Lab Week 2 – Module γ_1

Derivative Structures

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OBJECTIVES

- ✓ Review principles of x-ray scattering from crystalline materials
- ✓ Learn how to conduct x-ray powder diffraction experiments and use PDFs
- ✓ Study the inter-relationship of different crystal structures

SUMMARY OF TASKS

1) Calculate structure factor for materials to be investigated

2) Prepare samples for x-ray powder diffraction

2) Obtain x-ray scattering patterns for all materials

3) Compare obtained patterns with calculations and powder diffraction files (PDFs)

4) Perform peak fitting to determine percent crystallinity and crystallite size

BACKGROUND

## X-ray Diffraction from Crystalline Materials

As discussed in 3.012, a periodic arrangement of atoms will give rise to constructive interference of scattered radiation having a wavelength λ comparable to the periodicity d when Bragg's law is satisfied:

$$n\lambda = 2d \sin\theta \,\square$$

where n is an integer and θ is the angle of incidence.

Bragg's law tells us necessary conditions for diffraction, but provides no information regarding **peak intensities**. To use x-ray diffraction as a tool for materials identification, we must understand the relationship between structure/chemistry and the intensity of diffracted x-rays.

Recall from 3.012 class that for a 1d array of atoms, the condition for constructive interference can be determined as follows:
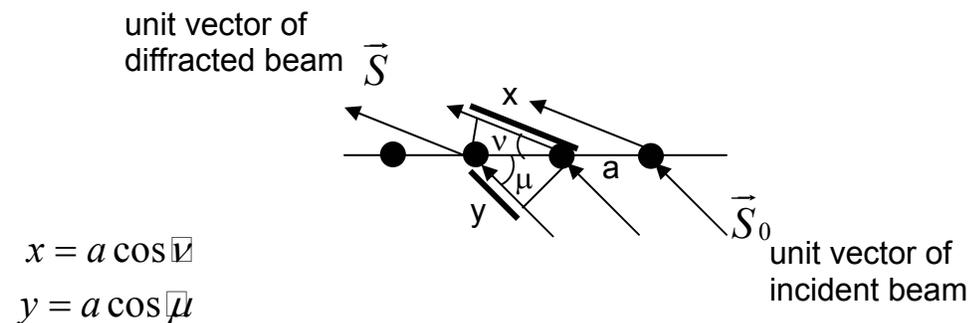
$$x = a\cos\square$$
$$y = a\cos\square\mu$$

The total path difference: $x - y = a\cos\square - a\cos\square\mu = h\lambda$

$$\left(\vec{S} - \vec{S_0}\right)\cdot\vec{a} = h\lambda$$

Defining $\vec{s} = \dfrac{\left(\vec{S} - \vec{S_{0\square}}\right)}{\lambda}$, the condition for 1d constructive interference becomes:

$$\vec{s}\cdot\vec{a} = h$$

For 3 dimensions, we have:

$$\vec{s} \cdot \vec{a} = h$$

$$\vec{s} \cdot \vec{b} = k$$

$$\vec{s} \cdot \vec{c} = l$$

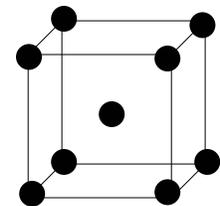where h, k and l are the Miller indices of the scattering plane.

For a single unit cell having M atoms, the scattered amplitude is proportional to the **structure factor**, defined as:

$$F(s) = \sum_{n=1}^{M} f_n \exp\left[2\pi i \vec{s} \cdot \vec{r_n} \right]$$

where $\vec{r_n}$ is the atomic position vector for the nth atom in the unit cell:
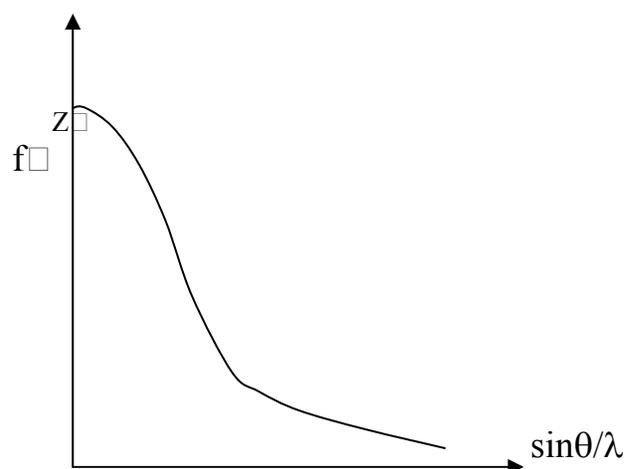
$$\vec{r_n} = x_n \vec{a} + y_n \vec{b} + z_n \vec{c}$$

where (x_n, y_n, z_n) are the atomic position coordinates.

Example: for a BCC structure, there are 2 atoms/cell at (0,0,0) and (1/2,1/2,1/2).

The parmater f_n is the **atomic scattering factor**, proportional to the atomic number *Z* of the nth atom. Hence, atoms of high *Z* scatter more strongly than light elements. The atomic scattering factor is a function of θ and λ.

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Substituting $\vec{r}_n$ into the structure factor:

$$F(s) = \sum_{n=1}^{M} f_n \exp\left[2\pi i \vec{s} \cdot (x_n \vec{a} + y_n \vec{b} + z_n \vec{c})\right]$$

$$F_{hkl} = \sum_{n=1}^{M} f_n \exp\left[2\pi i (hx_n + ky_n + lz_n)\right]$$

For a BCC crystal:

$$F_{hkl} = f \exp\left[2\pi i(0)\right] + f \exp\left[2\pi i \left(\frac{h}{2} + \frac{k}{2} + \frac{l}{2}\right)\right] = f + f \exp\left[\pi i(h + k + l)\right]$$

$$F_{hkl} = 2f \qquad h+k+l = \text{even}$$

$$F_{hkl} = 0 \qquad h+k+l = \text{odd}$$

The scattered intensity is related to the structure factor:

$$I_{coh} \propto FF^* = |F_{hkl}|^2 = 4f^2 \qquad h+k+l = \text{even}$$

$$I_{coh} = 0 \qquad h+k+l = \text{odd}$$

Note that the total coherent intensity will be a sum of the contributions of all unit cells in the crystal. For a BCC crystal, reflections from planes with Miller indices where h+k+l is an odd integer will be absent from the diffraction pattern, while reflections from (110), (200), (211), etc. will be present with reduced intensity as h+k+l increases.

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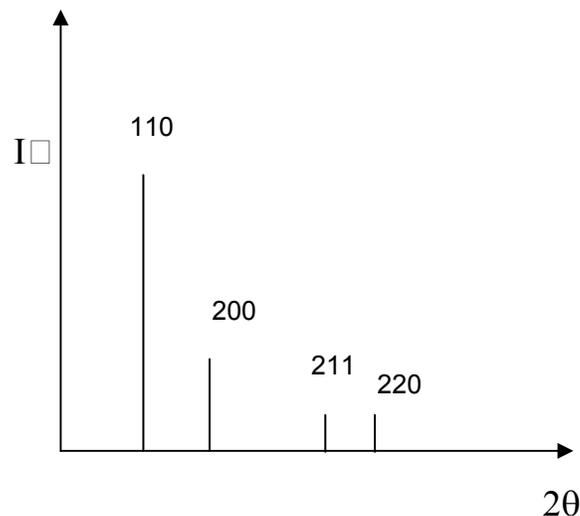
In our hypothetical case above, constructive interference occurs only at the exact Bragg angle and the I vs. 2θ curve exhibits sharp lines of intensity. In reality, diffraction peaks exhibit finite breadth, due both to instrumental and material effects. An important source of line broadening in polycrystalline materials is finite crystal size. In crystals of finite dimensions, there is incomplete destructive interference of waves scattered from angles slightly deviating from the Bragg angle. If we define the angular width of a peak as:

$$B = \frac{1}{2}\left(2\theta_1 - 2\theta_2\right)$$

then the average crystal size can be estimated from the Scherrer formula as:

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

Interplanar spacings can be calculated for different *hkl* planes from geometric relationships for a given crystal system:

Cubic: $d^{-2} = \dfrac{h^2 + k^2 + l^2}{a^2}$

Orthorhombic: $d^{-2} = \dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}$

Tetragonal: $d^{-2} = \dfrac{h^2 + k^2}{a^2} + \dfrac{l^2}{c^2}$

Hexagonal: $d^{-2} = \dfrac{4}{3}\left(\dfrac{h^2 + hk + k^2}{a^2}\right) + \dfrac{l^2}{c^2}$

Monoclinic: $d^{-2} = \dfrac{1}{\sin^2\beta}\left(\dfrac{h^2}{a^2} + \dfrac{k^2\sin^2\beta}{b^2} + \dfrac{l^2}{c^2} - \dfrac{2hl\cos\beta}{ac}\right)$

Bonding-Structure Relationships

Covalent bonding

Inorganic materials

Materials that exhibit covalent bonding pack in arrangements that reflect the directional nature of their bonds. For example, sp^3 hybridization in diamond and silicon mandates that atoms pack in these materials with tetrahedral coordination. These materials adopt the diamond cubic structure, a **derivative** of the FCC structure in which ½ of the tetrahedral interstitial sites are filled.

diamond cubic structure in 2 orientations
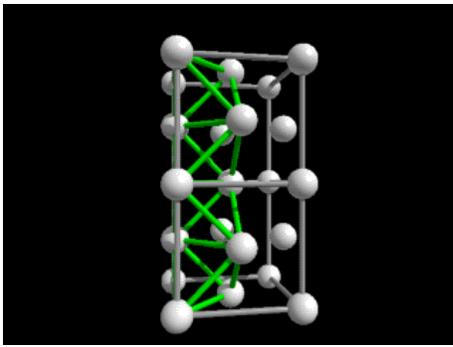
2 tetrahedral sites in a FCC lattice

Images from
http://www.uncp.edu/home/mcclurem/lattice/
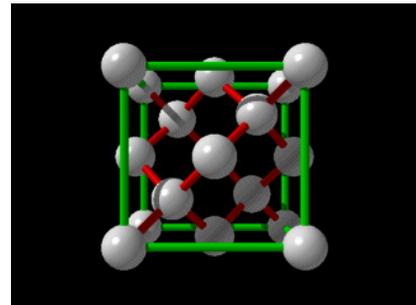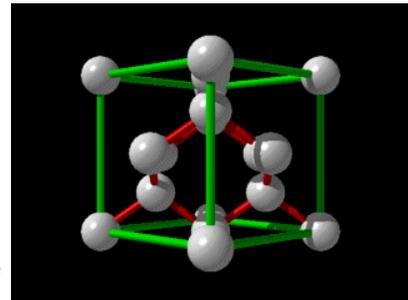
Courtesy of Dr. Mark McClure. Used with permission.

Along with silicon, numerous semiconductor alloys exhibit significant covalent character in their bonding, often adopting the zinc blende structure, a **derivative structure** of the diamond cubic structure. Examples include the III-V compounds GaAs, GaP, GaSb, AlP, AlAs, InSb, InP, InAs, and the II-VI compounds ZnS, ZnSe, ZnTe, CdTe.
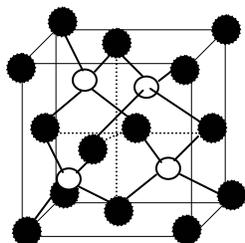
Zinc blende structure of ZnS: a FCC arrangement of sulfur atoms with zinc atoms filling ½ of the total tetrahedral sites

Chalcopyrite, CuFeS$_2$, a mineral, has a crystal structure that can be viewed as derivative of the zinc blende structure.

Structure of CuFeS$_2$: Cu (solid), Fe (shaded), S (unfilled).
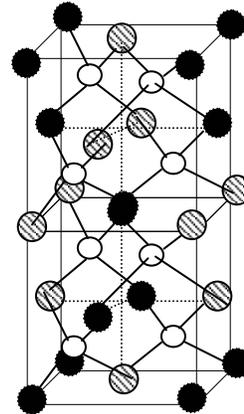
Polymers

Polymers are covalently bonded long chain molecules composed of repeating units made of carbon and hydrogen, and sometimes oxygen, nitrogen, sulfur, silicon and/or fluorine. As with inorganic materials, the covalent bonding in polymers imposes directionality on their spatial arrangement into periodic structures. Polymer chains exhibit weak intermolecular forces due to van der Waals attractions. The ability of polymer chains to pack into an ordered array depends strongly on the stereoregularity of their pendant groups. For example, depending on the method of polymerization, polystyrene may exhibit isotactic, syndiotactic or atactic structure. Atactic polystyrene, is entirely amorphous due to the random arrangement of the pendant phenyl groups, while syndiotactic and isotactic polystyrene, having more regular structures, exhibit crystallinity.

Isotactic PS (highly crystalline)

Styrene monomer

Syndiotactic PS (semi-crystalline)

Atactic PS (amorphous)
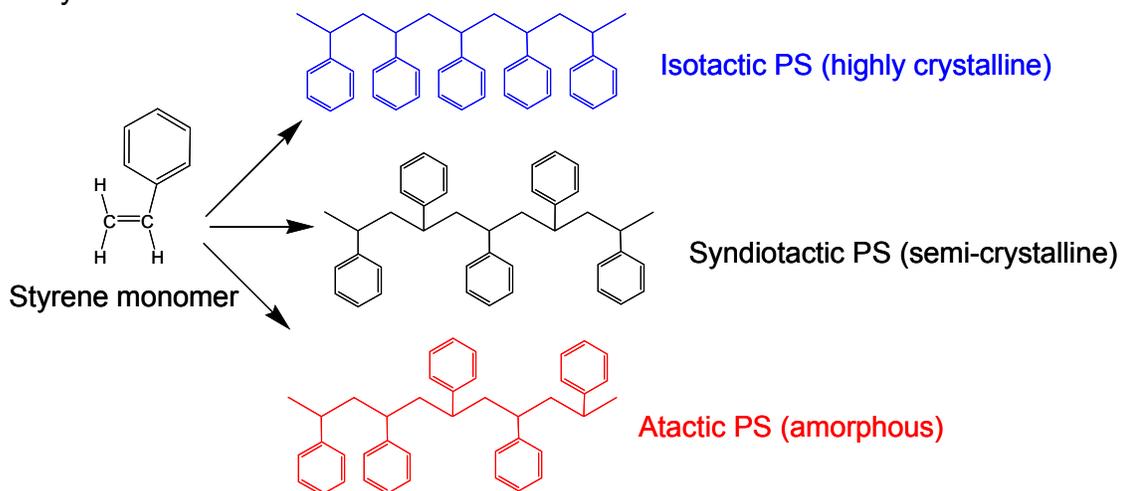
Polymers form into thin lamellar crystallites through a chain folding process, with their backbones oriented along one of the crystal axes, typically the c-axis. Chains may pack with zig-zag (all trans) or helical conformations of the backbone. Polyethylene, the largest volume commercial thermoplastic, arranges into an orthorhombic crystal with chains aligned along the c-axis in a zig-zag conformation.

unit cell of polyethylene

Figures removed due to copyright restrictions.

PE crystallite formed by
chain folding

Unlike inorganic materials, polymers never crystallize into cubic structures. This again can be explained based on the fact that bonding in polymer crystals is inherently anisotropic—strong covalent bonds exist along the chain axes, while weak secondary bonds provide cohesivity between chains.

Ionic Bonding

Many inorganic materials such as halides, oxides and silicates exhibit strong ionic character in their bonding. As a result, packing in these systems is dictated by

electrostatic forces—the structures chosen by nature are those that maximize interactions between ions of opposite charge while minimizing contact between like-charged ions and maintaining electrical neutrality. Pauling's rules codify this notion and provide rationalization for structural tendencies observed in systems with ionic bonding. As a consequence of electrostatics, ionic crystals create ordered arrangements of polyhedra, in which cations are in contact with a maximum number of surrounding anions, the number depending on the ratio of the cation to anion radius, R_C/R_A.

Coordination Number	Anion arrangement	Minimum stable R_C/R_A
8	corners of cube	0.732
6	Corners of octahedron	0.414
4	Corners of tetrahedron	0.225
3	corners of triangle	0.155
2	co-linear	0

Often ionic crystals consist of a close packed lattice of anions with cations placed into interstitial sites. An example of such a material is MgO, which exhibits a radius ratio of 0.593 and crystallizes in the halite (rock salt) structure. Other materials that crystallize in this structure include: NaCl, KCl, LiF, KBr, CaO, BaO, CdO, VO, FeO, CoO, NiO.
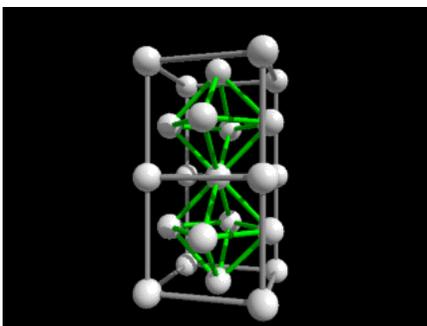

center octahedral sites in a FCC lattice
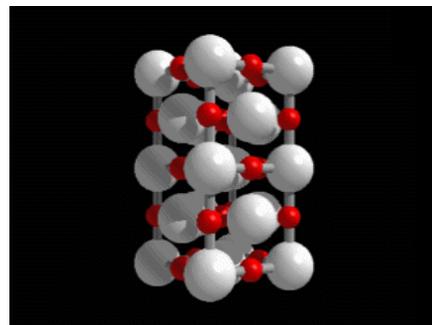
Halite structure of MgO: a FCC arrangement of O^{2-} ions with Mg^{2+} ions filling all octahedral sites.

Courtesy of Dr. Mark McClure. Used with permission.

Images from
http://www.uncp.edu/home/mcclurem/lattice/

Although of similar stoichiometry, the large radius ratio of CsCl, $R_C/R_A = 0.922$, favors a larger coordination number. This compound thus crystallizes in a BCC derivative structure in which Cl atoms sit on the cube corners and Cs atoms in the center of the cube.

CsCl structure
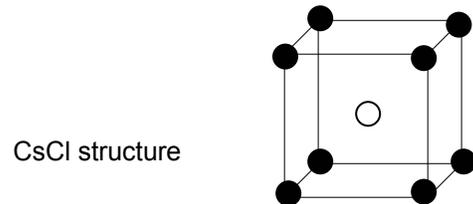
Metallic Bonding

Metal atoms in a metallic crystal bond through delocalization of valence electrons. The bonding in metals is largely nondirectional as a result, so that metals and metal alloys most often adopt close packed atomic arrangements, namely the face centered cubic (FCC) and hexagonal close-packed (HCP) structures, or the slightly lower density body-centered cubic (BCC) structure.

Materials

Materials to be investigated include: CsCl, NaCl, Fe, Al, Si, ZnS, $CuFeS_2$ (chalcopyrite), polyethylene, polypropylene

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