CHEMISTRY 448/548 Winter 2009

Assignment #1 (50 pts) - Due Jan 16th.

SHOW WORKING FOR FULL CREDIT.

ALL DRAWINGS MUST BE NEAT AND ACCURATE.

SLOPPY WORK WILL BE PENALIZED!

1. (5 pts) In class we discussed the rate of collision of molecules with a surface. McCash gives a formula for this (3.13). (a) Show that the units work out correctly (1 pt). (b) Calculate the number of collision per cm^2/sec of O_2 molecules with a surface at 25 °C and (i) 1 atm pressure and (ii) outer space (10^{-14} torr) (2 pts each)

Solution :

Collision rate = $Rate = \dfrac{P}{\left(2\pi\, m\, k_B T\right)^{1/2}}$ (given in McCash)

(a) First a units check.

$$Rate = \frac{P}{\left(2\pi\, m\, k_B T\right)^{1/2}} \equiv \frac{\text{kg m}^{-1}\text{ s}^{-2}\text{ (= Pa)}}{\left(\underbrace{\text{kg}}_{m}\times \underbrace{\text{kg m}^{2}\text{ s}^{-2}\text{ K}^{-1}}_{k_B} \times \underbrace{\text{K}}_{T}\right)^{1/2}} = \text{m}^{-2}\text{ s}^{-1} \quad \text{as required.}$$

(b) So $Rate(cm^{-2}s^{-1}) = \dfrac{10^{-4}\,P\text{ (Pa)}}{\left(2\pi\, m\, k_B T\right)^{1/2}} = C\,P$

With P in torr at 298K for O_2 we get

$$m = \left(\frac{32.0\text{ g}}{1\text{ mol}}\right) \times \left(\frac{1\text{ kg}}{1000\text{ g}}\right) \times \frac{1\text{ mol} \;/}{6.022\times 10^{23}\text{molecules}} = 5.31 \times 10^{-26}\text{ kg} \quad \text{and}$$

$$C = \frac{10^{-4}}{\left(2\pi \times 5.31 \times 10^{-26}\text{ kg} \times 1.381 \times 10^{-23}\text{ kg m}^2\text{s}^{-2}\text{ K}^{-1} \times 298\text{ K}\right)^{1/2}} = 2.70 \times 10^{18}$$

So $Rate$ (cm^{-2} s^{-1}) = 2.70×10^{18} P (Pa)

(i) P = 1 atm = 101,325 Pa

Rate = 2.70 × 10^{18} × 101,325 Pa = **2.73 × 10^{23} cm^{-2} s^{-1}**

(ii) P = 10^{-14} torr

$$Rate = 2.70 \times 10^{18} \times 10^{-14} \text{ torr} \times \left(\frac{1\text{atm}}{760 \text{ torr}}\right) \times \frac{101{,}325 \text{ Pa}}{1 \text{ atm}} = \mathbf{3.88 \text{ x } 10^{6} \text{ cm}^{-2} \text{ s}^{-1}}$$

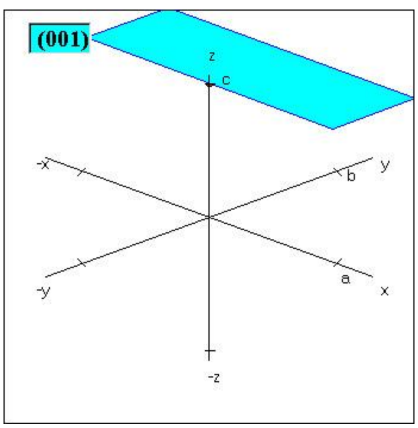
2. (9 pts) Sketch the following planes in a cubic lattice:

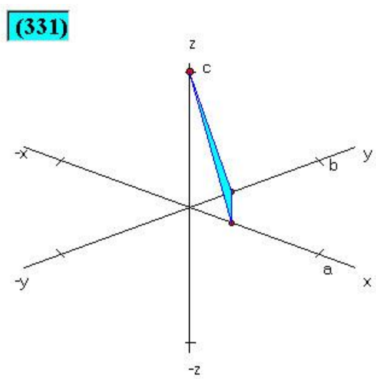
a) (001) b) (331) c) (-120)

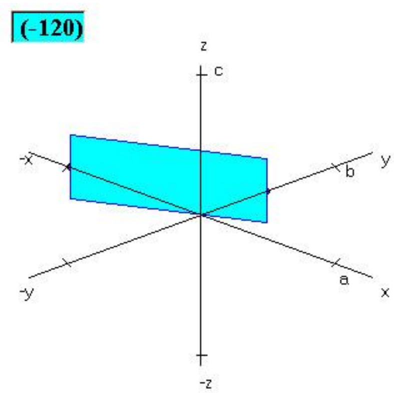
Make sure to indicate the axes and intercepts. (3 pts each)

Hint : a negative Miller index means that the plane intercepts the axis at a negative value relative to the origin.

Solution :





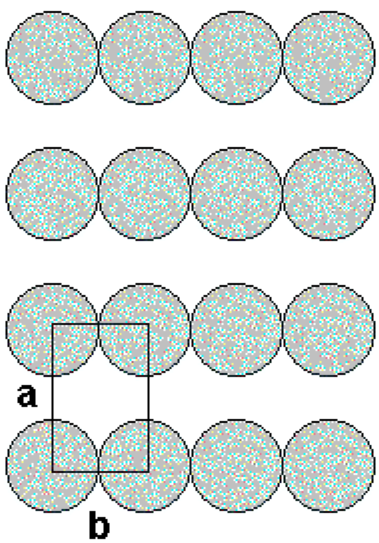


3. (12 pts) Rh crystallizes in the face-centered cubic lattice with a basis of one atom at each lattice point and a cell side of 382 pm. Rh atoms (radius 135 pm) touch across a *face-diagonal.* W crystallizes in the body-centered cubic lattice with a basis of one atom at each lattice point and a cell side of 316 pm. W atoms (137 pm) touch across a *body-diagonal.*

a) make realistic drawings of the Rh(110) and W(110) planes by using circles of appropriate size to represent the atoms. On the drawings indicate the smallest 2D surface unit cell possible and calculate its dimensions and area in each case. (8 pts)

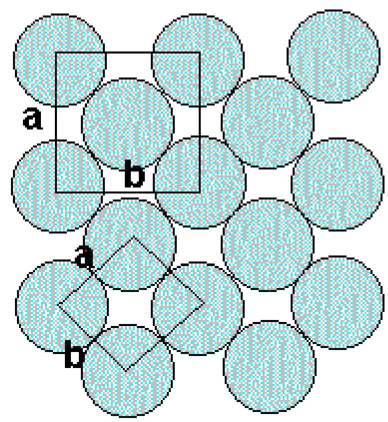
Solution :

Rh(110)



FCC(110)

W(110)



BCC(110)

Rh(110):

$\boldsymbol{a = (\sqrt{2}/2)\, a_0}$

$\boldsymbol{b = a_0}$

Area = *ab*

$= \{(\sqrt{2}/2) \times 382 \text{ pm}\} \times (382 \text{ pm})$

$= \mathbf{1.03 \times 10^5\ pm^2}$

W(110):

$\boldsymbol{a = b = (\sqrt{3}/2)\, a_0}$

Area = *ab*

$= \{(\sqrt{3}/2) \times (316 \text{ pm})\}^2$

$= \mathbf{7.49 \times 10^4\ pm^2}$

b) what will be the perpendicular distance between neighboring Rh(110) planes? (HINT : be careful to place the 2nd layer atoms in the correct location below the top layer) (4 pts)

Solution :

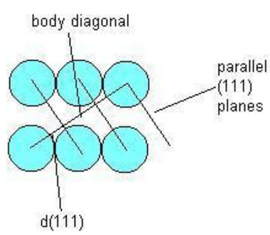
In an fcc crystal the face-centering atoms are the next layer below the (110) plane, so the interlayer distance between (110) planes will be 1/4 of a face diagonal or $(\sqrt{2}a_o)/4$.

So for Rh : $\boldsymbol{d}$**(110)** = 1.414 × 382 / 4 = **135 pm.**

4. (10 pts) The metal Cu crystallizes in a fcc lattice. We can regard this structure as being built up of (111) layers in an ABCABC . . . stacking where the atoms in each layer sit in hollows formed between triangles of atoms in the layer below.

a) show with appropriate diagrams that the interplanar distance between (111) planes is given by $d_{111} = a_0 / 3^{1/2}$ where a_0 is length of a side in the fcc unit cell. Express this in terms of atomic radii and in pm if a_0 for Cu is 362 pm (6 pts)

Solution :



fcc(111) interlayer distance projected onto a (110) plane

Parallel fcc(111) planes cut through the unit cell cube. As the body diagonal is $\sqrt{3}\,a_0$

then $\boldsymbol{d}$**(111)** $= \sqrt{3}\,a_0 / 3 = a_0 / \sqrt{3}$ = **209 pm**

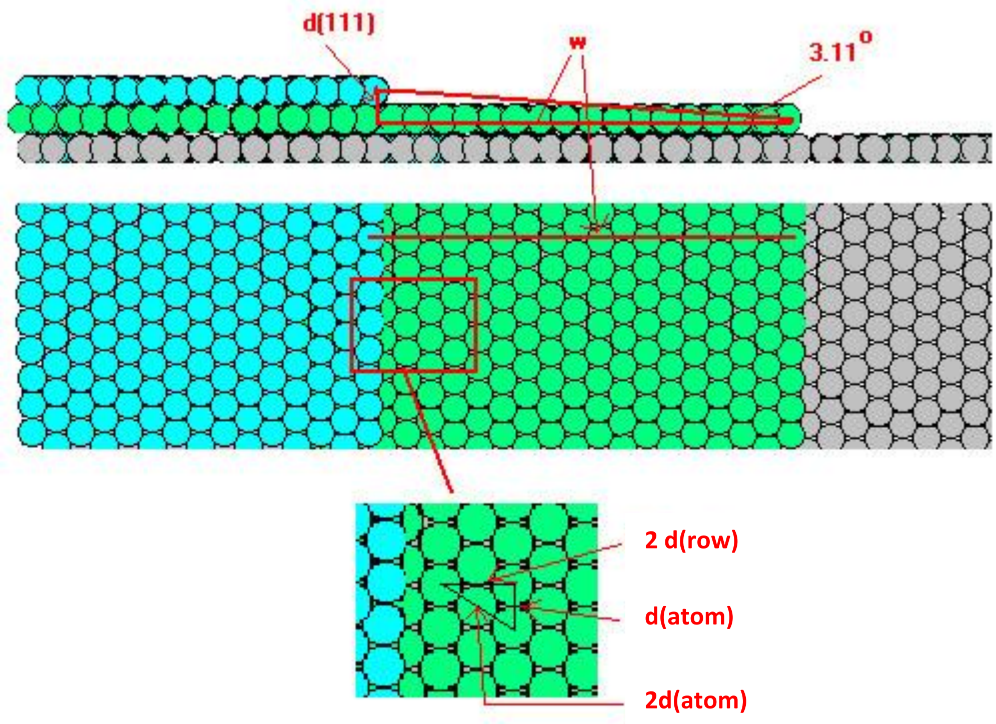
In the fcc structure atoms touch across the face diagonal so the distance across the diagonal is :

$\sqrt{2}\,a_0 = 4r$ (r = atomic radius) and $\boldsymbol{r} = \sqrt{2} \times 362 / 4$ = **128 pm**

so $d(111) = 4r / \sqrt{6}$ = **209 pm** as before.

b) consider a Cu crystal cut to expose a plane that has (111) terraces of width w separated by ledges (steps) 1 atom high in a regular fashion. The steps are formed by rows of atoms that touch in the (111) plane and the macroscopic angle of the surface relative to the (111) terraces (from one location at one step edge to an equivalent location at the next step edge) is 3.11°. Calculate the width of each terrace in pm. Approximately how many Cu atoms can fit across the width of this terrace – explain what assumptions you make. (4 pts)

Solution :



The step height is just *d*(111) so :

tan (3.11) = *d*(111) / *w* and so ***w*** = 209/ 0.05433 = **3864 pm**

However, things get a little tricky here. The layers of fcc(111) each lie in the hollows of the layer below meaning that atoms perpendicular to the step do not form rows of atoms that touch. As the inset shows, the inter-row separation perpendicular to the step is :

$d(\text{row}) = \sqrt{3}^{1/2}\, d(\text{Cu}) / 2 = \sqrt{3}\, r =$ **222 pm**

So the number of rows of Cu atoms in the terrace is

Hence, 3864 / 222 = **17.4**

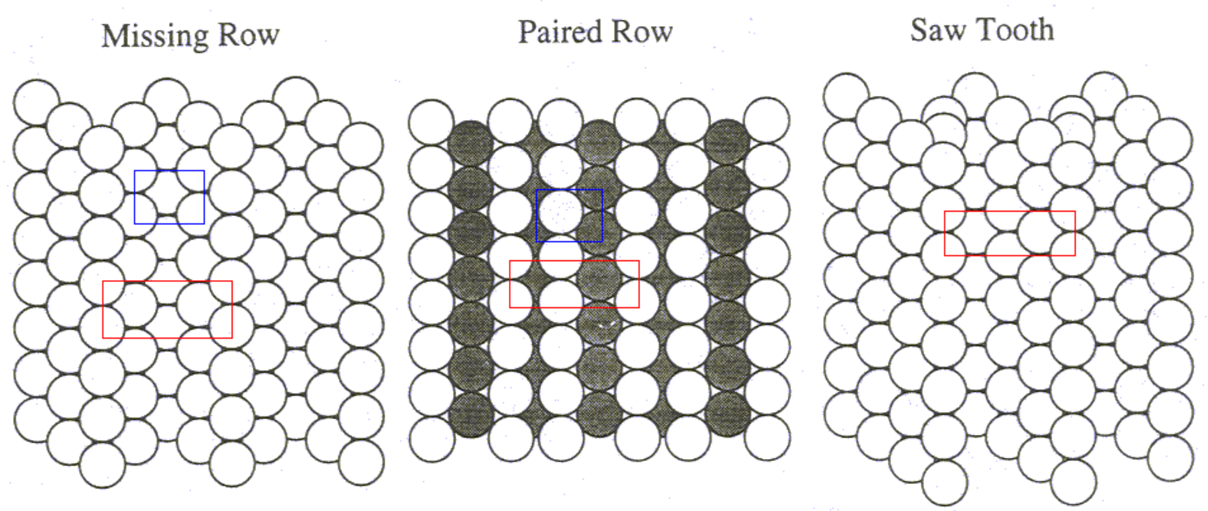
So, the terrace is 17.4 rows wide (the step atoms lie in dimples that are 1/3 of 2*d*(row) hence the fractional width).

5. (14 pts) The Pt(110) surface reconstructs in (2x1) manner. For some time there was controversy as to the actual surface structure. Three models shown below were proposed.

a) show that all three models have a (2x1) atomic arrangement (6 pts)

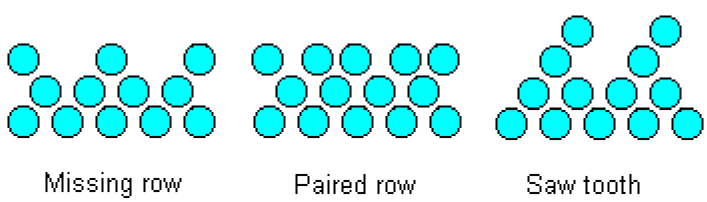
Solution :

The blue lines below show the original Pt(110) (1x1) mesh and the red lines the new surface mesh. Clearly in each case the new mesh has $a_s = 2\,a$ and $b_s = b$ and is a (2x1) reconstruction.



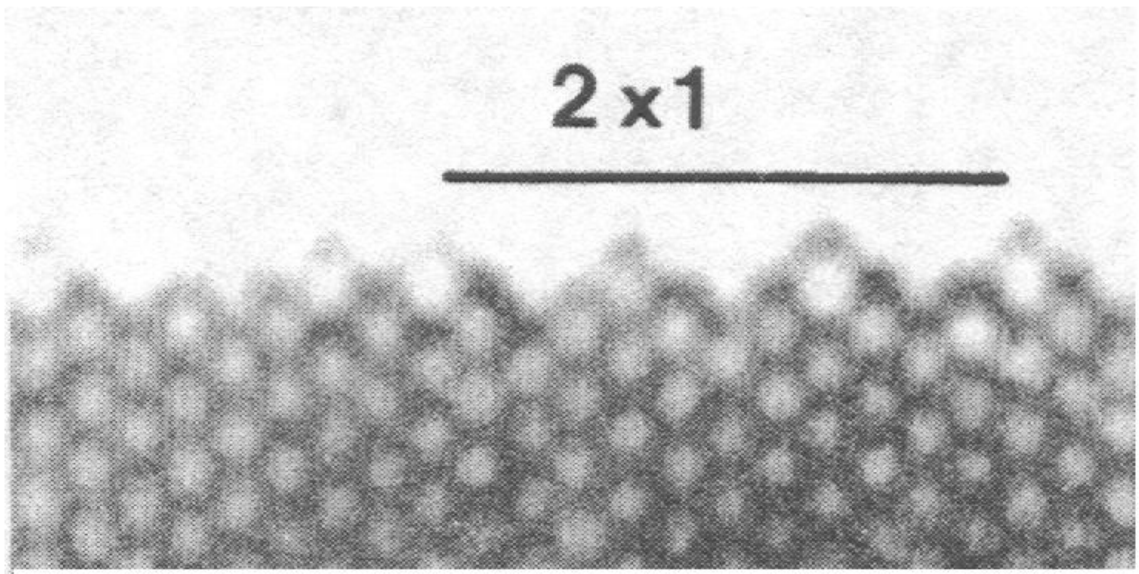
b) draw a side view of each structure (9 pts)

Solution :



c) compare each structure with the transmission electron microscope photo shown above and decide which model is probably correct (NOTE : in reality TEM data interpretation is subtle and we cannot simply in general infer a structure directly from a TEM image. However, in this case the TEM image and the actual structure do match). (5 pts)

Solution :



If we compare this TEM photo with the answers for part b) we see that the best correspondence is clearly with a missing row structure. The peaks are symmetric unlike the sawtooth model and there is no evidence of row pairing.