PROBLEM SET 2

#1) Problem # 1 in Omar

the set of vectors

$$\begin{cases} \vec{a} = \frac{a}{2}(\hat{i}+\hat{j}) \\ \vec{b} = \frac{a}{2}(\hat{j}+\hat{k}) \\ \vec{c} = \frac{a}{2}(\hat{k}+\hat{i}) \end{cases}$$

are the primitive ~~basis~~ basis vector for a fcc crystal

$$\begin{cases} \vec{a} \equiv \vec{a}_1 \\ \vec{b} \equiv \vec{a}_2 \\ \vec{c} \equiv \vec{a}_3 \end{cases} =$$

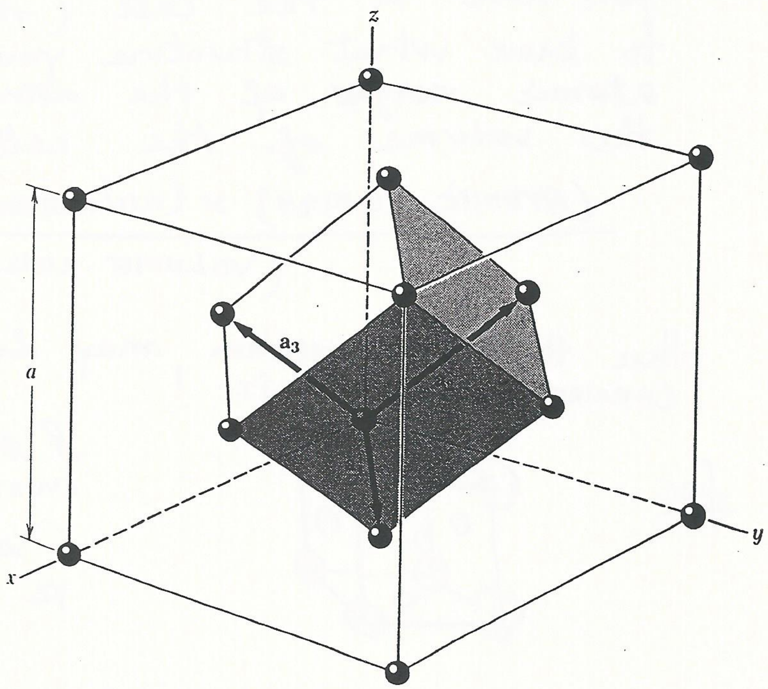


Figure 13 The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors a_1, a_2, a_3 connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

$$a_1 = \tfrac{1}{2}a(\hat{x} + \hat{y}) \ ; \qquad a_2 = \tfrac{1}{2}a(\hat{y} + \hat{z}) \ ; \qquad a_3 = \tfrac{1}{2}a(\hat{z} + \hat{x}) \ .$$

The angles between the axes are 60°. Here $\hat{x}$, $\hat{y}$, $\hat{z}$ are the Cartesian unit vectors.

#2)

(100) and 001 planes in the conventional fcc structure

Look at where the plane intercepts the $\vec{a}, \vec{b}$ & $\vec{c}$ axes :

(100 conventional) intercepts the $\vec{a}$ and $\vec{c}$ axes in $2|\vec{a}|$ and $2|\vec{c}|$ respectively. Therefore

$100_{conv.} \rightarrow 101$ primitive

3

Problem # 2 in Omar

Al → 26.98 amu
Fe → 55.85 amu

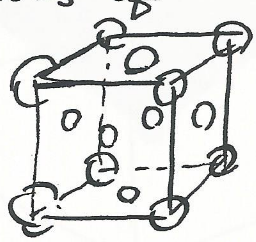
from table 1.2 →
Al → $a = 4.04$ Å (fcc)
Fe → $a = 2.86$ Å (bcc)

here you have to <u>count</u> how many atoms you have in the cell (that's why is important to know what structure you have). You know the atomic weight of the atoms, just calculate the volume of the cell.

$$\frac{(\text{ATOMIC WEIGH}) \times (\text{NUMBER ATOMS IN CELL})}{(\text{VOLUME CELL})} = \underline{\underline{\text{DENSITY}}}$$

here the only problem may be COUNTING & CONVERSIONS of UNITS!

fcc.



8 ATOMS @ CORNERS, BUT ONLY 1/8 BELONGS TO THIS CELL

6 ATOMS ON faces, BUT ONLY 1/2 BELONGS TO THIS CELL

$$\therefore \ \#_{\text{ATOMS IN CELL}} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = \underline{\underline{4}}$$

$$\text{DENSITY} = \frac{(26.98\ \text{AMU}) \times 4}{\underbrace{(4.04\text{Å})^3}_{\text{VOLUME CELL}}} = \underset{\text{CONVERSION!}}{\overset{\text{UNIT}}{\leadsto}} \leadsto \cong 2.7\ \text{g/cm}^3 \ \checkmark$$

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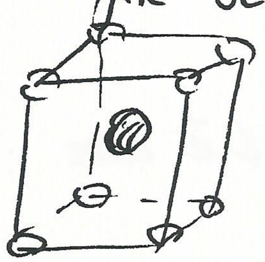
for Fe,

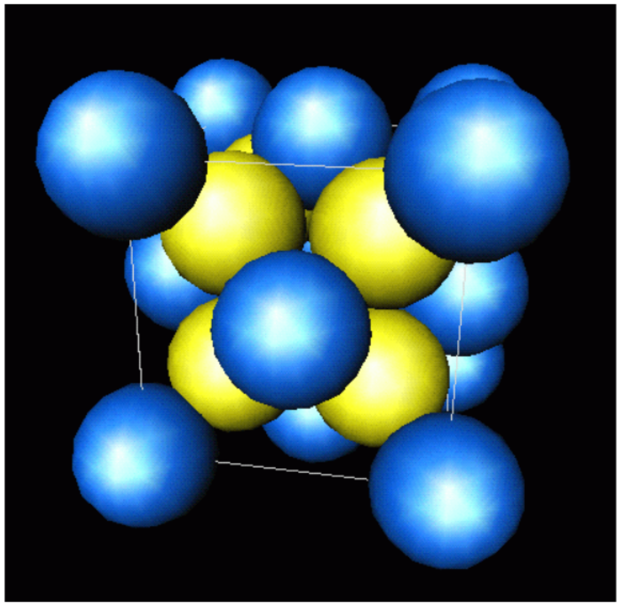


$$\#\ \text{ATOMS} = \frac{1}{8} \cdot 8 + 1 = \underline{\underline{2}}$$

$$\text{DENSITY} = \frac{(55.85\ \text{AMU}) \times 2}{(2.86\text{Å})^3} \underset{}{\overset{\text{CONVERSION!}}{\simeq}} \simeq 7.9\ \text{g/cm}^3$$

#4

Consider the crystal structure below, which is called fluorite. Each side of this unit cell has the same length, and all axes are orthogonal. There is no atom in the exact center of the unit cell.



(a) To which crystal system does this belong? Why? What is its Bravais lattice?

Bravais lattice is simple cubic (most obvious answer, with a more complex basis as shown below).

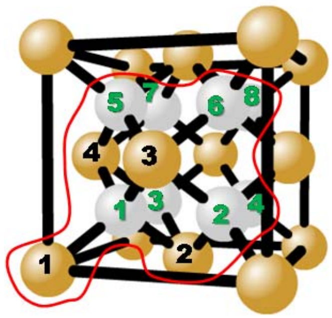
(b) What is the simplest formula for a compound with this crystal structure (with no common factor in the subscripts)? Indicate how you arrive at your answer.

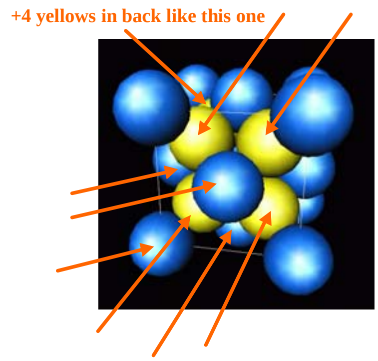
Blue atoms: (8 corners)x1/8 + (6 faces)x1/2 = 4

Yellow atoms: (8 interior to cell)x1 = 8

Therefore simplest formula is $(Blue)_4(Yellow)_8$ = $(Blue)_1(Yellow)_2$ with no common factors. In fact, this is the fluorite structure, with typical compound CaF_2.

(c) What is one possible atomic basis for this crystal? Indicate all atoms involved clearly, either on the color image or with a separate sketch. A good way to figure these out is to notice how many atoms of each type is in the unit cell, which we have done above. Then we must defined the coordinates of that no. for each, or 4 blue atoms and 8 yellow atoms, which give us one choice of the basis for simple cubic as follows, in two views:

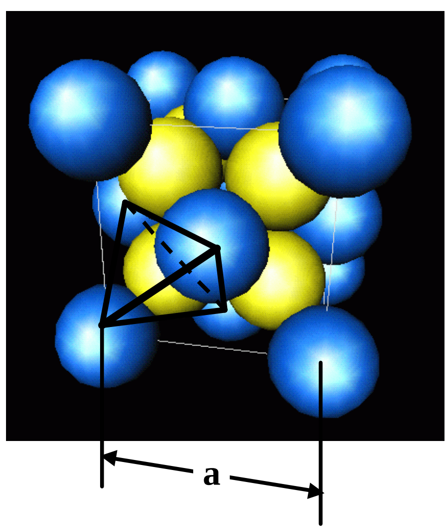




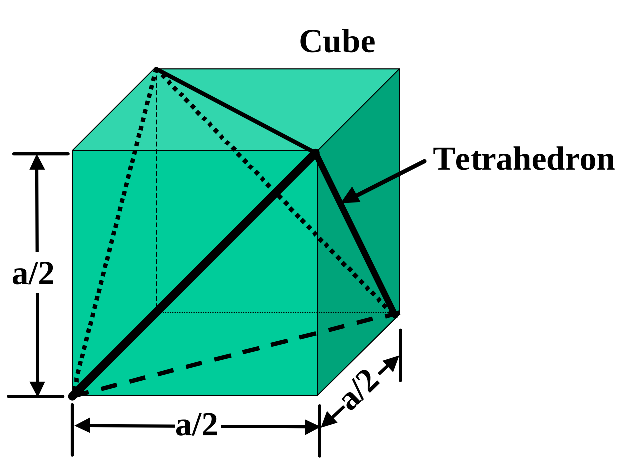
Note that this choice makes (Gold = Blue)$_4$(Gray = Yellow)$_8$ again, or with a 1:2 stoichometry.

(d) Show that the yellow atoms in fact are tetrahedrally bonded to the blue atoms, using one of them as an example.

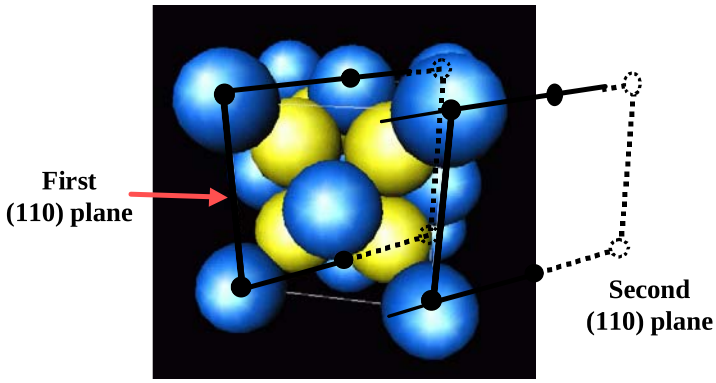
Can show in different ways, but could just note that the 5 atoms in the corner amount to something like the diamond lattice, with the yellow atom in the center of a tetrahedron of blue atoms:

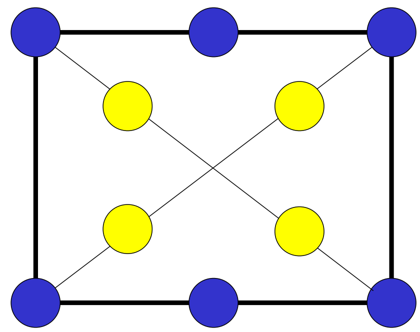


And there's a general argument to make, in that any cube can be used to form a tetrahedron, just by connecting lines along the diagonals of its faces. This is illustrated below for the cube of a/2 on a side in the lower left corner of the above image:



(e) Sketch the (110) plane for this crystal, and show where all blue and yellow atoms would be located on it.





(f) There is also a set of (110) planes, denoted {110}. Sketch the (110) plane lying just in front of the one in (e), and indicate the positions of the atoms on it. What is its perpendicular spacing with respect to its nearest-neighbor planes?

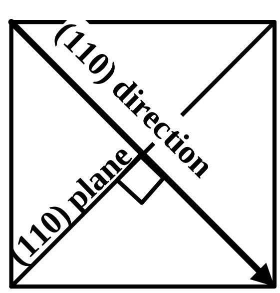
So the next plane of this type looks just like the first one, but passes through the two corner atoms on the front right side of the drawing just above. Because this is not a primitive unit cell, each set of planes does not pass through all atoms in the crystal.

For the distance between planes, it's easiest to use the formula from your book for distance between planes, which is finally half of face diagonal:

$$\mathbf{d}_{\mathbf{hk}\ell} = \frac{\mathbf{n}}{\left[\dfrac{\mathbf{h}^2}{\mathbf{a}^2} + \dfrac{\mathbf{k}^2}{\mathbf{b}^2} + \dfrac{\ell^2}{\mathbf{c}^2}\right]^{1/2}} = \frac{\mathbf{1}}{\left[\dfrac{\mathbf{1+1+0}}{\mathbf{a}^2}\right]^{1/2}} = \mathbf{a}/\sqrt{\mathbf{2}} = \sqrt{\mathbf{2}}\mathbf{a}/\mathbf{2} = \textit{half of face diagonal}$$

(g) Finally, show that the direction [110] is perpendicular to the {110} planes.

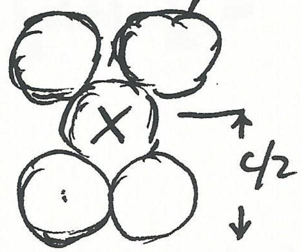
No need to do fancy mathematics here. Just look in from the top of the drawing above:



#5 / Problem #3 - Omar

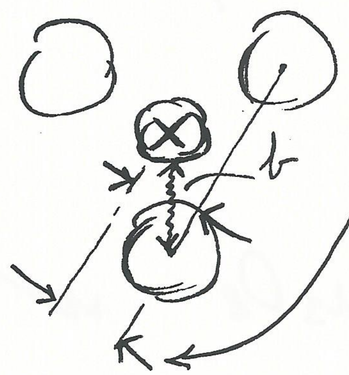
Look @ this figure (from Omar) from this side and from the top:

Side



the ⊗ ATOM is displaced (towards the page) by an amount which which is indicated by the arrows in the top view

Top

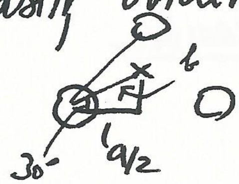


At this point we apply Pitagora's theorem:

side view: sphere in contact, means distance is a

need distance b

this is easily obtained by looking @ this triangle:



$$b = \frac{a/2}{\cos 30^\circ} \Rightarrow b = \frac{a}{2}\cdot\frac{2}{\sqrt{3}} = \frac{a}{\sqrt{3}}$$

$$\therefore\ b^2 + \left(\frac{c}{2}\right)^2 = a^2 \Rightarrow \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 = a^2 \quad \text{or}$$

$$-\frac{a^2}{3} + a^2 = \frac{2a^2}{3} = \frac{c^2}{4} \Rightarrow c^2 = \frac{8}{3}a^2 \Rightarrow c = \sqrt{\frac{8}{3}}\,a \quad \checkmark$$

6

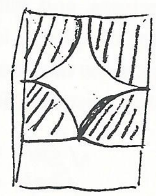
6. The face-centered cubic is the most dense and the simple cubic is the least dense of the three cubic Bravais lattices. The diamond structure is less dense than any of these. One measure of this is that the coordination numbers are: fcc, 12; bcc, 8; sc, 6; diamond, 4. Another is the following: Suppose identical solid spheres are distributed through space in such a way that their centers

lie on the points of each of these four structures, and spheres on neighboring points just touch, without overlapping. (Such an arrangement of spheres is called a close-packing arrangement.) Assuming that the spheres have unit density, show that the density of a set of close-packed spheres on each of the four structures (the "packing fraction") is:

$$
\begin{array}{ll}
\text{fcc:} & \sqrt{2}\pi/6 = 0.74 \\
\text{bcc:} & \sqrt{3}\pi/8 = 0.68 \\
\text{sc:} & \pi/6 = 0.52 \\
\text{diamond:} & \sqrt{3}\pi/16 = 0.34.
\end{array}
$$

SIMPLE CUBIC

TOP VIEW



if the cube has a side of LENGHT L,

Then $V_{cube} = L^3$, each sphere has a radius of $\frac{L}{2}$

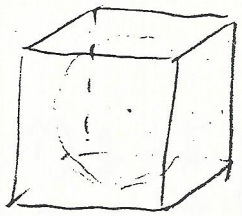
Therefore V OCCUPIED BY THE SPHERE INSIDE THE CUBE. IS !

$$(\#\ \text{SPHERES}) \times \left(\begin{array}{c}\text{PORTION of}\\ \text{SPHERE}\\ \text{INSIDE}\end{array}\right) \times \frac{4}{3}\pi\left(\frac{L}{2}\right)^3$$

$$\cancel{8} \times \frac{1}{\cancel{8}} \times \frac{4}{3}\pi \frac{L^3}{8} = \frac{\pi}{6} L^3$$

HENCE for S.C, $\frac{V_{SPHERE}}{L^3} = \frac{\pi}{6}$ 2/2

B.C.C.



$$V_{SPHERES} = \left(8\times\frac{1}{8}+1\right)\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}\right)^3,$$

since $R = \frac{\sqrt{3}}{4}$, i.e. FOURTH part of the BODY DIAGONAL

$$\frac{V_{SPHERES}}{V_{CUBE}} = \frac{8\pi}{3}\,\frac{3\sqrt{3}}{4\cdot4\cdot4} = \frac{\sqrt{3}\,\pi}{8}$$

1/2

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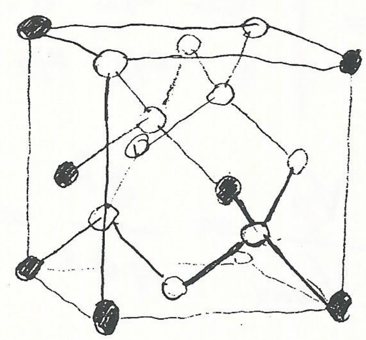
for THE DIAMOND STRUCTURE,



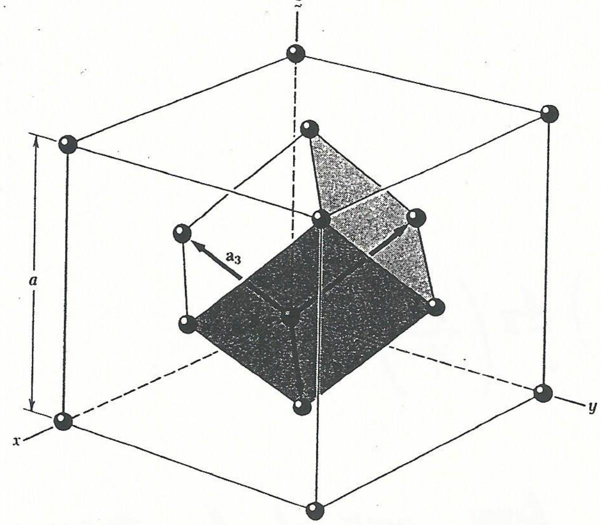
THE RADIUS of THE SPHERES MUST BE $\frac{\sqrt{3}}{8}$,

AND THE VOLUME of THE SPHERES WITHIN THE CUBE IS

$$\left(\underbrace{8\times\frac{1}{8}}_{\text{CORNERS}} + \underbrace{6\times\frac{1}{2}}_{\text{CENTRE of FACE}} + \underbrace{4\times1}_{\text{INSIDE THE CUBE}}\right)\frac{4}{3}\pi\left(\frac{\sqrt{3}}{8}\right)^3$$

#7

problem 7 in Omar



$$\begin{cases} \vec{a} = \frac{a}{2}(\hat{i}+\hat{j}) \\ \vec{b} = \frac{a}{2}(\hat{j}+\hat{k}) \\ \vec{c} = a/2(\hat{k}+\hat{i}) \end{cases}$$

$\vec{a}_1, \vec{a}_2, \vec{a}_3 \equiv$
$\vec{a}, \vec{b}, \vec{c}$ respectively

The volume of the parallelepiped spanned by the vectors $\vec{a}, \vec{b}$ and $\vec{c}$ is the volume of the primitive cell

$$V_p = (\vec{a}\times\vec{b})\cdot\vec{c} = (\vec{b}\times\vec{c})\cdot\vec{a} = (\vec{c}\times\vec{a})\cdot\vec{b}$$

invariant under cyclic permutations

$$\therefore \quad V_p = \begin{vmatrix} a/2 & 0 & a/2 \\ a/2 & a/2 & 0 \\ 0 & a/2 & a/2 \end{vmatrix} = \left(\frac{a}{2}\right)^3 \begin{vmatrix} 1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \end{vmatrix} = 2\cdot\frac{a^3}{8} = \frac{a^3}{4}$$

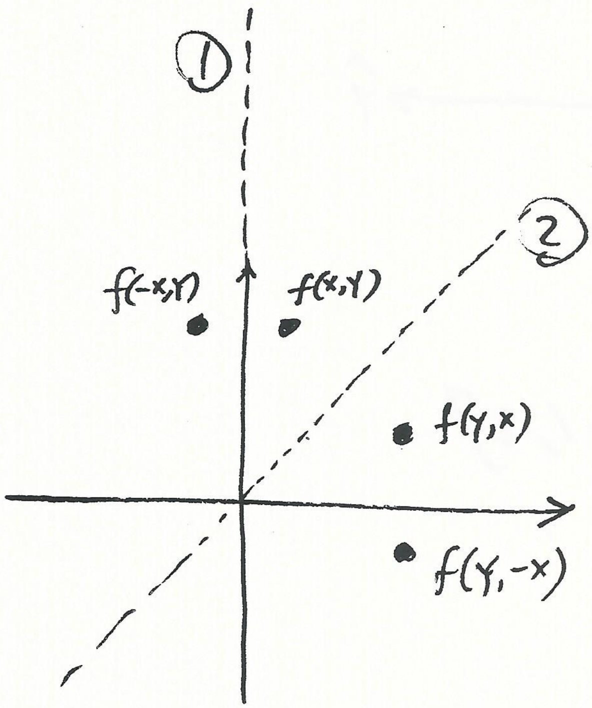
$$\therefore \quad \frac{V_p}{V_{conv}} = \frac{a^3}{4a^3} = 1/4$$

IMP: the volume of the PRIMITIVE CELL is 1/4 OF THE CONVENTIONAL ONE

from prob. # 3 $\rightarrow$ fcc conv. cell has 4 ATOMS
$\Rightarrow$ PRIMITIVE UNIT CELL MUST HAVE <u>1 ATOM</u>.

#8 – Problem 9 – Omar

Problem [8] - 9 in Omar. All symmetry operations mentioned here only act on 2 of the 3 coordinates of the object, leaving the one along the fourfold rotation axis unchanged. Then, one way to do this is to let the "object" be a function in 2D, say f(x,y). Then, if we for convenience take the first mirror plane to be along the y axis, it implies that f(x,y) = f(-x,y) for all x and y. Think about what the second rotation axis means in this sense, and then show by the same line of reasoning that the two together imply a clockwise rotation by 90 degrees as well.

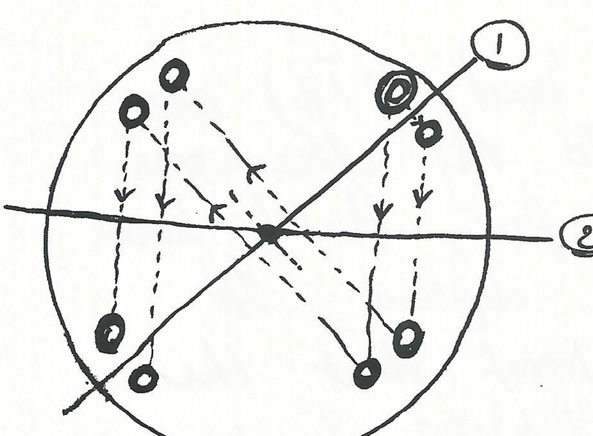


MIRRORS

1 : $f(x,y) \rightsquigarrow f(-x,y)$

2 : $f(x,y) \rightsquigarrow f(y,x)$

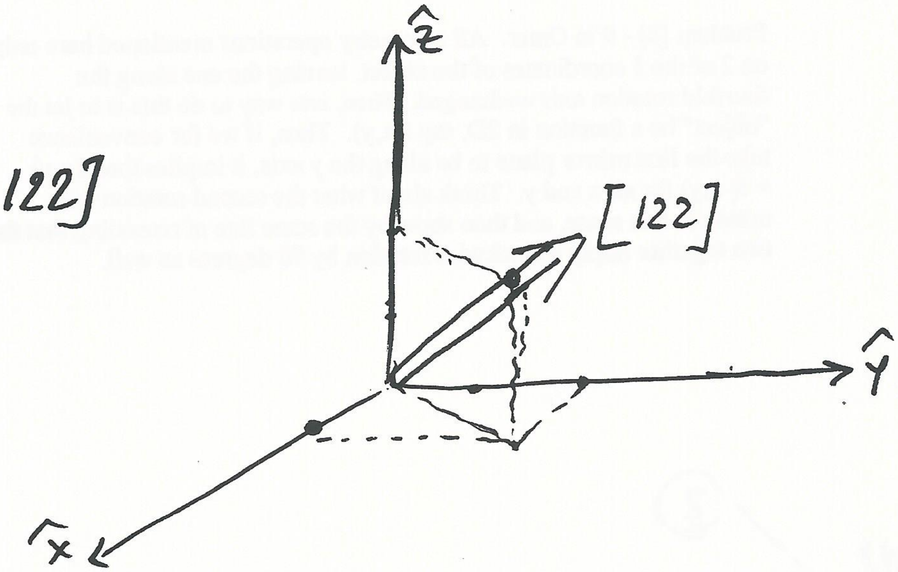
if you now mirror fold $f(-x,y)$ WRT 2 $\Rightarrow$ get $f(y,-x)$ which is exactly $f(x,y)$ rotated in the plane by $\pi/2$



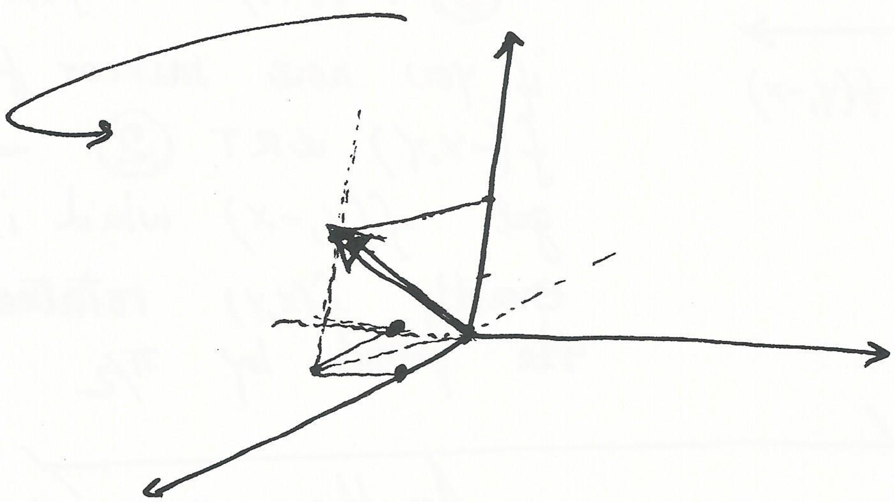
Another way would be to start with this object, and keep on mirror folding WRT 1 & 2 : you finally get this object, which has 1 & 2 as mirror planes and also reveals the 4-fold symmetry $\Rightarrow$ this group is called C_{4v}

#9 Problem 10 – Omar

[122]



[~~[illegible]~~] $[1\bar{1}2] = [1,-1,2]$



Now, the planes (122) and $(1\bar{1}2)$ are respectively **normal** to the directions $[122]$ and $[1\bar{1}2]$. In fact, that's how Miller indeces can be defined. It would be useful to proof that the plane (hkl) is $\perp$ to $[hkl]$ directions →

(hkl) means that

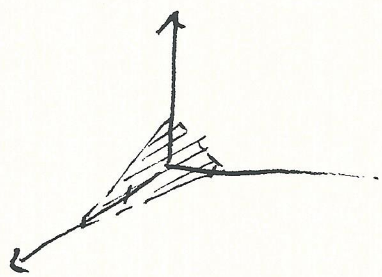
$$h:k:l = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3}$$

where x_1, x_2, x_3 is where the plane intersects the $\hat{x}, \hat{y}$ and $\hat{z}$ axes

$(122) \Rightarrow$

$$1:2:2 = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} \Rightarrow \frac{1}{2} : \frac{2}{2} : \frac{2}{2} = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} = \frac{1}{2} : 1 : 1$$

$x_1 = 2$, $x_2 = x_3 = 1$ intersections @ $(2,1,1)$

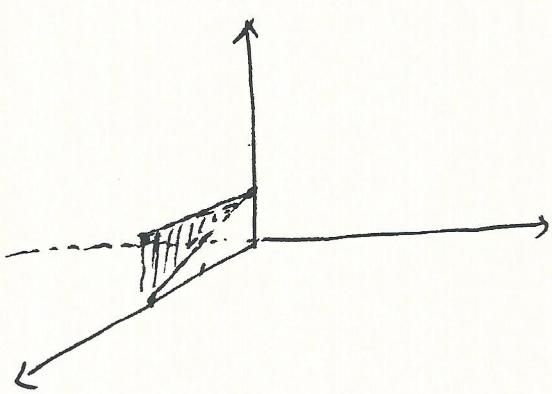


check, $\perp$ $[122]$

$(1\bar{1}2) = (1,-1,2)$

$$1 : -1 : 2 = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} \Rightarrow \frac{1}{2} : -\frac{1}{2} : 1 = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} \Rightarrow$$

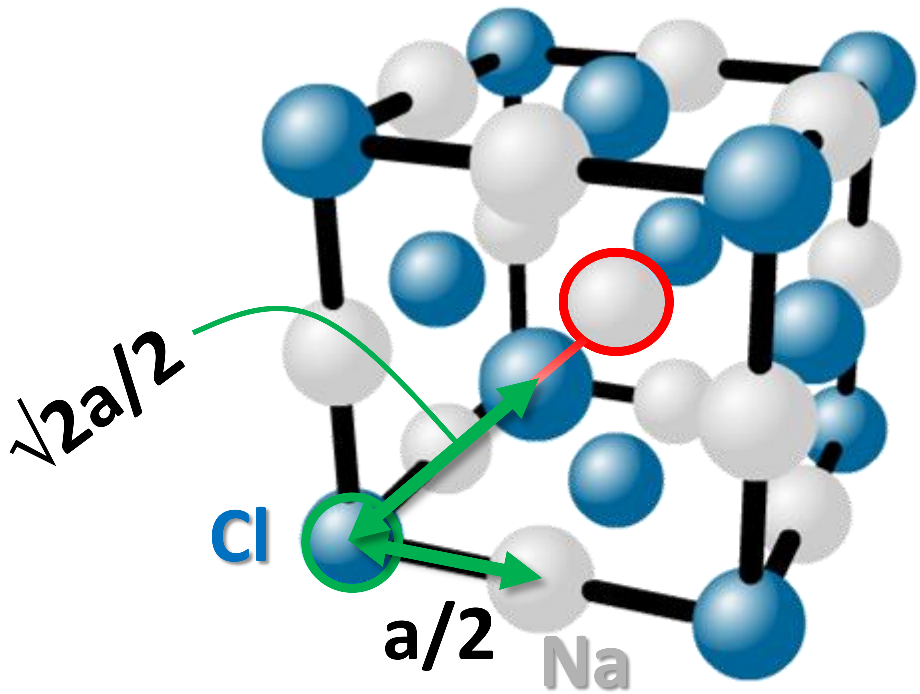
intersections @ $(2,-2,1)$



check, $\perp$ $[1\bar{1}2]$

[10]

NaCl



Ideal cation/anion ionic radii ratio from:

$r_{Na} + r_{Cl} = a/2 = 0.500a$

So $r_{Na} = 0.500a - r_{Cl}$

$2r_{Cl} = \sqrt{2}a/2 = -.7071a$

So

$r_{Cl} = -.7071a/2 = 0.3535a$

and

$r_{Na} = 0.5a – 0.3535a = 0.1465a$

Therefore, for the ideal NaCl structure

$r_{Na}/r_{Cl} = 0.414$

For real NaCL, the nos. are:

$r_{Na}/r_{Cl} = 1.16$ Å/1.67 Å = 0.694, so larger, but not so large that it ends in the CsCl structure, with ideal ratio of 0.732

[11] (a) $$\varphi_{\vec{k}}(\vec{r}) = C\sum_{Ai}^{N} e^{i\vec{k}\cdot\vec{R}_A} C_{Ai,\vec{k}}\,\varphi_{Ai}^{AO}(\vec{r}-\vec{R}_A)$$

$$\varphi_{\vec{k}}(\vec{r}+\vec{R}) = C\sum_{Ai}^{N} e^{i\vec{k}\cdot\vec{R}_A} C_{Ai,\vec{k}}\,\varphi_{Ai}^{AO}(\vec{r}-\vec{R}_A+\vec{R}) =$$

$$= C\sum_{Ai}^{N} e^{i\vec{k}\cdot\vec{R}_A} e^{-i\vec{k}\cdot(\vec{r}+\vec{R})} e^{i\vec{k}\cdot(\vec{r}+\vec{R})} C_{Ai,\vec{k}} \times$$

$$\times\, \varphi_{Ai}^{AO}(\vec{r}-\vec{R}_A+\vec{R})$$

$$= \underbrace{e^{i\vec{k}\cdot\vec{r}}}_{\uparrow\, e^{i\vec{k}\cdot\vec{R}}\,\uparrow \text{ phase factor due to translation}}\; C\,\underbrace{\sum_{Ai}^{N} e^{-i\vec{k}\cdot(\vec{r}-\vec{R}_A+\vec{R})} C_{Ai,\vec{k}}\,\varphi_{Ai}^{AO}(\vec{r}-\vec{R}_A+\vec{R})}_{\text{periodic}}$$

See sketch on next page

$$\varphi_{\vec{k}}(\vec{r}) = u(\vec{r})e^{i\vec{k}\cdot\vec{r}} \Rightarrow \varphi_{\vec{k}}(\vec{r}+\vec{R}) = u(\vec{r}+\vec{R})e^{i\vec{k}\cdot(\vec{r}+\vec{R})} \Rightarrow$$

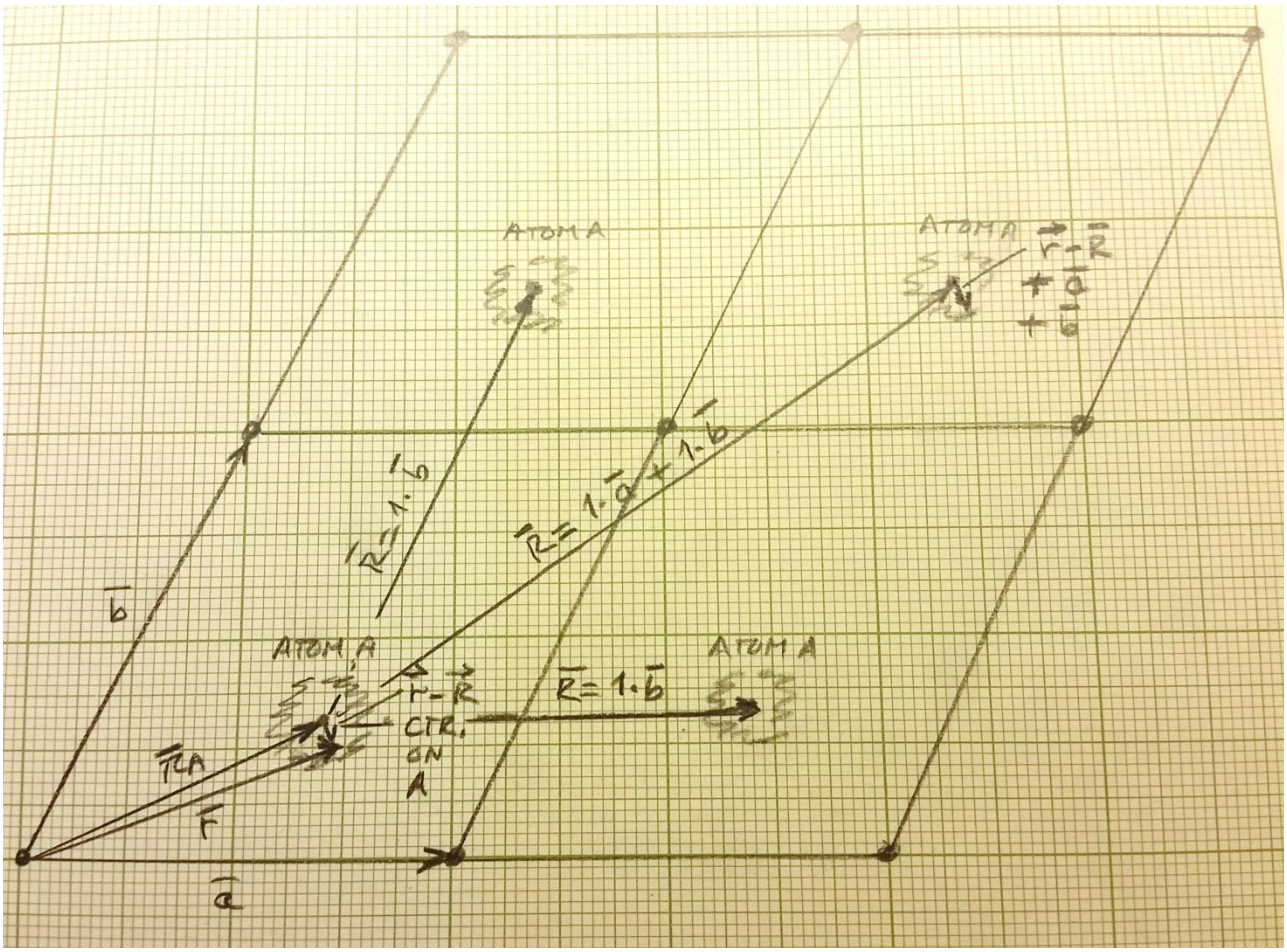
$$\Rightarrow \varphi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\, e^{i\vec{k}\cdot\vec{r}}\, u(\vec{r}) =$$

$$= e^{i\vec{k}\cdot\vec{R}}\,\varphi_{\vec{k}}(\vec{r})$$

Bloch Theorem

[11] (a)

Sketch to illustrate vectors and periodicity for tight-binding function



[11] (b)

$$\langle \varphi_{\vec{k}}(\vec{r}) | \varphi_{\vec{k}}(\vec{r}) \rangle = 1 =$$

$$= |C|^2 \langle \sum_{Ai} e^{i\vec{k}\cdot\vec{R}_A} C_{Ai,\vec{k}} \varphi^{AO}_{Ai}(\vec{r}-\vec{R}_A) | \sum_{Bj} e^{i\vec{k}\cdot\vec{R}_B} C_{Bj,\vec{k}} \varphi^{AO}_{Bj}(\vec{r}-\vec{R}_B) \rangle$$

$$= |C|^2 \sum_{ABij} C^*_{Ai,\vec{k}} C_{Bj,\vec{k}} e^{i\vec{k}\cdot(\vec{R}_B-\vec{R}_A)} \langle \varphi^{AO}_{Ai}(\vec{r}-\vec{R}_A) | \varphi^{AO}_{Bj}(\vec{r}-\vec{R}_B) \rangle$$

And, due to the zero overlap of the atomic orbitals on different atoms,

$$= |C|^2 \sum_{A}^{N} \sum_{ij} C^*_{Ai,\vec{k}} C_{Aj,\vec{k}} \langle \varphi^{AO}_{Ai} | \varphi^{AO}_{Aj} \rangle =$$

And, due to the orthonormality of the atomic orbitals on same atom,

$$= |C|^2 N \sum_{ij} C^*_{Ai,\vec{k}} C_{Aj,\vec{k}} \delta_{ij} = |C|^2 N \sum_{i} |C_{Ai,\vec{k}}|^2 = 1$$

$$|C|^2 = \frac{1}{N \sum_i |C_{Ai,\vec{k}}|^2}$$

[12]

a) it's a metal. There is no band gap at Fermi level. Some bands cross the Fermi level

b) # of spin-up bands greater than ↓ bands so this material is magnetic

c) Exchange interaction between electrons that tries to minimize the energy

d) Note further that the only bands that cross near the Fermi Energy are spin-up, so this is furthermore a special type of material we call a **half-metallic ferromagnet**; that is, it is only a metal in the magnetic spin-up electrons, in spin-down it is an insulator. Such materials are very interesting for use in magnetic logic devices, like the magnetic tunnel junction, in which changing magnetic order between two layers can drastically alter the resistance in a trilayer structure.