**Test 1, PHY4905, Spring 2016**

**Chaps. 1-3, 5 February 8, 2016**

**1. Consider the hexagonal compound CaCu5, which has the Ca atoms (light blue) at the corners (shown is one third of a full hexagon) and four of the Cu atoms on the faces (note that the top and bottom faces (which are NOT square) have two Cu atoms each while the other four faces (which are square) only have one) with the fifth Cu atom in the body centered position. The a and b lattice parameters in the base are equal, and equal to 5.082 Å, while the c-axis = 4.078 Å. The atoms are described by the following positions (see picture of the conventional cell) (take the origin 0,0,0 at the back rear of the bottom plane):**

**Ca: one at 0,0,0**

**Cu (3 different symmetry sites): one atom at: ½, ½, ½; one atom at ½, 0, ½ (left side face) and one atom at 0, ½, ½ (back side face) and one atom at 2/3, 1/3, 0 and one atom at 1/3, 2/3, 0 (note that a and b are not orthogonal but rather have a 120 o angle between them)**

**a.) (2 pts) what is the physical mass density, units of g/cm3, of CaCu5, if the molar mass of Ca is 40.078 g and of Cu 63.546 g?**

**in one unit cell, vol=a dot bxc=91.21 Å3 (since b and c are orthogonal, the magnitude of b x c is (bc) and the direction is perpendicular to the b-axis. Thus, a dot b x c is (abc) times cos 60o since a perpendicular to the b-axis makes a 30o angle with the a-axis. (you can also just use trig with the base as given in the picture.)**

**in this cell are 1 Ca atom (=1/8 \* 8 for the cube corners) plus 5 Cu atoms. The masses are 1 \*(40.078 g/mole)/6.022x1023 atoms/mole and 5\*63.546 gmole/6.022 1023 atoms/mole = (357.808)x10-23 g/6.022 \* 91.21 10-24 cm3=6.51 g/cm3**

**b.) (2 pts) Using fCa and fCu for the atomic form factors of Ca and Cu respectively, write down the structure factor, SG, using the 6 atom positions given above for the basis,**

**SG = Σj fj exp(-i2π[ hxj + kyj + lzj ]) where the sum is over j=1 to 6 for the basis atoms and the positions of the basis atoms are**

**rj =** x**j a1 +** y**j a2 +** zj**a3 and the ai are the conventional cell vectors. (Note again that a1 and a2 are not orthogonal.)**

**SG=fCa(1) + fCu(exp(-πi(h + k + l)) + exp(-πi(h + l)) + exp(-πi(k + l)) + exp(-2πi(2/3h + 1/3k)) + exp(-2πi(1/3h + 2/3k)**

**c.) 4 pts What is the structure factor for the following (hkl) values:**

**(hkl) = (100), (001), (101), (110), (111)? (This is more than the three – 100, 101, and 111 - asked for on the test, just for you information) (please convert to numbers, rather than leaving it as, for example, an answer that contains exp(iπ) (which is -1) or exp(-i2π/3) which is -0.5 -i√3/2. So, if the answer should be 0, and you have the sum of a bunch of exponentials that *would* add to zero if you did the conversions, you don't get credit.)**

**plug these hkl into answer to b. and look for a pattern**

**100 gives fCa(1) + fCu(-1-1+1-1/2+i√3/2 -1/2 - i√3/2 ) = fCa -2fCu**

**001 gives fCa(1) + fCu(-1-1-1+1+1) = fCa - fCu**

**101 gives fCa(1) + fCu(+1 +1 -1 -1/2 + i√3/2 -1/2 - i√3/2) = fCa**

**110 gives fCa(1) + fCu(+1-1-1+1+1)= fCa + fCu**

**111 gives fCa(1) + fCu(-1 +1 +1 +1 +1) = fCa + fCu(3)**

**d.) 2 pts The above values are amplitudes, and the measured xray intensities for each hkl line are arrived at via Shkl\* x Shkl, where S\* is the complex conjugate of S. Assume that the atomic form factors are just simply the Z (number of electrons) values, so fCa=20 and fCu=29. What hkl gives the largest intensity? All the amplitudes are real. (100) gives -38, (101) gives 20, and (111) gives 107 for amplitudes. Squaring these . . . (111) is the largest, which in fact agrees with the xray pattern. In fact, (100) [(-38]2 =1444] and (101) (202=400) also have relative intensities that agree with what we calculate.**

**2. Consider the van der Waals (also known as Lennard Jones) potential, where dipole-dipole attractions lead to a –(σ/R)6 attraction term. We discussed in class how a +(σ/R)12 repulsive potential term is added to represent hard core repulsion. We learned how, over the entire crystal, that the potential U was summed over all atoms j (not including atom i where the interaction was being considered as being on, and then the result is multiplied by N, the number of atoms in the crystal):**

**Eq. 1: U = 2Nε [ Σj’ (σ/pijR)12 - Σj’ (σ/pijR)6 ] where pijR is the distance between reference atom i and any other atom j, expressed in terms of the nearest neighbor distance R. For computational purposes, one can assume various repulsive terms *instead* of the (1/R12) term. One such assumption is the so-called Lennard Jones 9-6 potential, where the potential energy of two atoms at separation R is:**

**U = A/R9 – B/R6, where A≡2εR09 and B≡3εR06, where R0 is the equilibrium separation between two atoms.**

**a.) 1 pt In terms of A and B, calculate R0**

**equilibrium is when the potential energy is at its minimum (or, equivalently, when the force= -dU/dR = 0.) -9A/R10 + 6B/R7 =0 => 6B=9A/R03 or R0=(1.5A/B)1/3**

**b.) 1 pt At the equilibrium separation R0, calculate U in terms of ε.**

**U at R0 = A/R09 – B/R06. Substitute the given for A and B: 2εR09/R09 - 3εR06/R06 = -ε**

**which is just the equilibrium separation energy ε0.**

**c.) 1 point In fcc for the Lennard Jones 12-6 potential, the sum Σj’ (1/pij)12 = 12.13188 and Σj’ (1/pij)6 = 14.45392 For the 9-6 potential, the second sum is the same but the first one is different. *Qualitatively*, in fcc, would you expect the sum Σj’ (1/pij)9 to be larger, smaller, or the same as 12.13188? Explain your reasoning.**

**There are 12 nearest neighbors in fcc. When the sum Σj’ (1/pij)12 is calculated, pij for the nearest neighbors is just 1, and thus the nearest neighbors contribute already 12 to the sum of 12.13188. The next nearest neighbors in fcc, instead of being (√2/2)a distant (where a is the lattice cube edge length) is just ‘a’, which is √2 longer than the nearest neighbor distance. When you sum (1/√2)12 over the number (6) of next nearest neighbors in fcc, you get 6\*(1/64)=0.09375. And so on. If you add 6 times (1/√2)9, you already get 12 + 0.2652, so the sum of Σj’ (1/pij)9 in fcc is *larger.***

**d.) 2 points Using your answer from c.), would you expect the calculated equilibrium separation for a lattice of atoms (Eq. 1 above) arranged in the fcc structure to be larger, smaller, or the same using a Lennard Jones 9-6 potential instead of the usual 12-6 potential?**

**Just as we did when we had the 12-6 potential, take the first derivative of**

 **Σj’ (σ/pijR)9 - Σj’ (σ/pijR)6 to get 9\*(>12.2652) σ9/R010 – 6\*14.45392 σ6/R07 = 0 and solve**

**9\*(>12.2652) σ3/R03 – 6\*14.45392 = 0 or R03/σ3 = 9\*(>12.2652)/ 6\*14.45392, so we see that the equilibrium separation is larger. In real calculations, when the sum of Σj’ (1/pij)9 is done completely, the answer computationally is about 1.7% larger R0, which is not bad considering that 12.2652 is already 1.1% larger than 12.13188.**

3. **Einstein Model of the Specific Heat at constant volume:**

**As given in Kittel, in 3 dimensions (where N is Avogadro’s number for the number of atoms in 1 mole, and kB=1.38 10-23 J/K and ω0 is the Einstein frequency**

**CVE = 3 N kB (ħω0/(kBT))2 [exp(ħω0/(kBT)]/[exp(ħω0/(kBT)) – 1)]2**

**a.) What is the numerical value of CVE, in units of J/molK, at a temperature = ½ ħω0/kB**

**CVE =3R 4 exp2/[exp2 – 1]2 =3 \* 8.314 J/molK \* 4 \* 7.389/[6.389]2 = 24.942 \* 0.724 = 18.06 J/molK**

**b.) From the graph below and your result for part a, what would be the approximate Einstein temperature for Si?**

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**About 480 K**

**c.) What is the high temperature value of CVE? Show your calculation.**

**Call ħω0/(kBT) =x, so CVE = 24.942 (x)2 [exp(x)]/[exp(x) – 1)]2 ; as T->large, x->0; expand exp(x) = 1 + x, so have CVE (T->∞) = 24.942 (x)2 \* (1+x)/x2 = 24.942 J/molK, or 3 R, which is just the Dulong Petit value.**