090605 Quiz 6 X-ray Diffraction

1) Calculate the structure factor $F^2(h,k,l)$, for salt, NaCl. Which simple cubic reflections are missing?

2) Describe the orthorhombic unit cell structure of polyethylene. Also, sketch a plot of the thermal expansion coefficient for the three crystallographic directions.

3) Describe the nano-scale structure of polyethylene crystals (lamellar) and show how this structure relates to the degree of crystallinity.

5) Derive the Hoffman-Lauritzen equation for polymer lamellar thickness.

4) Describe the micron-scale, spherulitic structure of polyethylene.

ANSWERS: 090605 Quiz 6 X-ray Diffraction

1)

e) NaCl is an FCC structure with Cl's located at the [0,0,1/2] edge positions. Both Na and Cl alone form an FCC structure so the unit cell has 4 atoms of each or a total of 8 atoms:

Na 000 1/2 1/2 0 1/2 0 1/2 0 1/2 1/2
Cl 1/2 1/2 1/2 0 0 1/2 0 1/2 0 1/2 0 0

The structure factor for this unit cell contains 8 terms:

$$F = f_{Na}[1+ e^{pi(h+k)}+ e^{pi(h+l)}+ e^{pi(k+l)}]$$

$$+f_{Cl}[e^{pi(h+k+l)}+ e^{pi(l)}+ e^{pi(k)}+ e^{pi(h)}]]$$

Since both Na and Cl can form an FCC structure independently, you might expect that this common FCC structure factor, $[1+ e^{pi(h+k)}+ e^{pi(h+l)}+ e^{pi(k+l)}]$ could be "factored-out" leaving the translation of the Cl lattice relative to the Na lattice. This is what is done:

$$F = [1+ e^{pi(h+k)}+ e^{pi(h+l)}+ e^{pi(k+l)}]\ [f_{Na} + f_{Cl}\ [e^{pi(h+k+l)}]]$$

FCC Na and Cl with Translation

Thus, the FCC NaCl unit cell shows FCC rules modified for two atoms at a lattice site:

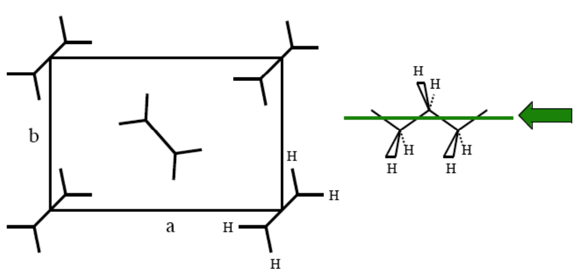
MIXED INDICES F = 0 (FCC rule)

UNMIXED INDICIES

$(h + k + l)$ even $F = 4(f_{Na} + f_{Cl})$

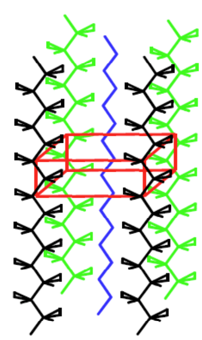
2)

Polyethylene Unit Cell



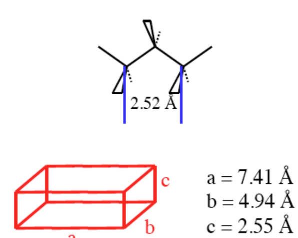
- The view is from above, looking along the chain axis.
- There are **two chains per unit cell** for polyethylene.
- The orthorhombic unit cell has high packing efficiency; 73% of space is occupied.

Polyethylene Unit Cell



Orthorhombic unit cell

- Each polyethylene chain is in an extended **planar zigzag** conformation.
- The **c axis** is always along the **chain direction**.



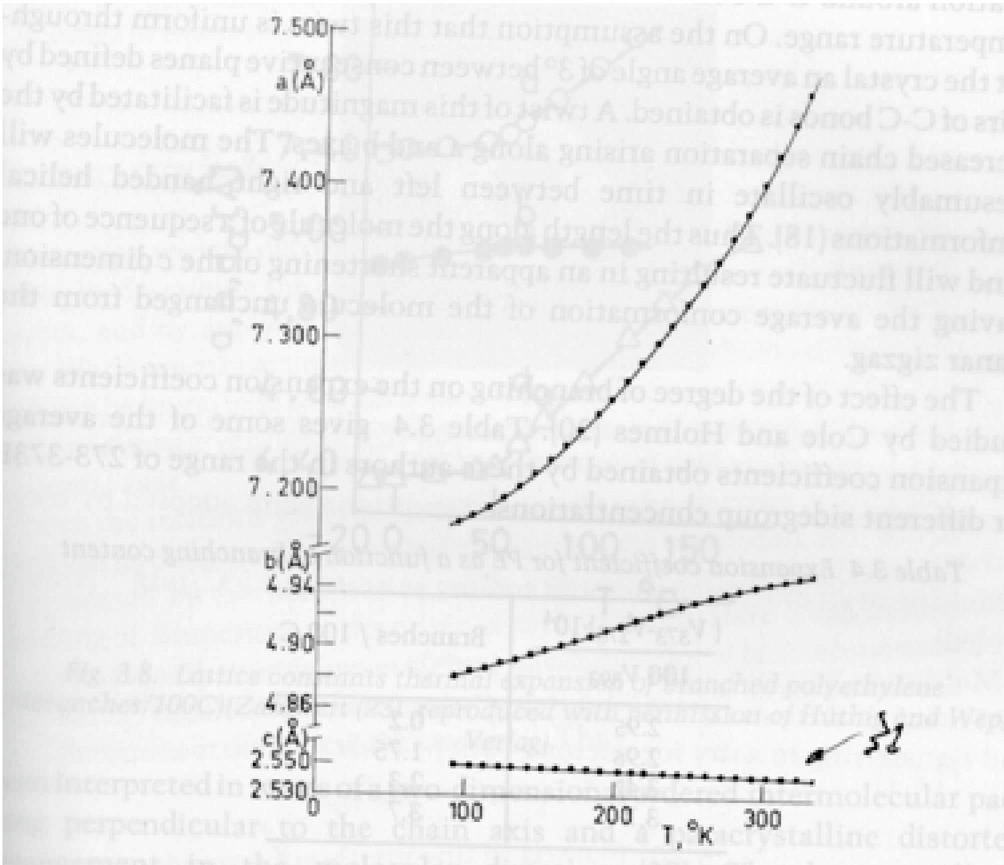
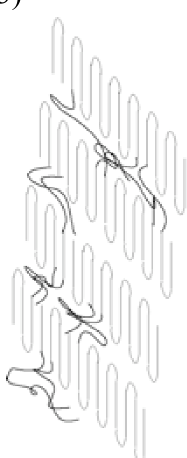


Fig. 3.7. Lattice constants thermal expansion for linear polyethylene (Davis et al.,24)

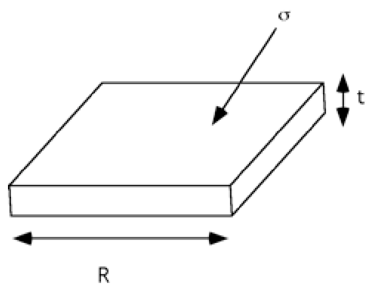
3)



Stacks of chain folded lamellar crystals separated by amorphous regions. The degree of crystallinity is the lamellar thickness divided by the repeat distance, L.

4)

Hoffman's law can be obtained very quickly for a free energy balance following the "Gibbs-Thomson Approach" (Strobl pp. 166) if on considers that the crystals will form asymmetrically due to entropically required chain folds and that the surface energy for the fold surface is much higher than that for the c-axis sides..



At the equilibrium melting point $[Delta]G_{[infinity]} = 0 = [Delta]H - T_{[infinity]} [Delta]S$, so $[Delta]S = [Delta]H/ T_{[infinity]}$.

At some temperature, T, below the equilibrium melting point, The volumetric change in free energy for crystallization $[Delta]f_T = [Delta]H - T [Delta]S = [Delta]H(1 - T/T_{[infinity]}) = [Delta]H(T_{[infinity]} - T)/ T_{[infinity]}$.

The crystallite crystallized at "T" is in equilibrium with its melt and this equilibrium state is adjusted by adjusting the thickness of the crystallite using the surface energy, that is,

$[Delta]G_T = 4Rt [sigma]_{side} + 2R^2 [sigma] - R^2t [Delta]f_T = 0$ at T.

That is, At T the crystallite of thickness "t" is in equilibrium with its melt and this equilibrium is determined by the asymmetry of the crystallite, t/R. If $[Delta]f_T = [Delta]H(T_{[infinity]} - T)/ T_{[infinity]}$. is use in this expression,

$4t [sigma]_{side} + 2R [sigma] = R\, t [Delta]H(T_{[infinity]} - T)/ T_{[infinity]}$.

Assuming that $[sigma]_{side}$ <<< [sigma], and "t"<<<"R" then,

$t = 2 [sigma] T_{[infinity]} /([Delta]H(T_{[infinity]} - T))$

which is the Hoffman law.

The deeper the quench, $(T_{[infinity]} - T)$, the thinner the crystal and for a crystal crystallized at $T_{[infinity]}$, the crystallite is of infinite thickness. (Crystallization does not occur at $T_{[infinity]}$).

5) Stacks of lamellae grow from a nucleation site (see below) with low angle branching so that they fill space. The growth of these semi-crystalline spherulites ends when it reaches an impinging spherulite to form polygons that display the Maltese cross as shown in the optical micrographs between crossed polars below.