Write your name here: _____

Instructions:

- Answer all questions to the best of your abilities. Be sure to write legibly and state your answers clearly.
- The point values for each question are indicated.
- You are not allowed to use notes, friends, phones, etc.
- You can use calculators.
- There are a total of 100 points.
- Feel free to ask questions, but only for clarification purposes.

I hope you all do really well.

It was a pleasure teaching you.

- DCC

| Problem Number	Score
1	/ 10
2	/ 10
3	/ 10
4	/ 10
5	/ 10
6	/ 10
7	/ 10
8	/ 10
9	/ 10
10	/ 10
Total	/ 100

1. The figure below (on the left) is part of a crystal containing a dislocation. The perfect crystal is displayed on the right. The x_3 direction points out of the page toward you, and conincides with six-fold axes of rotation in the perfect crystal.
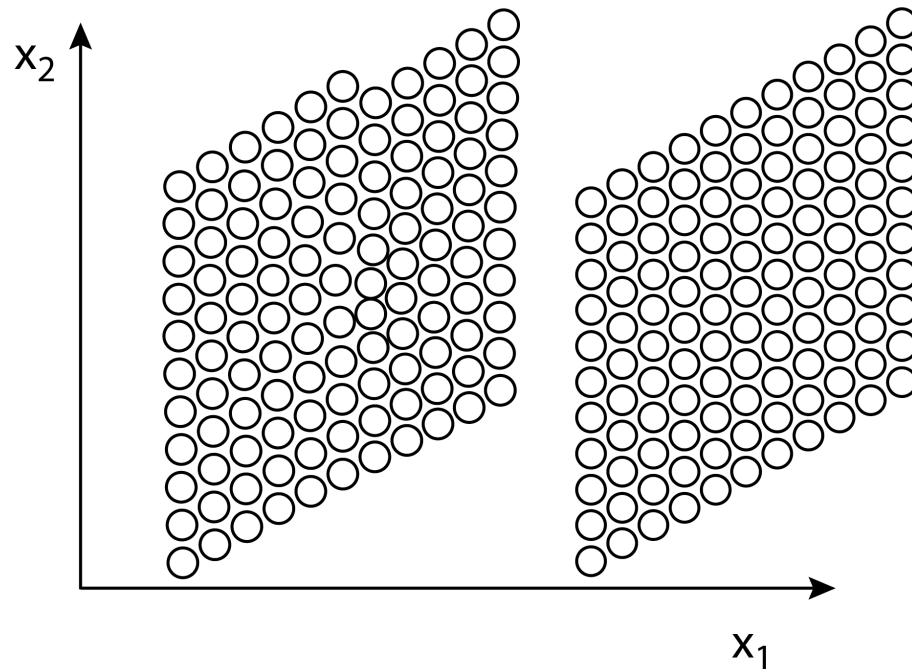
(a) Remembering that a Burgers circuit is just path that circles the dislocation, construct the Burgers circuit for the dislocation on the left [2 points], and identify the Burgers vector on the right panel [3 points].

(b) [1 point] What is the line direction of the dislocation? [1 point] Give a vector that is normal to the slip plane of the dislocation.

(c) Assume that the stress given below is applied to the crystal. [2 points] Compute the force exerted on the dislocation by the applied stress. [1 point] Assuming that the dislocation is only allowed to glide, in which direction does the dislocation move under the applied stress ? (Give an explicit vector describing the direction.)

Assume that $\sigma = \begin{bmatrix} \sigma_1 & -\sigma_o & 0 \\ -\sigma_o & \sigma_2 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ with $\sigma_o > 0$ and $\sigma_1 > 0$ and that $|b| = b$.

(This page for algebra for problem 1, if you need…)

(a) CsCl structure   (b) NaCl structure

Cs+
Cl-   Na+
             Cl-

a
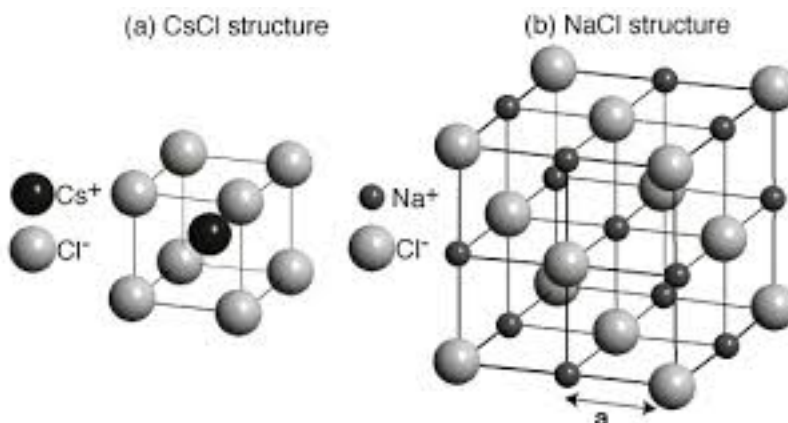
2. [10 points] MgO has the NaCl crystal structure. This structure is built on a cubic F-lattice, with two atoms per lattice point. However, you are wondering if it might not also form in the CsCl structure, which is a cubic lattice, again, with two atoms per lattice point. (Both of these structures are shown above – sorry about the fuzziness, these were shamelessly borrowed from Google images...) Using the data below, estimate the difference in energy per MgO formula unit, between MgO in the NaCl and CsCl structures. Based on your calculated energies, state whether or not you expect to find MgO in the CsCl structure, and explain your answer.

Note that in the table below, the ionization energy is the energy required to remove two electrons from the ion and the electron affinity is the energy to doubly ionize the doubly charged anion:
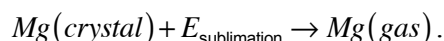
$$Mg + \text{Ionization energy} \rightarrow Mg^{2+} + 2e^-$$
$$O^{2-} + \text{Electron affinity} \rightarrow O + 2e^-$$
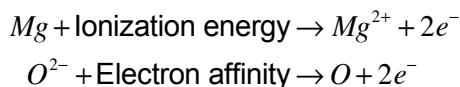
Also, we define the lattice energy, $U_{lattice}$ here to be the energy reduction upon forming the lattice from the ions separated by infinity:

$$Mg^{2+}(gas) + O^{2-}(gas) - U_{lattice} \rightarrow MgO(crystalline).$$
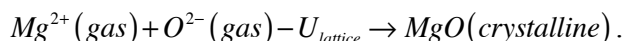
The dissociation energy is the energy required to dissociate the dimer:

$$O_2(gas) + E_D \rightarrow 2O(gas).$$
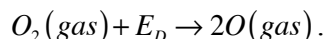
Finally, the sublimation energy is the energy required to take a Mg atom from the crystal to a gaseous state:

$$Mg(crystal) + E_{sublimation} \rightarrow Mg(gas).$$

Sublimation Energy of Mg	Dissocation Energy of O_2	Ionization energy of Mg	Electron Affinity of O	$U_{lattice}$ NaCl	$U_{lattice}$ CsCl
1.52 eV	5.15 eV	22.68 eV	-7.46 eV	39.33 eV	27.32 eV

3. [10 points] A simple hexagonal crystal is pulled in the $\mathbf{e}_3$ direction defined in the figure.
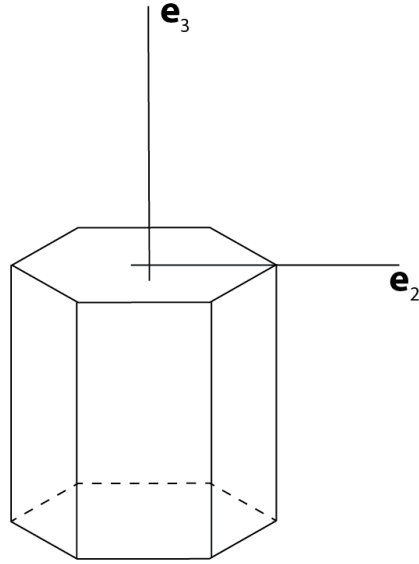
Find Young's modulus in terms of the Voigt elastic constants for the crystal. The Voigt index mapping reads:

index pair	11	22	33	23 or 32	13 or 31	12 or 21
Voigt index	1	2	3	4	5	6

The elastic constant matrix, in Voigt notation, is given by:

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix},$$

with $C_{66} = \frac{1}{2}(C_{11} - C_{12})$.
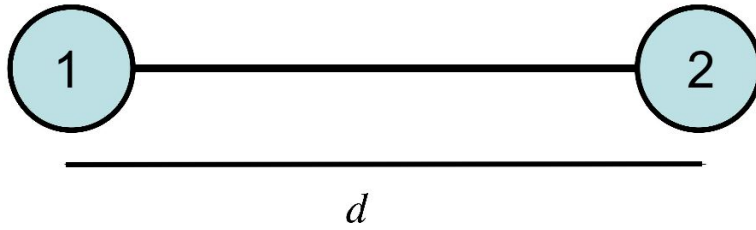
4. The Hamiltonian matrix for an electron bound to a dimer with bond length d, determined using a basis composed of the S states of the bare atoms, is given by:

$$H = \begin{pmatrix} E_1 & -V_o(d) \\ -V_o(d) & E_2 \end{pmatrix}$$

Here, E_1 and E_2 are the energy levels for an electron in the bare atoms labeled 1 and 2, respectively.

(a) [2 points] What energies might one measure for an electron bound to the dimer?

(b) [4 points] Sketch the eigenfunction associated with the *bonding* state. Assume the atomic basis states are $\psi_{100}(\mathbf{r})$ states of the respective atoms. Assume that $E_2 > E_1$, and and state in words how this is reflected in your sketch. (Plot the eigenfunction along the line connecting the nuclei of the dimer, as we did in class. There is no need to compute directly the eigenvectors – a sketch with the correct features will do.)

(c) Assume now that $E_2 = 4$ eV, and $E_1 = 3$ eV and d is chosen such that $V_o(d) = 2$ eV.
[2 points] Sketch the energy level diagram for the dimer.

[1 point] If there are three electrons in the molecule, two from atom 1, and one from atom 2, what is the change in electronic energy associated with forming the bond?

[1 point] Now suppose that $E_2 = E_1 = E_o$ and that the repulsive energy for the nuclei is given by:

$$E_{rep}(d) = 3[V_o(d)]^2.$$

Compute the ground state energy of the dimer with three electrons.

5. Simple metals, such as Na, can be thought of in the following way. If one removes 1 electron from a Na, the remaining electronic configuration is that of Ne, and if relatively stable. The removed electron can minimize its kinetic energy by spreading throughout the volume of the solid, and is modeled as doing so. In fact, each atom within the Na solid can be thought of as donating one electron to a sea of electrons (which we assume to be non-interacting). The remaining positively charged atom cores (in the Ne configuration) are assumed to be smeared continuously throughout the solid so that they yield a constant background Coulomb potential of $-V_o$. The time-independent Schrödinger equation for the electrons becomes:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) - V_o\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

Solving this problem is straightforward, but we need to make some simplifying assumptions.

First and foremost, we will assume that the electrons occupy a cube of edge length L, with volume L^3. Eventually, we will take the limit $L \to \infty$, but for now, we assume that L is finite.

In order to continue solving, we must choose a boundary condition for the edge of the box. For the particle in the box, we chose the box walls to be impenetrable. Here, we make a different assumption: We impose periodic boundary conditions. The idea is that we want to perturb the electron states minimally by our boundaries. One way to do this is to assume that when an electron leaves the box on one side, it "magically" reenters the box from the other side. In effect we impose the conditions on the eigenfunctions that

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + L\mathbf{e}_x) = \psi(\mathbf{r} + L\mathbf{e}_y) = \psi(\mathbf{r} + L\mathbf{e}_z).$$

In effect, the electrons' world is a 3-D torus...

The general solution to Schrödinger equation is given by a simple plane wave:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{L^{3/2}}.$$

[2 points] Based on the boundary conditions we imposed, what are the constraints on the vector $\mathbf{k}$?

[2 points] Given your solution for the constraints, what are the possible values that one might measure for an electron in this system?

[3 points] Assume that there are n electrons in the box. Compute the electronic energy of the electrons in terms of the density of the electrons in the box, assuming that the potential $-V_o = 0$. In general, this calculation would proceed as follows. One would sort the energy eigenvalues that you computed from low to high energy, and place up to two electrons in each level until all n electrons have been placed into levels. The electronic energy is simply the sum of the energies of the individual electrons.

For a small number of electrons, this is a straightforward exercise. For 10^{23} electrons, this task, as described, is impossible. We can, however, make progress if we first note that the energy of an electron in the eigenstate $\psi_\mathbf{k}(\mathbf{r})$ has an energy of $\frac{\hbar^2 k^2}{2m}$. Thus the states of equal energy are distributed in $\mathbf{k}$-space on spheres. The spheres with the smallest radii correspond to lowest energies. So when viewed in $\mathbf{k}$-space, the filled states occupy a sphere centered on the origin of volume $\frac{4\pi}{3}k^3$. If we knew the number of states per unit "volume" in $\mathbf{k}$-space, we could compute the radius of the sphere. From your solution to the previous part of this problem, you should be able to calculate this density, which we can call (for now) Ω_k. With this value, one can compute the radius of the sphere, defined to be the Fermi wavevector, k_f, according to

$$n = 2\Omega_k \frac{4\pi}{3} k_f^3 \, .$$

Here, the factor of 2 accounts for the spin – each **k** -state can take two electrons, one spin up and one spin down. The total energy of the electrons can then be written as the integral:

$$E_{electronic} = 2 \int_0^{k_f} dk \, 4\pi \, k^2 \Omega_k \frac{\hbar^2 k^2}{2m}$$

[3 points] The Fermi wavevector can be used to define a number of Fermi "things." For example, the Fermi energy is given by $E_f = \dfrac{\hbar^2 k_f^2}{2m}$, the Fermi velocity is given by $v_f = \dfrac{\hbar k_f}{m}$, and the Fermi temperature is given by $T_f = \dfrac{E_f}{k_B}$, with k_B Boltzmann's constant. Assume that the free electrons in Na can be modeled as a non-interacting electron gas. Compute the Fermi energy, velocity and temperature for Na. The cubic lattice parameters for Na, which crystallizes with the cubic I-lattice structure, with one atom per unit cell, is $a_o = 4.2906$ Å. ($\hbar = 1.0545617 \times 10^{-34}$ J-sec, $k_B = 1.38065 \times 10^{-23}$ J/K, and $m = 9.109383 \times 10^{-31}$ kg)

6. Below is a 2D crystal with C atoms represented by circles and N atoms represented by squares.
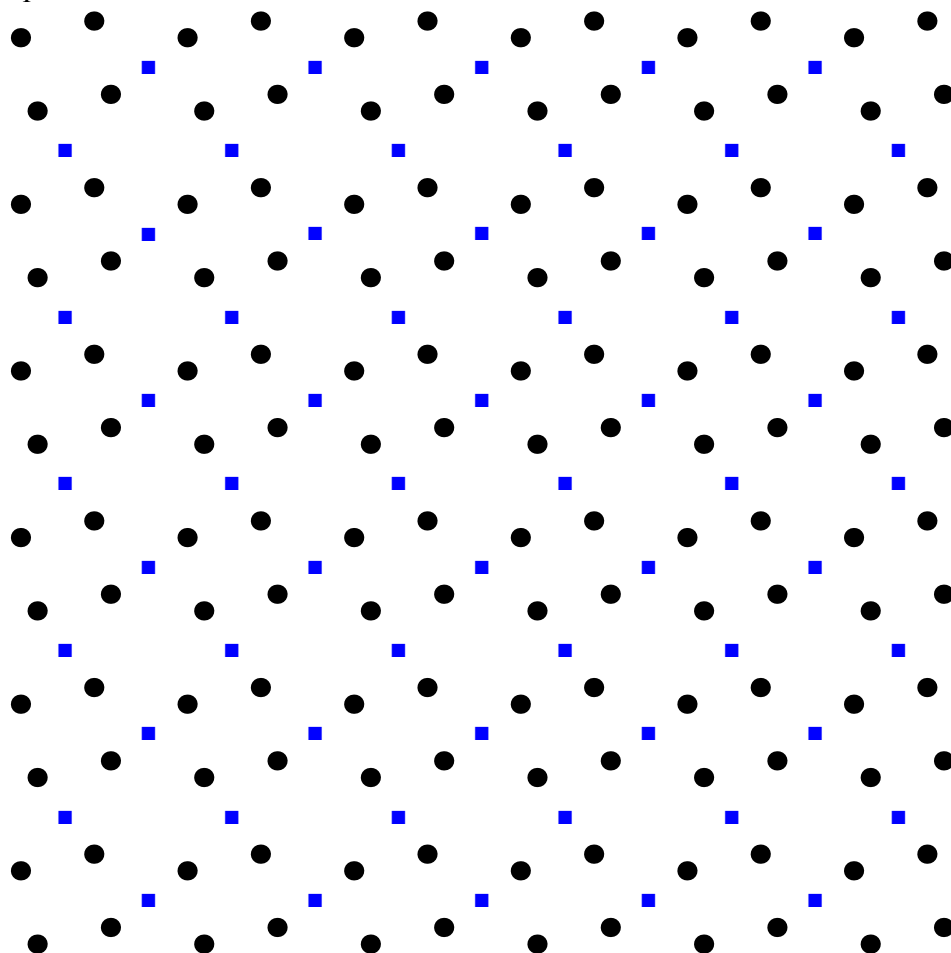
Use a plane group table to answer following questions and **label your answers clearly**:
(a) [1 point] Identify a set of the lattice points, marking each with "×".
(b) [1 point] Identify a set of primitive lattice vectors and a primitive unit cell.
(c) [1 point] Draw the direction $[\bar{1}\ 2]$ based on your primitive lattice vectors.
(d) [1 point] How many atoms are in each primitive unit cell?
(e) [1 point] Which plane group describes the symmetry of this crystal?
(f) [1 point] Sketch the asymmetric unit in a **separate** unit cell.
(g) [1 point] Give the Wyckoff positions of C atoms and N atoms.
(h) [3 point] Use the graph paper on the following page to sketch the diffraction pattern. Identify spots where C atoms contribute using an "×" and the spots to which N atoms contribute using an "O". Spots where that have contributions from both types of atoms should be represented by both symbols. Be sure to label the origin and axis correctly.
For each diffraction pattern you need to draw at least 15 symbols.
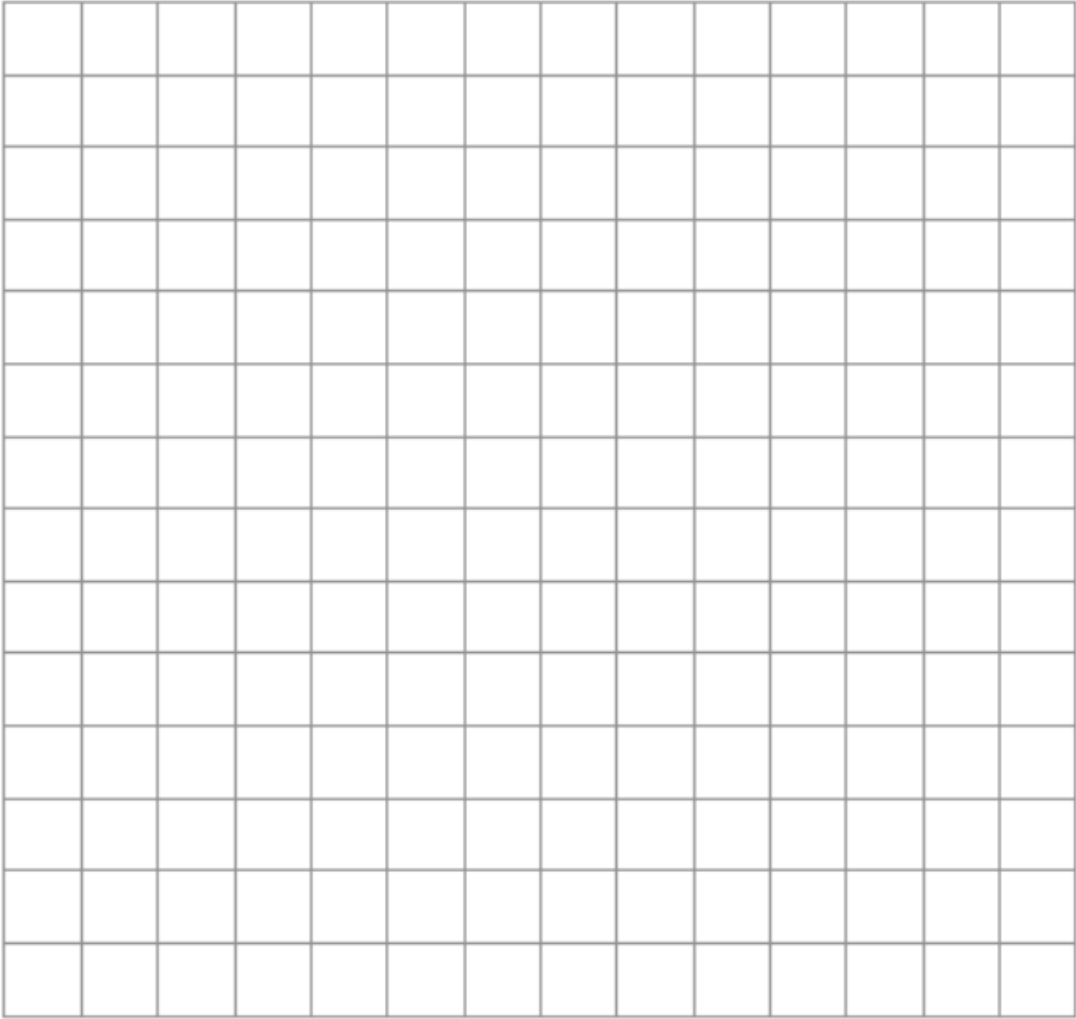
7. [10 points] The formation energy of a MgO vacancy pair (one cation and on anion) is 6.75 eV. The cubic lattice parameter of MgO (MgO forms in the NaCl structure) is 4.212 Å. How many vacancies do you expect to find per cubic centimeter at a temperature of 1000 K. Boltzmann's constant is 8.6173×10^{-5} eV/K.

8. [10 points] Piezoelectricity is the materials property wherein a material subject to an applied stress (as you know, a second rank tensor) develops an electric dipole moment (a vector quantity). The mathematical relationship relating the stress, σ, and the electric polarization, $\mathbf{p}$, is given by:

$$p_i = d_{ijk}\sigma_{jk},$$

with d_{ijk} the elements of a third rank tensor known as the piezoelectric constants of the material.

(a) [2 points] In general, how many elements does the tensor $\mathbf{d}$ include.

(b) [4 points] Using what you know about the transformation matrix of first and second rank tensors, derive the transformation rule for a third rank tensor. Be sure to justify any mathematical equations you write down with a brief explanation.

(c) [4 points] Now suppose that you have a material with inversion symmetry. Can this materials be piezoelectric? Why or why not? Justify your answer with a rigorous mathematical proof.

9. (a) [5 points] State the four postulates underlying theory of quantum mechanics.

(b) [5 points] Explain why a metal with a completely filled energy band and a gap in energy states above, is not a metallic conductor.

10. [5 points each] Complete the stereograms below by identifying all symmetrically equivalent directions, drawing all additional symmetry elements, and enumerating all elements of the point group.