

1. Lattices and symmetry.

- a. A pair of periodic two-dimensional patterns are presented on the following sheets. We have defined the concept of “lattice” and “lattice points” prior to our discussion of diffraction. Sketch in an array of lattice points on each pattern and connect them to construct the conventional unit cell. (Remember that the definition of a lattice is a collection of geometric points that summarize the translational periodicity of a pattern. A motif in the same orientation must “hang” at the same distance and in the same orientation at each point. The unit cell chosen by convention uses the two shortest translations in the lattice and, in addition, is selected to show any specialization of the cell – for example, rectangular, square, etc.)
- b. As an **optional exercise** locate any symmetry elements, such as rotation axes or mirror planes, that are present.

2. On a piece of ordinary graph paper draw an array of lattice points that define a square lattice.

- a. Connect the lattice points to define
 - i. a primitive cell
 - ii. a double cell
 - iii. a triple cell
- b. For the primitive cell that you have drawn:
 - i. Draw lines in the directions defined by [12] and [21].
 - ii. Draw the “planes” (lines, actually, in two dimensions but which are defined by indices h and k analogous to what one does in 3-D) with indices (13) and (31).
 - iii. For each of the above planes, show that ‘hanging’ a plane in this orientation on a sufficient number of lattice points in the neighborhood of the origin divides the interval between the origin of the lattice and the intercept plane into $(h \times k)$ parts.

3. Consider a one-dimensional crystal composed of identical atoms separated by a translation $a = 10 \text{ \AA}$. The crystal is irradiated with an x-ray beam having wavelength $\lambda = 1.0 \text{ \AA}$ that is incident on the crystal at an angle $\mu = 30^\circ$.

Using the Laue equation for diffraction by a one-dimensional crystal:

- Compute the **total** number of diffraction cones that are produced.
 - What is the maximum index, m , among the set of diffraction cones that are produced?
 - To what value of μ must the angle of incidence be changed in order to have the cone with the next highest value of m just come into existence?
4. **Using Maxwell relations and the variable-change theorem.** Let's determine a Maxwell relation for a new thermodynamic function, the Gibbs free energy. Free energies are extremely useful for determining phase behavior in multicomponent systems at constant temperature and pressure, and we will be making great use of this function soon. The Gibbs free energy is defined by:

$$G = H - TS$$

- Show that the Maxwell relation for the Gibbs free energy is $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$, as given in class.
- Use the variable change theorem and Gibbs free energy Maxwell relation to prove the following equation:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

5. **Compressing a solid.** The pressure on 100g of nickel is increased reversibly and isothermally from 0 to 500 atm. Assume the density of the sample is initially $8.90 \times 10^3 \text{ kg/m}^3$ and the isothermal compressibility remains constant at $6.75 \times 10^{-12} \text{ Pa}^{-1}$ respectively during this process.
- Calculate the final volume of the sample and determine the % change in volume that occurs.
 - Calculate the work done. (Hint: First, recast the work equation in terms of an integral over dP using the definition of compressibility; second, can any of the terms be assumed approximately constant during the integration?)
6. **Energy storage in polarized materials.** Consider the following two-step process. TiO_2 , when placed in an electric field parallel to the c-axis of the crystal, exhibits a strong polarization due to the high dielectric constant along this crystal direction ($\epsilon_r = \frac{\epsilon}{\epsilon_0} = 170$). A 1 cm^3 crystal of TiO_2 is polarized by placing it in an electric field of 10^6 Volts/m at constant temperature (298K) and volume. (Assume we can predict the polarization behavior using the linear isotropic model, despite the anisotropy in this case.)
- What is the work done in polarizing the sample?
 - If the energy absorbed by the crystal in this process were subsequently converted to heat by an adiabatic process within the crystal, will the temperature of the crystal be significantly changed?

Data for TiO_2 :

$$\text{MW} = 79.88 \text{ g/mole}$$

$$\rho = 4 \text{ g/cm}^3$$

$$C_p = 67.29 + 0.0187T \text{ J/mole K (T=200-2000 K)}$$