SOLUTIONS

SID: ______________________________

Signature: ______________________________

Materials Science and Engineering 102
Structure and Bonding

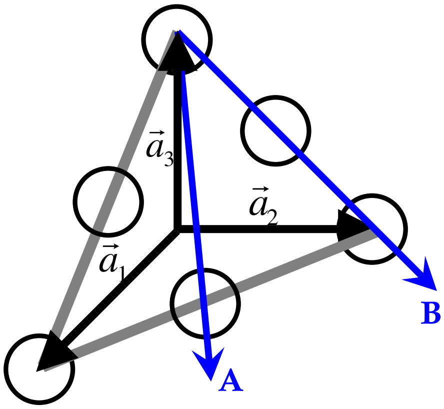
Prof. Stephen L. Sass

Midterm Examination
Duration: 1 hour 20 minutes

Closed book. Closed notes. No calculator allowed.

Please check that there are twelve pages in this packet.
There are four questions, and each is worth 25 points.

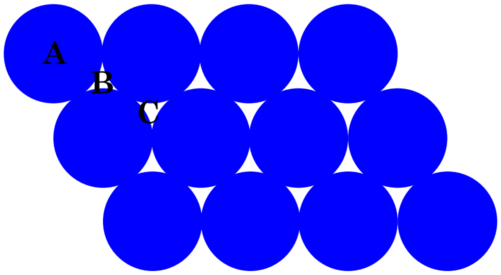
1.) (25 points)



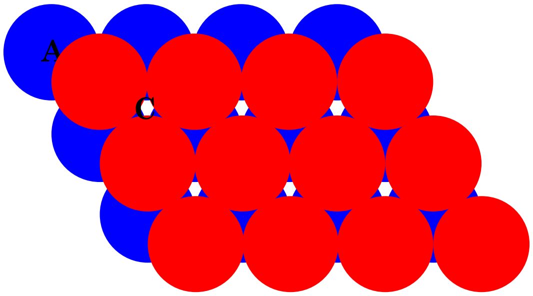
(a) (i) What are the Miller indices of the plane drawn above? (4 points)
(ii) What are the Miller indices of directions A and B? (5 points)
(iii) Show how two different crystal structures can be obtained by the stacking of the close-packed plane shown above. Use the ABC… notation for the stacking of these planes. Identify the crystal system of each of these structures. (8 points)

(b) For the f.c.c. structure:
(i) Show the location of an octahedral void. (4 points)
(ii) Consider a f.c.c. structure of A atoms, with B atoms inserted into every octahedral void. What is the ratio of number of B atoms to the number of A atoms (e.g. 1B:1A, 2B:1A, 1B:2A, etc) in this new structure? (4 points)

(a) (i) **(111)** plane
(ii) **A =** $[11\bar{2}]$ **B =** $[01\bar{1}]$
(iii) Shown below is a close-packed plane. *A* identifies the atomic positions on this close-packed plane. *B* and *C* are positions where another close-packed plane can be stacked above to maintain the close-packed structure.

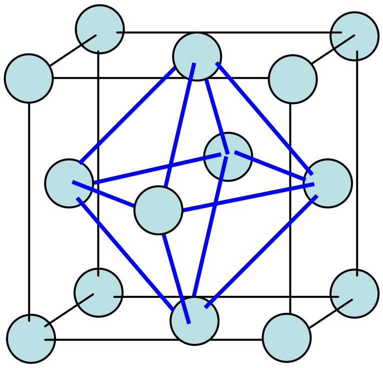


If a close-packed plane is stacked on the B positions, we get the resulting structure. The C positions remain available for the stacking of the next plane.



The next plane can be placed on the A or C positions.
ABCABC – FCC structure
ABABAB – HCP structure

(b) (i) void at ½½½



(ii) There are four A atoms. There are four octahedral voids in the FCC structure (one at the center and three on the edges).

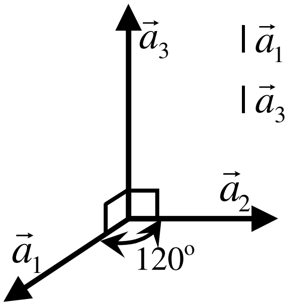
1A:1B

2.) (25 points)

(a) Show that a 7-fold rotation axis cannot be combined with translations to build up a two-dimensionally periodic crystal. (8 points) You may find the following numbers helpful:

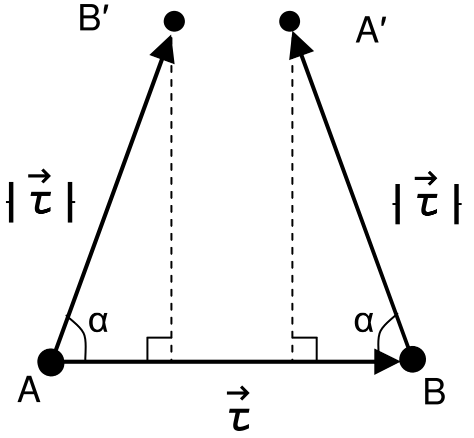
$$\cos\left(\frac{360^o}{7}\right) = 0.62 \qquad \sin\left(\frac{360^o}{7}\right) = 0.78 \qquad \tan\left(\frac{360^o}{7}\right) = 1.25$$

(b) Derive an equation for the plane spacing, d_{hkl}, in the hexagonal system, which has the unit cell shown below. (17 points)



$$|\vec{a}_1| = |\vec{a}_2| = a$$
$$|\vec{a}_3| = c$$

(a) Given a 2-D periodic crystal with translation vector $\vec{\tau}$, assume an n-fold rotation, corresponding to $\alpha = 360°/n$ exists and is compatible. Starting from lattice point **A**, apply the translation to generate **B**. Similarly, we exercise the rotational symmetry to generate **A′** from **A** and **B′** from **B**. This generates a diagram as below. **A′** and **B′** are lattice points, so should be separated by an *integer* number of lattice translations. Plugging in n=7, we find this rotation symmetry creates a statement which cannot be true, therefore a 7-fold rotation is not compatible.



$$m\,|\vec{\tau}| = \overline{\mathrm{AB}} \qquad m \in \mathbb{Z}$$

$$m\,|\vec{\tau}| = \overline{\mathrm{AB}} - 2\,|\vec{\tau}|\cos\alpha$$

$$m\,|\vec{\tau}| = |\vec{\tau}| - 2\,|\vec{\tau}|\cos\alpha$$

$$\frac{M}{2} = \frac{1-m}{2} = \cos\alpha \qquad M \in \mathbb{Z}$$

$$\text{for } n = 7,\ \text{RHS} = \cos\frac{360\,°}{7} = 0.62 \neq \frac{M}{2}\ \text{[LHS]}$$

Please note that this drawing is not unique; however, geometric variants will still confirm this result.

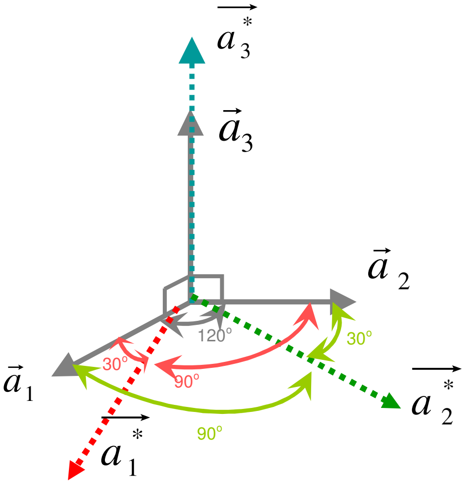
(b) The plane spacing, d_{hkl}, is related to the reciprocal lattice vector, $\overrightarrow{g_{hkl}}$, normal to its surface by:

$$\frac{1}{{d_{\text{hkl}}}^2} = \vec{g}_{\text{hkl}} \cdot \vec{g}_{\text{hkl}} \quad \text{where} \quad \vec{g}_{\text{hkl}} = h\,\vec{a_1}^* + k\,\vec{a_2}^* + l\,\vec{a_3}^*$$

(3 points)

$$\begin{aligned}\frac{1}{{d_{\text{hkl}}}^2} = {} & h^2\,\vec{a_1}^*\cdot\vec{a_1}^* + k^2\,\vec{a_2}^*\cdot\vec{a_2}^* + l^2\,\vec{a_3}^*\cdot\vec{a_3}^* \\ & + h\,\vec{a_1}^*\cdot\left(k\,\vec{a_2}^* + l\,\vec{a_3}^*\right) \\ & + k\,\vec{a_2}^*\cdot\left(h\,\vec{a_1}^* + l\,\vec{a_3}^*\right) \\ & + l\,\vec{a_3}^*\cdot\left(h\,\vec{a_1}^* + k\,\vec{a_2}^*\right)\end{aligned}$$

Applying the definitions (cross-products) of the reciprocal lattice vectors, we can determine the relationship between the reciprocal lattice vectors. Geometrically:



$$\vec{a_1}^* \perp \vec{a_3}^* \text{ and } \vec{a_2}^* \perp \vec{a_3}^* \Rightarrow \vec{a_1}^*\cdot\vec{a_3}^* = \vec{a_2}^*\cdot\vec{a_3}^* = 0$$

$$\vec{a_i}^*\cdot\vec{a_i}^* = \left|\vec{a_i}^*\right|^2$$

$$\frac{1}{{d_{\text{hkl}}}^2} = h^2\left|\vec{a_1}^*\right|^2 + k^2\left|\vec{a_2}^*\right|^2 + l^2\left|\vec{a_3}^*\right|^2 + 2\,\text{hk}\,\vec{a_1}^*\cdot\vec{a_2}^*$$

(4 points)

$$\vec{a_i}^*\cdot\vec{a_j} = \delta_{\text{ij}} = \left|\vec{a_i}^*\right|\left|\vec{a_j}\right|\cos[\text{angle between}]$$

$$\left|\vec{a_1}^*\right| = \frac{1}{a\cos[30\,°]}$$

$$\left|\vec{a_2}^*\right| = \frac{1}{a\cos[30\,°]}$$

(3x2 points)

$$\left|\vec{a_3}^*\right| = \frac{1}{c}$$

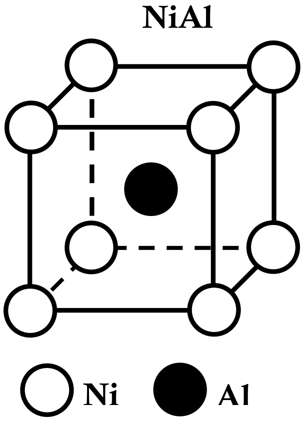
$$\vec{a_1}^*\cdot\vec{a_2}^* = \left(\frac{1}{a\cos[30\,°]}\right)^2\cos[60\,°] \qquad \cos[60\,°] = \frac{1}{2};\quad \cos[30\,°] = \frac{\sqrt{3}}{2}$$

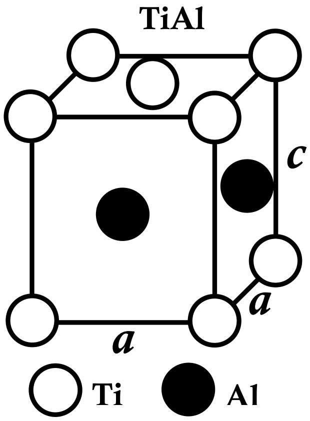
$$\boxed{\frac{1}{{d_{\text{hkl}}}^2} = \frac{4}{3\,a^2}\left(h^2 + k^2 + \text{hk}\right) + \frac{1}{c^2}\,l^2}$$

(4 points)

3.) (25 points)

Ordered intermetallic compounds are being considered as candidates for the next generation of jet turbine blade materials. They exist in a variety of different structures and compositions. Two intermetallic compounds and their crystal structures are shown below, where NiAl is in the cubic crystal system, and TiAl is tetragonal with c/a = 1.05. (For clarity, the atoms on the back faces are not shown on the TiAl schematic.)





You are working during the summer at the General Electric Research Laboratory. Your boss knows that you did very well in MSE 102, and therefore asks you to identify which of the two compounds is present in a powder sample.

(a) Which X-ray diffraction technique would you use to identify the crystal structure of the compound? Would you use white radiation or a single wavelength?
(5 points)

(b) What calculations must you perform in order to interpret the diffracted intensities observed in part (a)? Carry out these calculations for the two structures and explain how you could identify which compound is present.
(20 points)

(a) Powder diffraction (3 points), using a single wavelength (2 points),

(b) Diffracted intensities ➔ We need to calculate the *structure factor.* (2 points)

$$\text{Structure factor} = f \equiv \sum_{\substack{\text{atoms in}\\ \text{unit cell}}} f_m \operatorname{Exp}\left[i\, 2\pi\, \vec{S} \cdot \overrightarrow{u_m} \right] \quad \text{(2 points)}$$

where

$$\vec{S} = \vec{g}_{\text{hkl}} = h\,\vec{a}_1^{\,*} + k\,\vec{a}_2^{\,*} + l\,\vec{a}_3^{\,*}$$

$$\overrightarrow{u_m} = x_m\,\vec{a}_1 + y_m\,\vec{a}_2 + z_m\,\vec{a}_3, \text{ using fractional coordinates}$$

Find the atom positions (2x4 points), in fractional coordinates, then insert (2x1 point):

For NiAl

$$\text{Ni}: 0\,0\,0 \qquad f_{\text{NiAl}} = f_{\text{Ni}} + f_{\text{Al}}\,\text{Exp}[i\,\pi\,(h+k+l)]$$

$$\text{Al}: \frac{1}{2}\;\frac{1}{2}\;\frac{1}{2} \qquad f_{\text{NiAl}} = \begin{cases} f_{\text{Ni}} + f_{\text{Al}} & \text{for } h+k+l = 2\,n,\;\; n \in \mathbb{Z} \\ f_{\text{Ni}} - f_{\text{Al}} & \text{otherwise} \end{cases}$$

For TiAl

$$\text{Ti}: 0\,0\,0 \qquad f_{\text{TiAl}} = f_{\text{Ti}}\,(1 + \text{Exp}[i\,\pi\,(h+k)]) + f_{\text{Al}}\,(\text{Exp}[i\,\pi\,(h+l)] + \text{Exp}[i\,\pi\,(k+l)])$$

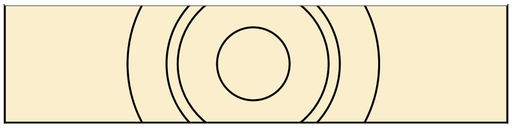
$$\frac{1}{2}\;\frac{1}{2}\;0$$

$$\text{Al}: \frac{1}{2}\;0\;\frac{1}{2} \qquad f_{\text{TiAl}} = \begin{cases} 2\,(f_{\text{Ti}} + f_{\text{Al}}) & \text{if } h,\,k,\,l \text{ same parity} \\ 2\,(f_{\text{Ti}} - f_{\text{Al}}) & \text{if } h,\,k \text{ same parity, } l \text{ not} \\ 0 & \text{otherwise} \end{cases}$$

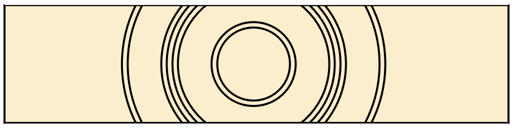
$$0\;\frac{1}{2}\;\frac{1}{2}$$

(6 points) To distinguish between these two structures, we notice that NiAl is cubic, whereas TiAl is tetragonal. Crystal structures with higher symmetry (cubic) should result in fewer diffractions rings in powder diffraction. Specifically for cubic vs. tetragonal, having the $c \neq a$ implies that (100) and (010) are no longer equivalent to (001), so the (001) diffraction will be different and contribute another ring, and similarly for other hkl.

cubic



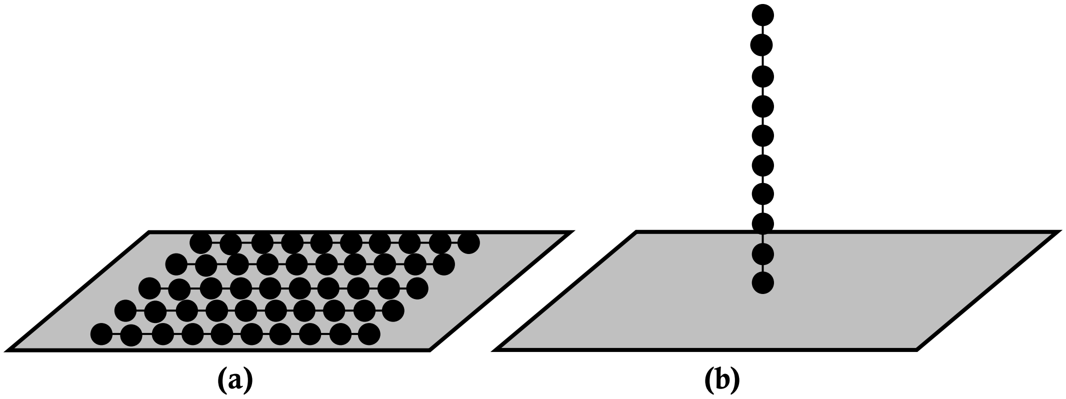
tetragonal



In addition, we notice that the intensities should be different for the expected hkl diffractions as calculated in the structure factors (since $I \propto F^{*}F$) based on the differing motifs of these crystals. This means that the diffractions will not strictly follow the cubic vs. tetragonal disparity since some of the expected tetragonal diffractions are not allowed due to the structure factor. Comparing the rules to the generated intensities should yield the mystery compound.

4.) (25 points)

A new form of silicon is thought to exist where long straight one-dimensional chains of silicon atoms are in either one of the two orientations shown below. Figure (a) shows one such structure where the chains lie parallel to the surface in a well-ordered two-dimensionally periodic array. Figure (b) shows a second structure where an individual chain is oriented perpendicular to the surface.



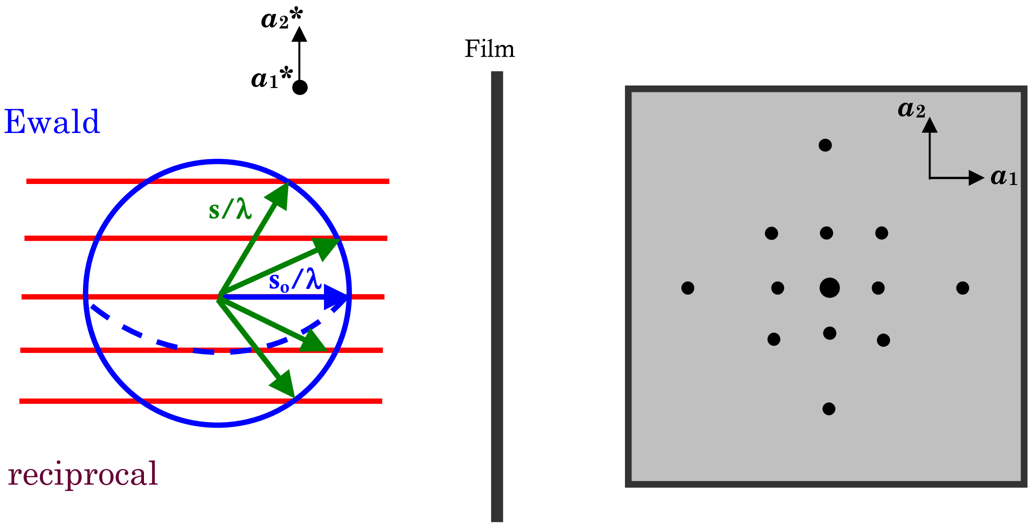
(a) Describe the reciprocal lattice of each of the two structures. How did you arrive at this answer? (A long derivation is not required. Be brief.) Show the orientation of the reciprocal lattice with respect to the real space structure.
(12 points)

(b) Describe in detail a diffraction experiment that you would perform to determine which of these two structures actually exists. Assume that the flat surfaces on which the silicon chains sit are thin and can be ignored in the diffraction experiment. (13 points)

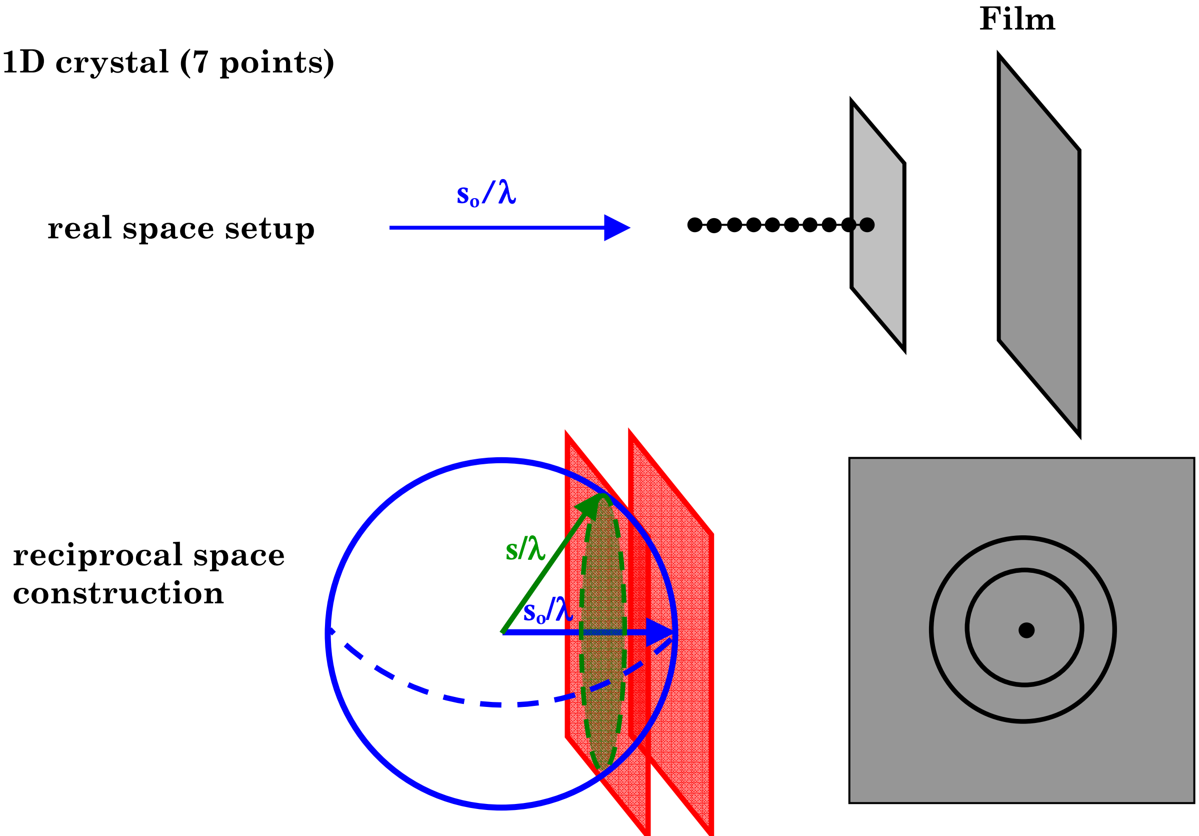
(a) As defined in class, the reciprocal lattice is composed of the regions in reciprocal space where we can achieve high diffracted amplitude (2 points). In a **2D crystal** (structure a), this can be attained if two independent Laue conditions are satisfied. That is, $\mathbf{S}\cdot\boldsymbol{a}_1$ and $\mathbf{S}\cdot\boldsymbol{a}_2$ are integers (4 points). Define $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ to be in-plane lattice vectors, and $\boldsymbol{a}_3$ to be the out-of-plane lattice vector. Each Laue condition defines a set of parallel planes at which the **S** vector can end. Since $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are not parallel vectors, satisfying both Laue conditions simultaneously can be visualized as the intersection of two sets of planes. **The reciprocal lattice is a set of lines, orthogonal to the $\boldsymbol{a}_1$-$\boldsymbol{a}_2$ plane** (3 points).
In a 1D crystal (structure b), high diffracted amplitude can be attained by satisfying just one Laue condition. **The reciprocal lattice is a set of parallel planes, orthogonal to the $\boldsymbol{a}_3$ axis, spaced $1/|\boldsymbol{a}_3|$ apart** (3 points).

(b) Perform an X-ray diffraction experiment using monochromatic radiation, orient the surface orthogonal to the incoming beam, and place the film at a position to detect forward scattered beams (4 points).

2D crystal, *Side View* (2 points)



1D crystal (7 points)



not showing all reciprocal lattice planes for clarity

Concentric rings

By comparing the real diffraction pattern with the ones above predicted for each structure, we should be able to identify which one actually exists. Note that in using the Ewald Sphere construction, you have to make sure the $\mathbf{s}_o/\lambda$ vector ends on a reciprocal lattice point, line, or plane.

Scores

1)

2)

3)

4)

Total