Homework 3 Solutions

2. (a). Referring to the figure on the right, we see the given 2D lattice is not a Bravais lattice because it violates the requirement that the arrangement of lattice points look the same from all lattice sites. To prove this, look along the vectors designated by (1) and (2) in the figure. A lattice point is observed in both cases, but the distance is different. We see, however, that it is a lattice with a two-atom basis. The fundamental Bravais type is the triangular lattice, and there is one "satellite" atom per lattice point, designated by the small black dots in the Figure.

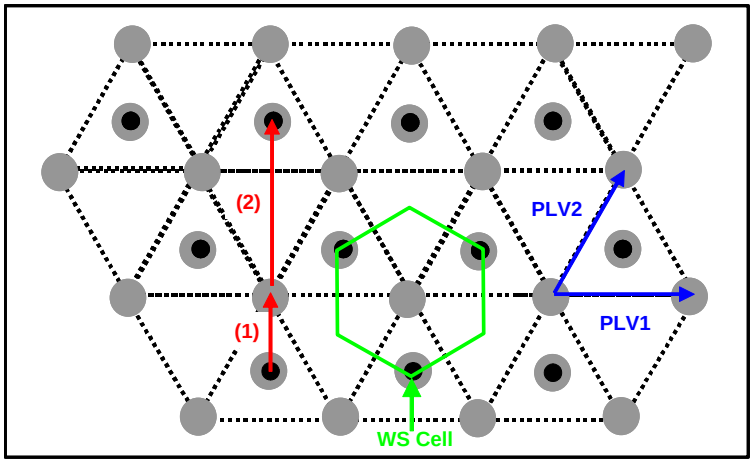


Figure for Problem 2

(b). Because the triangular lattice is two-dimensional, there are only two primitive lattice vectors, but a limitless number of possible choices. The pair having minimum length and minimum included angle is shown in the Figure as PLV1 and PLV2. The associated Wigner –Seitz cell is also shown, its form being a 2D equilateral hexagon.

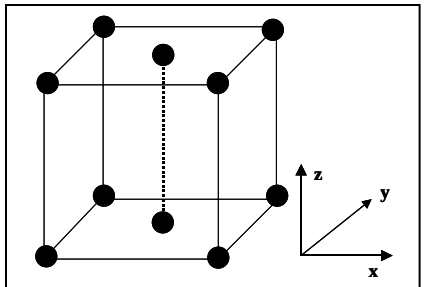
3. The NaCl crystal can be considered as two interpenetrating fcc lattices with the Na atoms on one fcc lattice and the Cl atoms on the other. For any fcc lattice the volume of the primitive cell is $\left(\frac{1}{4}\right) a^3 \Rightarrow$ atoms/volume = $4/a^3$, where a is the conventional cubic lattice constant. So overall crystal density $\rho = \frac{M}{V} = M_1 \frac{4}{a^3} + M_2 \frac{4}{a^3}$, where $M_1 = mass\ of\ Na\ atoms = 22.99 \times m_p = 3.85 \times 10^{-26}\ KG$ and m_p is the proton rest mass (1.67×10^{-27} KG). Similarly, $M_2 = mass\ of\ Cl\ atom = 35.45 \times m_p = 5.93 \times 10^{-25}$ KG. Finally, because the NaCl has a = 5.63 Ang, we get $\rho = 863 + 1439 = 2.19 \times 10^3$ KG/m3 at 300 K.

4. (a) By "ideal" hcp stacking, we mean the stacking of triangular lattices in a cannonball fashion. Since the cannonballs are identical, the center-to-center spacing between balls in the triangular lattice should be the same as the center-to-center nearest-neighbor spacing between layers. This means that the three points of a triangular unit cell and the point from the layer above them form the corners of a four-sided tetrahedron as shown in the figure to the right. The length of the hcp c axis is then half the height of the tetrahedron, and a is the length along the base. From trigonometry the distance d between a corner of the

base and the center of the base is given by a/(2d) = cos(30°). By the Pythagorean theorem, $(c/2)^2 = a^2 - d^2 = a^2 - a^2/(2\cos 30^o)^2$, or $c = 2a(1 - 1/3)^{1/2}$ or $c = (8/3)^{1/2}\, a$.

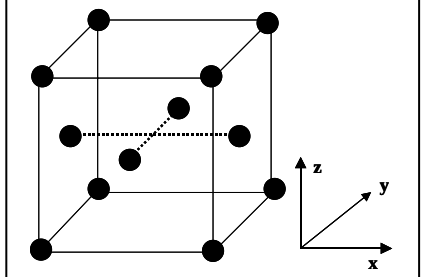
(b) The hcp lattice can be thought of as a simple hexagonal lattice with a single-atom basis (i.e., two atoms per primitive unit cell). So the density is given by 2/v where v is the primitive cell volume given by cA, where A is the area of the base of the tetrahedron. From trigonometry, $A = (3)^{1/2}a^2/2$ so the density is $\rho_{hcp} = 4/[(3)^{1/2}a^2c] \equiv (2)^{1/2}/[(a_{hcp})^3]$. For the three common cubic lattices, simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc), we have densities $\rho_{sc} = 1/(a)^3$, $\rho_{bcc} = 2/a^3$ and $\rho_{fcc} = 4/a^3$ where a is the conventional cubic lattice constant. Assuming the densities stay fixed, we derive the following relationships: $a_{hcp} = [(2)^{1/2}]^{1/3} \cdot a_{sc} = [(2)^{1/2}/2]^{1/3} \cdot a_{bcc} = [(2)^{1/2}/4]^{1/3} \cdot a_{fcc}$

5. (a) Base-centered cubic (simple cubic plus one atom at the center of the top and bottom faces) is shown in the sketch at right. The arrangements of points around each lattice site is identical and the orientation is the same from point to point. So, yes, it is a Bravais lattice. Three primitive lattice vectors are: $\mathbf{a}_1 = (a/2)(\mathbf{x} + \mathbf{y})$, $\mathbf{a}_2 = (a/2)(\mathbf{x}+\mathbf{y})$, and $\mathbf{a}_3 = a\,\mathbf{z}$.



Base-centered cubic lattice

(b) Side-centered cubic (simple cubic plus one atom at the center of each of the fours sides) is shown in the sketch at right. This lattice has an orientation problem. Unlike the base-centered lattice, an atom in one of the side facets does not have the same environment as one in the bottom or top facets unless a rotation operation is also performed. So, no, it is not a Bravais lattice.



Side-centered cubic lattice

6. (a) We write the total potential energy of the linear chain in terms of the total number of atoms (ions) 2N:

$$U(R) = N\left(\frac{ZA}{R^n} - \frac{\alpha q^2}{4\pi\varepsilon_0 R}\right) = N\left(\frac{2A}{R^n} - \frac{2\ln 2\, q^2}{4\pi\varepsilon_0 R}\right) = 2N\left(\frac{A}{R^n} - \frac{(\ln 2)q^2}{4\pi\varepsilon_0 R}\right)$$

for $Z = 2$, and for $\alpha = 2\ln 2$ – the Madelung constant for the chain. To find the equilibrium position R_0, we differentiate with respect to R and set this to zero:

$$\left.\frac{dU}{dR}\right|_{R_0} = 0 = 2N\left(\frac{-nA}{R^{n+1}} + \frac{(\ln 2)q^2}{4\pi\varepsilon_0 R^2}\right)\Bigg|_{R_0} \Rightarrow R_0^{-n} = \frac{q^2 \ln 2}{nAR_0 4\pi\varepsilon_0}$$

Substitution back into U(R) yields $U(R_0) = \frac{2N\ln 2 \cdot q^2}{4\pi\varepsilon_0 R_0}\left(\frac{1}{n} - 1\right)$ which becomes $\frac{-N\ln 2 \cdot q^2}{4\pi\varepsilon_0 R_0}\left(1 - \frac{1}{n}\right)$

if N is the number of atomic ions rather than 2N.

(b) If the linear chain is compressed so that $R_0 \rightarrow R_0(1 - \delta)$ and δ is small, we can Taylor expand

$$f(x) = f(x_0) + \left.\frac{df}{dx}\right|_{x=x_0}(x - x_0) + \frac{1}{2}\frac{d^2 f}{dx^2}(x - x_0)^2$$

with the mapping $x \rightarrow R_0(1-\delta)$, , $x_0 \rightarrow R_0$, and $f \rightarrow U(r)$.

We get $U\left[R_0(1-\delta)\right] - U(R_0) \equiv \Delta U = \frac{1}{2}\left.\frac{d^2U}{dR^2}\right|_{R=R_0}(R_0\delta)^2$ with $\left.\frac{d^2U}{dR^2}\right|_{R=R_0} = \frac{2N\ln 2q^2}{4\pi\varepsilon_0 R_0^3}(n-1)$

So the mechanical work per unit length is, $\Delta U' \equiv \Delta U/(2NR_0) = \frac{1}{2}C\delta^2/R_0$ with $C = \frac{\ln 2 \cdot q^2}{4\pi\varepsilon_0 R_0}(n-1)$.

7. (a)To get U_0 in terms of α, r, and R_0, we use fact that in equilibrium

$$dU/dR|_{R0} = 0 \Rightarrow \left|\frac{N}{2}\left[\frac{-z\lambda}{\rho}e^{-R/\rho} + \frac{\alpha q^2}{4\pi\varepsilon_0 R^2}\right]\right|_{R=R_0} = 0 \text{ or } z\lambda e^{-R_0/\rho} = \frac{\alpha q^2 \rho}{4\pi\varepsilon_0 R_0^2}$$

So that, $U_0 = \frac{1}{2}N\left[\frac{\alpha q^2\rho}{4\pi\varepsilon_0 R_0^2} - \frac{\alpha q^2}{4\pi\varepsilon_0 R_0}\right] = \frac{N\alpha q^2}{8\pi\varepsilon_0 R_0}\left[\frac{\rho}{R_0} - 1\right]$

(b) For NaCl structure R_0 = nearest neighbor distance = a/2.

So $\rho = \left[\frac{4\pi\varepsilon_0 a U_0}{N\alpha q^2} + 1\right]\frac{a}{2} = (-0.87+1)\frac{a}{2}$ = 0.2726 Angstrom

Where the last step uses a = 4.215 Ang, U_0/N = -5.20 eV/N, α = 1.7476, and q = e

(c) We re-arrange the Madelung expression to get

$$\frac{2U}{N} + \frac{\alpha q^2}{4\pi\varepsilon_0 R_0} = z\lambda\exp(-R_0/\rho) \text{ or } \lambda = \frac{\exp(a/2\rho)}{z}\left[\frac{2U}{N} + \frac{\alpha q^2}{2\pi\varepsilon_0 a}\right]$$

which for z = 6 becomes $\lambda = (2279/6)[-10.4 + 11.94]$ eV

or λ = 584.9 eV = 9.371×10^{-17} J

(d) In zincblende structure, we expect ρ and λ to stay the same since they depend only on Mg and O pair. But α goes to 1.6381 because of the lattice change.

So, given that ρ = 0.2726 and R_0 = 1.959 Ang, $\frac{U_0}{N} = \frac{\alpha q^2}{8\pi\varepsilon_0 R_0}\left[\frac{\rho}{R_0} - 1\right]$ = - 5.18 eV

8. (a) Energy per ion $U' = \frac{1}{2}\left[\left[z\lambda\exp(-R/\delta\right] - \frac{\alpha q^2}{4\pi\varepsilon_0 R}\right]$

We want to write this as $U' = U_0' + A(\delta R)^2 + B(\delta R)^3$ where

$\delta R = \delta R - R_0$. This invites a Taylor expansion about the equilibrium point:

$$U' = U'\Big|_{R=R_0} + \frac{dU'}{dR}\Big|_{R=R_0}\left(R-R_0\right) + \frac{1}{2}\frac{d^2U'}{dR^2}\Big|_{R=R_0}\left(R-R_0\right)^2 + \frac{1}{6}\frac{d^2U'}{dR^3}\Big|_{R=R_0}\left(R-R_0\right)^3 + \ldots$$

So,

$$A = \frac{1}{2}\frac{d^2U'}{dR^2}\Big|_{R=R_0},\ B = \frac{1}{6}\frac{d^3u'}{dR^3}\Big|_{R=R_0}$$

$$\frac{dU'}{dR} = \frac{1}{2}\left[\frac{-z\lambda}{\rho}\exp\left(\frac{-R}{\rho}\right) + \frac{\alpha q^2}{4\pi\varepsilon_0 R^2}\right]$$

$$\frac{d^2U'}{dR^2} = \frac{1}{2}\left[\frac{z\lambda}{\rho}\exp\left(\frac{-R}{\rho}\right) - \frac{\alpha q^2}{2\pi\varepsilon_0 R^3}\right]$$

$$\frac{d^3U'}{dR^3} = \frac{1}{2}\left[\frac{-z\lambda}{\rho^3}\exp\left(\frac{-R}{\rho}\right) + \frac{3\alpha q^2}{2\pi\varepsilon_0 R^4}\right]$$

From equilibrium condition

$$\frac{dU'}{dR}\Big|_{R=R_0} = 0 \Rightarrow \frac{z\lambda}{\rho}\exp\left(\frac{-R_0}{\rho}\right) = \frac{\alpha q^2}{4\pi\varepsilon_0 {R_0}^2}$$

So in terms of R_0, ρ, and α, we have:

$$A = \frac{1}{2}\frac{d^2U'}{dR^2}\Big|_{R=R_0} = \frac{1}{4}\left[\frac{\alpha q^2}{4\pi\varepsilon_0 {R_0}^2\rho} - \frac{\alpha q^2}{2\pi\varepsilon_0 {R_0}^3}\right] = \frac{\alpha q^2}{16\pi\varepsilon_0 {R_0}^2}\left[\frac{1}{\rho} - \frac{2}{R_0}\right]$$

$$B = \frac{1}{6}\frac{d^3U'}{dR^3}\Big|_{R=R_0} = \frac{1}{12}\left[\frac{-\alpha q^2}{4\pi\varepsilon_0 {R_0}^2\rho^2} + \frac{3\alpha q^2}{2\pi\varepsilon_0 {R_0}^4}\right] = \frac{\alpha q^2}{16\pi\varepsilon_0 {R_0}^2}\left[\frac{-1}{3\rho^2} + \frac{2}{{R_0}^2}\right]$$

(b) For sodium chloride R_0 = 2.82 Å, ρ = 0.321 Å, α = 1.748 $\Rightarrow \frac{\alpha q^2}{16\pi\varepsilon_0 {R_0}^2} = 1.265\times10^{-9}$,

$$A = 1.265\times10^{-9}\left(3.115\times10^{-10} - 7.092\times10^{9}\right) = 30.4$$

$$B = 1.265\times10^{-9}\left(-3.235\times10^{20} + 2.515\times10^{19}\right) = -3.77\times10^{11}$$

(c) From thermal expansion expression, we find

$$<\delta R> = \frac{-3B}{4A^2}k_B T = +1.26\times10^{-12}\,m = +0.0126\ \text{Å}$$

so that $CTE = \frac{<R>-R_0}{R_0 T} = \frac{<\delta R>}{R_0 T} = 14.9\times10^{-6}$

This is about 38% of the actual experimental value of $CTE = 39.5\times10^{-6}$.