HOMEWORK ASSIGNMENT 1
SOLID STATE
DUE MAR 13, 2008

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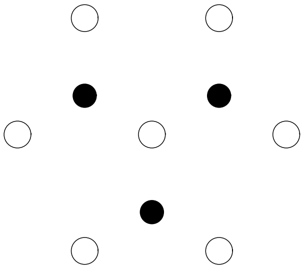
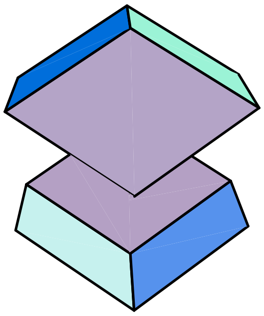
1a. *Prove the reciprocal lattice of a face centered cubic lattice is a body centered cubic lattice.* Take three primitive vectors of the FCC lattice, for instance $\boldsymbol{v}_1 = (1, 0, 0)$, $\boldsymbol{v}_2 = (\frac{1}{2}, \frac{1}{2}, 0)$ and $\boldsymbol{v}_3 = (0, \frac{1}{2}, \frac{1}{2})$. The reciprocal lattice is generated by the cross-products $\boldsymbol{w}_3 := \boldsymbol{v}_1 \times \boldsymbol{v}_2 = (0, 0, \frac{1}{2})$, $\boldsymbol{w}_1 := \boldsymbol{v}_2 \times \boldsymbol{v}_3 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $\boldsymbol{w}_2 := \boldsymbol{v}_3 \times \boldsymbol{v}_1 = (0, \frac{1}{2}, -\frac{1}{2})$ (each multiplied by $2\pi/det(\boldsymbol{v}_1, \boldsymbol{v}_2, \boldsymbol{v}_3) = 8\pi$, but this constant factor does not change the type of lattice. Adding $\boldsymbol{w}_3$ to $\boldsymbol{w}_2$ and doubling all three vectors we get $(0, 0, 1)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and $(0, 1, 0)$, which we recognize as the generators of a BCC lattice.

1b. *Sketch the Wigner–Seitz primitive cell for HCP crystal structure.* To answer this we take a lattice point at the origin and its 12 nearest neighbors: six are on the xy-plane forming a hexagon, three are on the next plane above forming a triangle, and three more on the plane below, directly underneath the three above. This is the view down the z-axis:

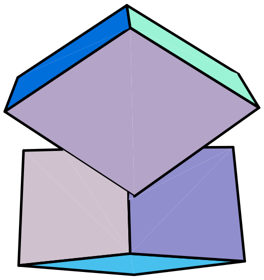


To construct the Wigner–Seitz primitive cell, then, we can start with a hexagonal prism around the z-axis. We then make three cuts above the xy-plane, and the three corresponding cuts below, mirroring the roof. The vertices of the Wigner–Seitz cell are always equidistant from (at least) four lattice points, so we can think of the vertices of the roof as midpoints of tetrahedral holes, squeezed between two lattice layers. Since two out of three layers are shared between the HCP and the FCC, the roof is the same as for the FCC Wigner–Seitz cell, namely, three diamonds having a $1 : \sqrt{2}$ diagonal ratio. The difference is that in the FCC the "antiroof" at the bottom is rotated 60 degrees, but here it is aligned with the roof:

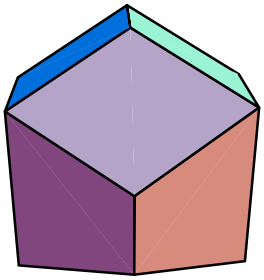
FCC WS cell without side walls



HCP WS cell without side walls



complete WS cell



2. *For a cubic lattice with lattice constant a, prove* $1/d_{hkl}^2 = (h^2 + k^2 + l^2)/a^2$. *Calculate the d values for* (110), (102), (121) *planes in a cubic lattice with* $a = 5$ Å.

First suppose that $a = 1$. The plane P intersects the coordinate axes at $(h, 0, 0)$, $(0, k, 0)$, $(0, 0, l)$, and so has equation $x/h + y/k + z/l = 1$ and normal vector $(1/h, 1/k, 1/l)$. Since h, k, l don't all share a common factor, the exists integers n_1, n_2, n_3 such that $n_1 h + n_2 k + n_3 l = 1$. Translating the plane P by the vector (n_1, n_2, n_3) gives a lattice plane whose distance to P is minimal. Projecting (n_1, n_2, n_3) onto the normal vector $(1/h, 1/k, 1/l)$ we obtain a vector of length $1/\sqrt{h^2 + k^2 + l^2}$, which is by construction perpendicular to P (so its length is the interplane distance d_{hkl}).

Now scale everything by a factor of a to conclude that the interplane distance in the general case is $a/\sqrt{h^2 + k^2 + l^2}$.

The d values for the selected planes are 5Ådivided by $\sqrt{2}$, $\sqrt{5}$ and $\sqrt{10}$, respectively, that is, 3.53Å, 2.27Å, and 1.58Å, respectively.

3a. *Powder specimens of three monatomic cubic crystals are analyzed with a Debye-Scherrer camera. The approximate positions of the first four diffraction rings in each case are:*

A: 42.2, 49.2, 72.0, 87.3 degrees
B: 28.8, 41.0, 50.8, 59.6 degrees
C: 42.8, 73.2, 89.0, 115 degrees

Identify the crystal structures of A, B and C (FCC, BCC, diamond).

First we calculate $\sin^2(\psi/2)$, since $h^2 + k^2 + l^2$ is proportional to that quantity.

A: 0.129, 0.173, 0.345, 0.476; proportional to 3, 4, 8, 11.
B: 0.062, 0.123, 0.184, 0.247; proportional to 1, 2, 3, 4 (or r, $2r$, $3r$, $4r$).
C: 0.133, 0.355, 0.491, 0.711; proportional to 3, 8, 11, 16.

The FCC structure requires either all even or all odd, so $(h, k, l) = (1, 1, 1) \rightarrow h^2 + k^2 + l^2 = l$, (2,0,0) → 4, (2,2,2) → 8, (3,1,1) → 11. Hence **A is FCC**.

The BCC requires $h + k + l$ even, so (1,1,0) → 2, (2,0,0) → 4, (2,1,1) → 6, (2,2,0) → 8, (3,1,1) → 10. This matches B with $r = 2$. Hence **B is BCC**.

The diamond structure requires either h, k, l to be all odd or for $h + k + l$ to be 4 times an integer (1,1,1) → 3, (2,2,0) → 8, (3,1,1) → 11, (4,0,0) → 16. Hence **C is the diamond structure**.

3b. *If the wavelength of the incident X-ray beam is 1.5*Å, *what is the length of the side of the conventional cubic cell in each case?*

We use the value $\lambda = 1.5$Å in the expression

$$\lambda = 2d \sin\frac{\phi}{2} = 2\frac{a}{\sqrt{j^2 + k^2 + l^2}} \sin\frac{\phi}{2}.$$

Thus, taking the first signal in each case, we have for A

$$1.5\text{Å} = 2 \times 0.360 \times \frac{a}{\sqrt{3}} \Rightarrow a = 3.61\text{Å}.$$

For B:

$$1.5\text{Å} = 2 \times 0.249 \times \frac{a}{\sqrt{2}} \Rightarrow a = 4.26\text{Å}.$$

For C:

$$1.5\text{Å} = 2 \times 0.365 \times \frac{a}{\sqrt{3}} \Rightarrow a = 3.56\text{Å}.$$

3c. *If the diamond structure were replaced by a zinc blende structure with a cubic unit cell of the same side, at what angles would the first four rings now occur?*

The difference between the zinc blende structure and the diamond structure is that in the former, half the sites are filled with one atom and half with another. Thus the total structure factor comes from two *not necessarily equal* FCC structure factors:

$$S_{\text{total}}(hkl) = S_{\text{fcc}}(hkl)\big(A + B\exp(i/2)(h+k+l)\big).$$

This means that only the constraint that $h+k+l$ to be 4 times an integer becomes simply $h+k+l$ to be an even integer. The other possibility, h, k, l to be all odd, remains the same. Thus we have (1,1,1) → 3, (2,0,0) → 4, (2,2,0) → 8, (3,1,1) → 11, (2,2,2) → 12. Hence the first four rings occur at when $\sin^2(\psi/2) = 0.133, 0.177, 0.355, 0.491$, or $\psi = 42.8, 49.7, 73.2, 89.0$.

4a. *The common building blocks for most high temperature superconductors are copper oxide layers. Assume the distance between copper atoms (filled circles) is a. For simplicity let us also assume that in the third dimension these* CuO_2 *layers are simply stacked with spacing c, and there are no other atoms in the crystal. In first approximation the layers have fourfold symmetry; the crystal is tetragonal. Sketch the Bravais lattice and indicate a possible set of primitive vectors for this crystal: what is the unit cell, and what is the basis? What is its reciprocal lattice?*

The Bravais lattice is a stretched version of simple cubic lattice (stretched in the z direction by a factor c/a, where "stretched" is to be interpreted as "compressed" if $c < a$). A possible set of primitive vectors is given by $\boldsymbol{v}_1 = (a, 0, 0)$, $\boldsymbol{v}_2 = (0, a, 0)$, $\boldsymbol{v}_3 = (0, 0, c)$. The unit cell is the parallelepiped whose edges are these three vectors. The basis is made up of one Cu atom at $(0, 0, 0)$ and two O atoms at $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$.

Reciprocal lattice: recall that the reciprocal lattice of a simple cubic lattice of size a is also simple cubic, of size $2\pi/a$. In the case of a tetragonal lattice, the correspondence is also simple, as can be seen from the equations

$$\boldsymbol{w}_1 = 2\pi\frac{\boldsymbol{v}_2 \times \boldsymbol{v}_3}{\boldsymbol{v}_1 \cdot (\boldsymbol{v}_2 \times \boldsymbol{v}_3)}$$

and its counterparts for $\boldsymbol{w}_2$ and $\boldsymbol{w}_3$. That is, the reciprocal lattice is also tetragonal, with generating vectors $\boldsymbol{w}_1 = (2\pi/a, 0, 0)$, $\boldsymbol{w}_2 = (0, 2\pi/a, 0)$, $\boldsymbol{w}_3 = (0, 0, 2\pi/c)$.

4b. *In* La_2CuO_4 *one discovers, at closer inspection, that* CuO_2 *lattice is actually not flat, but that the oxygen atoms are moved in a small amount out of the planes ("up" and "down") in an alternating fashion. What is the primitive cell and lattice spacing for this crystal?*

Now we can take as primitive vectors $\boldsymbol{v}_1 = (a, a, 0)$, $\boldsymbol{v}_2 = (0, -a, 0)$, $\boldsymbol{v}_3 = (0, 0, c)$, where the coordinate axes are still directed as before. The system is still tetragonal, but the size of the primitive cell in the "horizontal" directions is $\sqrt{a}$.

5a. *Fleming and coworkers describe the structure of various alkaline metal-doped* C_{60} *compounds in Fleming et al. Nature,* **352***, 701 (1991). In Figure 2a of the paper and fcc structure of* A_3C_{60} *is indicated. In the usual representation of the fcc structure the* C_{60} *molecules would be placed on the corners, e.g. at positions* $(1, 0, 0)$, $(0, 1, 0)$, $\ldots$, $(1, 1, 1)$*, and the face centers of the unit cell. The figure certainly does not look like a cube; what is a possible choice for the conventional* (x, y, z) *coordinates of the* C_{60} *molecule in the middle of Figure 2a from the paper?*

The face of the standard FCC cube is a vertical diagonal plane of the box shown in the figure. The conventional coordinates of the ball in the center would be $(0, \frac{1}{2}, \frac{1}{2})$, for instance.

5b. *Assume you perform a powder X-ray diffraction measurement on a Rb doped* C_{60} *material with* $\lambda = 0.9$Å *X-rays. You want to compare your results to Fleming's to see what stoichiometry your compound is. What are the positions* (2θ*, in degrees) of the first five diffraction peaks for the three observed structures (doping = 3, 4 and 6 in table 2 of the paper).*

[Out of time.]

6. *Derive a simplified structure factor master equation for the perovskite structure of* $SrTiO_3$*. Atomic coordinates are Sr:* $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$*; Ti:* $(0, 0, 0)$*; O:* $(\frac{1}{2}, 0, 0)$*;* $(0, \frac{1}{2}, 0)$*;* $(0, 0, \frac{1}{2})$.

The underlying Bravais lattice is simple cubic. We must add the contributions of each of the 5 elements of the basis:

$$S_{\boldsymbol{K}} = S_{\mathrm{Sr}} + S_{\mathrm{Ti}}\, e^{i\pi(n_1+n_2+n_3)} + S_{\mathrm{O}}(e^{i\pi n_1} + e^{i\pi n_2} + e^{i\pi n_3}).$$

The second term partially cancels out the first when $n_1 + n_2 + n_3$ is odd; they reinforce each other when $n_1 + n_2 + n_3$ is even. The multiplier for S_{O} can be $-3, -1, 1, 3$.

7a. *An ammonium halide, NH_4X, has the CsCl structure at room temperature.* $a = 4.059$Å, *and transforms to the NaCl structure at* $138 \circ C$, $a = 6.867$Å. *The density of the room temperature polymorph is* 2.431 *g/cm^3. Identify the substance.*

The volume of the unit cell being $V = 4.059^3$Å $= 66.87 \times 10^{-24}\,\mathrm{cm}^3$ and the density $\rho = 2.431\mathrm{g/cm}^3$, we see that the molar mass is $V\rho$ times Avogadro's number, or 97.90, so the halogen is bromine.

7b. *Calculate the percentage difference in molar volume between the two polymorphs, ignoring thermal expansion effects.*

The molar volume of the high-temperature polymorph is $\frac{1}{4}6.867^3$ Å $= 80.95$, which is 21% higher than the low-temperature one.

7c. *Assuming an effective radius of* 1.50Å *for the spherical $NH_4{}^+$ ion and that anions and cations are in contact, calculate the radius of the anion in each structure. Are the anions in contact in the two structures?*

In the CsCl structure the cation and anion are in contact along a diagonal of the cube, of half-length 3.515Å; thus the anion has a radius of 2.01Å. The anions are very close to touching (their centers are 4.06Å apart).

In the NaCl structure the cation and anion are in contact along an edge of the cube, whose half-length is 3.433Å; thus we must assing the anion a radius of 1.93Å. This time the anions are far from touching (centers 4.85Å apart).

8. *Starting with a cubic close packed array of anions, what structure types are generated by (a) filling all the tetrahedral sites with cations; (b) filling one half of the tetrahedral sites, e.g. the T_+ sites, with cations; (c) filling all the octahedral sites with cations; (d) filling alternate layers of octahedral sites with cations. Give an example for each of these structures.*

(a) There are 2 cations per anion; this is the antifluorite structure, found in $\mathrm{Li_2O}$. (The fluorite structure is the same but with cations and anions interchanged.)

(b) This is the zinc blende structure (one the polymorphs of ZnS).

(c) This is the rock salt structure (NaCl).

(d) The prototype here is cadmium chloride, $\mathrm{CdCl_2}$.

9. *Repeat the above question for a hexagonal close packed array of anions.*

(a) I wasn't able to find an example of this structure.

(b) This is the wurtzite structure (the other polymorph of ZnS).

(c) This is the nickel arsenide structure (NiSb).

(d) This structure is represented by cadmium iodide, $\mathrm{CdI_2}$.