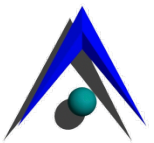
X-ray diffraction: *the basics*



Alan Goldman

IOWA STATE UNIVERSITY

What's wrong with this picture?

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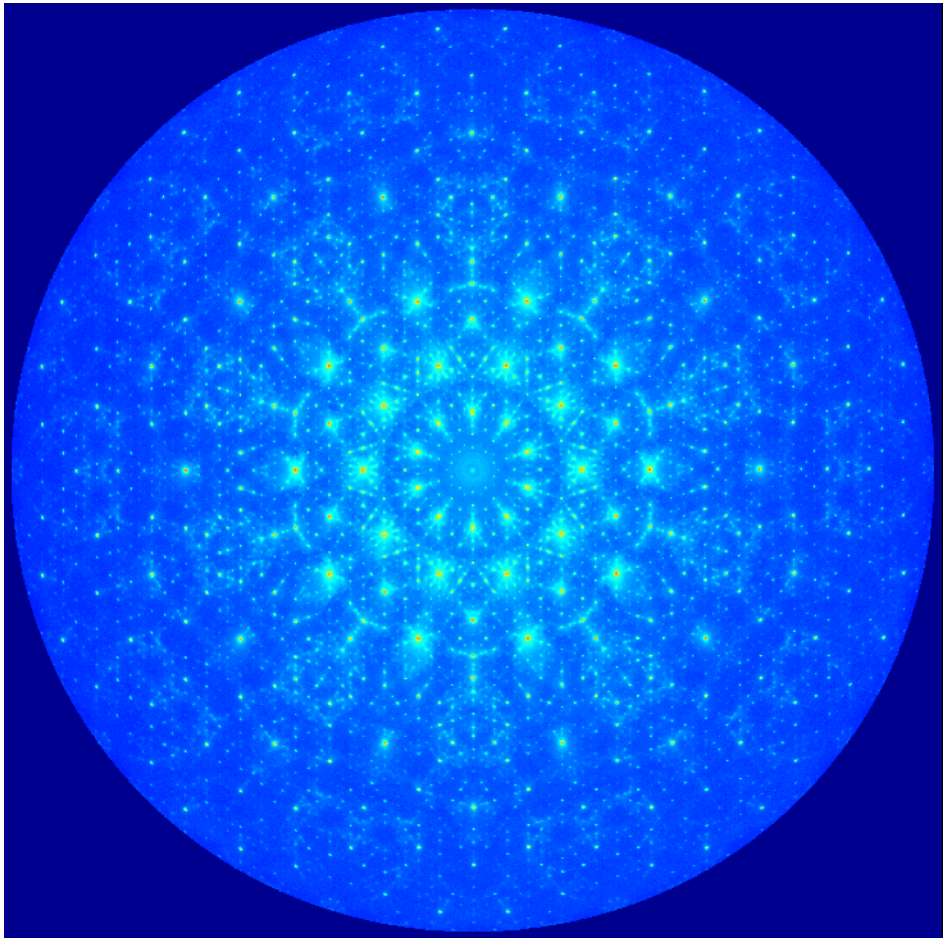

What is the atomic scale structure?

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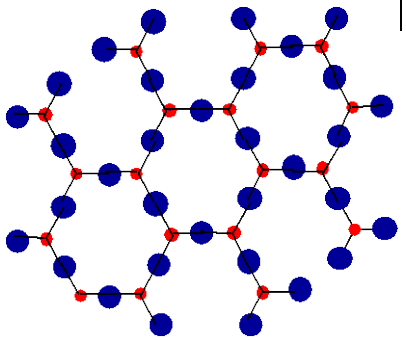
Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of: -metals
  -many ceramics
  -some polymers



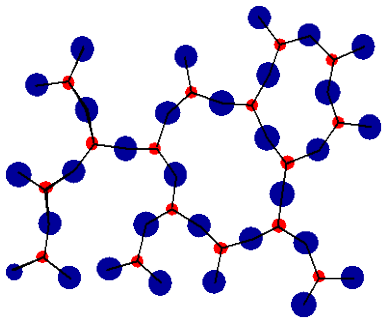
crystalline SiO_2

Adapted from Fig. 3.18(a), *Callister 6e.*

Noncrystalline materials...

- atoms have no "regular" packing
- occurs for: -complex structures
  -rapid cooling

• Si • Oxygen



noncrystalline SiO_2

Adapted from Fig. 3.18(b), *Callister 6e.*

"Amorphous" = Noncrystalline

Distance between atoms ~ Å (10^{-10} m)

How do we use x-rays to study crystal structures?

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X-rays →

Visible light →

Resolution ~ wavelength

So, 10^{-10} m resolution
Requires $\lambda \sim 10^{-10}$ m

Different probes

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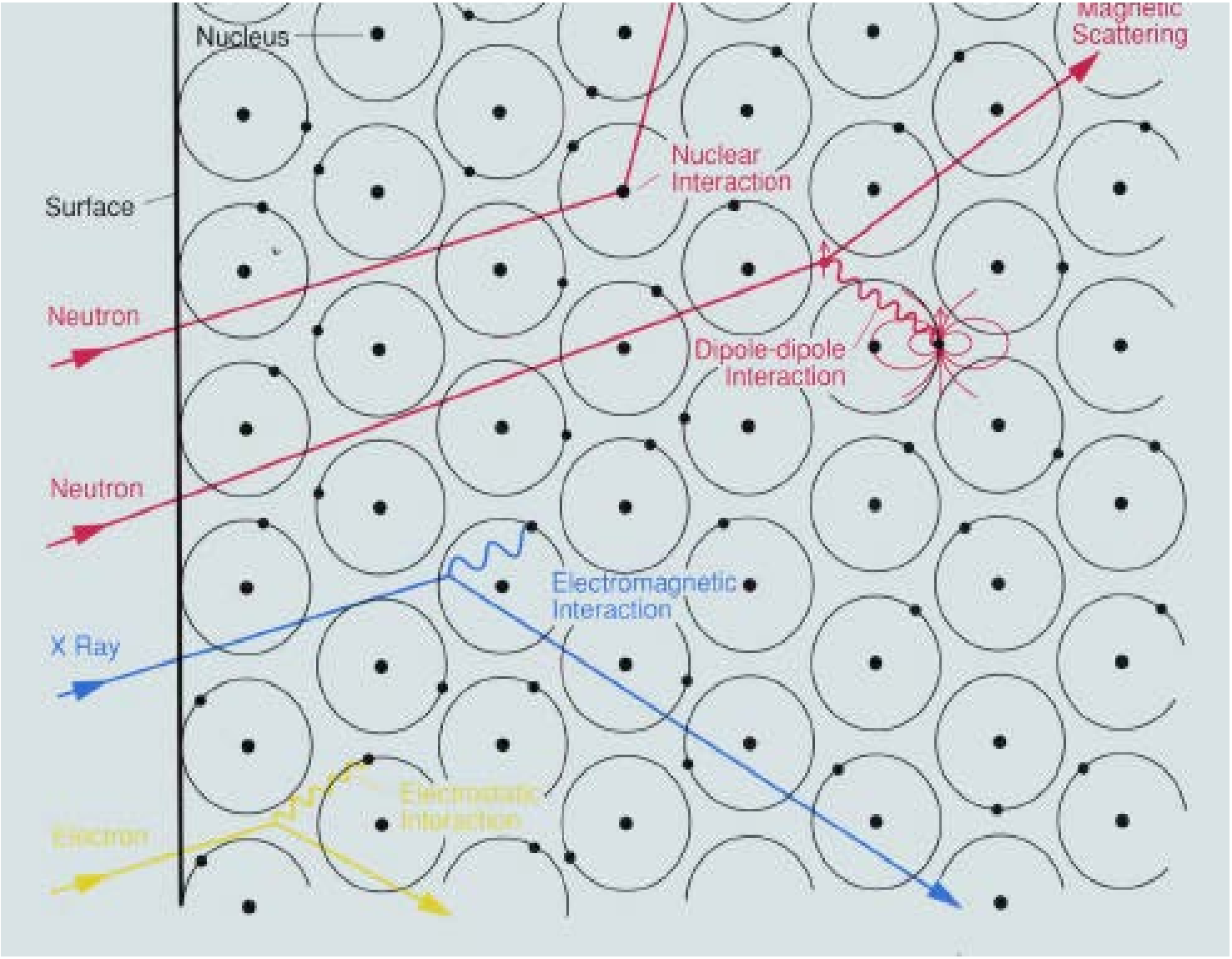

Different probes

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	NEUTRONS	X-RAYS	ELECTRONS
Wavelength range	0.4 - 10 Å	0.1 - 5 Å	0 .04 - 0.2 Å
Energy range	0.001 - 0.5 eV	3000 - 100000 eV	6000 - 120000 eV
Cross-section	10^{-25} barns	10^{-25} Z^2 barns	~10^{-22} barns
Penetration depth	~ cm	~ μm	~ nm
Typical flux	10^{11} s^{-1} m^{-2}	10^{24} s^{-1} m^{-2}	10^{26} s^{-1} m^{-2}
Beam size	mm-cm	μm-mm	nm-μm
Typical sample	Any bulk sample	Small crystals, powders, surfaces	Surfaces, thin films, grains, gases
Techniques	**Diffraction** Inelastic scattering Reflectivity	Diffraction Photon absorption Photoemission Inelastic scattering	Microscopy Diffraction Emission spectroscopy EELS
Phenomena	**Magnetic/crystal structures** collective excitations (phonons, spin waves) electronic excitations (crystal-field, spin-orbit)	Crystal structures, electronic transitions (photoemission, absorption),	microstructure crystal structures electronic transitions

Why x-rays??

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- Easily accessible in the laboratory
- Penetration ~ microns to millimeters (tuned with energy)
  - Low-energies can be used to probe surface and near surface regions
  - High energies can probe the bulk of a sample
- High flux at National Facilities
  - Allows you to throw a lot of photons away → high energy and momentum resolution
  - Is highly polarized and highly collimated
  - Is continuously tunable across a wide range of energies (1 keV → 200 keV)
- Wavelength range ~ interatomic spacing (1-2 Å) → diffraction
  - interacts with electrons
  - Magnetic interactions are higher order

Production of x-rays

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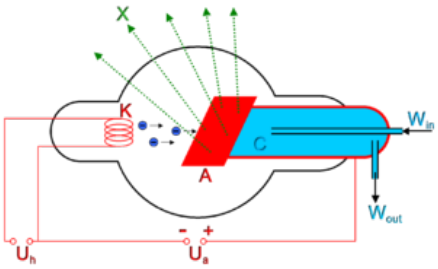
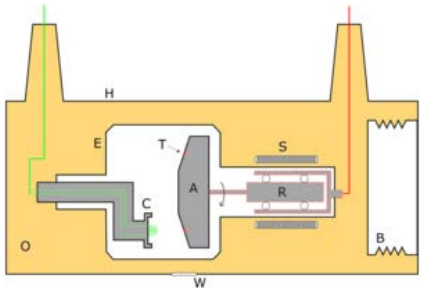
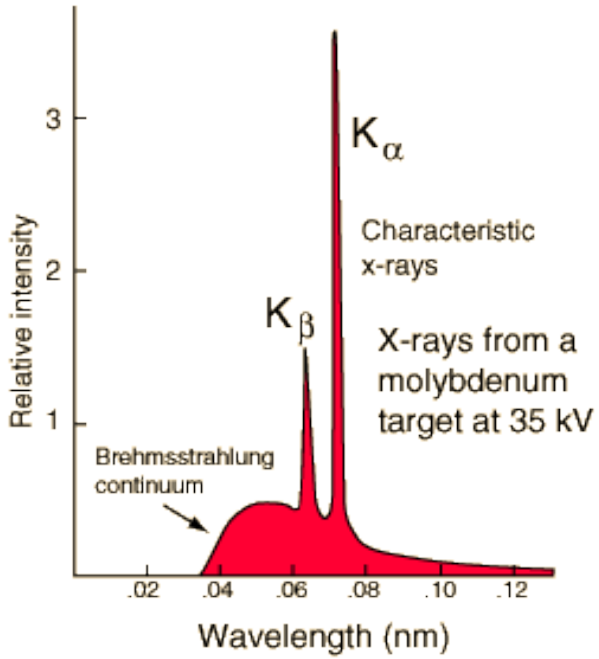


X-ray tube



Rotating anode



X-rays from a synchrotron source

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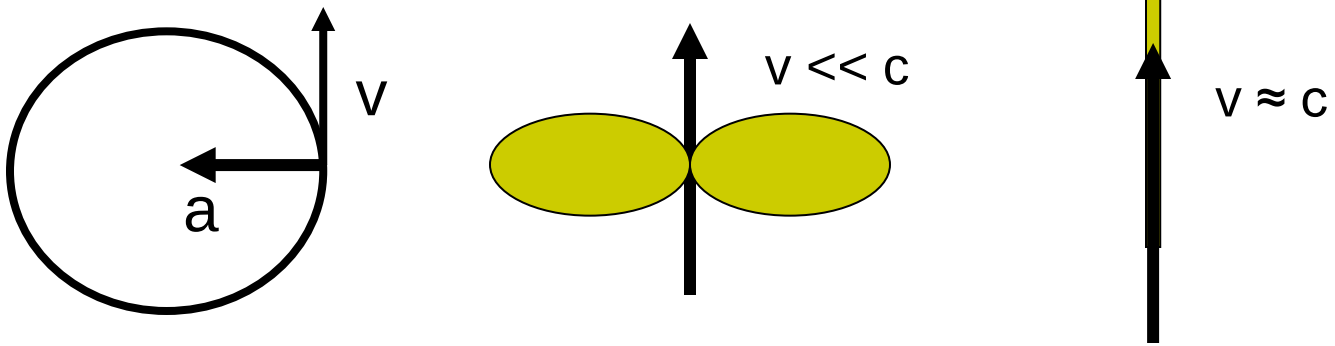
- Static charge ---- Electric field
- Charge moving at constant v ---- Magnetic field
- Accelerating charge --- Electromagnetic radiation



Synchrotron radiation is

highly collimated
highly linearly polarized
highly brilliant
continuous wavelength distribution (beyond Cu, Mo, etc..)

Bending magnet radiation

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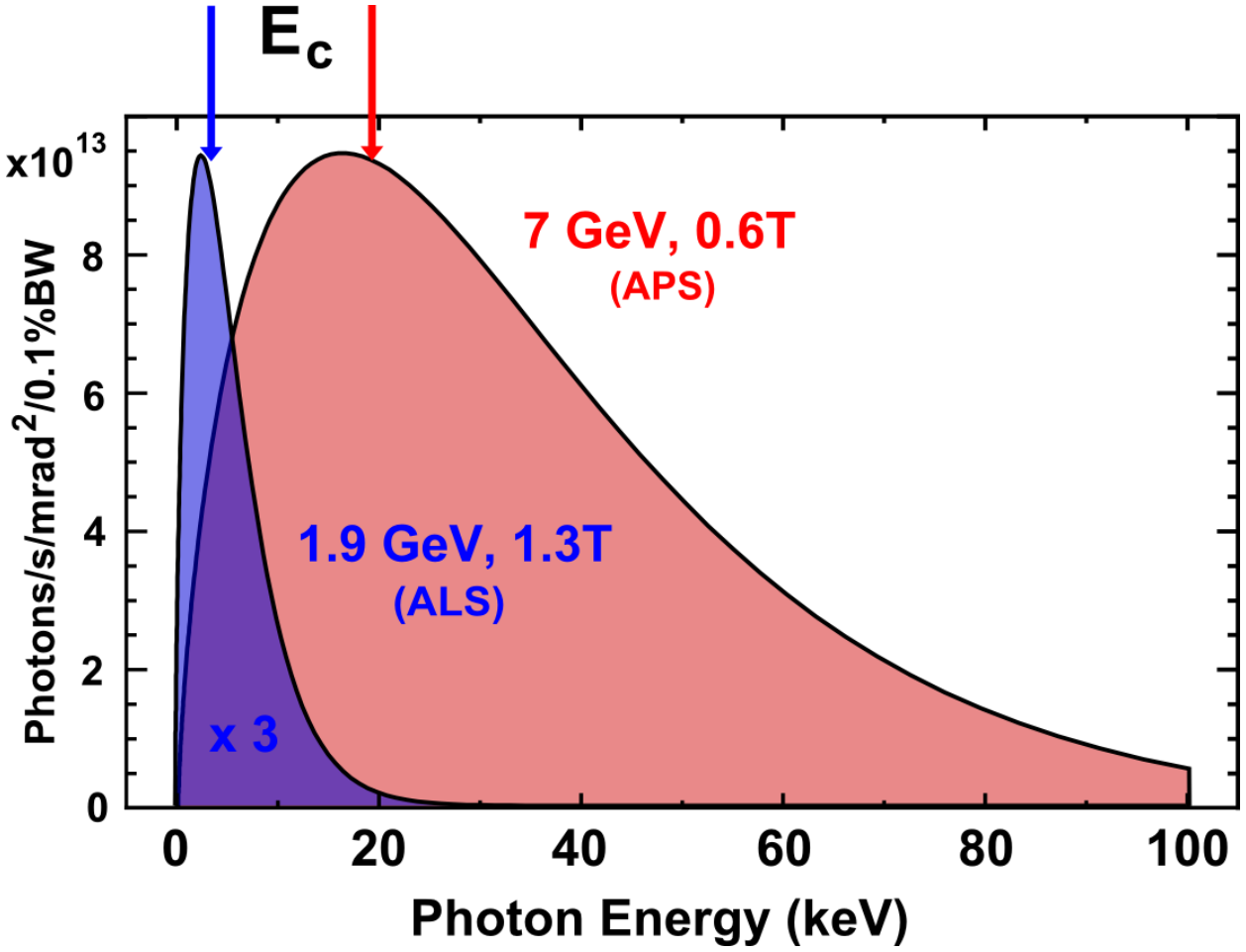

Places to go

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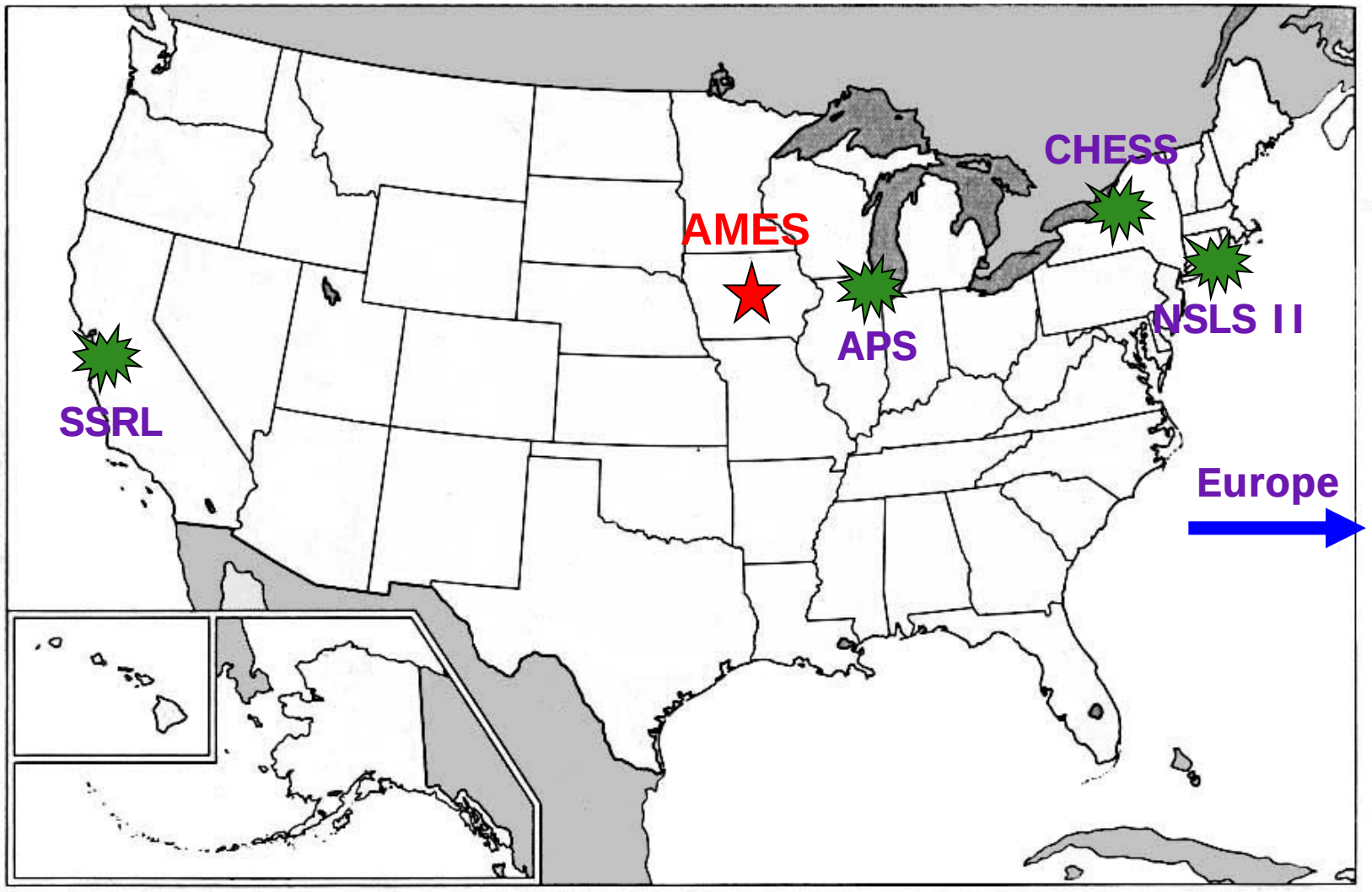

Advanced Photon Source

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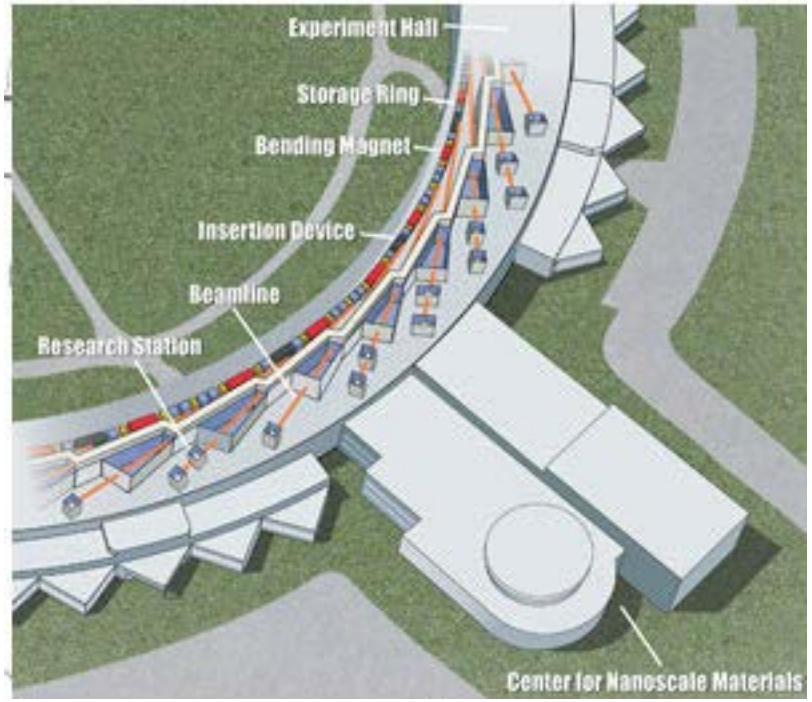
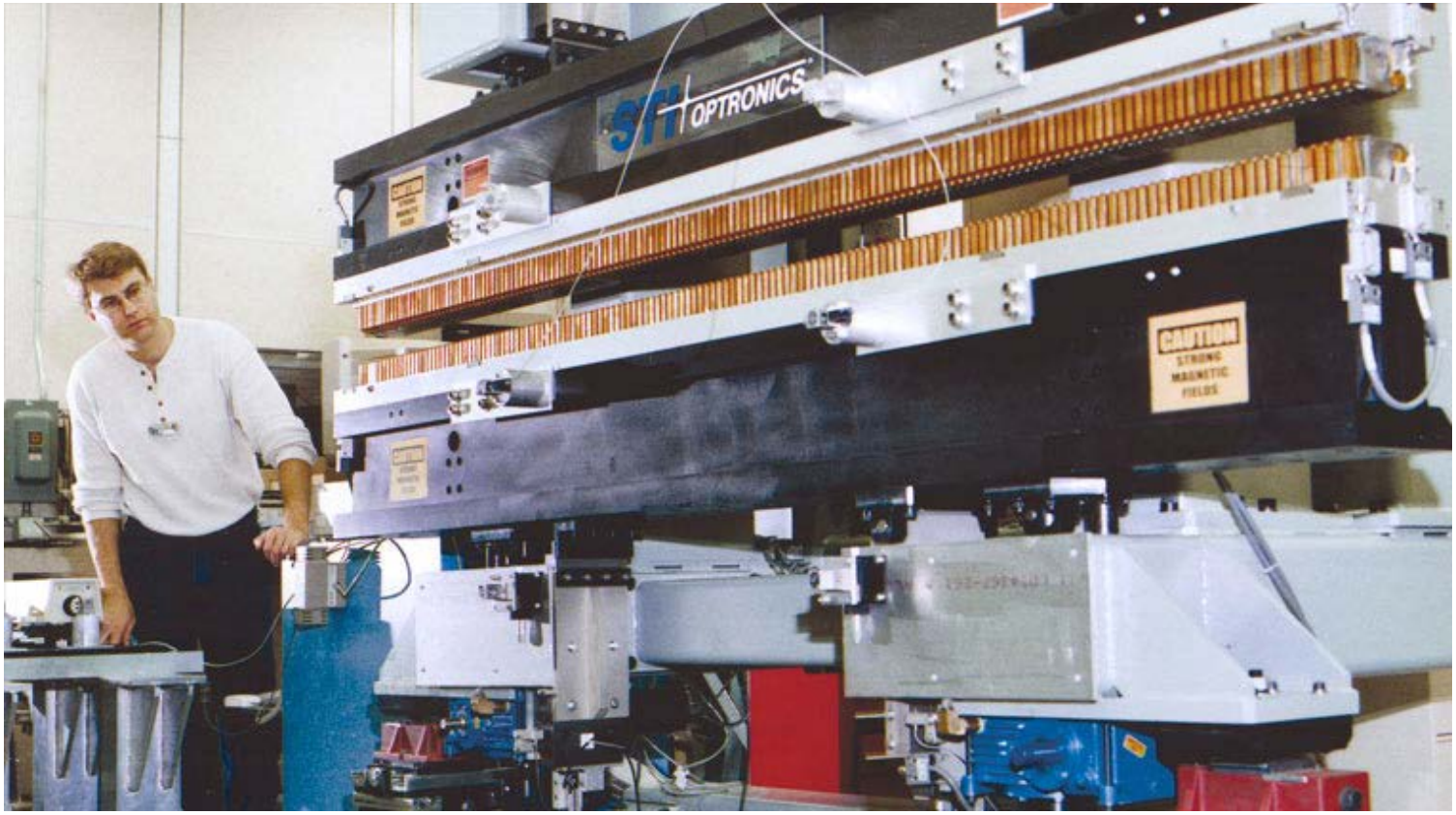
Synchrotron




B200


SFT
OPTRONICS
CAUTION
STRONG
MAGNETIC
FIELDS

Insertion Devices

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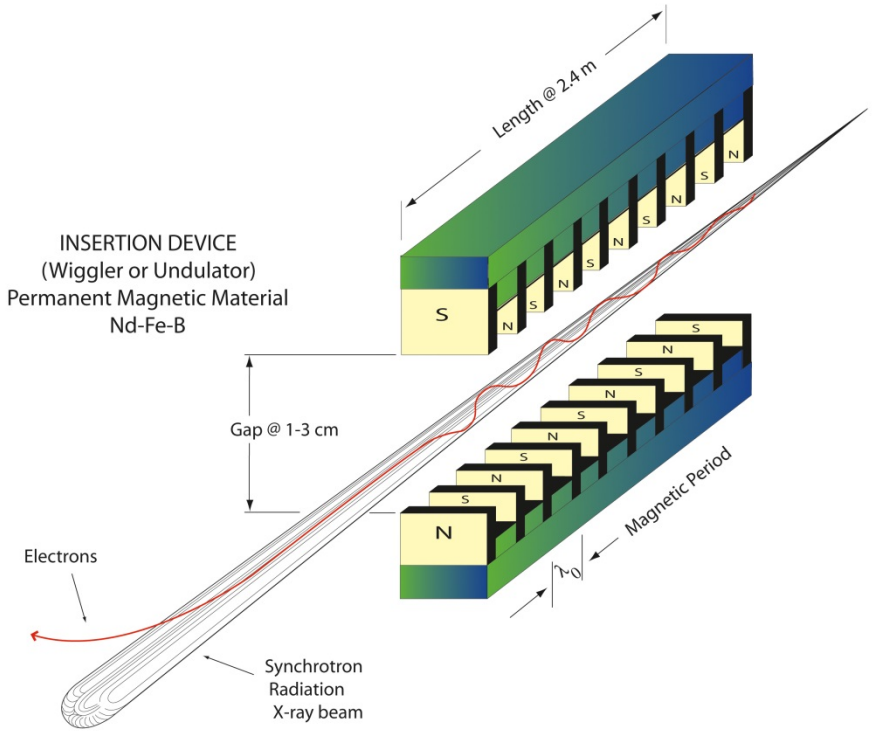
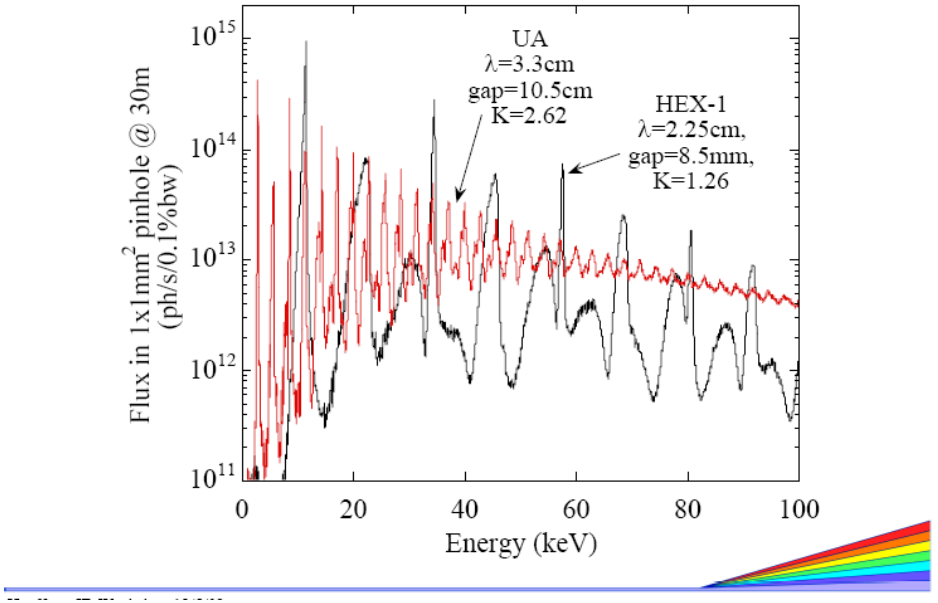


High Energy Undulator Flux



Bragg's Law –the view in real space

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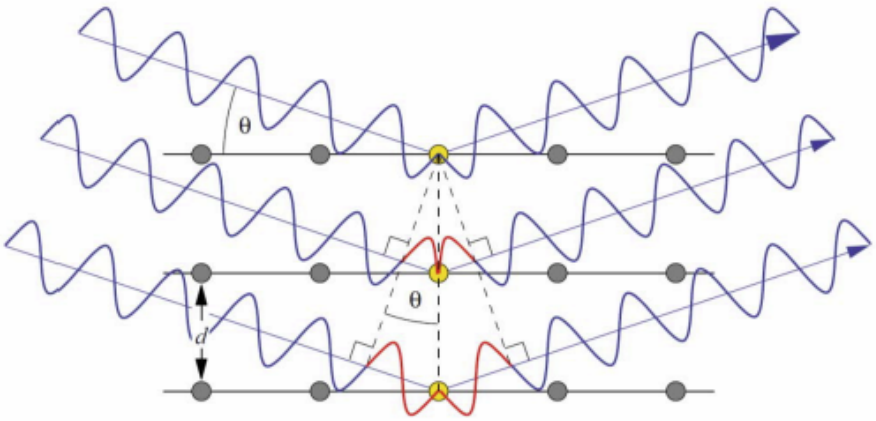
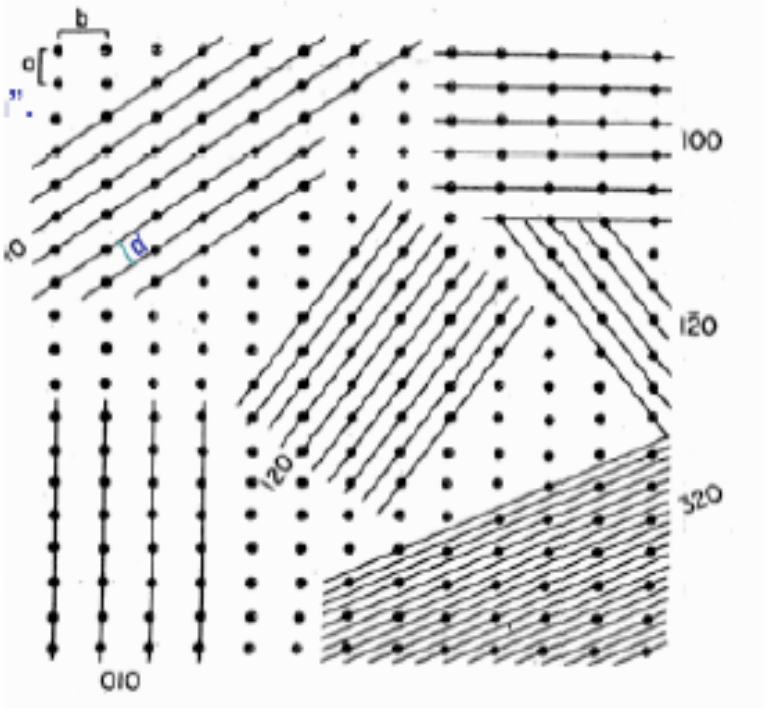


Constructive interference when $n\lambda = 2dsin\theta$



But Physicists live in reciprocal space

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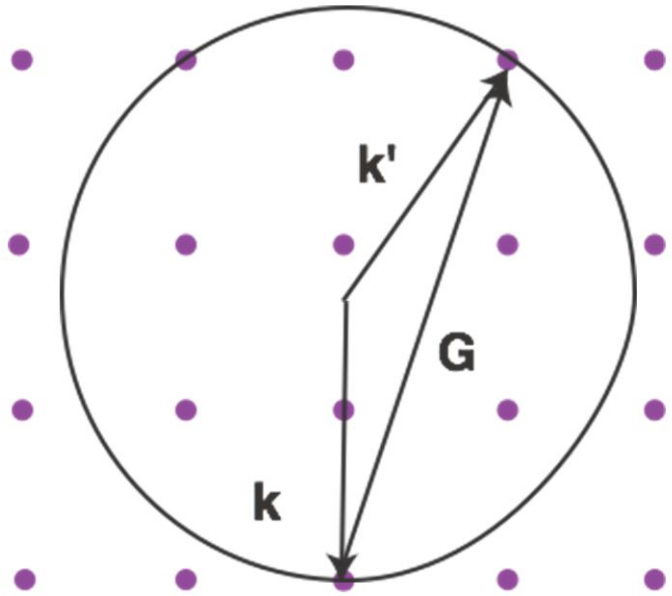
The Ewald construction

Laue condition $\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}$ if **G** is a rec. lat. vec.

- Draw (cut through) the reciprocal lattice.
- Draw a **k** vector corresponding to the incoming x-rays which ends in a reciprocal lattice point.
- Draw a circle around the origin of the **k** vector.
- The Laue condition is fulfilled for all vectors **k'** for which the circle hits a reciprocal lattice point.



89

Diffraction peak intensities

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Generally speaking:

Whereas the dimensions and symmetry of the unit cell determine peak positions, peak intensities are governed by how the atoms are arranged within the unit cell.

$$I_{hkl} \propto |F_{hkl}|^2$$

$$F_{hkl} = \sum_{j=1}^{m} N_j f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$

- where the atoms are on the atomic planes
  - this is expressed by the fractional coordinates x_j y_j z_j
- what atoms are on the atomic planes
  - the scattering factor f_j quantifies the efficiency of X-ray scattering at any angle by the group of electrons in each atom
    - The scattering factor is equal to the number of electrons around the atom at 0° θ, the drops off as θ increases
  - N_j is the fraction of every equivalent position that is occupied by atom j

Single-crystal diffraction

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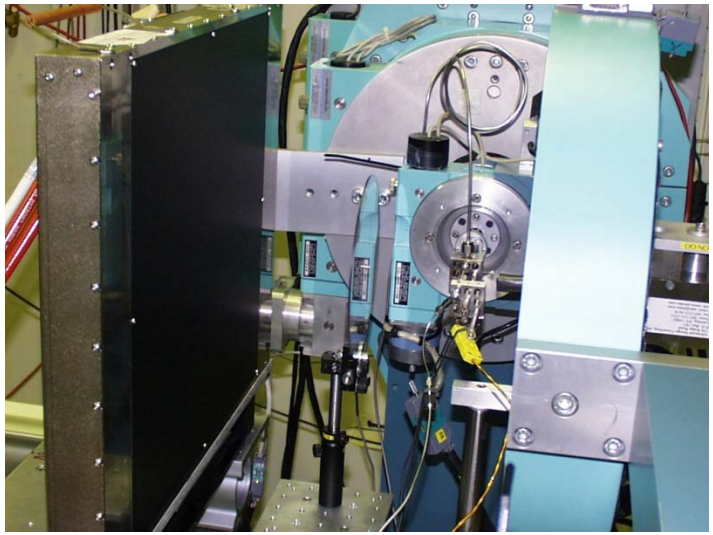
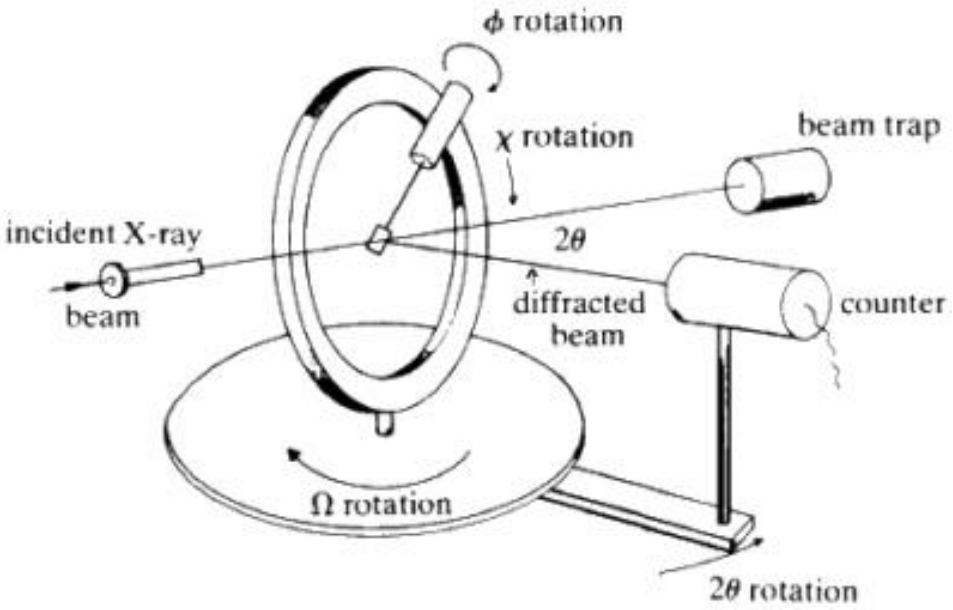
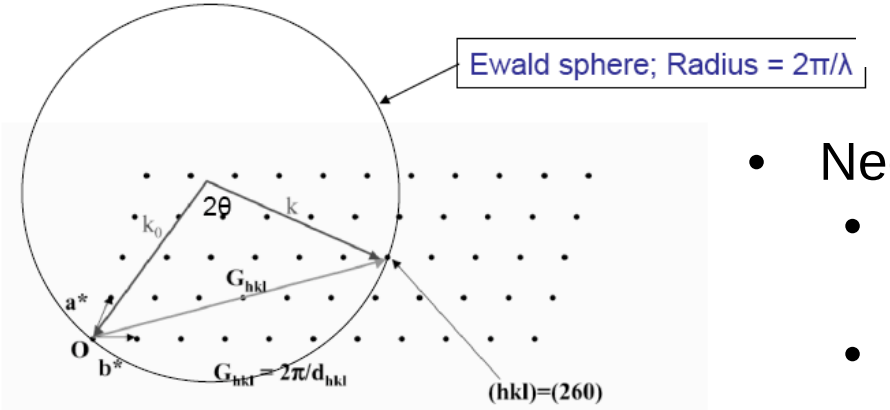
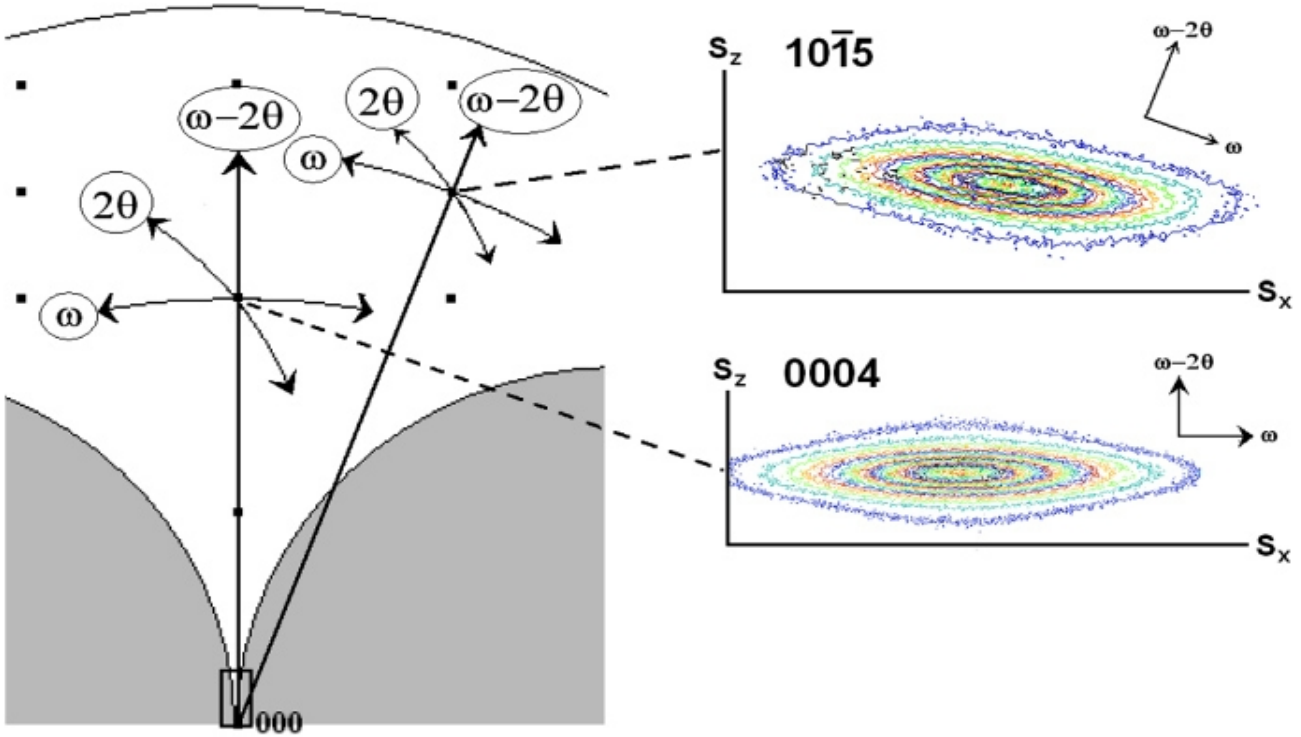




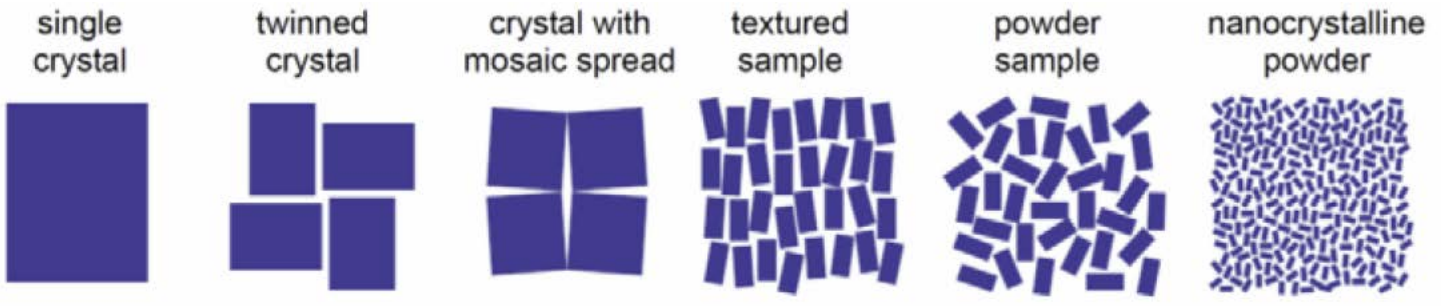


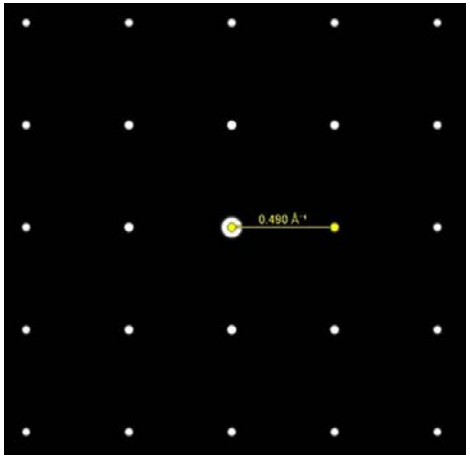
- Need to rotate through several angles
  - It's easy to get "lost in reciprocal space"
  - But you get a lot more detail!

Scanning reciprocal space

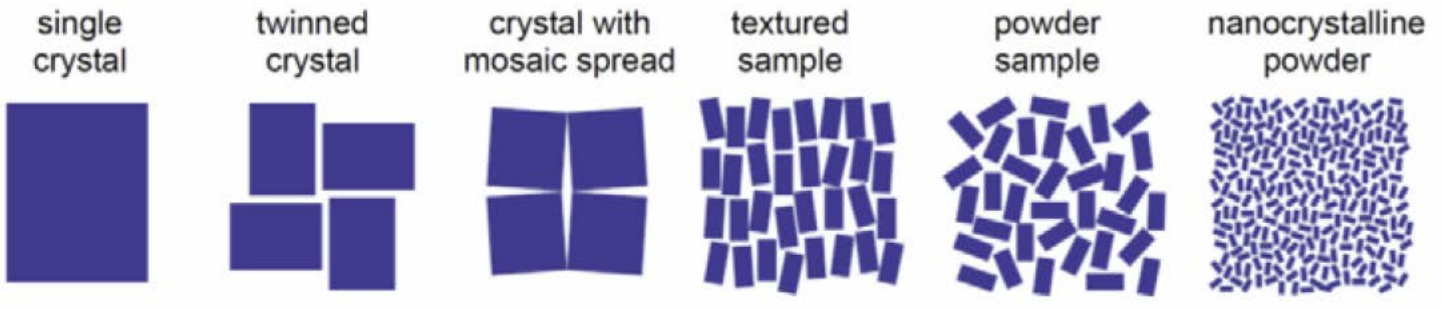


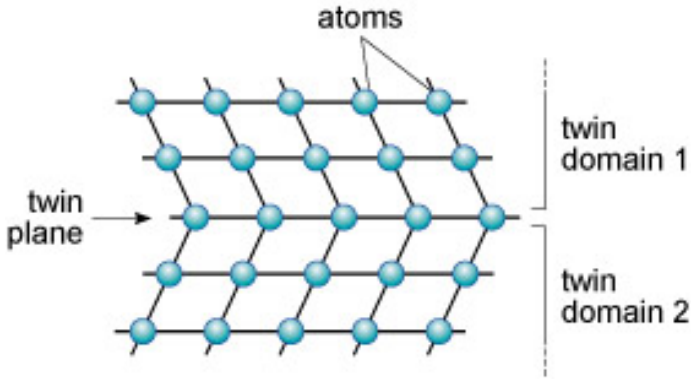
Flavors of samples

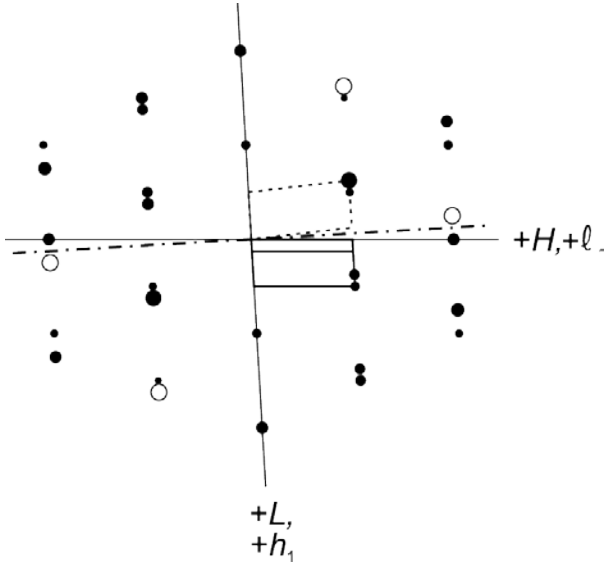




Twinned crystals







Is this just a nuisance?

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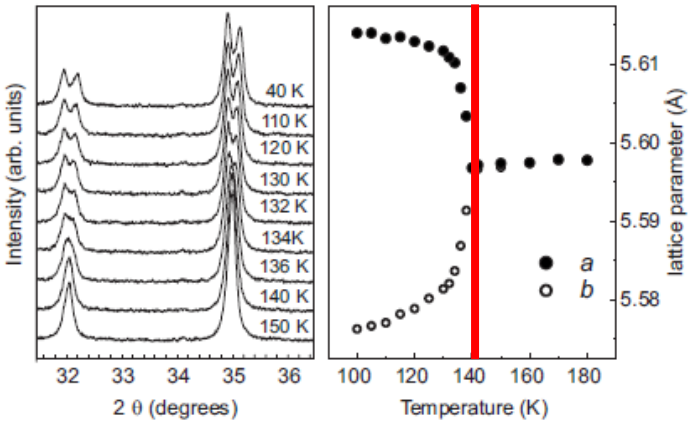
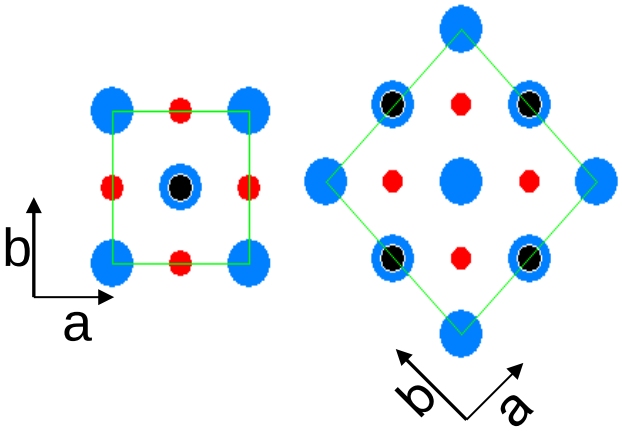
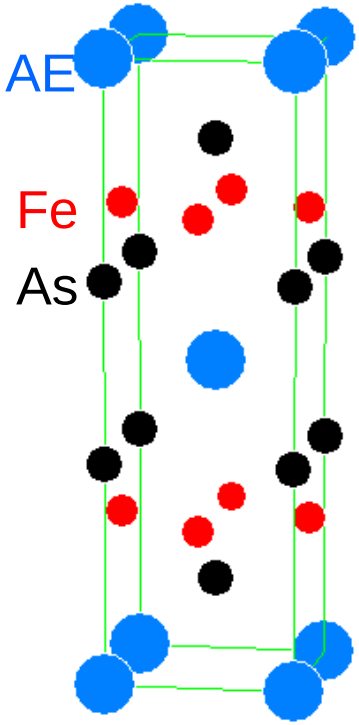
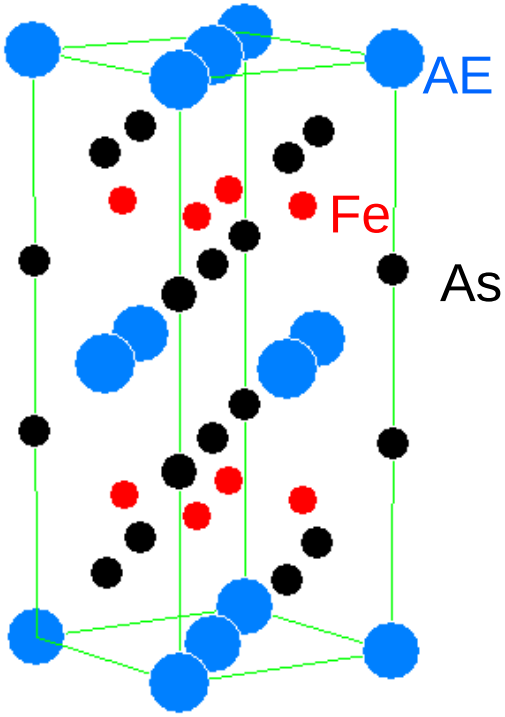


Structural phase transition

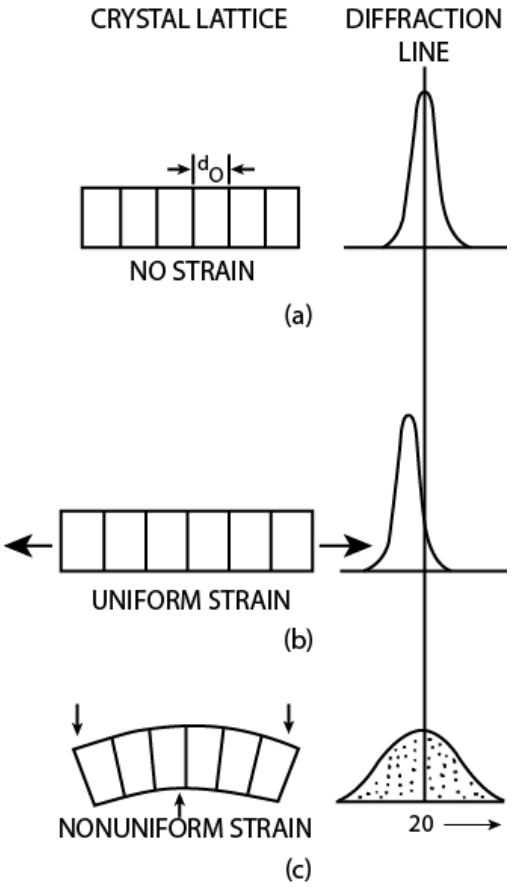
I4/mmm → *Fmmm*



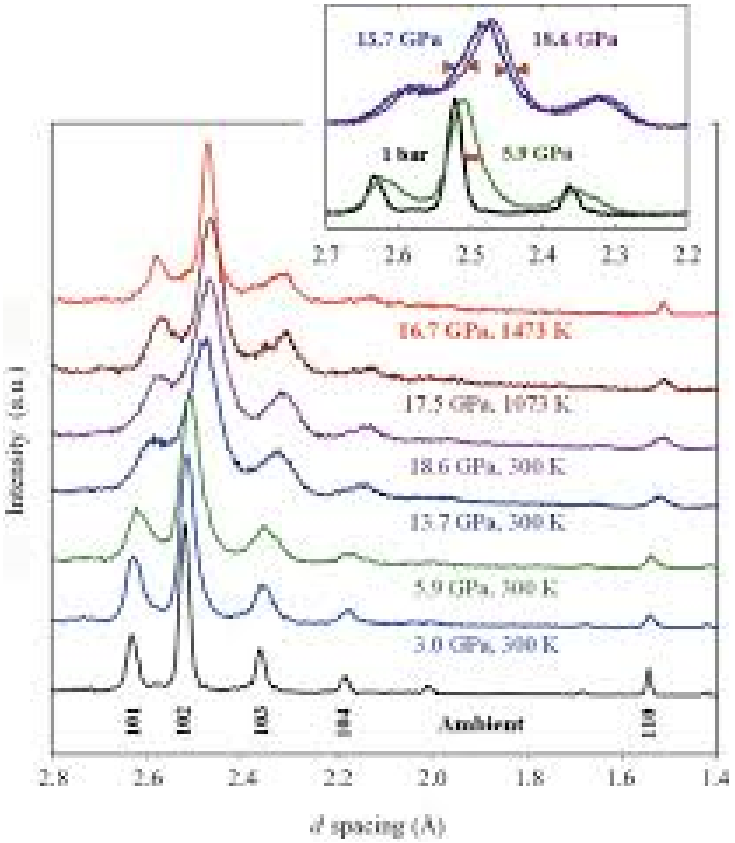




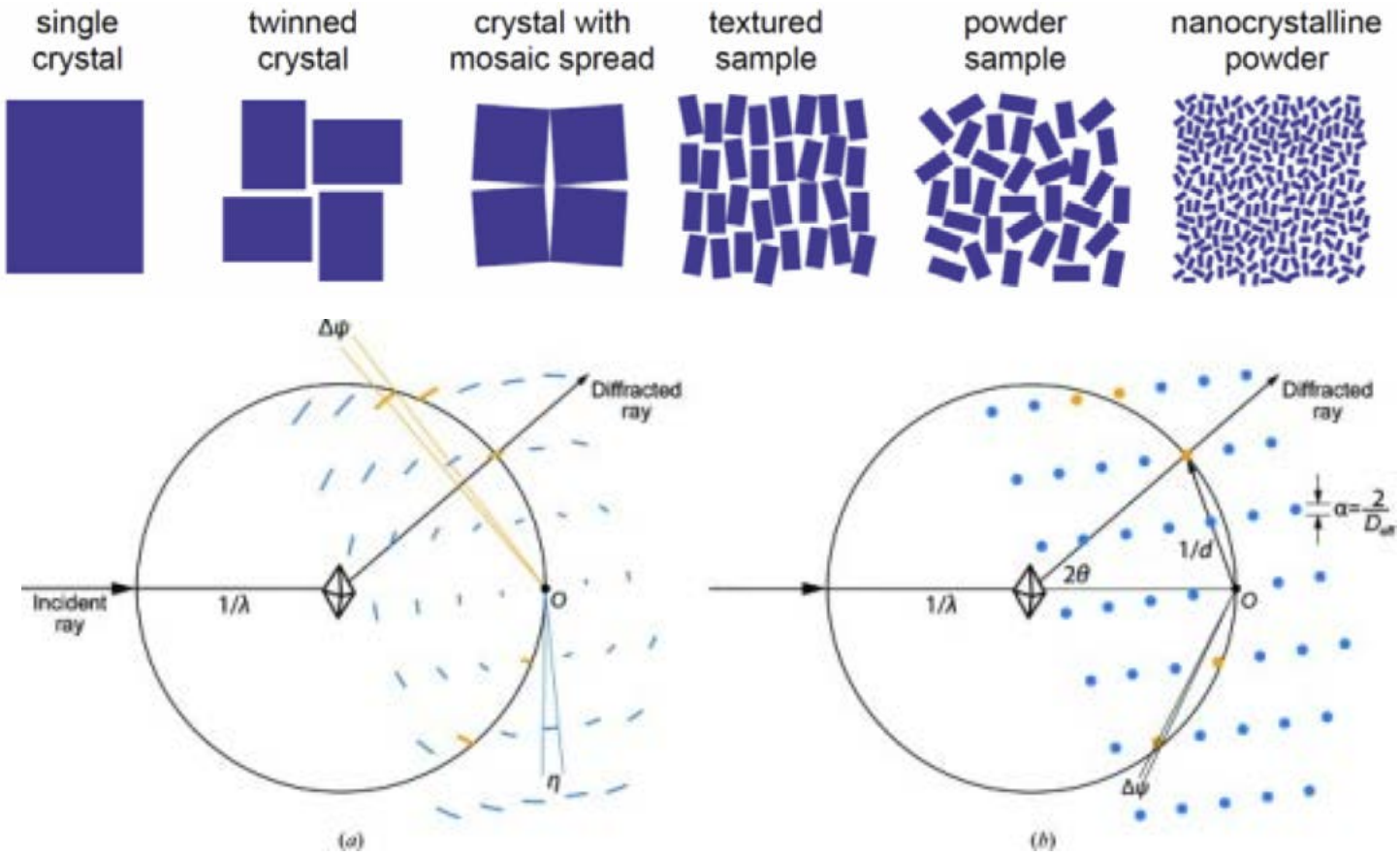
Strained samples



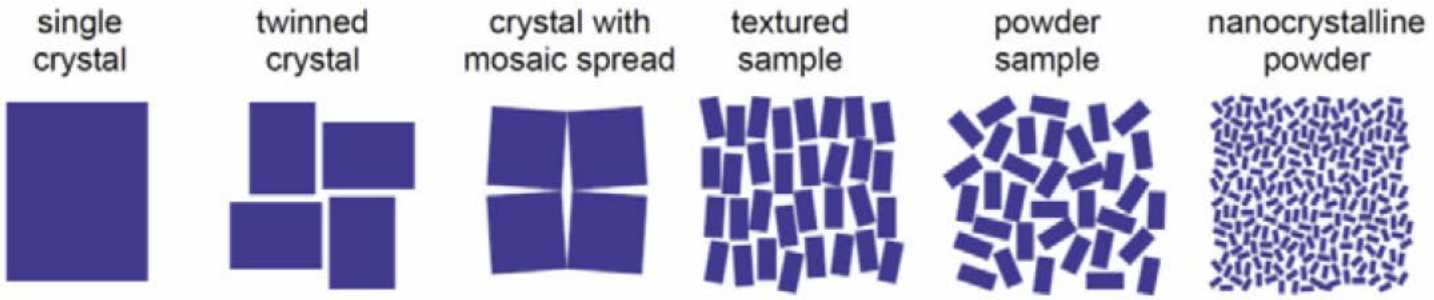
Samples under pressure

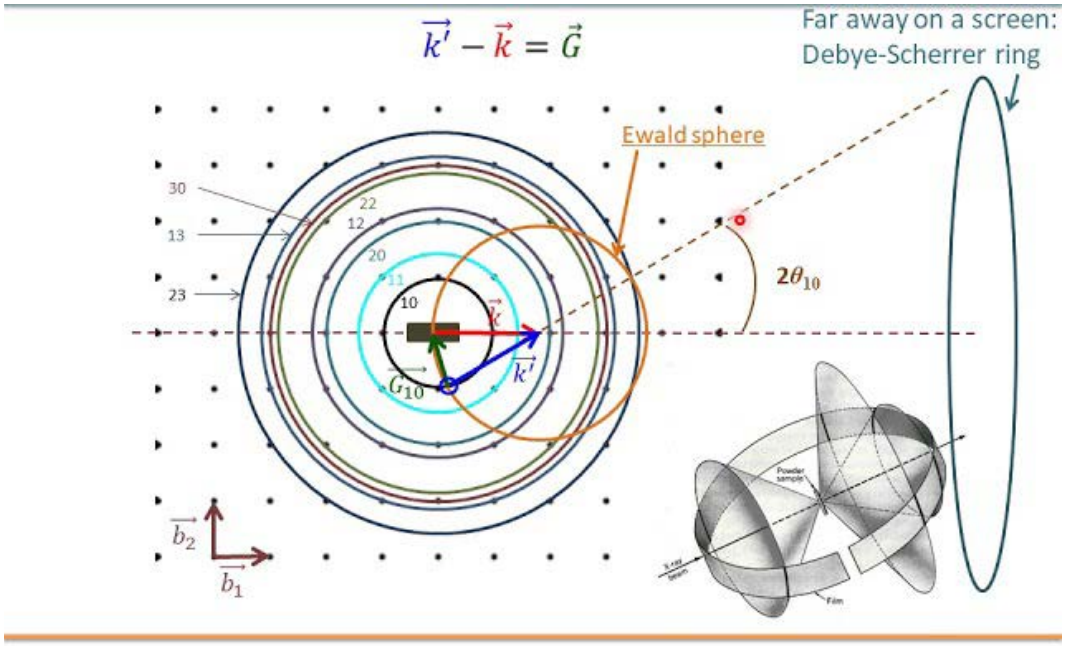


Mosaic crystals



Ideal powder samples





Powder diffraction

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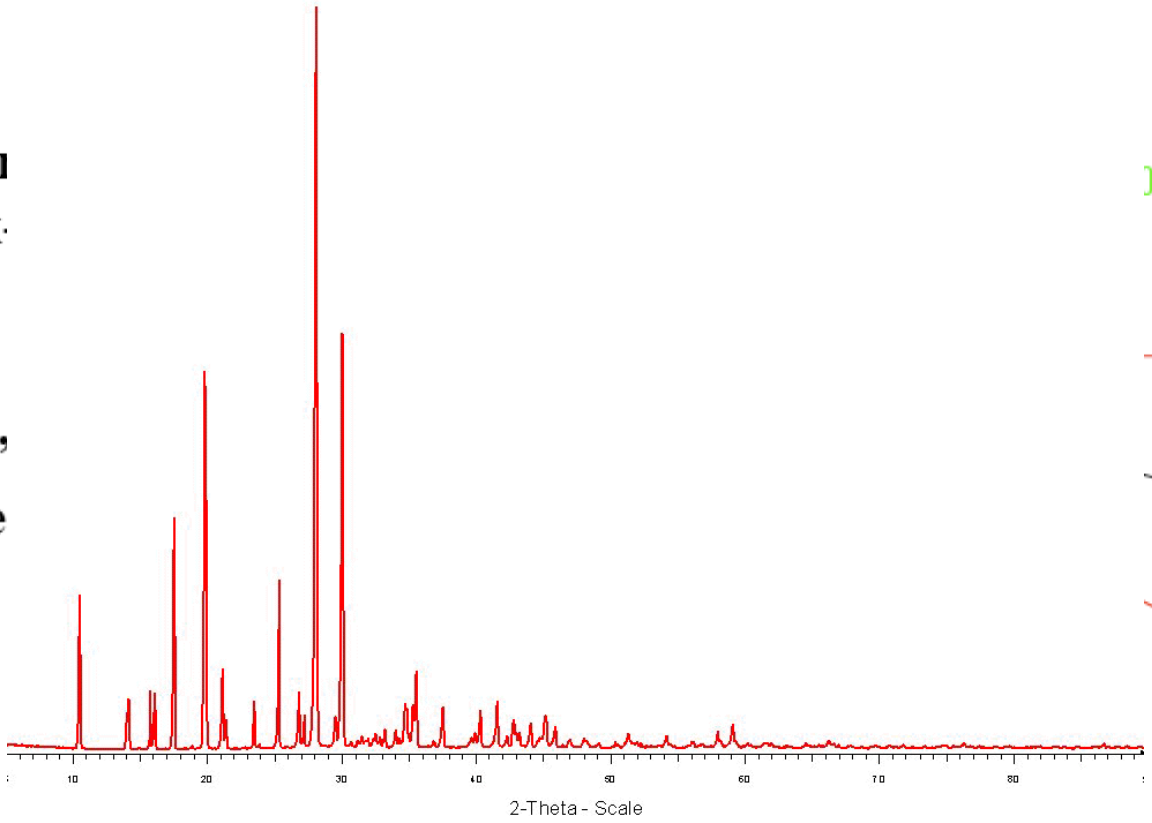
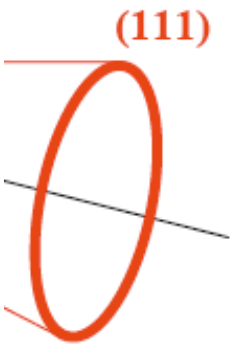
In

x-

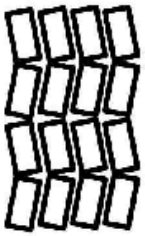
Bragg'

Powde





Types of powder samples



Textured powder
(preferred orientati

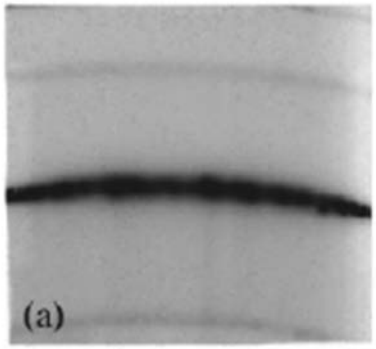
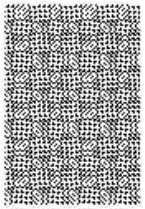
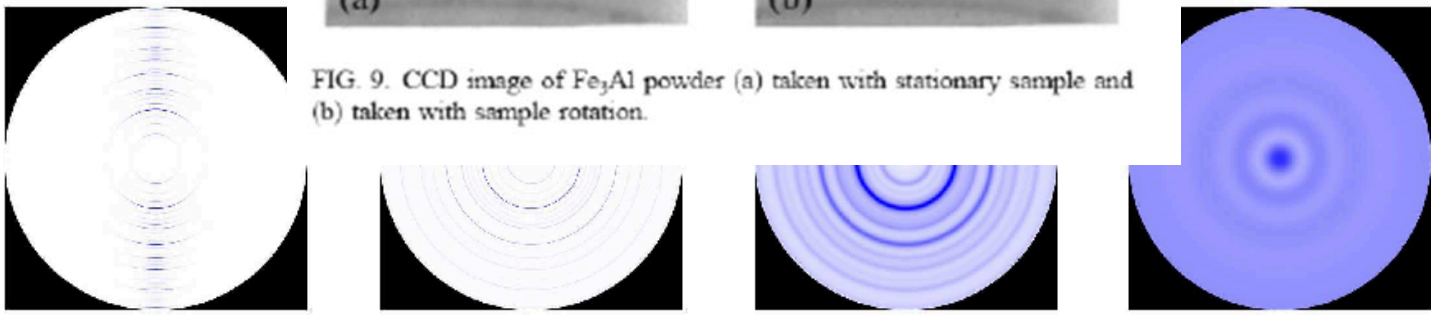


FIG. 9. CCD image of Fe_3Al powder (a) taken with stationary sample and (b) taken with sample rotation.



Amorphous



Fitting diffraction data

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- **Rietveld refinement**
  - Lattice constants
  - space group
  - Atom positions
  - Site disorder/vacancies
  - Thermal vibration amplitude
  - Strain broadening
  - R-factor

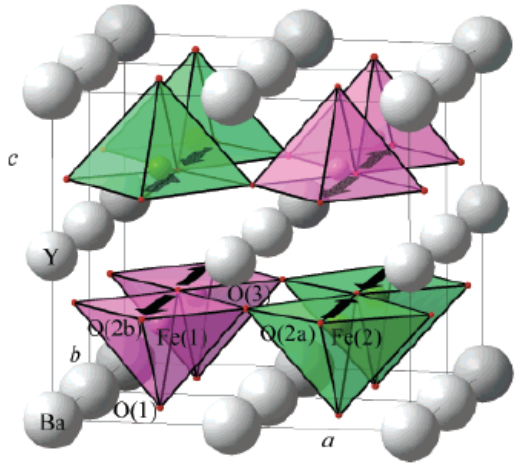

Figure 3. Crystal and magnetic structure of the class-I MV (charge-ordered) $YBaFe_2O_5$ at 20 K. Magnetic unit cell ($a \times 2b \times c$) is drawn.

Table 4. $YBaFe_2O_5$ Structure Refinement Results from NPD Data

T (K):	20	280	300	320	340
λ (Å)	1.5402	2.0783	2.0783	2.0783	2.0783
R_{wp}	0.0671	0.0789	0.0907	0.0783	0.0748
χ^2	4.78	1.38	1.91	1.25	1.17
space group	*Pmma*[a]	*Pmma*[a]	*Pmma*[a]	*Pmmm*[b]	*Pmmm*[b]
a (Å)	8.0251(1)	8.0162(2)	8.0141(2)	3.93329(7)	3.93181(7)
b (Å)	3.83834(6)	3.85238(7)	3.85511(9)	3.91342(7)	3.91717(7)
c (Å)	7.5312(1)	7.5541(2)	7.5577(2)	7.5652(1)	7.5683(1)
$a_s - b_s$(Å)[c]	0.1742	0.1557	0.1520	0.0199	0.0146
V (Å^3)	231.983(8)	233.28(1)	233.49(1)	116.447(5)	116.563(5)
Fe(1) z	0.2542(4)	0.2568(9)	0.257(1)	0.2640(2)	0.2641(2)
Fe(2) z	0.2695(4)	0.2662(9)	0.265(1)		
O(1) z	0.003(1)	0.001(3)	0.000(3)	0	0
O(2a) z	0.3213(7)	0.324(2)	0.325(2)	0.3137(5)	0.3140(6)
O(2b) z	0.3132(7)	0.307(2)	0.308(2)		
O(3) x	0.0098(7)	0.012(1)	0.011(2)	0	0
O(3) z	0.3119(3)	0.3130(4)	0.3115(4)	0.3127(5)	0.3125(6)
Y U_{iso} (Å^2)	0.0063(4)	0.0123(9)	0.013(1)	0.0152(8)	0.0137(7)
Ba U_{iso} (Å^2)	0.0039(6)	0.014(1)	0.017(1)	0.017(1)	0.0144(9)
Fe U_{iso}/U_{eqv} (Å^2)[d,e]	0.0039(3)	0.0124(6)	0.0139(8)	0.0132	0.0122
O(1) U_{eqv} (Å^2)[d]	0.0080	0.0138	0.0159	0.0181	0.0136
O(2) U_{eqv} (Å^2)[d,f]	0.0065	0.0123	0.0129	0.0186	0.0188
O(3) U_{eqv} (Å^2)[d]	0.0078	0.0128	0.0141	0.0146	0.0138
Fe M_y (μ_B)	3.82(2)	3.41(3)	3.26(3)	2.88(2)	2.76(2)
Fe M_z (μ_B)	0	0	0	−0.17(8)	−0.20(8)
Fe M_{Total} (μ_B)	3.82(2)	3.41(3)	3.26(3)	2.89(2)	2.77(2)

[a] Wyckoff positions for space group *Pmma* (nuclear cell) are: Ba at 2a (0,0,0); Y at 2c (0,0,$^1/_2$); Fe(1) and O(1) at 2f ($^1/_4$,$^1/_2$,z); Fe(2) at 2f ($^3/_4$,$^1/_2$,z); O(2a) at 2e ($^3/_4$,0,z); O(2b) at 2e ($^1/_4$,0,z); O(3) at 4j (x,$^1/_2$,z). [b] Wyckoff positions for space group *Pmmm* (nuclear cell) are: Ba at 1a (0,0,0); Y at 1c (0,0,$^1/_2$); Fe at 2t ($^1/_2$,$^1/_2$,z); O(1) at 1f ($^1/_2$,$^1/_2$,0); O(2) at 2s ($^1/_2$,0,z); O(3) at 2r (0,$^1/_2$,z). [c] Orthorhombic distortion; refers to the single-perovskite-type subcell. [d] U_{eqv} values are given for those atoms where anisotropic displacement parameters were used in the refinement. The U_{eqv} values are defined as one-third the trace of the diagonal matrix describing the shape of the thermal ellipsoid. A complete list of the anisotropic displacement parameters is given in the Supporting Information. [e] The displacement parameters for Fe(1) and Fe(2) were constrained to be equal. An isotropic displacement parameter was used in the charge-ordered state; anisotropic displacement parameters were used for the MV state. [f] The displacement parameters for O(2a) and O(2b) were constrained to be equal.

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