Advanced Physical Chemistry
Exam III
110 points; 100 points = 100%

Suggestions. Scan through the entire exam. Note that there is a 15-point essay question at the end of the exam. You may wish to write an outline of this question first, and then leave time at the end to answer it fully. Budget your time carefully.

Crystal properties (34 points)

1. (3 points) The violet color of fluorite (CaF_2) is due to an imperfection in the crystal lattice. Describe the imperfection in one or two sentences.

2. (5 points) We also observed the fluorescence of fluorite. Draw an energy-level diagram and use arrows to show the process of fluorescence. Label the diagram.

3. (4 points) A crystal of calcite ($CaCO_3$) causes printed words to appear doubled. This property of crystals is called _____ or _____.

4. (6 points) Briefly describe any two methods of crystallization. (Diagrams may be helpful.)

5. (2 points) Aaron described a mineral that was crystallized under a pressure of 0.4 GPa. Convert this pressure to bar (1 bar = 1.01 x 10^5 Pa). Is this high or low pressure?

6. (4 points) In a few sentences describe how can one tell if a crystal is a single crystal or twinned.

7. (10 points) Why is a *single crystal* needed for X-ray diffraction? What property of the crystal is important? (Write 2-3 sentences; don't try to fill up this page.)

Crystals and Symmetry (18 points)

8. (2 points) What are the characteristics of an *orthorhombic* unit cell?

9. (5 points) What is a *space group*? What is the significance of the mathematical term *group*? Use as an example space group *P*2/m, which has four equivalent positions:
   1) x,y,z
   2) $\bar{x},y,\bar{z}$
   3) $x,\bar{y},z$
   4) $\bar{x},\bar{y},\bar{z}$

10. (3 points) If a molecule crystallizes in space group *P*2/m and $Z = 2$, what can you conclude about the molecule, in one sentence?

11. (3 points) Some space-group operators involve translations. Write the operator that corresponds to the *c* glide plane in monoclinic space groups with the **b** axis unique:

---

12. (5 points) Draw a projection of the monoclinic cell on the **ab** plane. Draw a small circle to represent an atomic position and label it *1*. Draw another small circle (labeled *2*) that shows the equivalent position after the 2_1 rotation/translation operation. (The screw axis is parallel to the **b** axis in conventional monoclinic orientation.)

Diffraction Pattern (31 points)

13. (3 points) Where in the diffraction pattern are the high-angle reflections? (A diagram may help.)

14. (5 points) If we want 0.5 Å resolution for a small-molecule structure (in order to locate the H atoms) and we are using Mo K_α radiation (0.71073 Å), what is θ_{max} for the diffraction pattern? (Set your calculator on degrees.)

15. (4 points) Why is it difficult to locate H atoms in the electron-density map? (Use the proper terminology.)

16. (4 points) A metal such as polonium crystallizes in a primitive cubic structure at a pressure of 1 atm. Suppose that at a pressure of 50 atm the metal forms a body-centered cubic structure with the same cell constants. How would the diffraction patterns of the two forms differ? Be as specific as possible.

17. (4 points) Aaron described the structure of a mineral at two different temperatures. What differences in the diffraction pattern were seen at the two temperatures? Be as specific as possible.

18. Below are the equivalent positions for the most common space group for small molecules, $P2_1/c$.

1) x, y, z

2) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$

3) $x, \bar{y} + \frac{1}{2}, + \frac{1}{2} z$

4) $\bar{x}, \bar{y}, \bar{z}$

a. (3 points) If the identity position of Co is 0.5335, .4267, .8077, give the equivalent position after the rotation/translation symmetry operation:

_____

b. (8 points) Assume that a Patterson map was calculated for a cobaloxime complex similar to the ones Greg described in his oral report. For space group $P2_1/c$ calculate four Co-Co vectors if the Co position is 0.5335, .4267, .8077.

Structure Factors and Electron Density (12 points)

19. (6 points) Write the Fourier series for the structure factor F_{023} in space group $P2_1/c$ after the Co position was deduced from the Patterson map. Because the cobaloxime structure in question 18 is centrosymmetric, the expression for the structure factor is simplified. Substitute numbers in the equation, estimating if necessary. The Co position is 0.5335, .4267, .8077. No other atomic positions are known at this stage in the structure determination.

20. (6 points) After calculating all the structure factors as you showed in question 19, what calculation would be done next in a typical crystal structure determination? Write out the Fourier series as part of your answer to this question. Define all terms in the equation. In a few sentences, tell how this calculation helps to determine the crystal structure.

General (15 points)

21. (15 points) Essay question. List what we can learn by analyzing the results of a crystal structure. Give specific examples of each item on your list from the CSD structure you chose, from the Crystal-Maker structure you examined, from the article in your oral report, or from class discussion.