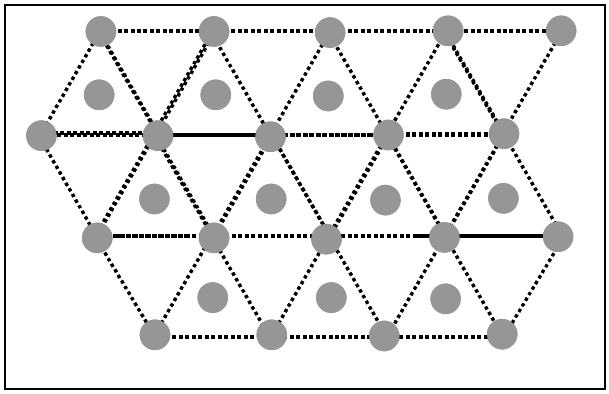
HW#3 Problems, Atomic Theory and Crystal Structure

1. With reference to the figure to the right, is the two dimensional crystal shown (atoms = dark circles) a pure Bravais lattice ? Why or why not ? Is it a Bravais lattice with a basis ? If not, say why. If so, what is the Bravais lattice type, and mark all the "satellite" atoms. (b) How many primitive lattice vectors (PLVs) are there ? Draw the shortest possible PLVs having the minimum possible angle between them. Then draw the *Wigner-Seitz* primitive unit cell. What geometric shape does it have ?



2. Using known values of the crystal structure, lattice constant, and atomic weights, calculate the density of crystalline NaCl and crystalline Cu from first principles.

3. (A good exercise in crystal geometry and structural transformation). With the rapid development of the nitrides and oxides in material science, crystals having hexagonal symmetry are becoming increasingly important.

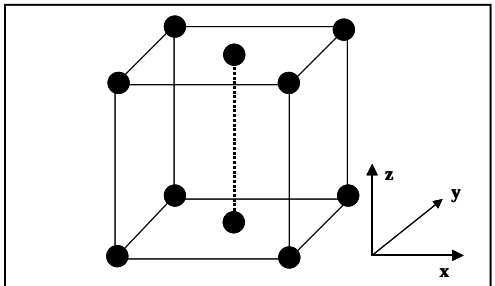
(a) Prove that the ideal c/a ratio for an ideal hexagonal close-packed (hcp) structure is $(8/3)^{1/2}$.

(b) Some materials transform from hcp to cubic form as a function of temperature and or pressure. Assuming that the density remains fixed through this transition, find the relationship between the in-plane lattice constant a_{hcp} in the hcp phase relative to the lattice constant in cubic phase a_{cube} for simple cubic, body-centered-cubic, and face-centered cubic.

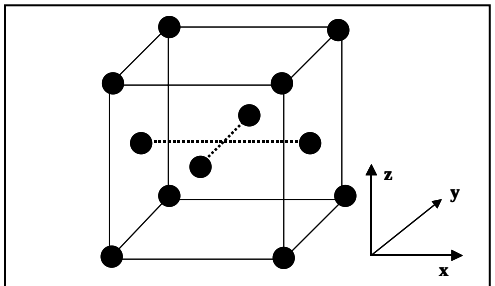
4. Referring to the figures on the right, indicate whether each structure is a Bravais lattice. If it is, give three primitive vectors. If it is not, describe it as a Bravais lattice with the smallest possible basis.

(a) Base-centered cubic (simple cubic plus one atom at the center of the top and bottom faces)

(b) Side-centered cubic (simple cubic plus one atom at the center of each of the fours sides).



Base-centered cubic lattice



Side-centered cubic lattice

5. (Back to elasticity of solids, but now crystalline). Consider a linear lattice of 2N atoms of alternating charge +/-q and equilibrium separation R_0 , and a repulsive potential energy AR^{-n} between nearest neighbors only.

(a) Show that at the equilibrium separation, $U(R_0) = [-2N\ln(2)q^2/(4\pi\varepsilon_0 R_0)]\,[1 - n^{-1}]$.

(b) Let the crystal be compressed so that $R_0 \rightarrow R_0\,(1 - \delta)$. Show that the mechanical work done per unit length has a term $(1/2)C\delta^2$ where $C = (n-1)\ln(2)q^2/(4\pi\varepsilon_0 R_0)$.

6. (Cohesive energy for an upcoming class of crystalline materials) The materials science field has growing interest in metal oxides, such as MgO, ZnO, VOx, BSTO, and the YBCO discovered to display high temperature superconductivity. MgO usually crystallizes in the NaCl structure, with a room-temperature lattice constant a = 4.215 Ang

and a cohesive energy of U_0 = 5.20 eV per atom. Since it has an ionic character, the cohesive energy of MgO can be estimated using the Madelung model discussed in class: $U = 0.5*N[z\lambda\exp(-R/\rho) - (\alpha q^2)/(4\pi\varepsilon_0 R)]$, where N is the number of ionized atoms, z is the number of nearest neighbors, λ and ρ are fitting parameters, α is Madelung's constant, and R is the nearest-neighbor separation.

(a) Derive an expression for the equilibrium cohesive energy U_0 in terms of α, ρ, R_0 (equilibrium separation), N and fundamental constants.
(b) Use this expression and the experimental cohesive energy per atomic ion to evaluate the nuclear repulsive range parameter, ρ.
(c) Now evaluate the repulsive energy parameter λ.
(d) Under conditions possible in microelectronic devices, crystalline MgO may take on the zincblende structure. Use the above information to estimate the cohesive energy of cubic MgO.

7. Assume that the cohesive energy per ion of an ionic solid is given by the Madelung expression, $U' = 0.5*[z\lambda\exp(-R/\rho) - (\alpha q^2)/(4\pi\varepsilon_0 R)]$, where z is the number of nearest neighbors, λ and ρ are fitting parameters, and α is Madelung's constant

(a) Derive expressions for the quadratic and cubic coefficients in an expansion $U' = U'_0 + f(\delta R)^2 + g(\delta R)^3$ in terms of α, ρ, and R_0, where $\delta R = R - R_0$ and R_0 is the equilibrium ion separation (clue: use a Taylor's expansion) .
(b) Calculate the f and g coefficients in MKS units and in eV for sodium chloride, which has the following parameters: R_0 = 2.820 Angstrom, ρ = 0.321 Angstrom and α = 1.748 (hints: q = e = 1.602e-19, ε_0 = 8.85e-12).
(c) Apply these values of f and g to determine the thermal expansion CTE = $3gk_BT/4f^2$, for T = 300 K. Formulate and evaluate the coefficient of thermal expansion (CTE).

8. (Combination of crystal-lattice, thermodynamic, and elasticity principles) GaN is deposited on a (hexagonal) sapphire substrate oriented with its c-axis perpendicular to the plane of the substrate. The growth occurs by MBE at 753 K, the wafer is then cooled to 294 K.

(a) Calculate the strain in the GaN layer in plane parallel to the a-plane of the sapphire due to the difference in thermal contraction (see Table I below) and resulting lattice mismatch. Assume: (1) that the substrate and the layer are rigidly bonded over the whole temperature range and that the growth is "pseudomorphic" (i.e., the GaN conforms to the sapphire, so the sapphire is assumed to be unstrained at all temperatures); (2) that at the growth temperature, a perfect lattice match occurs by virtue of the c axis of the GaN being at an angle with respect to the c axis of the sapphire; and (3) that the in-plane strain in the GaN can be approximated by $3^{1/2}(\Delta a/a)$. Is the in-plane elastic state of the GaN in compression or tension ?
(b) Of course, elasticity theory requires that the in-plane strain in (a) must be correlated to a perpendicular strain in the GaN as well. Assuming the strain components to all be equal and Y = 3.45 x 10^{11} N/m^2 in all directions, how much elastic potential energy (per unit volume) is stored in the GaN film at the heterointerface ?

9. Common Crystal Structures. For the following common crystal structures: (1) Sodium Chloride, (2) Cesium Chloride, (3) Hexagonal Close Packed, (4) Diamond, and (5) Zincblende:

(a) Inspect each of these for centrosymmetry and, therefore, piezoelectricity.
(b) Inspect each for both centrosymmetry and a unique polar axis and, therefore, pyroelectricity. If one exists, describe the direction of the unique polar axis relative to the atomic structure.

	GaN bulk				GaN layer				Sapphire			
T (K)	c (Å)	α_c (10^{-6} K^{-1})	a (Å)	α_a (10^{-6} K^{-1})	c (Å)	α_c (10^{-6} K^{-1})	a (Å)	α_a (10^{-6} K^{-1})	c (Å)	α_c (10^{-6} K^{-1})	a (Å)	α_a (10^{-6} K^{-1})
294	5.18561		3.1880		5.1857		3.1871		12.9907		4.7577	
		2.8		3.1		2.0		3.8		3.9		4.3
343	5.18633		3.1885		5.1863		3.1877		12.9927		4.7587	
		2.8		3.1		2.8		3.7		4.3		4.6
403	5.18699		3.1891		5.1870		3.1884		12.9960		4.7598	
		2.8		3.8		3.1		3.8		5.1		5.1
453	5.18772		3.1897		5.1878		3.1890		12.9993		4.7610	
		2.8		3.8		3.1		4.4		5.7		5.9
503	5.18841		3.1903		5.1886		3.1897		13.0030		4.7624	
		2.8		4.4		3.1		4.4		7.1		6.7
553	5.18911		3.1910		5.1894		3.1904		13.0076		4.7640	
		3.8		4.4		5.4		5.6		7.4		4.1
603	5.19009		3.1917		5.1908		3.1913		13.0124		4.7657	
		4.6		5.0		5.8		5.6		7.4		7.1
653	5.19232		3.1925		5.1922		3.1922		13.0172		4.7674	
		5.0		6.2		5.8		5.6		8.9		7.1
703	5.19360		3.1935		5.1936		3.1931		13.0230		4.7691	
		6.1		6.2		5.8		7.9		9.3		9.2
753	5.19520		3.1945		5.1952		3.1942		13.0291		4.7713	
	±0.0005	±0.3	±0.0001	±0.6	±0.0001	±0.6	±0.0002	±1.2	±0.0001	±0.3	±0.0001	±0.6

Data for Problem 8