Physics 725: Solid State Physics I

In-class Midterm Exam

Tuesday, October 4, 2016 / 11:00–12:15 / Room 104, Lewis Hall

Student's Name: _____

Instructions

There are 19 questions, some with multiple subparts. You should attempt all of them. Mark your response on the test paper in the space provided. **Please use a pen**. If in answering a question you sketch a diagram, please provide meaningful labels. Aids of any kind—including class notes, textbooks, cheat sheets, and calculators—are not permitted.

Good luck!

15 points	multiple choice	questions 1–12
9	short answer	13–18
11	long answer	19
35 points		

Multiple choice questions (15 points)

Answer by circling one of (a), (b), (c), etc. directly on the test paper. Be sure that your selection is clear and unambiguous.

1. Which of the following represents the state of *highest* symmetry?

   (a) amorphous solid
   (b) quasicrystal
   (**C**) homogenous, isotropic gas with no long-range correlations
   (d) stiff linear molecules in solution that form a nematic
   (e) crystal with a discrete set of rotation, reflection, and translation invariants

2. Which of the following statements about solidification is *incorrect*?

   (a) systems with only an excluded volume interaction are athermal
   (b) cohesion in materials is governed by potential energy (electrostatic) but solidification is largely driven by entropic considerations
   (c) for classical hard spheres, the hcp and fcc configurations (ABAB and ABCABC layer stacking, respectively) are degenerate; both correspond to close packing
   (**D**) for classical hard spheres, the ordered phase at temperature $T > 0$ is a state of low entropy

3. Which of the following statements is *incorrect*?

   (a) the liquid-solid phase transition is first order
   (**B**) the liquid-solid phase transition is continuous
   (c) a crystal has a latent heat of formation
   (d) liquid can be supercooled below its solidification temperature

4. Which of the following statements is *incorrect*?

   (a) the largest atoms are in the bottom-left portion of the periodic table
   (b) the atoms in the top-right portion of the periodic table are hardest to ionize
   (c) the halides generally have a high electron affinity
   (d) the noble gas elements are chemically inert
   (**E**) none of them

(2 points) 5. Indicate whether these are true or false statements.

(**T** / f) pure crystals are thermodynamically unstable to contamination by impurities
(**T** / f) near special stoichiometric ratios, alloys of two elements can form superlattices
(t / **F**) binary mixtures will always alloy rather than phase separate
(**T** / f) the dynamics of phase separation are diffusive
(t / **F**) quenching and annealing are synonyms for the same process

6. Which of the following materials is the least ionic in character?

   (**A**) Ge
   (b) GaAs
   (c) InSb
   (d) InAs
   (e) CdTe
   (f) ZnSe

7. Condensed matter physics largely considers physical processes over what range of energies?

   (a) μeV to eV
   (**B**) meV to keV
   (c) keV to MeV
   (d) MeV to GeV

8. What is the approximate distance between atoms in a copper crystal?

   (a) 30 Å
   (b) 300 Å
   (**C**) 0.3 nm
   (d) 30 nm
   (e) 3 μm

(2 points) 9. Which of the following exhibit collective excitations in response to shear?

(yes / **NO**) gas
(yes / **NO**) liquid
(**YES** / no) glass
(**YES** / no) regular solid

10. What kind of (carbon valence orbital) hybridization takes place in diamond?

    (a) sp
    (b) sp^2
    (**C**) sp^3

(2 points) 11. Assign each of these categories in the periodic table—

(a) semi-metals (b) non metals and halogens (c) noble gases
(d) alkali metals and alkaline earths (e) basic metals

—to the most appropriate group of elements below. Write the corresponding letter in the space provided. Each letter should appear exactly once.

b C N O P S F Cl Br I

a B Si As Te

d Li Na K Rb Cs Be Mg Ca Sr

e Al Ga In Sn Tl Pb Bi

c He Ne Ar Kr Xe

12. The pair distribution function $g(r) \sim \langle \sum_{i<j} \delta(r - |\boldsymbol{R}_i - \boldsymbol{R}_j|) \rangle$ describes the average separation between atoms. For a molten system, it is featureless—aside from a small hard-core exclusion region $0 \leq r < \sigma$. When the system is cooled and solidifies, $g(r)$ develops a sequence of strong peaks at positions $r > \sigma$. For each sequence below (showing the first three peak distances), identify the Bravais lattice type as

(a) body-centred cubic, (b) face-centred cubic, or (c) simple cubic.

Write the corresponding letter in the space provided. Each letter should appear exactly once.

a $\frac{\sqrt{3}}{2}a$, a, $\frac{\sqrt{11}}{2}a$, ...

b $\frac{1}{\sqrt{2}}a$, a, $\frac{\sqrt{10}}{2}a$, ...

c a, $\sqrt{2}a$, $\sqrt{3}a$, ...

Short answer questions (9 points)

Try to provide answers in concise prose. At most a few sentences are required for each question.

13. In what (mathematical) sense are the Bavais lattice vectors and reciprocal lattice vectors of a crystal *dual* to each other?

Each Bravais lattice $\{\boldsymbol{R}\} = \mathbb{Z}\boldsymbol{a}_1 + \mathbb{Z}\boldsymbol{a}_2 + \mathbb{Z}\boldsymbol{a}_3$ has a corresponding partner lattice—its dual—defined by $\{\boldsymbol{G}\} = \mathbb{Z}\boldsymbol{g}_1 + \mathbb{Z}\boldsymbol{g}_2 + \mathbb{Z}\boldsymbol{g}_3$ such that $\boldsymbol{g}_m \cdot \boldsymbol{a}_n = 2\pi\delta_{m,n}$ and hence $e^{i\boldsymbol{G}\cdot\boldsymbol{R}} = \exp(2\pi i \times \text{integer}) = 1$.

(2 points) 14. Describe two methods for obtaining a high-quality single crystal. There are many possible answers. (i) Pulling from a melt—silk thread raised slowly out of the molten material in a crucible; (ii) zone refining—polycrystalline sample packed in a long cylinder and drawn slowly throw a hot annulus; (iii) vapour deposition—atoms released from a furnace onto a substrate in an evacuated chamber.

(2 points) 15. What are x-rays? What energy or wavelength must they have if they're to be used in diffraction experiments for the purpose of characterizing crystal structure? When x-rays scatter from a material, are they interacting with protons, neutrons, or electrons?

X-rays are high-energy photons. To be useful in diffraction experiments on crystalline materials, they must have energies in the range of a few keV and wavelengths on the order of an Angstrom. X-rays predominantly scatter off the electronic charge distribution of the material.

16. The Madelung constant of a stable ionic solid is always positive. Why must that be so?

The potential energy of an ionic solid is $V = \sum_{i,j} q_i q_j / r_{i,j}$, where q_i is the net charge of the ion at position i and $r_{i,j}$ is the distance between ions at positions i and j. An ionic solid has a bipartite structure with ions of alternating charge on the two sublattices. If the nearest-neighbour distance is d, then $V = -\alpha e^2/d$, where the Madelung constant α is a positive geometric constant. If any particular ionic configuration leads to $\alpha < 0$, then $V > 0$ and the system is not stable. That is to say, the material would fly apart as a consequence of Coulomb repulsion.

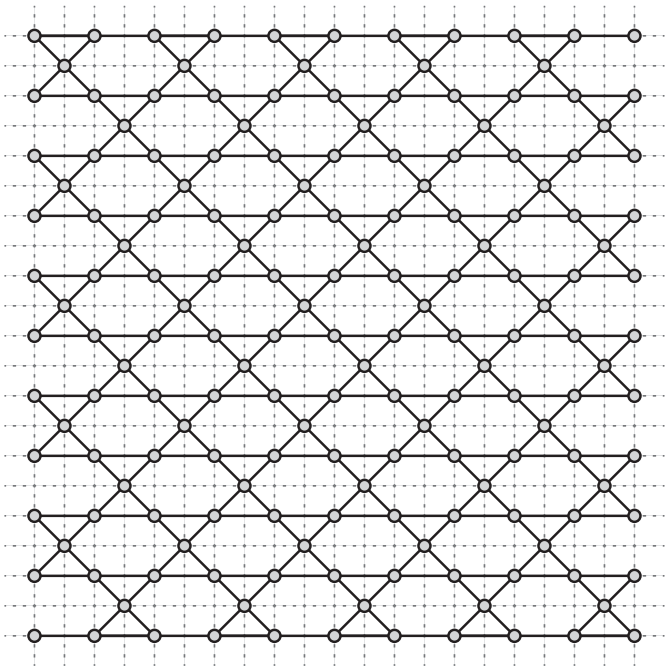
17. The free energy of a two-component system must behave in what way (as a function of relative concentration) for the system to be unstable to phase separation?

The free-energy curve of the uniform system must have more than one local minimum as a function of concentration.

(2 points) 18. The alloy Cu_3Au can form when a high-temperature liquid mixture of roughly 75% copper and 25% gold is cooled. What experimental signature marks the formation of the new intermetallic crystalline compound? What are the different outcomes when the system is quenched versus annealed?

The experimental signature is the appearance of new diffraction peaks. The superlattice forms when then system is annealed but not when it is quenched.

Long answer problems (11 points)



19. The figure above shows a two-dimensional crystal made up of a single kind of atom. The underlying grid of dotted lines is just a guide to the eye. (The dotted lines are spaced by a distance a.)

(2 points) (a) Find lattice vectors and a basis for the crystal.

The centres of all the "bowties" are connected by linear combinations of the lattice vectors $\boldsymbol{a}_1 = 4a\boldsymbol{e}_x$ and $\boldsymbol{a}_2 = 2a(\boldsymbol{e}_x + \boldsymbol{e}_y)$. [Another choice is $\boldsymbol{a}_1' = 2a(-\boldsymbol{e}_x + \boldsymbol{e}_y)$ and $\boldsymbol{a}_2' = 2a(\boldsymbol{e}_x + \boldsymbol{e}_y)$.] Taking the centre of the bowtie as the coordinate origin in the unit cell, we define a three-atom basis $\{\boldsymbol{\tau}_1, \boldsymbol{\tau}_2, \boldsymbol{\tau}_3\} = \{\mathbf{0}, a(-\boldsymbol{e}_x + \boldsymbol{e}_y), a(\boldsymbol{e}_x + \boldsymbol{e}_y)\}$

(b) Compute the area of the unit cell.

The area is $\Omega_0 = \boldsymbol{a}_1 \times \boldsymbol{a}_2 \cdot \boldsymbol{e}_z = [4a\boldsymbol{e}_x \times 2a(\boldsymbol{e}_x + \boldsymbol{e}_y)] \cdot \boldsymbol{e}_z = 8a^2[\underbrace{\boldsymbol{e}_x \times \boldsymbol{e}_x}_{=0} + \underbrace{\boldsymbol{e}_x \times \boldsymbol{e}_y}_{=\boldsymbol{e}_z}] \cdot \boldsymbol{e}_z = 8a^2$.

Equivalently, $\Omega_0 = \boldsymbol{a}_1' \times \boldsymbol{a}_2' \cdot \boldsymbol{e}_z = 4a^2[(-\boldsymbol{e}_x + \boldsymbol{e}_y) \times (\boldsymbol{e}_x + \boldsymbol{e}_y)] \cdot \boldsymbol{e}_z = 4a^2(2\boldsymbol{e}_z) \cdot \boldsymbol{e}_z = 8a^2$.

(c) Determine the corresponding reciprocal lattice vectors.

$$\boldsymbol{g}_1 = \frac{2\pi}{\Omega_0}\boldsymbol{a}_2 \times \boldsymbol{e}_z = \frac{2\pi}{8a^2}\, 2a(\boldsymbol{e}_x + \boldsymbol{e}_y) \times \boldsymbol{e}_z = \frac{\pi}{2a}(\boldsymbol{e}_x \times \boldsymbol{e}_z + \boldsymbol{e}_y \times \boldsymbol{e}_z) = \frac{\pi}{2a}(\boldsymbol{e}_x - \boldsymbol{e}_y)$$

$$\boldsymbol{g}_2 = \frac{2\pi}{\Omega_0}\boldsymbol{e}_z \times \boldsymbol{a}_1 = \frac{2\pi}{8a^2}\, 4a\boldsymbol{e}_x \times \boldsymbol{e}_z = -\frac{\pi}{a}\boldsymbol{e}_y$$

or

$$\boldsymbol{g}_1' = \frac{2\pi}{\Omega_0}\boldsymbol{a}_2' \times \boldsymbol{e}_z = \frac{2\pi}{8a^2}\, 2a(\boldsymbol{e}_x + \boldsymbol{e}_y) \times \boldsymbol{e}_z = \frac{\pi}{2a}(\boldsymbol{e}_x \times \boldsymbol{e}_z + \boldsymbol{e}_y \times \boldsymbol{e}_z) = \frac{\pi}{2a}(\boldsymbol{e}_x - \boldsymbol{e}_y)$$

$$\boldsymbol{g}_2' = \frac{2\pi}{\Omega_0}\boldsymbol{e}_z \times \boldsymbol{a}_1' = \frac{2\pi}{8a^2}\, \boldsymbol{e}_z \times 2a(\boldsymbol{e}_x + \boldsymbol{e}_y) = \frac{\pi}{2a}(\boldsymbol{e}_z \times \boldsymbol{e}_x + \boldsymbol{e}_z \times \boldsymbol{e}_y) = \frac{\pi}{2a}(-\boldsymbol{e}_x + \boldsymbol{e}_y)$$

(2 points) (d) Sketch the Brillouin zone that results from the Wigner-Seitz construction.

The Brillouin Zone is a square, rotated 45 degrees with respect to the cartesian axes.

(3 points) (e) Using the reciprocal lattice vectors $\boldsymbol{g}_1$ and $\boldsymbol{g}_2$ that you computed in part (c), parameterize arbitrary points in the reciprocal lattice with the linear combination

$$\boldsymbol{G} = \boldsymbol{G}(n_1, n_2) = n_1\boldsymbol{g}_1 + n_2\boldsymbol{g}_2$$

for integers n_1 and n_2. Assuming that the atomic form factors are identical for all the atoms, determine the geometric structure factor as a function of n_1 and n_2.

The reciprocal lattice vectors

$$\boldsymbol{g}_1 = \frac{\pi}{2a}(\boldsymbol{e}_x - \boldsymbol{e}_y), \quad \boldsymbol{g}_2 = -\frac{\pi}{a}\boldsymbol{e}_y$$

form linear combinations

$$\begin{aligned}\boldsymbol{G} = n_1\boldsymbol{g}_1 + n_2\boldsymbol{g}_2 &= n_1\frac{\pi}{2a}(\boldsymbol{e}_x - \boldsymbol{e}_y) - n_2\frac{\pi}{a}\boldsymbol{e}_y \\ &= \frac{\pi}{2a}(n_1\boldsymbol{e}_x - n_1\boldsymbol{e}_y) + \frac{\pi}{2a}(-2n_2\boldsymbol{e}_y) \\ &= \frac{\pi}{2a}[n_1\boldsymbol{e}_x - (n_1 + 2n_2)\boldsymbol{e}_y].\end{aligned}$$

Hence,

$$\begin{aligned}\sum_j f_j e^{i\boldsymbol{G}\cdot\boldsymbol{\tau}_j} &= f_0\sum_{j=1}^{3} e^{i\boldsymbol{G}\cdot\boldsymbol{\tau}_j} \\ &= f_0\left\{1 + \exp\left(\frac{i\pi}{2}[n_1\boldsymbol{e}_x - (n_1 + 2n_2)\boldsymbol{e}_y]\cdot(-\boldsymbol{e}_x + \boldsymbol{e}_y)\right)\right. \\ &\qquad \left. + \exp\left(\frac{i\pi}{2}[n_1\boldsymbol{e}_x - (n_1 + 2n_2)\boldsymbol{e}_y]\cdot(\boldsymbol{e}_x + \boldsymbol{e}_y)\right)\right\} \\ &= f_0\left\{1 + \exp\frac{i\pi}{2}[-n_1 - (n_1 + 2n_2)] + \exp\frac{i\pi}{2}[n_1 - (n_1 + 2n_2)]\right\} \\ &= f_0\left\{1 + \exp[-i\pi(n_1 + n_2)] + \exp(-i\pi n_2)\right\} \\ &= f_0\left\{1 + (-1)^{n_1+n_2} + (-1)^{n_2}\right\},\end{aligned}$$

and the structure factor is

$$S_{\boldsymbol{G}} = \left|\sum_j f_j e^{i\boldsymbol{G}\cdot\boldsymbol{\tau}_j}\right|^2 = |f_0|^2\left\{1 + (-1)^{n_2}[1 + (-1)^{n_1}]\right\}^2.$$

(2 points) (f) Determine which diffraction peaks have maximum intensity and explain why extinction never occurs.

The structure factor behaves as

$$\begin{aligned}
S_{\boldsymbol{G}} = S(n_1, n_2) &= |f_0|^2 \Big\{ 1 + (-1)^{n_2} \big[1 + (-1)^{n_1} \big] \Big\}^2 \\
&= |f_0|^2 \Big\{ 1 + 2(-1)^{n_2} \big[1 + (-1)^{n_1} \big] + (-1)^{2n_2} \big[1 + (-1)^{n_1} \big]^2 \Big\} \\
&= |f_0|^2 \Big\{ 1 + 2(-1)^{n_2} \big[1 + (-1)^{n_1} \big] + \big[1 + 2(-1)^{n_1} + (-1)^{2n_1} \big] \Big\} \\
&= |f_0|^2 \Big\{ 1 + 2(-1)^{n_2} \big[1 + (-1)^{n_1} \big] + 2 \big[1 + (-1)^{n_1} \big] \Big\} \\
&= |f_0|^2 \Big\{ 3 + 2(-1)^{n_1} + 2(-1)^{n_2} + 2(-1)^{n_1+n_2} + \Big\} \\
&= |f_0|^2 \Big\{ 1 + 2 \big[1 + (-1)^{n_1} \big] \big[1 + (-1)^{n_2} \big] \Big\} \\
&= |f_0|^2 \times \begin{cases} 9 & \text{if } n_1 \text{ and } n_2 \text{ are both even} \\ 1 & \text{otherwise} \end{cases}
\end{aligned}$$

The peak intensities are as follows:

n_1	n_2	$S(n_1, s_2)/\lvert f_0 \rvert^2$
0	0	9
0	1	1
1	0	1
0	$\bar{1}$	1
$\bar{1}$	0	1
0	2	9
1	1	1
2	0	9
0	$\bar{2}$	9
1	$\bar{1}$	1
$\bar{1}$	1	1
$\bar{1}$	$\bar{1}$	1
$\bar{2}$	0	9
0	3	1
1	2	1
2	1	1
3	0	1
⋮	⋮	⋮

Since the crystal basis is nontrivial, extinction can't be ruled out. But it turns out not to occur: there are no reciprocal lattice vectors $\boldsymbol{G}$ for which $S_{\boldsymbol{G}}$ vanishes. This is so because $\sum_{j=1}^{3} e^{i\boldsymbol{G}\cdot\boldsymbol{\tau}_j}$ comprises three terms with value ± 1, and there's no way for these to sum to zero.