Class Notes: Chapter 2

Homework 3: Chapter 2: 6, 7, 9 and Chapter 3: 3

XRD and Crystalline Structure:

Crystals and the crystalline state can be defined in a number of different ways, density, enthalpy or free energy change on heating, spectroscopic associations, presence of certain planes of registry in microscopy for instance. For XRD a crystal is defined as **perfect 3-D order**. This corresponds to the strictest definition of a crystal. For a semi-crystalline polymer, for instance, 100% crystallinity is never obtained by this definition since there are large interfacial regions where some degree of disorder is present. Perfect 3-D order means that the structure repeats in all directions so that by describing the structure locally (in a repeating 3-d unit) the entire structure can be uniquely described.

Nomenclature

Point Lattice = An array of points in space so arranges that each point has identical surroundings **Unit Cell** = a collection of 3 vectors along **Crystallographic axes** each of which is described by a magnitude or length and an angle from the origin. These 6 parameters (3 magnitudes and 3 directions) are the **Lattice parameters**.

There are several ways to categorize crystals. One involves the **7 crystal systems** described on pp. 35 of the text. The crystal systems are described in terms of the Lattice parameters.

Cubic	$a=b=c = = = = 90^{\circ}$	S, FC, BC
Tetragonal	$a=b = = =90^{\circ}$	S, BC
Orthorhombic	$= = = = 90^{\circ}$	S, FC, BC, BaseC
Rhombohedral (Trigonal)	a=b=c = = Not 90	D° S
Hexagonal	a=b = =90°	=120° S
Monoclinic	= =90°	S, BaseC
Triclinic		S

Primitive Cell (Simple above) = One Lattice Point per cell **Non-Primitive** = More than one point per cell

Points per cell = N = $N_{interior} + N_{face}/2 + N_{corner}/8 + N_{edge}/4$

Figure 2-3 shows Unit Cells.

In addition to classification according to Lattice Parameters, crystal structures can be classified according to symmetry operations that can be performed on them. There are 4 symmetry operations: Reflection Rotation Inversion

Rotation/Inversion

Figure 2-6 shows symmetry elements for a cube with some of the symbols associated with these operations.

Symmetry operations were used to choose the 7 crystal systems above.

A combination of symmetry operations and translations are used to construct crystal systems. There are 3 translations commonly used,

Body Centering Face Centering Base Centering

Lattice Directions and Planes It is important to remember the standard use of brackets in crystallography: [**u**,**v**,**w**] is a direction (Square brackets) a bar over u, v or w indicates a negative direction <**uvw**> are directions of a form (pointy brackets) this is a class of similar directions <111> [111],[11],[11],[11]]

(**hkl**) are the **miller indicies** for a plane. h,k,l are fractional intercepts, 1/u, 1/v, 1/w of a plane with the **a,b,c** axies. Actual intercept is a/u, b/v, c/w, Miller indices are fractional intercepts, i. e. intercept divided by magnitude of a, b, c.

<u>NOTE</u>: We have mentioned that there is an inverse relationship between the angle of diffraction (sin) and the d-spacing of a set of planes, (hkl). Miller indicies are a natural way to refer to plane spacing using a set of inverse distances. This is discussed in appendix 1 and we will touch on this later. Here we should mention that the miller indicies (hkl) can be multiplied by a set of unit vectors in "inverse space", \underline{b}_1 , \underline{b}_2 , \underline{b}_3 , which are related to the "real space" lattice parameters by cross products i.e. $\underline{b}_i = 1/V$ ($\underline{a}_{i+1} \times \underline{a}_{i+2}$). The magnitude of the vector defined by (h, k, l) is the d-spacing. Diffraction occurs when a vector defined by sin() equals the inverse vector associated with (h,k,l).

In fact, Miller indices and much of the crystallographic nomenclature is intimately tied with the XRD experiment.

For the Cubic system [hkl] is perpendicular to the plane (hkl)

{hkl} are planes of a form (script brackets)

{100} are the faces of a cube (100),(010), (001), ($\underline{1}$ 00),(0 $\underline{1}$ 0), (00<u>1</u>) these are generated by the symmetry operation of 4-fold rotation

Planes of a Zone: A group of planes all parallel to one line, the **Zone Axis** [uvw]. Any plane belongs to a zone if : hu + kv + lw = 0

Any 2 non-parallel planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ belong to a zone and the zone axis [uvw] is defined by: $\mathbf{u} = \mathbf{k}_1\mathbf{l}_2 - \mathbf{l}_1\mathbf{k}_2$ $\mathbf{v} = \mathbf{l}_1\mathbf{h}_2 - \mathbf{h}_1\mathbf{l}_2$

$\mathbf{w} = \mathbf{h}_1 \mathbf{k}_2 - \mathbf{k}_1 \mathbf{h}_2$

Plane Spacings

Plane Spacings, d_{hkl} , are defined according to the crystal system to which the planes belong. Equations for plane spacings are given in appendix 3 on page 501.

For the cubic system $d_{hkl} = a/(h^2+k^2+l^2)^{1/2}$

Some Specific Crystal Systems:

Crystals can be thought of as having two descriptive features. First there is a repetitive pattern of structure in 3-d space which is assumed to proceed infinitely in all directions. Since there are a fixed number of ways 3-d space can be arranged into an infinite pattern there are fixed number of crystal systems and Bravis lattices.

The second component of a crystal is the material which is placed at each lattice site. In some cases this is simply an atom (figure 2-14), BCC -Fe, Cr, Mo, V..., FCC -Fe, Cu, Pb, Ni... In many cases the structure at each lattice site is composed of several atoms (polymer crystals) or huge bio-molecules, proteins.

XRD measures both the structure of the lattice as well as the structure of a lattice site. For protein crystallography, for instance, the lattice structure is generally known and XRD is used to describe the protein secondary and tertiary structure at each lattice site. For metals the structure of a lattice site is usually quite simple and XRD is used to determine the lattice structure.

Figures 2-15 and 2-16 show a case where two atoms are associated with a single lattice site, HCP (Zn, Mg, Be, -Ti. In this case the two associated atoms are shown in 2-15 (b) by dashed lines. These two atoms are considered to occupy a lattice site as a unit.

HCP and FCC (-Fe, Cu, Pb, Ni...) structures both display hexagonal planes, (111) in FCC, (figure 2-16) and both represent the densest crystalline arrangements, occupied volume =74%. The difference between these two systems involves the relative arrangement of the hexagonal planes which follow an ABAB sequence in HCP and an ABCABC pattern in FCC. FCC and HCP are the dominant crystalline arrangements in simple symmetric systems such as colloidal crystals where density is the dominant consideration. For example, a can of marbles will naturally arrange in one of these structures.

Note: Twinning (pp. 59 Cullity)

Since there is strong similarity between HCP ABABAB pattern in the hexagonal planes and the FCC ABCABC pattern in the (111) planes and because there is no density difference between the two crystal systems it might seem logical that during crystal growth or under deformation mistakes could be easily made in the stacking of (111) planes. For instance the stacking of FCC could proceed ABCABABCABCABABC. Such a defect is a twin. A twin is a defect involving no for HCP density differences. Similarly, structure you might а see ABABABCACACACACACACABABAB where the insertion of a C plane is a twinning defect. The latter might occur under shear of an HCP lattice on the (111) plane.

Twinning can be described as rotation about an axis (180° rotation normal to the (111) plane) or reflection about a plane (reflection about the (111) plane). The 111 plane shared by the two crystalline structures of a twin is called the *composition plane* or the twinning plane.

There are two kinds of twins in metallurgy,

- 1) Annealing twins for FCC metals (Cu, Ni, Al, a-brass)
- 2) Deformation twins in HCP metals (Zn, Mg, Be) and BCC metals (-Fe, W).

Figure 2-23 on page 60 shows typical appearance of a twinned grain in the microscope.

Studies of twinning and the formation of twins under deformation are active areas of research in metallurgy. Cullity gives some insight in to this fascinating area and a number of other resources

are available if you are interested. V. J. Vasudevan in our department is an expert in this area and he or his graduate students are an excellent source of information on twinning.

Prediction of Crystal System:

Despite the long history of crystallography, there remains no reliable way to predict what crystalline system will be chosen by a specific material. For simple situations we can consider some of the features which lead to the choice of one system over another. The FCC/HCP systems are useful in this sense because the density is identical. For symmetric lattice site systems where maximization of density is the critical feature, the choice of FCC or HCP will depend on second order interactions between planes, i.e. the A and C planes in FCC vs HCP.

One possible reason for deviation from FCC and HCP systems is that the lattice site is not symmetric. A typical crystal lattice for a polymer is orthorhombic or triclinic where a b and c are all different. The reason for this is the different bonding/molecular association schemes in different directions for a polymer crystal. Typically the chain axis is taken as the c-axis. Association of chains in this direction are through covalent bonds. In the a and b directions weaker hydrogenbonds or van der Waals interactions occur.

-uranium, Figure 2-17 is base centered orthorhombic with a fairly odd ball pairing of atoms to form lattice sites. Uranium atoms shows a preferred diadic association, U_2 .

NaCl (table salt) was the first crystal studied by Bragg. This is a crystal composed of two atoms of which there are many examples, $A_x B_y$. Two basic rules (pp. 51) are useful for these cases, 1) The lattice for A considered independently is the same as that for B considered independently and is the same as that for the crystal as a whole.

2) Body or face centering translations must begin and end on the same atom.

With these rules in mind NaCl is FCC. Similarly, CsCl is simple cubic. Since there are many crystals which mimic these, the group is referred to as a **system**, for example the NaCl System includes KCl, CaSe, PbTe (figure 2-18) and CsCl system includes CsBr, NiAl, -brass, and CuPd.

The Diamond system includes Silicon and Germanium (Semiconductor systems). It has 8 atoms per unit cell (1 corner 3 face and 4 internal). The diamond system is FCC with two atoms for lattice site (figure 2-19). Zinc Blende (ZnS) has the same structure but with two different atoms occupying the two lattice sites.

Solid solutions

Solid solutions are crystalline systems that contain at least two types of atoms where the distribution of one of the two has some type of disorder in its arrangement. One atom is the solvent (mostly ordered arrangement, i.e. crystal lattice) and the other the solute (mostly disordered arrangement) There are two common ways to do this:

1) Substitutional = Replace lattice sites of solvent with solute in a random way. This occurs when the two atoms are of similar size, 10% Molybdenum in Chromium BCC lattice.

2) Interstitial = Solute fits between some of the lattice sites of the solvent. Ferrite, Carbon in Iron BCC 0.1% carbon.

3) An ordered solid solution is also possible where the solute orders in regular sites of a substitutional solid. The lattice of the solute is different than that of the solvent (the base crystal). The solute's lattice is called a **super-lattice**. AuCu3 (Gold Copper alloy) at high temperature it is FCC with Au and Cu at random on the lattice sites (Substitutional Solid Solution). At low

Temperature Au goes to the corners and Cu goes to the Face Center positions (simple cubic). There are two Simple cubic lattices with different lattice dimensions.

Atomic size and Coordination

XRD is a primary means to determine atomic sizes and coordination. Typically, a spherical model is used for simple atoms. For space filling spheres in a HCP lattice c/a = 1.633, (occupied volume =74%).

For typical metals c/a is 1.58 (Beryllium) 1.89 Cadmium. This is interpreted as non-spherical atoms. Atoms must be ellipsoidal. This is part of how atoms "choose" a crystal system.

For BCC (-Iron) the closest approach is along the [111] direction, BCC closest approach = $a \frac{3}{2} = 0.866 a$.

For FCC closest approach is 2/2 = 0.707 = 0.707 a.

For HCP closest approach in hexagonal plane is a

between atoms in hexagonal plane and next hexagonal plane closest approach is $(a^2/3 + c^2/4)$

From these equations applied to atoms in different crystal structures several things can be said, 1) atomic size remains fairly constant in different crystalline structures

2) atomic size has a fairly predictable change with coordination number (number of nearest neighbors)

CRYSTAL	Coordination Number
FCC or HCP	12
BCC	8
Diamond Cubic	4

In this series diameter decreases by about 3% from FCC/HCP to BCC and by about 9% from BCC to Diamond Cubic.

Atomic size also changes slightly with the type of bonding (ionic, covalent, metallic, van der Waals)