

# Structural characterization

## Part 1

# Experimental methods

- X-ray diffraction
- Electron diffraction
- Neutron diffraction
- Light diffraction
- EXAFS-Extended X-ray absorption fine structure
- XANES-X-ray absorption near edge structure
- A number of other methods can give important additional information such as:
  - Electron spin resonance
  - Nuclear magnetic resonance
  - Mössbauer spectroscopy

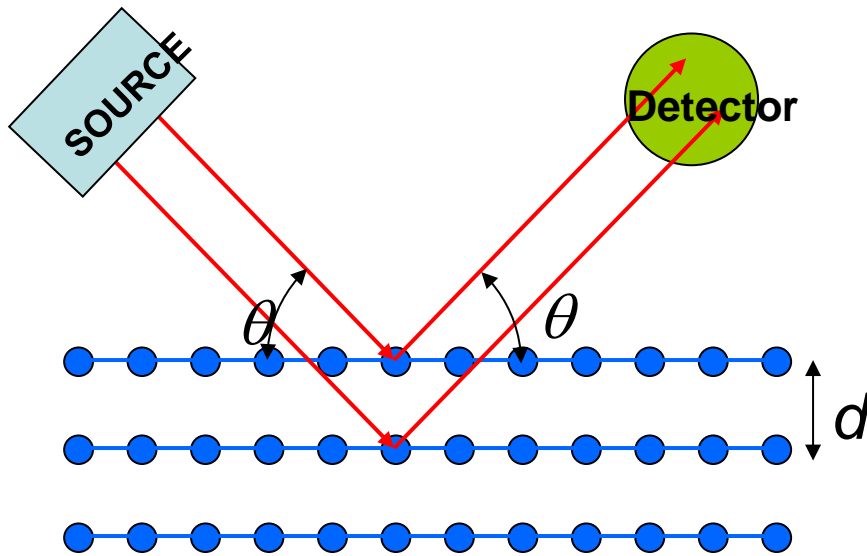
# X-ray and electron diffraction

- X-ray scattering:
- Elastic scattering from electrons
- Powders or thick ( $\sim\mu\text{m}$ ) films
- Thin films at glancing incidence
- Atomic form factor  $f(Q)$  decreases with scattering vector  $Q$ , but can be computed.
- Electron scattering:
- Elastic scattering from screened Coulomb fields of atoms
- Thin films in an electron microscope
- Strong multiple scattering for thicker films
- Inelastic background
- Quantitative analysis difficult

# Neutron scattering

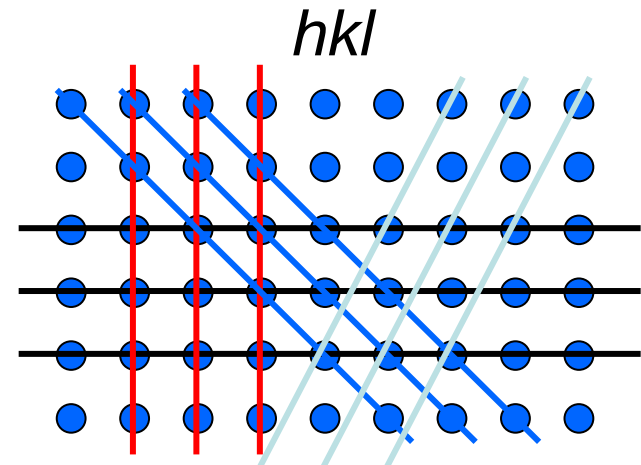
- Inelastic scattering from atomic nuclei
- Short range nuclear interaction
- Scattering length  $b$ , independent of  $Q$ .
- $b$  varies between elements and is dependent on isotope
- Wavelength and energy of thermal neutrons comparable to atomic spacings and vibrational excitations
- Both structure and dynamics can be studied
- Bulk materials, powders
- Isotope substitution
- Scattering from magnetic structure
- Few large international facilities

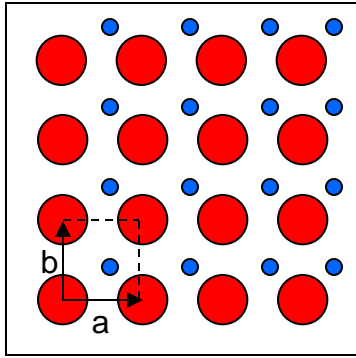
# Diffraction from crystals



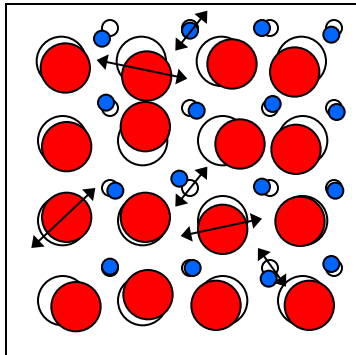
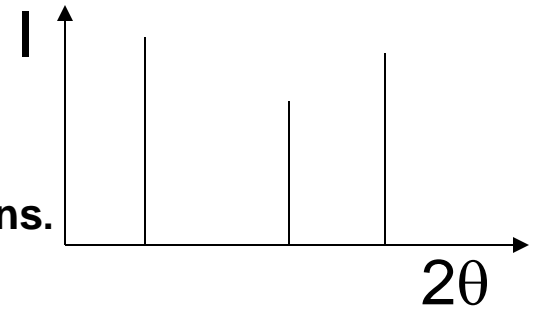
Bragg's law

$$\lambda = 2d_{hkl} \sin \theta$$

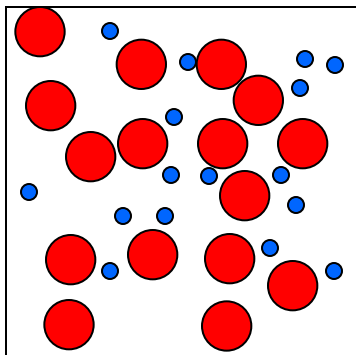
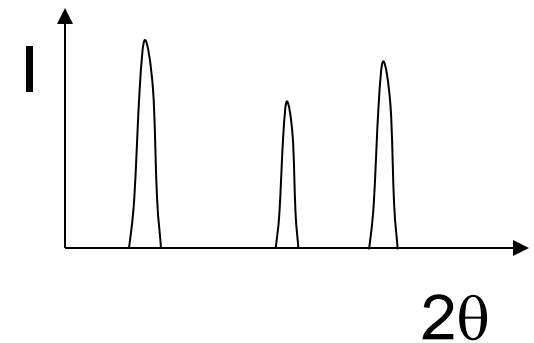




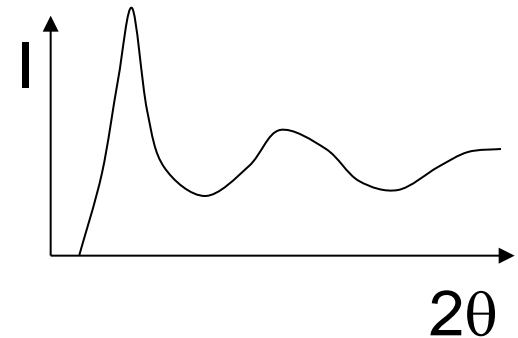
**Perfect crystal**  
 All atom positions are defined by the lattice parameters  
 Diffraction pattern consists of Bragg-peaks which are delta functions.



**Crystal with thermal vibrations of the atoms.** Lattice parameters define a mean position of the atoms and we obtain broadened Bragg-peaks.  
 In polycrystals broadening occurs primarily from small grain sizes.



**Amorphous material**  
 Long range order lost, but some short range order still exists  
 Diffraction pattern consists of broad peaks

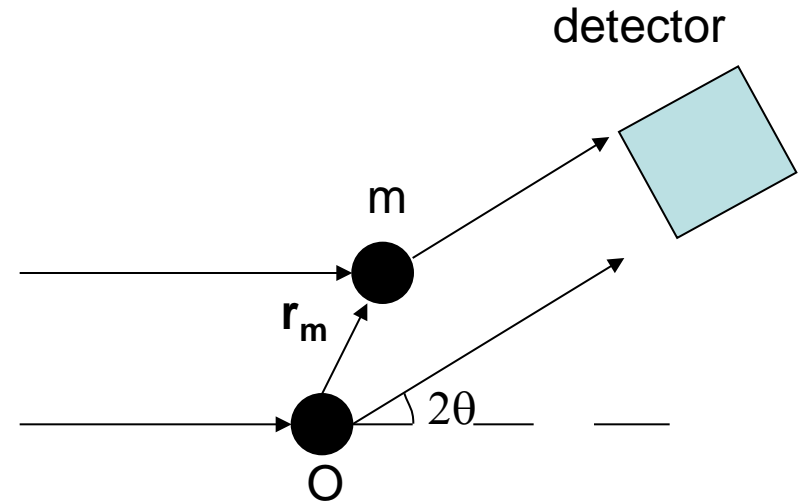


# Amorphous materials

- No crystalline order – the reciprocal lattice does not exist!
- An interpretation of diffraction experiments in terms of atomic planes or reciprocal lattice vectors is not possible
- We must sum up the waves scattered from each atom in the whole sample
- Gives experimental information on atomic distances and their distributions, as specified by the radial distribution function

# Ex: X-ray scattering

- Elastic scattering  
 $|\mathbf{k}_i| = |\mathbf{k}_f| = k$
- Single scattering
- Momentum transfer:  
 $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ ,  $Q = 2k \sin(\theta)$
- Phase difference  $\mathbf{Q} \cdot \mathbf{r}_m$
- Atomic form factor  $f_m(\mathbf{Q})$
- Scattering amplitude  $A(\mathbf{Q})$
- Intensity  $I(\mathbf{Q}) = A^*(\mathbf{Q})A(\mathbf{Q})$



Schematic geometry

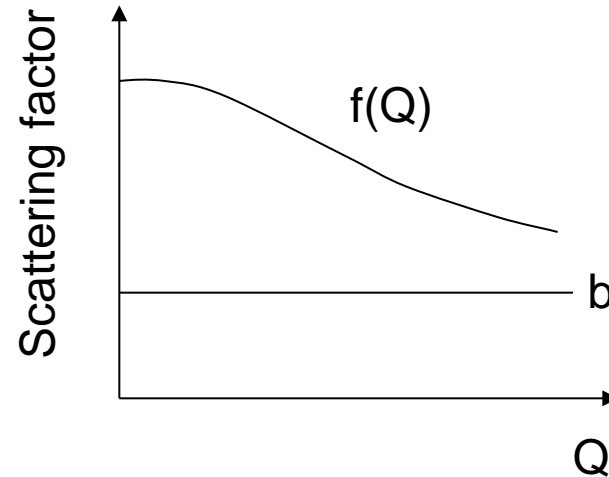


# Scattering from an atom

- Atomic form or scattering factor

$$f_m(\mathbf{Q}) = \int_{atom} n_e(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r}$$

- $n_e(\mathbf{r})$  is electron concentration around an atom
- This is the same equation as in the theory of X-ray diffraction from crystals!



- Comparison of X-ray and neutron factors
- $f_e$  larger than  $f_m$ , but similar shape

# Scattered intensity

- Scattering amplitude

$$A(\mathbf{Q}) = \sum_m f_m \exp(-i\mathbf{Q} \cdot \mathbf{r}_m)$$

- Intensity

$$I(\mathbf{Q}) = \sum_m \sum_n f_m f_n \exp(i\mathbf{Q} \cdot (\mathbf{r}_m - \mathbf{r}_n))$$

- Normalized to the intensity scattered by a single electron  
 $I_e(\mathbf{Q}) = |f_e(\mathbf{Q})|^2$
- Isotropic material: Average over all orientations of  $\mathbf{r}_m - \mathbf{r}_n$

$$I(Q) = \sum_m \sum_n f_m f_n \sin(Qr_{mn}) / Qr_{mn}$$

# Monatomic solid - general

- N atoms in sample, we put  $f_m = f_n = f$
- Sum terms with  $m \neq n$  separately

$$I(\mathbf{Q}) = Nf^2 \left[ 1 + \sum_{m \neq n} \exp(i\mathbf{Q} \cdot (\mathbf{r}_m - \mathbf{r}_n)) \right]$$

- The sum over the atoms  $m$  around a given atom  $n$  can be converted to an integral over the pair distribution function  $g_2(\mathbf{r})$ . Note that  $\mathbf{r} = \mathbf{r}_m - \mathbf{r}_n$ .

$$I(\mathbf{Q}) = Nf^2 \left( 1 + n_0 \int g_2(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \right)$$

# Monatomic isotropic solid

- Isotropic materials

$$I(Q) = Nf^2 \left( 1 + n_0 \int 4\pi r^2 g_2(r) \left( \frac{\sin Qr}{Qr} \right) dr \right)$$

$$I(Q) = Nf^2 \left( 1 + \frac{n_0}{Q} \int 4\pi r \sin Qr dr + n_0 \int 4\pi r^2 (g_2(r) - 1) \left( \frac{\sin Qr}{Qr} \right) dr \right)$$

- The second term gives forward scattering, which cannot be separated from the incident beam
- The first and third terms constitute the structure factor,  $S(Q)$

# Pair distribution function

- The pair distribution function can be written in terms of the structure factor by an inverse Fourier transformation

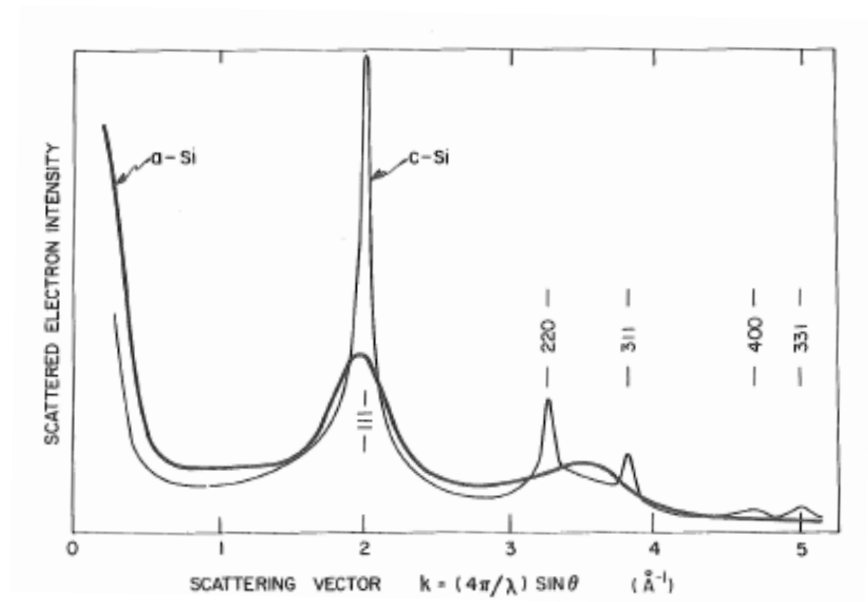
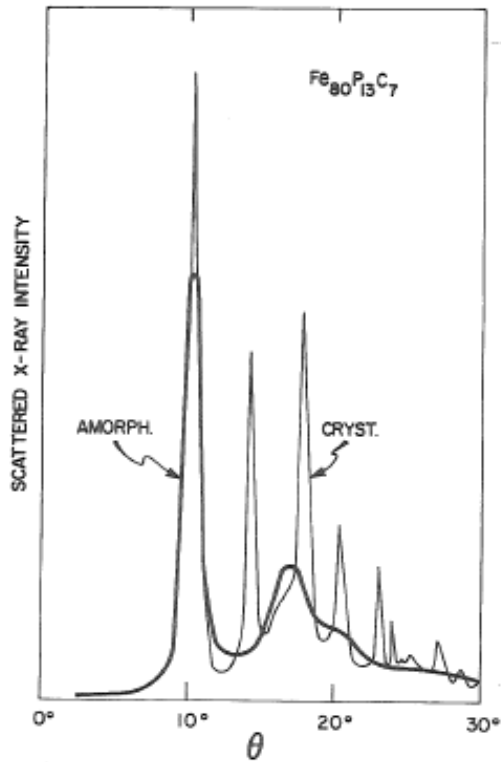
$$S(Q) = 1 + 4\pi n_0 \int r^2 (g_2(r) - 1) \left( \frac{\sin Qr}{Qr} \right) dr$$

$$g_2(r) = 1 + (8\pi^3 n_0)^{-1} \int 4\pi Q^2 (S(Q) - 1) \left( \frac{\sin Qr}{Qr} \right) dQ$$

- PDF can be inferred from experimental data
- Truncation errors from integral – data for a restricted range of Q.

# Amorphous vs. crystalline

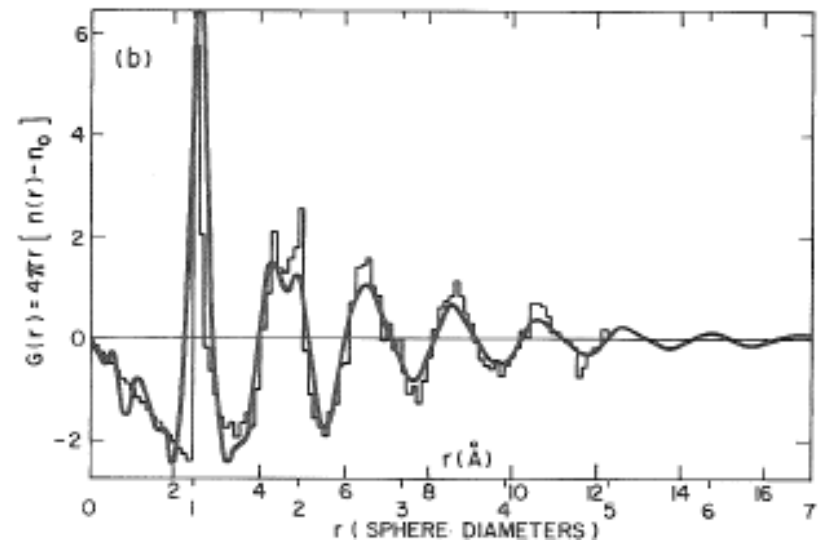
- Amorphous metal alloy
- Crystallized by heating
- Amorphous Si
- Partial crystallization



Source: Zallen, The Physics of amorphous solids

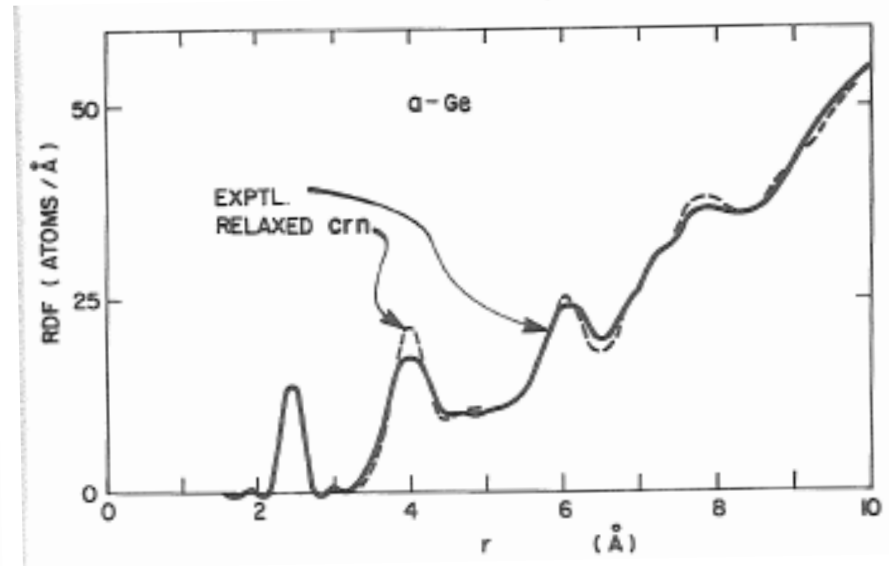
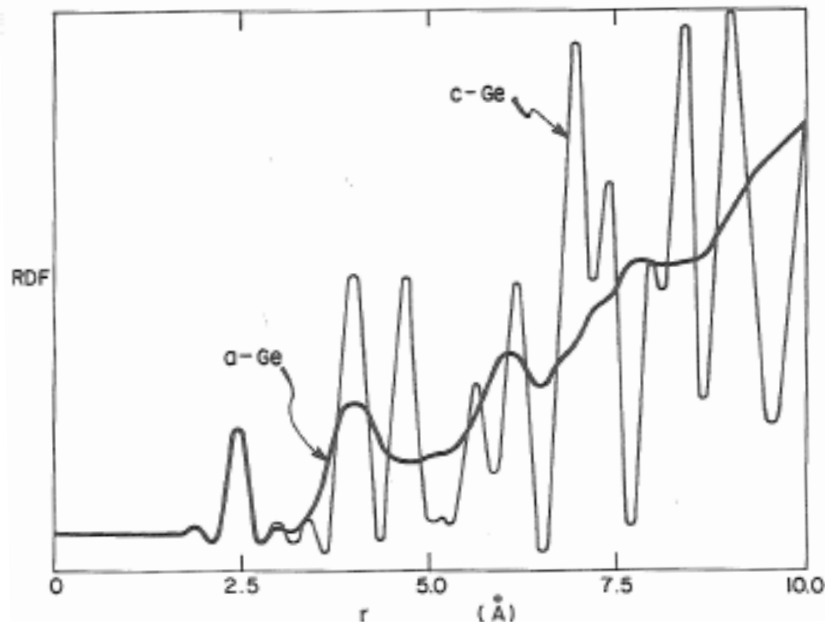
# Amorphous metals: RSP model

- Actually an alloy  $\text{Ni}_{76}\text{P}_{24}$ .
- Radii of Ni and P similar, hence comparison with RSP model reasonable
- Reduced pair distribution function is plotted
- $G(r) = 4\pi r n_0 (g_2(r) - 1)$
- Very good agreement – even for example splitting of second peak!



Source: Zallen, The Physics of amorphous solids

# Amorphous Ge: CRN model



Source: Zallen, The Physics of amorphous solids

- Radial distribution function  $4\pi r^2 n_0 g_2(r)$
- Very good agreement with CRN model
- Microcrystalline models do not give so sharp first peaks without also giving to sharp peaks at larger  $r$

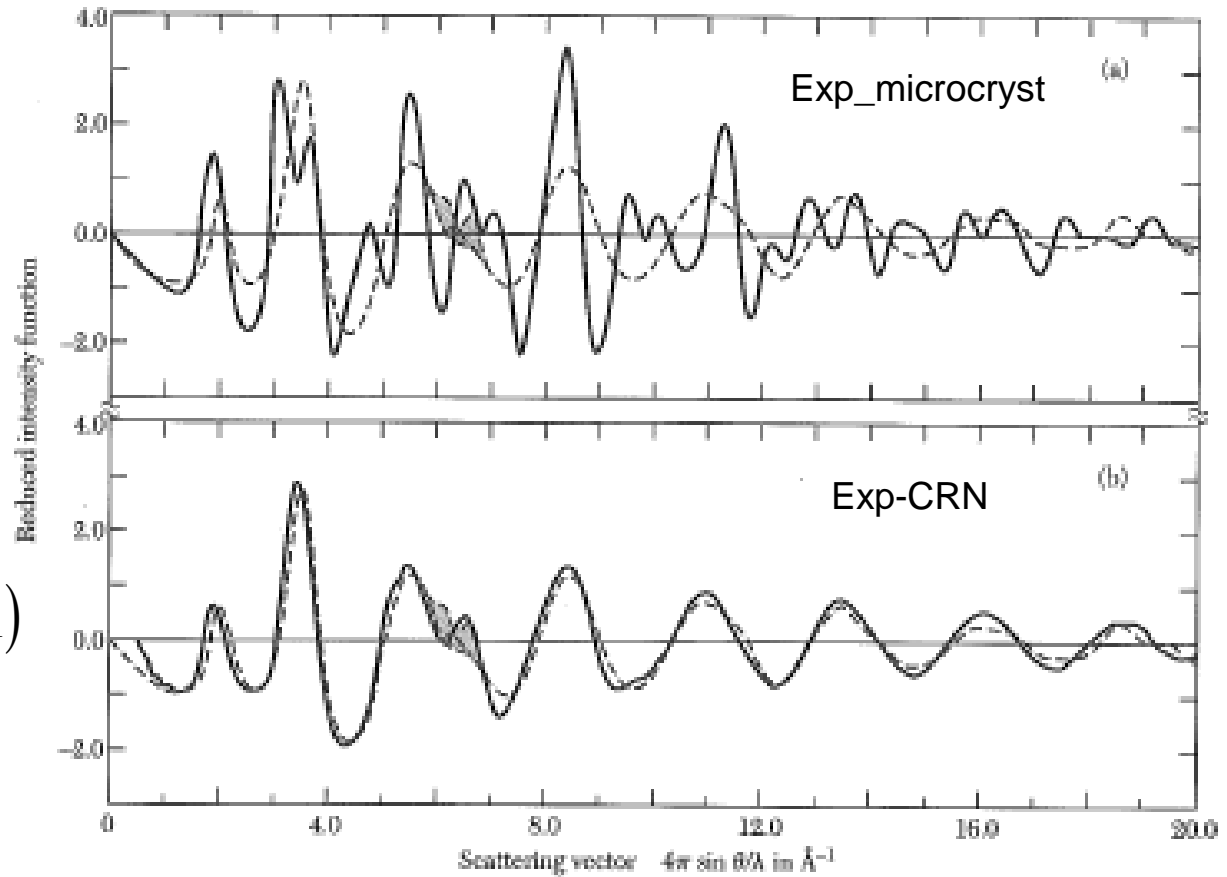


# CRN vs. microcrystalline model

a-Ge

exp-dashed

$$F(Q) = Q((I / Nf^2) - 1)$$



Source: C. Kittel: Introduction to Solid State Physics

# Compounds

- Materials that consist of more than one kind of atom
- In general we must use the partial pair distribution functions  $g_{2,ij}(r)$  to describe the structure – needs EXAFS measurements!
- One can define an effective total  $g_2(r)$  from the partial functions
- For binary compounds one can analyze diffraction experiments in a way analogous to the case of a monatomic material.

# Polyatomic solid -1

- Sum over p different kinds (i) of atoms of number  $N_i$  and with atomic fractions  $x_i$
- Scattering intensity for isotropic material (m,n enumerate the atoms)

$$I(Q) = \sum_m \sum_n f_m f_n \sin(Qr_{mn}) / Qr_{mn}$$

$$I(Q) = Nf^2 \left( 1 + n_0 \int 4\pi r^2 g_2(r) ((\sin Qr) / Qr) dr \right)$$

- Perform first the summation over the N terms with  $m=n$ . The term  $Nf^2$  becomes now a sum over  $N_i f_i^2$ .
- The next sum is when m and n are not equal. The sum over the N atoms at the origin becomes a sum over  $N_i f_i$  and the integral over each partial pair distribution function  $g_{2,ij}(r)$  is weighted by  $f_j$  for each atom type j.

# Polyatomic solid - 2

- Hence the relation for a monatomic solid

$$I(Q) = Nf^2 \left( 1 + n_0 \int 4\pi r^2 g_2(r) \left( (\sin Qr) / Qr \right) dr \right)$$

- is generalized to (i-atom at origin)

$$I(Q)/N = \sum_{i=1}^P x_i f_i^2 + \sum_{i=1}^P \sum_{j=1}^P x_i f_i f_j n_0 \int 4\pi r^2 g_{2,ij}(r) \left( (\sin Qr) / Qr \right) dr$$

- $4\pi r^2 n_0 g_{2,ij}(r)$  is the average number of j-atoms at a distance r from an i-atom.
- Treat near forward scattering as for the monatomic case.

# Total pair distribution function

- Define a total pair distribution function by

$$g_2(r) = \sum_{ij} x_i f_i f_j g_{2,ij}(r) / \langle f \rangle^2$$

- Def:

$$\langle f \rangle = \sum_{i=1}^p x_i f_i$$

- We obtain an expression similar to the one for a monatomic solid

$$\langle f^2 \rangle = \sum_{i=1}^p x_i f_i^2$$

$$I(Q)/N = \langle f^2 \rangle + \langle f \rangle^2 n_0 \int 4\pi r^2 (g_2(r) - 1) ((\sin Qr)/Qr) dr$$

- Inversion difficult when f depends on Q
- Radial distribution function (RDF)
- $n_0 \rho(r)$  (in units of  $e^{-}/\text{\AA}$ )

$$\rho(r) = 4\pi r^2 \langle f \rangle^2 g_2(r)$$

# Ex: Binary compound - 1

- Two kinds of atoms A,B
- Formula unit  $A_xB_y$  – scattered intensity normalized by number of formula units M instead of number of atoms N
- Sum PDF and RDF over a formula unit of the material

$$n_0\rho(r) = 4\pi r^2 n_0 (xf_A^2 g_{2,AA}(r) + yf_B^2 g_{2,BB}(r) + \\ + xf_A f_B g_{2,AB}(r) + yf_A f_B g_{2,BA}(r))$$

- Note that  $g_{BA}/g_{AB}=x/y$
- Integration over a peak in the RDF gives the number of electrons giving rise to it

# Binary compound - 2

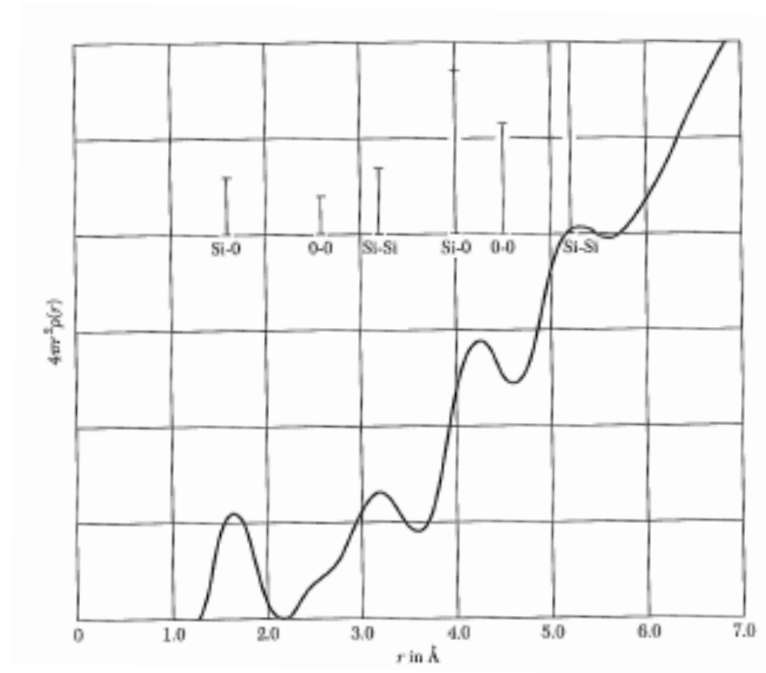
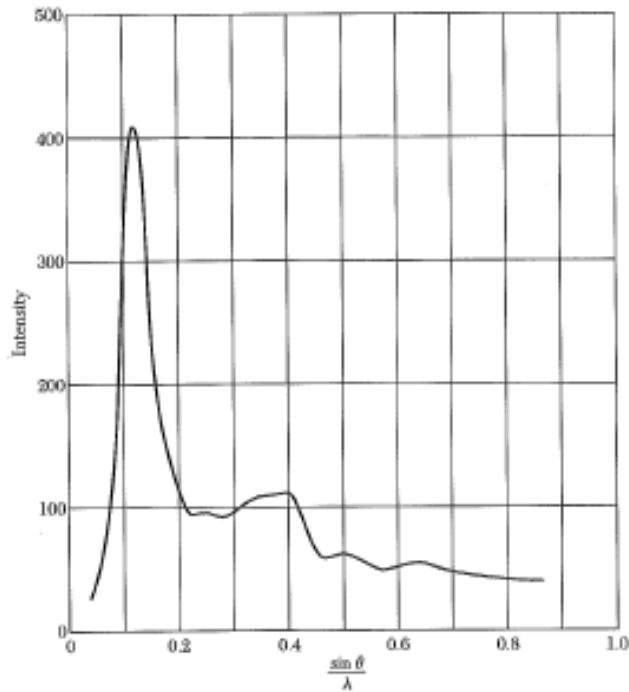
- First coordination shell: Contributions from AB and BA terms
- Number of B atoms surrounding an A atom:  $n_{AB}$
- Number of A atoms surrounding a B atom:  $n_{BA}$
- They are related by the stoichiometry  $n_{BA}/n_{AB}=x/y$
- Area under the first peak of the generalized RDF

$$A = f_A f_B (x n_{AB} + y n_{BA}) = 2x f_A f_B n_{AB}$$

- Second peak: AA, BB or maybe both. May be difficult to resolve

# Vitreous SiO<sub>2</sub>

- Scattered X-ray intensity
- Radial distribution function

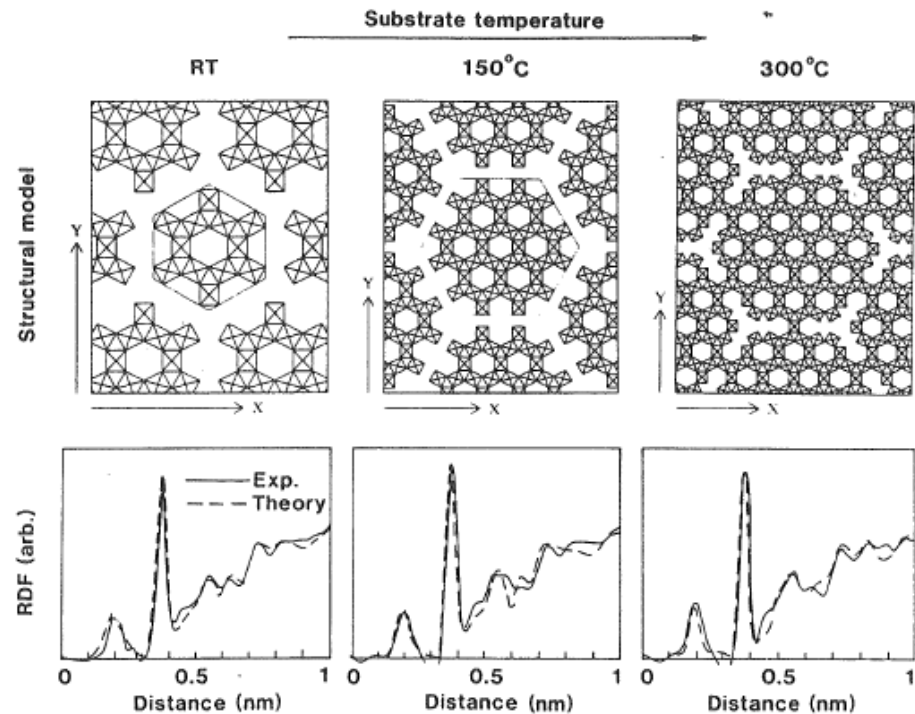


Source: C. Kittel: Introduction to Solid State Physics



# Structural modeling of amorphous $\text{WO}_3$

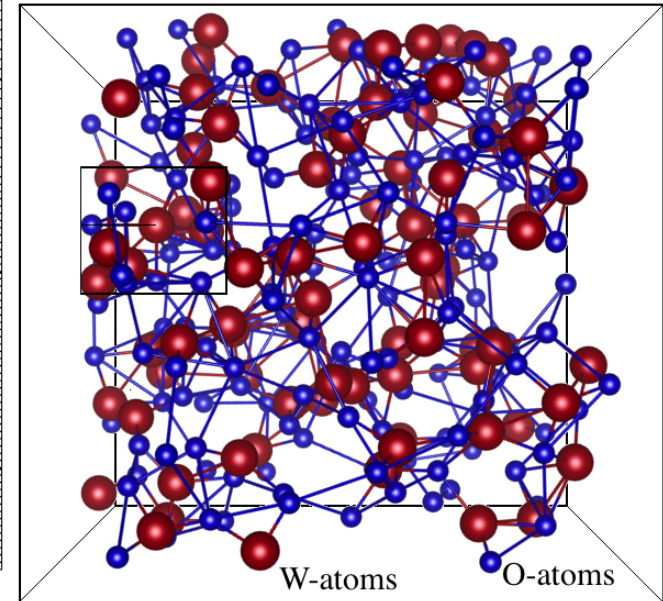
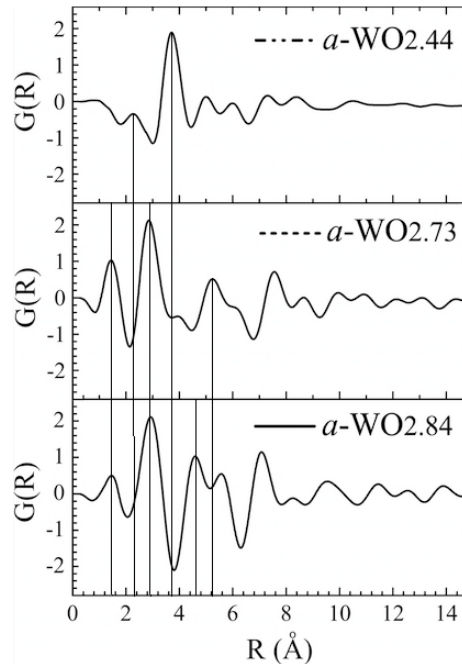
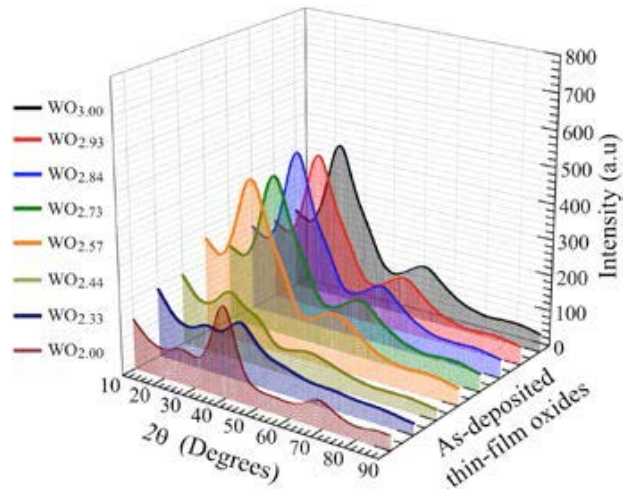
- RDF from X-ray diffraction for  $\text{WO}_3$  films evaporated at different substrate temperature.
- Compared to models based on connected  $\text{WO}_6$  octahedra
- Good agreement with nanocrystalline model and more so at higher substrate temperatures.



Source: Nanba and Yasui, J. Solid state Chem. 83 (1989) 304

# Sputtered $\text{WO}_{3-x}$ thin films

- More "amorphous" than evaporated films
- C. Triana, lic. thesis



$$G(r) = 4\pi r n_0 (g(r) - 1)$$

(reduced radial distribution function)

# Summary

- We have concentrated on X-ray scattering
- Neutron scattering and EXAFS: Later lecture
- Broadened diffraction peaks give short range order
- Featureless spectrum at larger length scales for a disordered material
- Spectrum can be inverted to obtain pair distribution function
- Ex: Monatomic solids and binary compounds with amorphous structure