

IN RESPONDING TO THIS PROBLEM IT MIGHT HAVE BEEN USEFUL TO PLACE BOUNDS ON POSSIBLE ANSWERS. IN TWO DIMENSIONS THERE ARE ONLY FOUR POSSIBLE OPERATIONS:

Structure. (50 points total)

1.

- (a) REFLECTION,  $\sigma$  OR GLIDE  $\sigma_T$  (THESE CHANGE  $R \rightarrow L$  OR  $L \rightarrow R$ )
- (b) TRANSLATION,  $T$  OR ROTATION;  $A_n$  (THESE LEAVE "HANDEDNESS" UNCHANGED)

THUS, IF THE SEQUENCE OF OPERATIONS  $op\#2 \cdot op\#1$  HAS CHANGED  $R \rightarrow L$  (OR VICE VERSA)

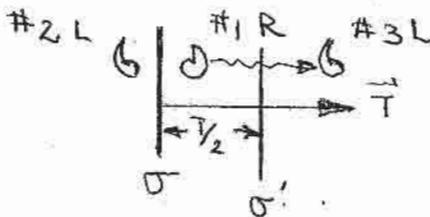
THE ONLY POSSIBLE ANSWER IS (a): REFLECTION OR GLIDE

CONVERSELY, IF THE SEQUENCE OF OPERATIONS HAS LEFT THE CHIRALITY UNCHANGED ( $R \rightarrow R$  OR  $L \rightarrow L$ ), THE ONLY POSSIBLE ANSWER IS (b): TRANSLATION OR ROTATION.

- a. (10 points) Addition of a symmetry operation to a two-dimensional space defines a way in which an initial motif, #1, will be mapped to a new location, #2. Introduction of a second operation will result in mapping of motif #2 to a new motif #3. As all three motifs are symmetry-related, some new operation #3 must unavoidably have arisen and will define an operation that maps #1 directly to #3. This may be expressed as a 'combination theorem' for these operations:

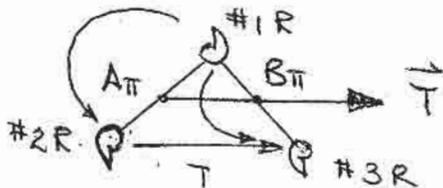
$$op\#2 \cdot op\#1 = op\#3$$

Please complete the two combination theorems stated below and illustrate each with a sketch that shows the sequential mapping of the initial motif.



$$T \cdot \sigma = ?$$

$\vec{T} \cdot \sigma = \sigma'$  A REFLECTION IN A PLANAR LOCUS PARALLEL TO THE FIRST AND SEPARATED FROM IT BY  $\vec{T}/2$ .



$$T \cdot A_\pi = ?$$

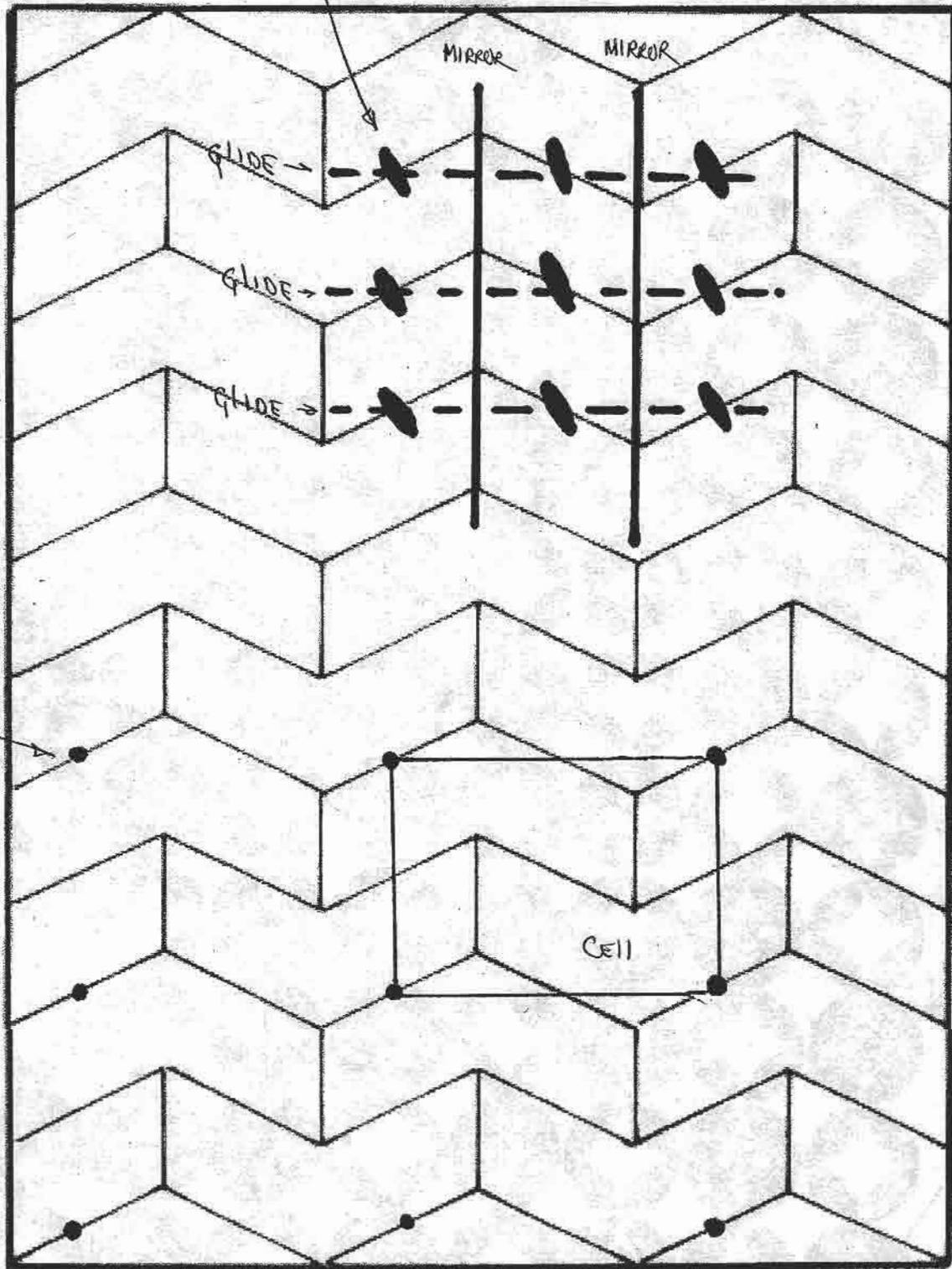
$\vec{T} \cdot A_\pi = B_\pi$  A NEW ROTATION OPERATION OF  $180^\circ$  ABOUT A POINT B THAT IS LOCATED HALF WAY ALONG  $\vec{T}$  FROM  $A_\pi$

b. (16 points). A pair of translationally-periodic two-dimensional patterns are on the following sheets. An extra copy of each is provided so that you can use on for scratch work. Directly on the sheets:

- ② i. Sketch in an array of bold dots as lattice points that show the translational periodicity.
- ② ii. Connect the lattice points to indicate the conventional unit cell.
- ④ iii. Sketch in, using conventional symbols, the location of all symmetry elements that are present within the cell.

c. **Bonus: a 3.012 challenge:** State the symbol for the plane group displayed by each of the patterns: one bonus point for each if you are correct, no loss of points if you are wrong.

2-fold Axes



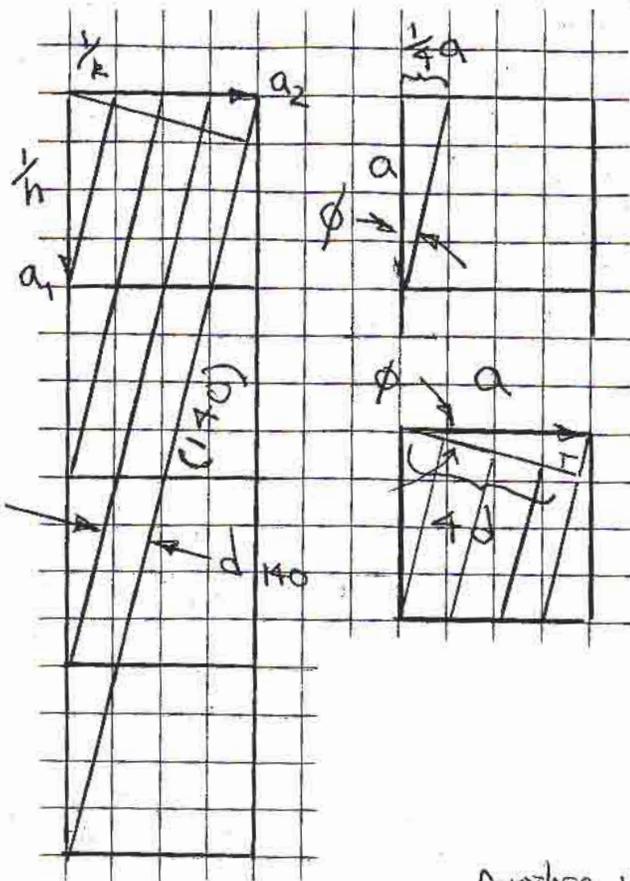
CELL IS  
PRIMITIVE  
RECTANGULAR  
LATTICE

This is PLANE GROUP  $P2_1mg$

2.

- a. (8 points). For a cubic crystal with a lattice constant  $a = 12.4 \text{ \AA}$ , compute the spacing of the (1 4 0) planes.

BECAUSE  $l = 0$  COMPUTATION OF  $d_{hkl}$  BECOMES A TWO-DIMENSIONAL PROBLEM THAT IS RELATIVELY EASY. LET'S RECALL THAT, FOR A PLANE WITH MILLER INDICES  $(hkl)$ , THE FIRST PLANE FROM THE ORIGIN CUTS  $a$  AT  $\frac{1}{h}$ ,  $b$  AT  $\frac{1}{k}$  AND  $c$  AT  $\frac{1}{l}$



THE STACK OF PLANES (140), SHOWN AT FAR LEFT CUTS  $a_2$  AT  $\frac{1}{4}, \frac{2}{4}, \frac{3}{4}, \dots$  AND  $a_1$  AT 1, 2, 3, 4

← THE ANGLE  $\phi$  IS GIVEN BY

$$\tan \phi = \frac{\frac{1}{4}a}{a} = \frac{1}{4}$$

$$\phi = \tan^{-1} \frac{1}{4} = 14.036^\circ$$

←  $\cos \phi = \frac{d}{a}$

$$\begin{aligned} \text{so } d_{140} &= \frac{a}{4} \cos 14.036^\circ \\ &= \frac{12.4 \text{ \AA}}{4} \cos 14.036^\circ \end{aligned}$$

$$d_{140} = 3.0074 \text{ \AA}$$

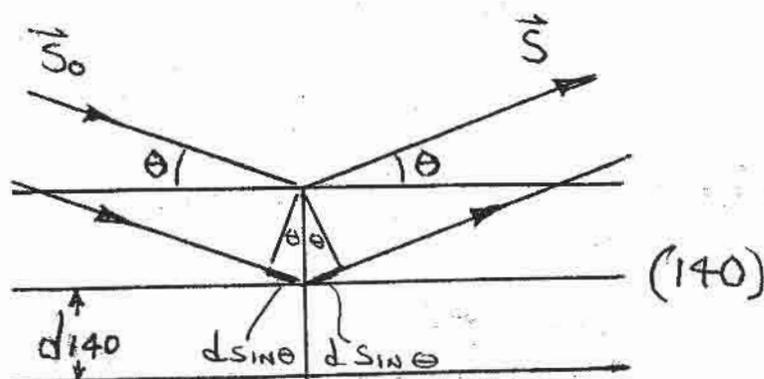
ANOTHER WAY OF EVALUATION OF  $d_{140}$  IS TO USE THE FOLLOWING FORMULA THAT GIVES  $d_{hkl}$  FOR A CUBIC CRYSTAL IN TERMS OF  $a$  AND  $hkl$

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{\frac{1}{2}}}$$

$$\begin{aligned} \text{from which } d_{140} &= \frac{a}{(1^2 + 4^2)^{\frac{1}{2}}} = \frac{12.4 \text{ \AA}}{\sqrt{17}} \\ &= \underline{\underline{3.0074 \text{ \AA}}} \end{aligned}$$

(I DON'T EXPECT YOU TO BE FAMILIAR WITH THIS RELATION BUT, HEY, IF YOU WERE, THERE'S NOTHING WRONG WITH USING IT!)

- b. (8 points). This set of planes is shown below indicating the direction of unit vectors  $S_0$  and  $S$  of X-radiation that might be diffracted from this set of planes according to Bragg's law.



At what value or range of values of the incident wavelength,  $\lambda$ , will there fail to be a diffracted beam for any value of the angle of incidence  $\theta$ ?

From the above diagram one can see that the path difference between rays scattered from neighboring planes in the stack (hkl) is given by  $2d \sin \theta$ . This leads directly to Bragg's law, the relation between path difference and the number of integral wavelengths in that path difference if constructive interference is to occur in the rays scattered from adjacent planes:

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

This relation says that

- As  $d$  increases we can get  $n$  wavelengths path difference at smaller values of  $\theta$
- As  $\theta$  increases we get a larger path difference for a given  $d$  and  $\lambda$
- As  $\lambda$  increases we need a larger  $\theta$  to produce a given path difference of  $n\lambda$

For the experiment described above, the interplanar spacing is given and fixed at  $d_{140} = 3.0074 \text{ \AA}$ . We must have at least  $n=1$ , one wavelength path difference, to produce constructive interference. If  $\lambda$  were to increase, one could increase  $\theta$  to maintain a path difference of one wavelength. However, once  $\theta = 90^\circ$  and  $\sin \theta = 1$ , we have run out of room to maneuver!

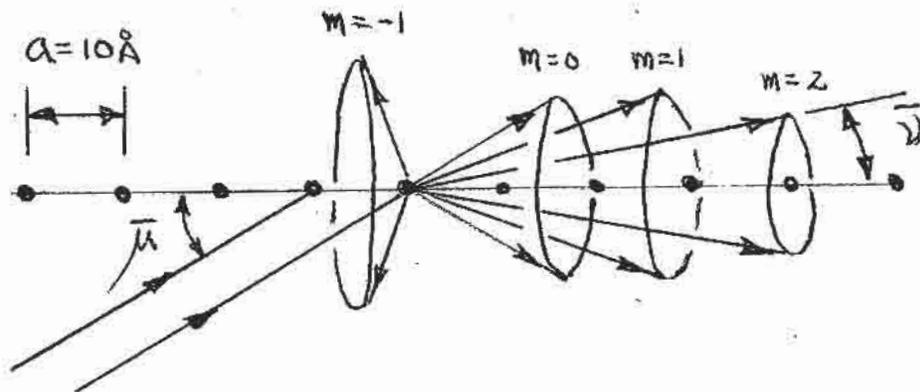
Therefore, no diffraction peak will be produced for  $\lambda$  greater than the  $\lambda_{\text{max}}$  for which  $2d_{140}(\sin \theta_{\text{max}}) = 2d_{140} \cdot 1$

$$\therefore \lambda > 2d_{140} = 6.014 \text{ \AA} \quad \text{cannot produce a diffraction peak}$$

- c. (8 points). Let us now consider diffraction from a one-dimensional crystal with a lattice constant  $a = 10 \text{ \AA}$ . The crystal is irradiated with an X-ray beam having a wavelength  $\lambda$  that is incident on the crystal at an angle  $\bar{\mu}$  of  $30^\circ$ . Diffraction must now be described by the Laue equation for scattering by a one-dimensional crystal:

$$\cos \bar{\nu} = \cos \bar{\mu} + \frac{m\lambda}{a}$$

where  $m$  is an integer and  $\bar{\nu}$  is the angle between the lattice row and the diffracted beam. Let us now ask the same question as in problem 2(b): Is there a value or range of values of  $\lambda$  for which this crystal would be unable to produce any scattered beams at all?



$$\cos \bar{\nu} = \cos \bar{\mu} + m\lambda/a$$

$\cos \bar{\nu} \leq \cos \bar{\nu} \leq 1$  AND THIS CONSTRAINT LIMITS THE VALUES OF  $\bar{\mu}$ ,  $m$  AND  $\lambda$  FOR WHICH A DIFFRACTION CONE CAN OCCUR.

(THE CRYSTAL WE DECIDE TO EXAMINE FIXED  $a$ , SO WE WILL NOT BOTHER TO EXAMINE THE EFFECT OF CHANGING  $a$ )

FOR THE CONES ON THE RIGHT-HAND SIDE OF THE DIAGRAM

$$1 \leq \cos \bar{\nu} = \cos \bar{\mu} + m\lambda/a$$

therefore with other variables constant

AS  $\bar{\mu} \uparrow$   $\cos \bar{\mu} \downarrow$   $\cos \bar{\nu} \downarrow$   $\bar{\nu} \uparrow$

AS  $m \uparrow$   $\cos \bar{\nu} \uparrow$   $\bar{\nu} \downarrow$

SO THE DIFFRACTION CONES OPEN UP, WHEN  $\bar{\mu}$  BECOMES SUFFICIENTLY LARGE A NEW CONE WITH  $m+1$  WILL POP UP AND BECOMES PART OF THE SET.

SO THE DIFFRACTION CONES CLOSE UP AND EVENTUALLY WE WILL HIT AN INTEGER FOR WHICH  $\cos \bar{\nu} > 1$  AND THAT CONE WILL BE IMPOSSIBLE. (NOTE THAT THIS

IS THE WAY THE CONES ARE LABELED IN SEQUENCE IN THE ABOVE DIAGRAM, SO THE LABELING IS CORRECT IF  $\bar{\mu}$  IS DEFINED AS ACUTE (SEE FURTHER DISCUSSION BELOW.)

As  $\lambda \uparrow$   $\cos \bar{\nu} \uparrow$   $\bar{\nu} \downarrow$  THE DIFFRACTION CONES WILL CLOSE UP AND WINK OUT ONE-BY-ONE AS THE RIGHT HAND SIDE OF THE EQUATION BECOMES  $> 1$ . THE CONE FOR  $m=1$  WILL HIT  $\bar{\nu} = 0$  AND DISAPPEAR WHEN  $\cos \bar{\mu} + \lambda/a = 1$  AND  $\lambda = a(1 - \cos \bar{\mu})$ . OR, FOR THE PARAMETERS LISTED,  $\lambda = a(1 - \cos 30^\circ) = 1.340 \text{ \AA}$

DOES THIS PROVIDE THE WAVELENGTH BEYOND WHICH NO DIFFRACTION OCCURS? NOT NECESSARILY! WE STILL HAVE TO CONSIDER THE CONES AT THE LEFT SIDE OF THE LATTICE ROW:

$$\boxed{-1 \geq \cos \bar{\nu} = \cos \bar{\mu} + m \frac{\lambda}{a}}$$

THESE CONES, WILL HAVE NEGATIVE VALUES OF  $m$  IF  $\bar{\nu}$  IS  $> 90^\circ$  — THAT IS, WE CONTINUE TO MEASURE  $\bar{\nu}$  IN A COUNTER-CLOCKWISE DIRECTION FROM THE RIGHT-HAND END OF THE LATTICE ROW SO  $\bar{\nu}$  IS OBTUSE AND  $\cos \bar{\nu}$  IS NEGATIVE

As  $\bar{\mu} \uparrow$   $\cos \bar{\mu} \downarrow$  AND IS  $\oplus$   $\cos \bar{\nu} \uparrow$  (IS LESS NEGATIVE) SO THE DIFFRACTION CONES OPEN UP. A NEW CONE WITH  $(-m-1)$  MAY APPEAR

As  $-m \downarrow$  (BECOMES MORE NEGATIVE)  $\cos \bar{\nu} \downarrow$  (IS MORE NEGATIVE) DIFFRACTION CONES CLOSE DOWN — i.e., HALF-ANGULAR OPENING MEASURED FROM THE LEFT END OF THE LATTICE ROW CLOSES DOWN AND MAY DISAPPEAR

As  $\lambda \downarrow$   $\cos \bar{\nu} \downarrow$  (IN MORE NEGATIVE) DIFFRACTION CONES CLOSED DOWN AND THE ONE WITH LARGEST  $-m$  MAY DISAPPEAR

THE CONE THAT IS CLOSEST TO THE DIRECTION OF THE CONTINUATION OF THE INCIDENT BEAM — THE ONE WITH  $m=-1$  — WILL DISAPPEAR WHEN

$$\cos \bar{\nu} = -1 = \cos \bar{\mu} - 1 \frac{\lambda}{a}$$

$$\frac{\lambda}{a} = \cos \bar{\mu} + 1$$

$$\lambda \geq a(\cos \bar{\mu} + 1) \geq 10 \text{ \AA} (\cos 30^\circ + 1) \geq 10.660 \text{ \AA}$$

THIS IS A GREAT DEAL LARGER THAN THE WAVELENGTH  $\lambda \geq 1.340 \text{ \AA}$  FOR WHICH CONES WITH POSITION  $m$  WILL DISAPPEAR. THE REASON IS THAT THERE ARE A GREAT MANY MORE DIFFRACTION CONES WITH NEGATIVE  $m$  AS OPPOSED TO POSITIVE  $m$ . LET'S COMPUTE THE RANGES FOR THE PARAMETERS SPECIFIED ABOVE AND A PARTICULAR  $\lambda$  — SAY  $10 \text{ \AA}$

$$\begin{aligned} \text{for } +m \quad \cos \bar{\nu} = 1 &= \cos \bar{\mu} + m \frac{\lambda}{a} \\ &= \cos 30^\circ + m \frac{10 \text{ \AA}}{10 \text{ \AA}} \\ 1 &= 0.8660 + 0.1 m \end{aligned}$$

$$m_{\text{MAX}} \leq \frac{1 - 0.8660}{0.1} = 1.34$$

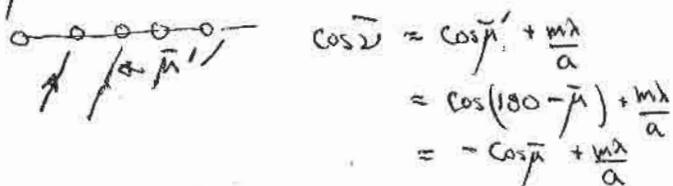
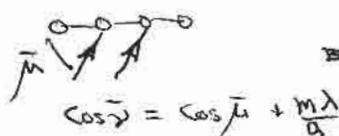
$$m_{\text{MAX}} = 1 \text{ ! ONLY ONE CONE!}$$

(9a)

But for  $-m$   $\cos \bar{\nu} = -1 < \cos \bar{\mu} - \frac{m\lambda}{a}$   
 $< 0.8660 - m \frac{1 \text{ \AA}}{10 \text{ \AA}}$   
 $-1 - 0.8660 < -m \cdot 0.1$   
 $|m_{\text{min}}| > \frac{-1.8660}{0.1} = -18.660 \quad m_{\text{min}} = -18!$   
 WOW! EIGHTEEN CONES!

TWO FINAL COMMENTS IN THIS TUTORIAL.

(a) WHAT CHANGES IF ONE USES THE OBTUSE ANGLE BETWEEN THE INCIDENT BEAM AND THE INCIDENT BEAM TO DEFINE  $\bar{\mu}$ ??



THIS LOOKS EXACTLY THE SAME AS OUR ORIGINAL RESULTS EXCEPT THAT WE HAVE CHANGED THE SIGN OF  $m$

$\cos \bar{\nu}$  IS DEFINED FOR NEGATIVE  $m$  AS LOW AS

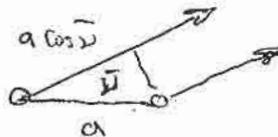
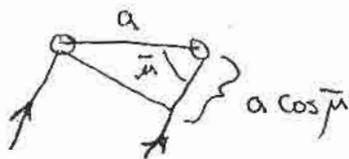
$$\cos \bar{\nu} \geq -\cos \bar{\mu} - \frac{m\lambda}{a} \geq -1$$

AND FOR POSITIVE  $m$  UP TO

$$\cos \bar{\nu} \leq -\cos \bar{\mu} + \frac{m\lambda}{a} \leq 1$$

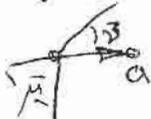
(b) THIS ABILITY, AS SHOWN ABOVE, TO SWITCH THE SIGN OF  $m$  WITHOUT CHANGING PHYSICALLY, WHAT IS HAPPENING, MAY SEEM STRANGE:  $m\lambda$  HAS PHYSICAL MEANING AS WELL! IT IS THE PATH DIFFERENCE BETWEEN RAYS SCATTERED FROM ADJACENT ATOMS IN THE CHAIN. BUT IS IT A PATH DIFFERENCE  $m\lambda$  (PHASE DIFFERENCE  $2\pi m$ ) OF THE ATOM ON THE LEFT RELATIVE TO THE ATOM ON THE RIGHT? OR VICE VERSA?

LET'S GO BACK TO THE WAY WE OBTAINED THE LAUE EQUATION



SO  $(a \cos \bar{\nu} - a \cos \bar{\mu})$  IS THE PATH DIFF OF THE ATOM TO THE LEFT RELATIVE TO THE ATOM ON THE RIGHT.

THIS RELATION CAN BE QUANTIFIED BY ASSIGNING A VECTOR SENSE TO THE LATTICE TRANSLATION  $\vec{a}$



THUS  $a \cos \bar{\nu} - a \cos \bar{\mu} = m\lambda$  MEANS NEIGHBORING ATOM AT THE

TERMINUS OF  $\vec{a}$  HAS PHASE  $2\pi m$  OR PATH DIFFERENCE  $m\lambda$  RELATIVE TO THE ATOM AT THE START OF  $\vec{a}$ .

In fact, we can place the Laue equation in a nifty vector form by

letting the direction of the incident beam be represented by a unit vector  $\vec{S}_0$  and the direction of the diffracted beam by a unit vector  $\vec{S}$ .

Then  $\vec{S}_0 \cdot \vec{a} = |\vec{a}| |\vec{S}_0| \cos \bar{\mu} = a \cos \bar{\mu}$   
 $\vec{S} \cdot \vec{a} = |\vec{a}| |\vec{S}| \cos \bar{\nu} = a \cos \bar{\nu}$  } so that the Laue equation may be written:

$$a \cos \bar{\nu} - a \cos \bar{\mu} = \vec{S} \cdot \vec{a} - \vec{S}_0 \cdot \vec{a} = \boxed{(\vec{S} - \vec{S}_0) \cdot \vec{a} = m\lambda}$$

which sidesteps any ambiguity on whether path difference is  $+m\lambda$  or  $-m\lambda$  and of whether path difference is that of atom on the left relative to atom on the right.

The preceding long-winded tutorial has hopefully conveyed some appreciation of the nuances of the Laue equation (hey! it was good for the 1915 Nobel Prize in physics!) and how one can cast it into a simple, compact form using vector algebra.

We have also shown that the diffraction cone for one wavelength path difference between atoms separated by  $\vec{a}$  disappears when  $\lambda \geq 1.390 \text{ \AA}$  and the diffraction cone for one wavelength path difference between atoms separated by  $-\vec{a}$  ( $m = -1$ ) disappears when  $\lambda \geq 18.660 \text{ \AA}$ .

This, however, is NOT the answer to the question "is there a value or range of values of  $\lambda$  for which this crystal would be unable to produce any scattered beams at all?"

The correct answer could have been given straightaway without further thought:

There is a diffraction cone with  $m=0$  (of which the incident beam is one generator) on which all beams are produced by atoms scattering exactly in phase. As the path difference between all scattered rays along this cone is zero this cone will be present for any wavelength in the incident beam regardless of how large or small the value of  $\lambda$  might be.

1. **Thermodynamics.** (50 points).

- a. (5 points each part, 30 points total) **True-False-explanation.** Read the statements below and decide if they are *completely* true, or false based on your understanding of thermodynamics. **Explain your choice** of true/false (in 1 or 2 *brief* sentences), and if necessary, show an equation that supports your statement.

- i. A first-order phase transition can be identified by a discontinuous increase in the value of several variables of a system at the transition temperature, including volume, heat capacity, enthalpy, and entropy.

**False.** First-order phase transitions are characterized by a discontinuity in each of these functions; however, the heat capacity may jump to a higher or lower value after the phase transition (e.g., transformation from a liquid to a gas), and volume also is not constrained to jump to a higher value (e.g. ice has a larger molar volume than liquid water).

- ii. If the entropy change of a first-order phase transformation at constant pressure  $\Delta S_{\text{trans}}$  is positive for stability, then the enthalpy of transformation  $\Delta H_{\text{trans}}$  must also be positive.

**True.** At a first-order phase transition at constant pressure, the enthalpy change and entropy change are related to one another by  $\Delta H_{\text{trans}} = dq_{\text{rev,trans}} = T_{\text{trans}} \Delta S_{\text{trans}}$ . Since the absolute temperature must be positive, the sign of the enthalpy and entropy changes must be the same.

- iii. Minimizing the Helmholtz free energy of the system + its surroundings under conditions of constant temperature and volume to determine the equilibrium state is equivalent to maximizing the entropy of the universe, in obedience to the second law.

**False.** Minimizing the free energy of the **system alone** at constant temperature and volume is equivalent to maximizing the entropy of the universe in a spontaneous process.

- iv. The entropy of materials decreases as temperature decreases, but if a hot liquid is placed in thermal contact with a cold reservoir, the liquid will spontaneously cool to the temperature of the reservoir, and this spontaneous process will not violate the second law.

**True.** Though the entropy of the material will be decreased in this process, the entropy of the surroundings will substantially increase in the process of accepting heat from the system (heat must leave the system in this process). Thus the entropy of the universe (system + surroundings) will increase.

- v. The work of polarizing an anisotropic single-crystal material by application of an electric field will depend on the direction in which the field is applied relative to the crystal orientation.

**True.** Anisotropic materials have electric displacements which may vary with direction in the crystal due to symmetries (or lack thereof) in the structure.

- vi. For an isolated system of two materials A and B brought into thermal contact, the entropies of the subsystems will be maximized at equilibrium, but the internal energies will **not** necessarily reach a maximum or minimum.

**False.** The entropies of the individual subsystems will **not** necessarily be maximized- the **sum** of the entropies of the two subsystems will be maximized, according to the second law.

- b. (20 points) Consider a liquid comprised of four components A, B, C, and D, mixed homogeneously in a single phase at constant temperature and pressure. The molecules can undergo an interconversion reaction:



The chemical potentials of the components are always positive ( $> 0$ ).

- (i) If the chemical potential of C in the system is initially greater than that of all the other components, will an increase in the number of B molecules in the system occur spontaneously? Show how your answer is proven by the equilibrium/spontaneity condition for this system.
- (ii) Write an expression showing the relationship between the chemical potentials of each species at equilibrium.
- (i) The direction of spontaneous processes for a system at constant temperature and pressure is determined by the Gibbs free energy:

$$dG_{system} < 0 \quad \text{spontaneous}$$

We can write an expression for the system free energy:

$$dG_{system} = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

We have a direct relationship between the moles of each component present due to the given interconversion reaction:

$$dn_A = dn_B = -dn_C = -dn_D$$

This relationship comes directly from the fact that every forward reaction that occurs consumes an A and a B molecule, and produces one C and one D molecules- likewise the opposite occurs for the reverse reaction. This allows us to simplify the spontaneity condition:

$$dG_{system} = (\mu_A + \mu_B - \mu_C - \mu_D)dn_A < 0$$

$$(\mu_A + \mu_B - \mu_C - \mu_D)dn_B < 0$$

We can answer the question by simply analyzing the last expression: if  $\mu_C$  is initially greater than all of the chemical potentials, (and all are positive), then the sum/differences of the chemical potentials in parentheses is negative. The system will be driven to the reverse reaction (C + D consumed to make more A + B)- with  $dn_B$  positive- in order to have the total free energy differential  $< 0$ . Thus, the amount of B molecules **will** spontaneously increase.

- (ii) The equilibrium condition on the chemical potentials is readily shown from the last equations derived above:

$$dG_{system} = (\mu_A + \mu_B - \mu_C - \mu_D)dn_A = 0 \text{ (condition for equilibrium)}$$

In order to maintain equilibrium regardless of small fluctuations in the number of molecules of any species present (e.g., nonzero  $dn_A$ ), we must have:

$$\mu_A + \mu_B - \mu_C - \mu_D = 0$$

*or*

$$\mu_A + \mu_B = \mu_C + \mu_D$$