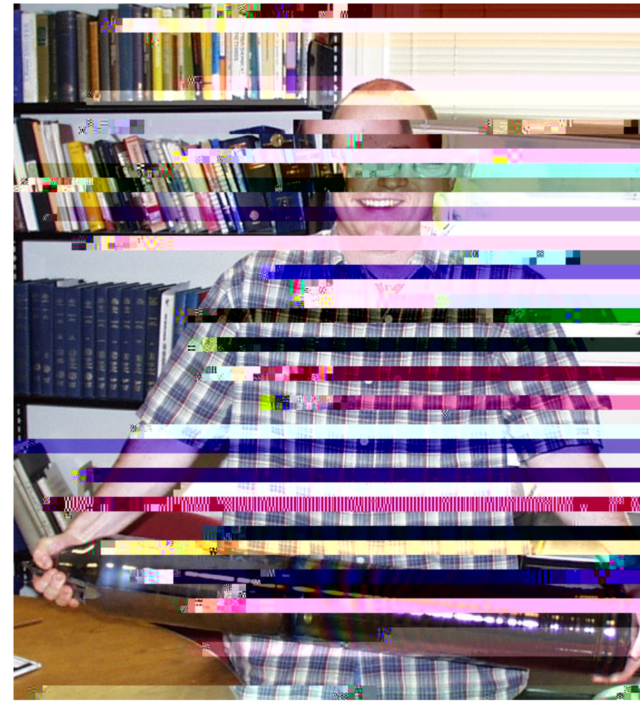
- Often used for growth from a molten “solvent” that dissolveve9tf ( )6.4 (d

- Most commonly used method
  (esp. in organic and biochemistry)
- Crystals form from a saturated solution
-

- First developed for the growth of metal single crystals
- Most commonly used commercial single crystal growth method
  - Well suited for semiconductors like Si, GaAs
  - Can also be applied to oxides, e.g., Nd:YAG, Ti:sapphire
- Growth is accomplished from a seed crystal that is slowly pulled out of the melt
  - Commonly produces crystals with 10 inches in diameter and several feet long


Laif Alden with a Si single crystal grown by the Czochralski method

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layered solvents of different density

“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

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- The angles between external faces of crystals are not arbitrary, but characteristic of a material
  - can be measured with a goniometer

- The external crystal faces

- Oldest methods relied on simple physical observations only
  - Example: Crystal habit
  - Could determine symmetry of crystal, but usually not atomic scale structure
- NMR has become one of the most powerful structural tools for organic molecules
  - Can also be used for amorphous materials
  - Often less straightforward for solids and/or non-standard nuclei
- Crystallographic methods
  -

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- Electron microscopy is a powerful tool for the visualization of particles and/or lattices (high resolution)
- Electrons can be focused using magnetic lenses
- Gives structural information on a short length scale
    - Provides a 2D image
    - Samples are often damaged by the intense electron beams
    - Only very thin samples can be measured
- Atomic resolution imaging is now possible
    - Images can be difficult to interpret

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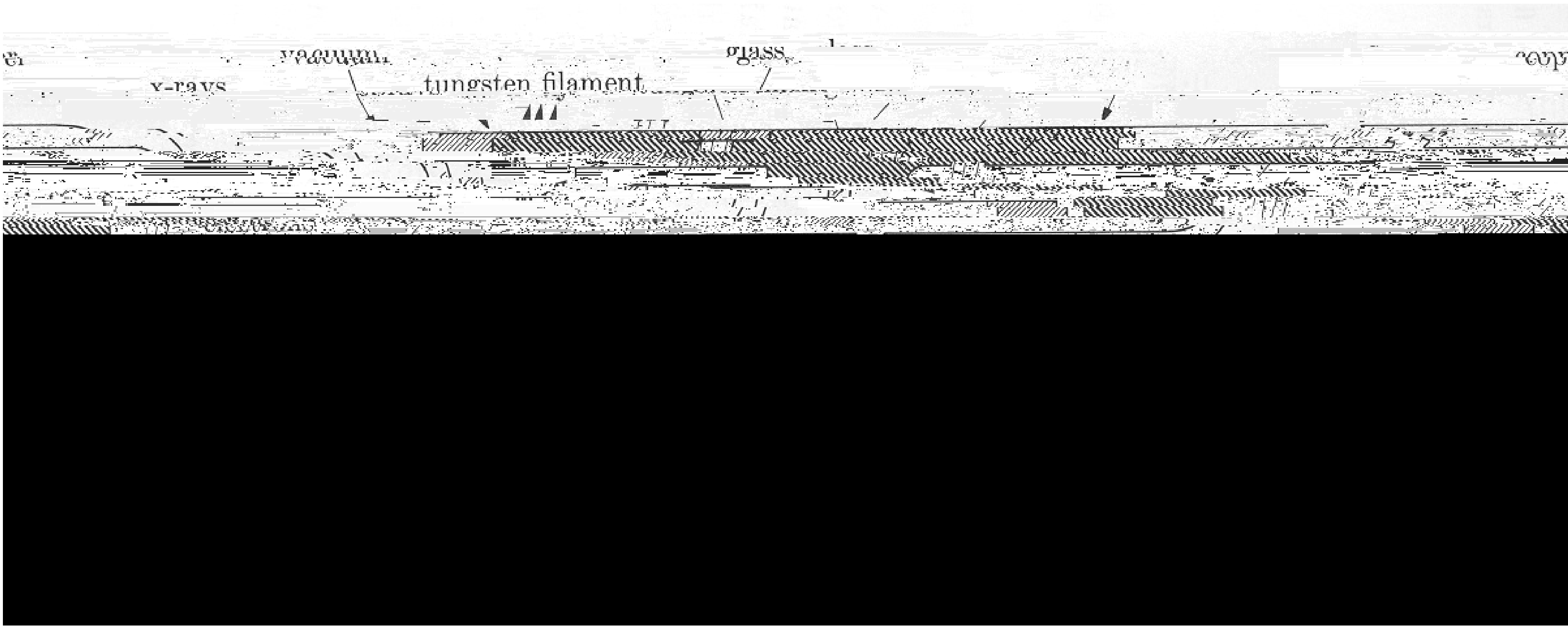
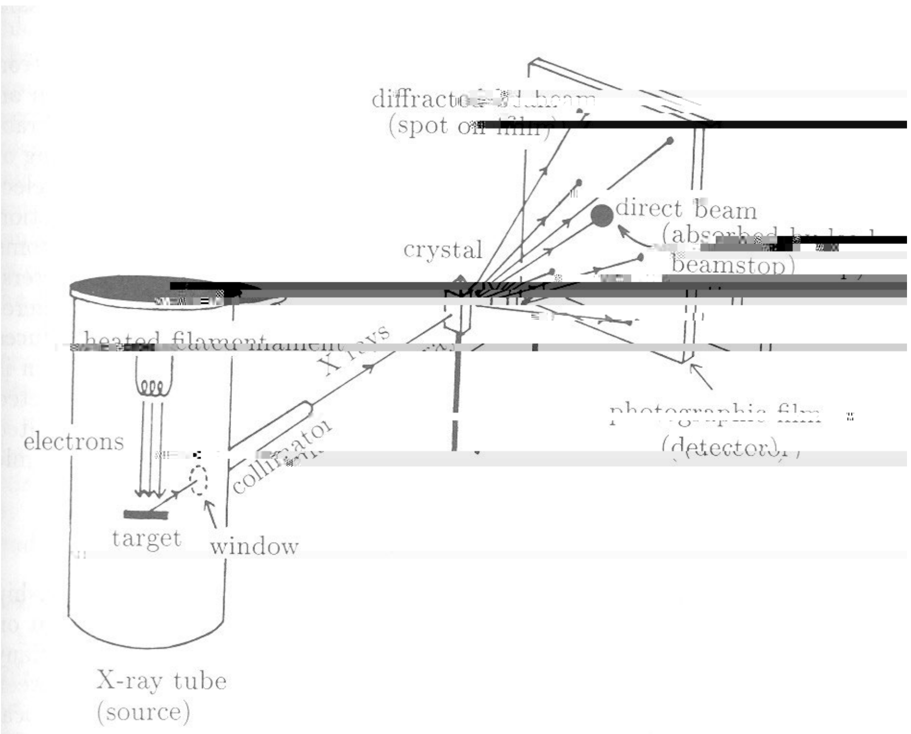
- There are no refractive lenses for X-rays, as the refractive index in all materials is close to 1
  - Between 0.99 and 0.999
- X-rays can be focused using diffraction-based optics
  - e.g., a “peak” of X-



Cullity, “Elements of X-ray Diffraction”



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