

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.
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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.

3.012

Structure PSET #3 Solutions.

Problem #1) see attached graph paper.

Problem #2) see attached grid paper

Problem #3) $a = 10 \text{ \AA}$; X-ray w/ $\lambda = 1.0 \text{ \AA}$; incident at $\theta = 30^\circ$

Laue equation: $m\lambda = a \cos \bar{\nu}_i - a \cos \bar{\nu}_f$

if $\cos \bar{\nu}_i = +1$, then: $m(1.0) = 10(1) - 10 \cos 30$, get $m = 1.34$

if $\cos \bar{\nu}_i = -1$, then $m(1.0) = 10(-1) - 10 \cos 30$, get $m = -18.66$

m must be an integer, therefore range is from $[-18 \rightarrow +1]$ inclusive.

This means m can take 20 different values, so there will be 20 diffraction cones.

b) At $\cos \bar{\nu}_i = +1$, $m = +1.34$, since m must be an integer $m = +1$ is the maximum index.

c) what value of θ to get $m = 2$?

$$m\lambda = a \cos \bar{\nu}_i - a \cos \theta$$

$$\cos \theta = \frac{a \cos \bar{\nu}_i - m\lambda}{a} = \frac{10(1) - 2(1)}{10} = 0.8$$

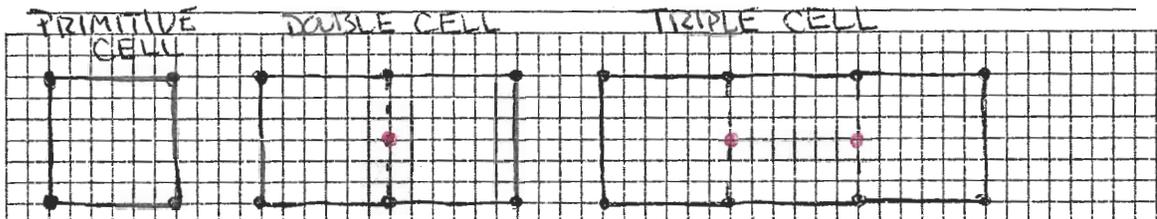
$$\cos^{-1} 0.8 = 36.87^\circ$$

$$\underline{\underline{\theta \approx 36.9^\circ}}$$

Assignment: Pset #3. Problem #2

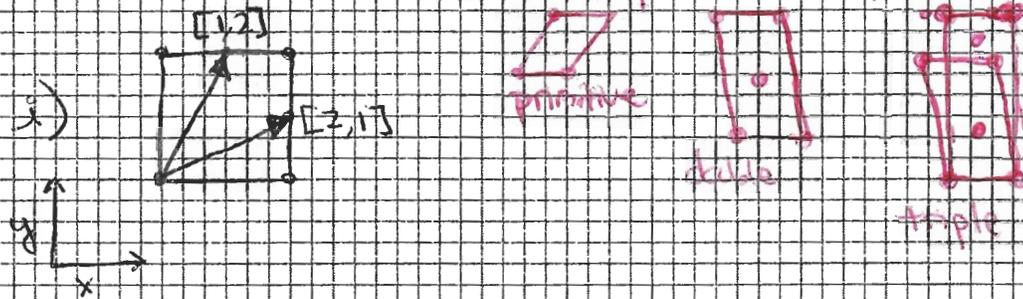
Date: _____

a)

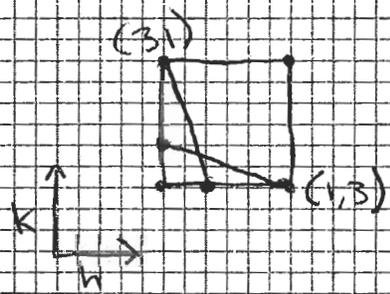


Also acceptable for 2a)

b)



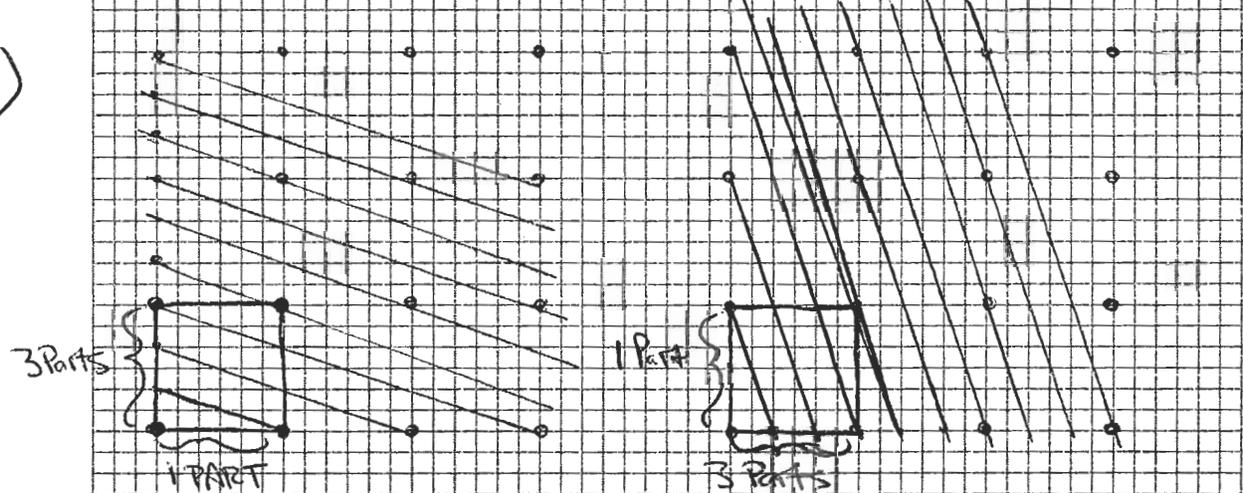
ii)



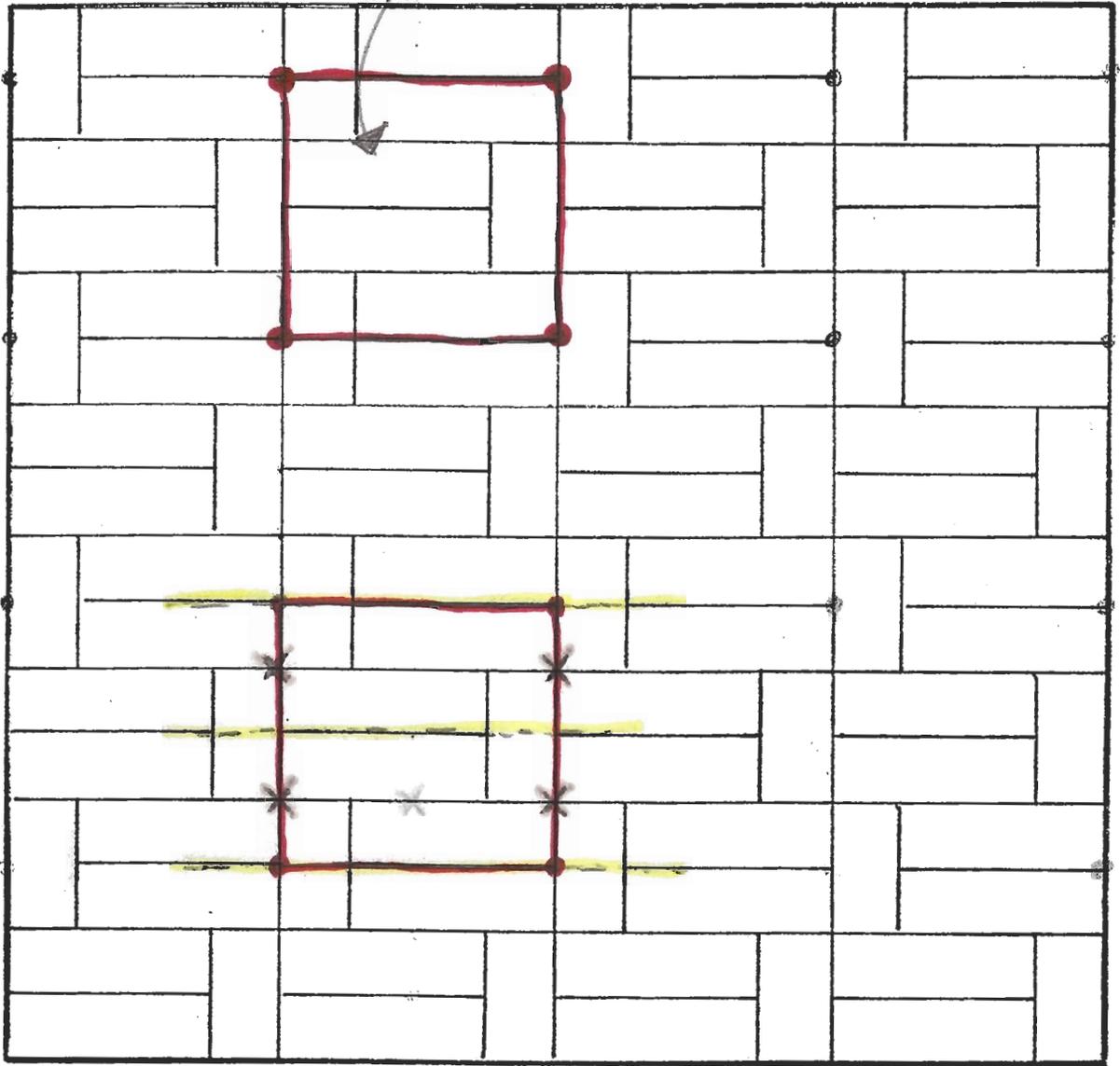
iii)

FOR (1,3) PLANAR ARRAY:

FOR (3,1) PLANAR ARRAY:



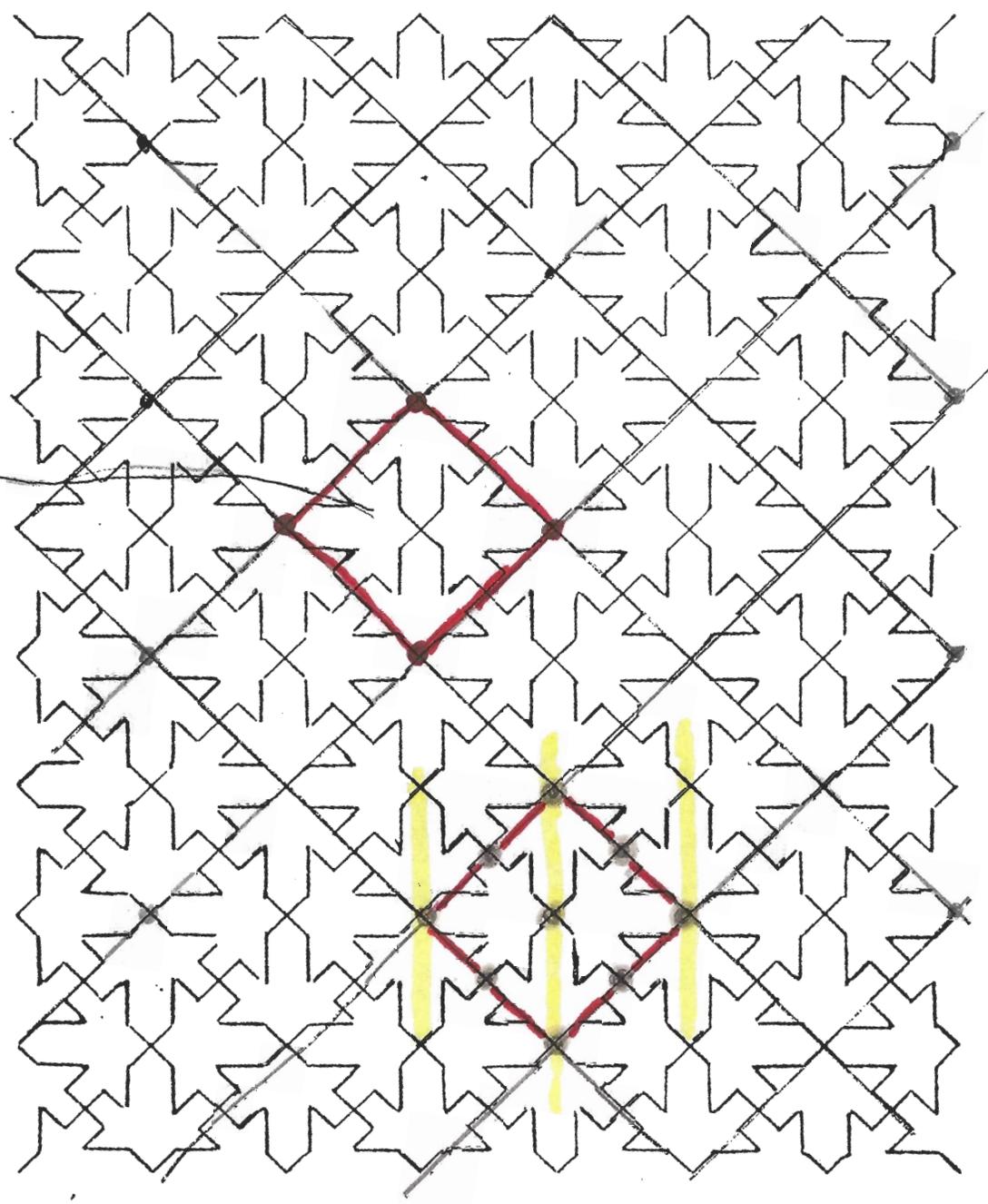
UNIT CELL



-mirror plane

-axes of rotation.

UNIT
CELL



axes of rotation

- mirror plane.

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**[DJI1]. 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.

First, we write the differential for the Gibbs free energy, and plug in known equalities to simplify it:

$$dG = dH - TdS - SdT = TdS + VdP - TdS - SdT = VdP - SdT$$

Now we equate the terms in the above expression with the partial differentials of G:

$$dG = VdP - SdT = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

Equating the terms in front of the differentials, we have:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

To obtain the Maxwell relation, we simply look at the second derivatives of G, taken in either order:

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P}$$

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

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

- b. Use the variable change theorem and Gibbs free energy Maxwell relation to prove the following equation:

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

We start by using the variable change theorem to obtain an expression for the partial derivative:

Variable change theorem: $\left(\frac{\partial x}{\partial f}\right)_z = \left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z$

Applying to our target partial derivative: $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_S + \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T$

We can now make use of Maxwell equations and partial derivative definitions to simplify this expression: First, we know that $\left(\frac{\partial H}{\partial P}\right)_S$ is V and $\left(\frac{\partial H}{\partial S}\right)_P$ is T by inspection of the differential form of enthalpy:

$$dH = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

Finally, the last term $\left(\frac{\partial S}{\partial P}\right)_T$ is eliminated using the Gibbs free energy Maxwell relation:

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

Substituting each of these equalities into the expression, we arrive at the expected result:

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

5. **Compressing a solid**[DJ12]. 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?)

(a) The volume change is determined from the isothermal compressibility:

$$\begin{aligned}\kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \\ \kappa dP &= -\frac{dV}{V} \\ \kappa \int_0^{100} dP &= -\int_{V_i}^{V_f} \frac{dV}{V} \\ \kappa \Delta P &= -\ln \frac{V_f}{V_i} = \ln \frac{V_i}{V_f} \\ \frac{V_f}{V_i} &= e^{-\kappa \Delta P} = e^{-(6.75 \cdot 10^{-12} \text{ Pa}^{-1})(100 \text{ atm})\left(\frac{1.0132 \cdot 10^5 \text{ Pa}}{1 \text{ atm}}\right)} = 0.9999316\end{aligned}$$

Thus the final volume ($1.122923 \times 10^{-5} \text{ m}^3$) is barely different from the starting volume, and the volume change is tiny- the fractional change is $\sim .006\%$, even for this respectable pressure change. The close packing in solids strongly resists further compression.

(b) The work done by hydrostatic pressure in this process is:

$$w = \int_{V_i}^{V_f} -PdV$$

We can recast this equation in terms of the pressure change by again employing the equation for isothermal compressibility:

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$-\kappa V dP = dV$$

$$\therefore w = \int_0^{500} \kappa V dP$$

Because we already know the volume is very very nearly constant during this process, we can make the approximation that V is constant and remove it from the integrand, giving us:

$$\therefore w = \kappa V \int_0^{500} P dP = \kappa V \frac{P^2}{2} \Big|_0^{500} = (6.75 \times 10^{-12} Pa^{-1}) (1.1229 \times 10^{-5} m^3) \frac{1}{2} (500 atm)^2 \left(\frac{1.0132 \times 10^5 Pa}{atm} \right)^2 = 0.0972 J$$

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 ($\epsilon_r = \frac{\epsilon}{\epsilon_o} = 170$). 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 :

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

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

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

The energy transferred to the system by the polarization is given by the work of polarization:

$$w = \int dw = \int_0^{10^5} V \epsilon E dE = V \epsilon \int_0^{10^5} E dE = V(170 \epsilon_0) \frac{(10^5)^2}{2}$$

$$w = (1 \times 10^{-6} m^3) \left(170 \cdot \left(8.854 \times 10^{-12} \frac{F}{m} \right) \right) \frac{\left(10^6 \frac{V}{m} \right)^2}{2} = 7.526 \times 10^{-4} J$$

If the polarization work is converted to heat in an adiabatic process, the heat is retained completely within the sample and will directly affect the temperature of the sample. We can already guess that this small amount of work will not have much of an impact on the temperature of the crystal. At constant pressure:

$$C_p = \left(\frac{dq_{rev}}{dT} \right)_p$$

$$q = 7.526 \times 10^{-4} J = \int_{298K}^{T'} n C_p dT = \int_{298K}^{T'} (0.05 \text{ moles}) (67.29 + 0.0187T) dT$$

$$7.526 \times 10^{-4} J = (0.05) \left[67.29(T - 298) + \frac{0.0187}{2} (T^2 - 88,804) \right]$$

This gives us a quadratic equation for T, which we can solve to confirm that the temperature change is **negligible** for this small amount of heat transfer. Note that we multiplied Cp by the number of moles n, since the heat capacity given was a molar quantity (heat capacity *per mole*).