

Homework 3

1. We stated that the covalent bond responsible for the strength of so many solids is tetrahedral in nature and occurs in many crystalline semiconductors such as silicon – arguably the world’s most important material for electronics. Calculate the angle between neighboring tetrahedral bonds using the geometric fact that the covalent bonds strive to be equidistant (to minimize potential energy).
2. 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  $a_{\text{hcp}}$  in the hcp phase relative to the lattice constant in cubic phase  $a_{\text{cube}}$  for simple cubic, body-centered-cubic, and face-centered cubic.
3. In each of the following cases indicate whether the 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 four sides).
4. 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,  $U(R_0) = [-2N\ln(2)q^2/(4\pi\epsilon_0R_0)] [1 - n^{-1}]$ .
  - (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  $C = (n-1)\ln(2)q^2/(4\pi\epsilon_0R_0)$ .
5. 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:  $U = 0.5*N[ z\lambda\exp(-R/\rho) - (\alpha q^2)/(4\pi\epsilon_0R)]$ , where  $N$  is the number of ionized atoms,  $z$  is the number of nearest neighbors,  $\lambda$  and  $\rho$  are fitting parameters,  $\alpha$  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  $\alpha$ ,  $\rho$ ,  $R_0$  (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,  $\rho$ .
  - (c) Now evaluate the repulsive energy parameter  $\lambda$ .
  - (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.
6. 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  $Y = Y = 3.45 \times 10^{11} \text{ N/m}^2$  in all directions, how much elastic potential energy (per unit volume) is stored in the GaN film at the heterointerface ?

TABLE I. Lattice constants and thermal expansion coefficients  $\alpha = [a(T1) - a(T2)] / \{(T2 - T1) \times 0.5 \times [a(T1) + a(T2)]\}$  of gallium nitride (bulk and epitaxial layer) and sapphire.

T (K)	GaN bulk				GaN layer				Sapphire			
	c (Å)	$\alpha_c$ ( $10^{-6} \text{ K}^{-1}$ )	a (Å)	$\alpha_a$ ( $10^{-6} \text{ K}^{-1}$ )	c (Å)	$\alpha_c$ ( $10^{-6} \text{ K}^{-1}$ )	a (Å)	$\alpha_a$ ( $10^{-6} \text{ K}^{-1}$ )	c (Å)	$\alpha_c$ ( $10^{-6} \text{ K}^{-1}$ )	a (Å)	$\alpha_a$ ( $10^{-6} \text{ K}^{-1}$ )
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	
	$\pm 0.0005$	$\pm 0.3$	$\pm 0.0001$	$\pm 0.6$	$\pm 0.0001$	$\pm 0.6$	$\pm 0.0002$	$\pm 1.2$	$\pm 0.0001$	$\pm 0.3$	$\pm 0.0001$	$\pm 0.6$

Data for Problem 6