Plan for single crystal diffraction on Synergy-I system

INTRODUCTION:
Single crystal X-ray diffraction is by far the most authoritative as well as convenient way for molecular structure determination. With only one nice single crystal, a reliable structure model can be obtained within one hour on a state-of-the-art diffractometer. For example, the structure of CuSO₄·5H₂O was fully determined on a Rigaku SuperNOVA X-ray diffractometer within 24 minutes, (5 minutes for mounting and centering the crystal sample, 9 minutes for data collection, another 10 minutes for solving and refinement.). The crystal system is triclinic, for a crystal in cubic, the data collection can be much shorter, similar to taking a photo. The unit cell parameters can be as precise as 10⁵ Å with suitable data acquisition strategy, and no other in-house technique can offer this precision!

Moreover, the resulting structure model is a perfect combination of both abstract and intuitive. All kinds of structural information, like unit cell dimension, crystal system,
space group, atoms positions and occupancies, …, etc., can be easily extracted from the structure model. (Question1: Can you name or list any other structural information?) And then, certain behaviors of the corresponding compound can be well explained through structure evaluation and/or comparison. In addition, all physique properties can be calculated or simulated based on this very X-ray structural model by using proper quantum calculation methods. (Suggestion: If you are interested, you can consult the manual of Guassian 09™ or Materials Studio®, to see which kind of properties can be obtained via quantum calculation.)

Now, you might sense the power of X-ray single crystal diffraction. Indeed, X-ray structure analysis is independent if you want publish a new compound, because all other methods, like spectrum analysis and thermal analysis can only offer partial or discrete structural information. But, single-crystal XRD is able to handle all kinds of crystal samples, range from very simple compound, like diamond with only one carbon atom, to super complicated one, such as protein and virus, with millions of atoms, and yields full structural information with very small uncertainty. And as well known, this situation won’t change in the foreseeable future.

However, the above mentioned function is only one of the main applications of single crystal XRD, and we just find where the atoms are (the relative positions of all atoms in the unit cell). We can follow what the atoms do via non-ambient XRD experiments. The structure might change with the variation of experiment conditions, such as temperature, pressure, moisture, … etc., (Suggestion: If you are interested, you can search and read papers about non-ambient single crystal diffraction in journals, like Crystal Growth & Design https://pubs.acs.org/loi/cgdeu and CrystEngComm https://pubs.rsc.org/en/journals/journalissues/ce#issueid=ce020035&type=current&issnonline=1466-8033.) So, a series of data collection can be performed at different conditions to get solid proves about phase transition. In this way, direct relationship between structures and physique properties can be built, and it’s very essential to understand the behaviors of certain system. (Questions: Why we need a single crystal with suitable (relative large) size for structure determination? What should we do if no qualified crystal sample can be found? Can you name any other techniques for structure analysis?)
PROJECT TARGETS:

1. Determine the X-ray single crystal structure of CuSO₄·5H₂O with the Synergy-I diffractometer from Rigaku;
2. Get familiar with the general procedure of single crystal diffraction;
3. Learn how to select qualified single crystal sample for diffraction;
4. Learn basic skill of structure refinement with ShelX and a GUI, like OLEX2;
5. Learn how to evaluate the results of single crystal structure refinement;
6. Learn to plot all kinds of crystallographic molecular figures;
7. Search structural databases, like CSD, ICSD, PDF4, and COD;
8. Compare structure models with similar structure models in the CSD database;
9. Try to simulate the polycrystalline powder pattern from the structure model;
10. Verify the purity of the sample;
11. Take photos of the crystal samples for morphology analysis;
12. Determine the miller indices for all visible facets of a single crystal (optional).

SUGGESTED PLAN FOR SUCCESSFUL AND EFFICIENT WORK:

Week one:
1. Visit the X-ray lab with both single crystal and powder diffractometers;
2. Take training about sample selection and mounting;
3. Practice using microscope to evaluate the crystals and taking photos;
4. Centering the crystal sample on the goniometer and take a diffraction pattern;
5. Taking patterns for different samples for comparison;
6. Try to search different databases and plotting structure figures;
7. Make a plan for the real structure determination in the second week.

Week two:
1. Review the skills about instruments operation taken from week one;
2. Select a well-qualified single crystal, mount it on goniometer and perform unit cell determination, and then start the full data collection for structure refinement;
3. Search the databases for more information about structure solving;
4. Practice ShelX with OLEX2 for structure refinement and report preparation;
5. Try using both Mercury and VESTA for structure plotting;
6. Take training about polycrystalline XRD on Empyrean diffractometer;
**Week three:**
1. Treat the frames collected in week two and try to solve and refine the structure;
2. Perform polycrystalline XRD experiment for the same compound;
3. Simulate the polycrystalline XRD pattern of the crystal and make comparison;
4. Take photos of the crystal samples for morphology analysis;
5. Determine the miller indices for all visible facets of a single crystal;
6. Plot molecular figures with the CIF file from the refinement;
7. Prepare the crystallographic table for publish.

**Week four:**
1. Q&A for all kinds of questions about single crystal XRD;
2. Introduction of crystallographic software and textbooks (optional);
3. More examples for structure solving and refinement;
4. Prepare the report or presentation.

**INFORMATION NEEDED IN THE REPORT:**

1. How to select a suitable single crystal for X-ray diffraction?
2. How to select X-ray diffractometer for structure determination?
3. How to mount and center the crystal sample on the goniometer?
4. How to make sure it’s a single crystal?
5. What’s the unit cell parameters of CuSO₄·5H₂O?
6. Can you find similar structure in CSD, COD and PDF4?
7. What’s the coordination of Cu/Fe and S in the unit cell?
8. What are the bond lengths of Cu/Fe-O? Are they similar? What can be the reason?
9. What’s the meaning of those values of bond length?
10. Plot a molecular figure showing only the asymmetry unit cell;
11. Plot a structure figure showing everything in the unit cell;
12. Provide a crystallographic table about refinement in the report;
13. Make a list of all H-bonding in the structure;
14. Simulate the theory polycrystalline XRD pattern;
15. Compare the simulated pattern with the real pattern on a powder diffractometer;
16. Is the sample pure or not? What’s the proof of your conclusion?
17. Take a photo for a crystal with nice facets, and determine the Miller indices of the facets, put a figure with the results in the report.

**OPTION:**

*a) Please offer solutions for single crystal XRD for samples with sensitivities:*

1. Sensitive to $O_2$
2. Sensitive to $H_2O$:
3. Sensitive to Temperature:
4. Sensitive to Lights:
5. Suffer from Efflorescence:

*b) Please explain the reason that why with the X-ray beam of ~0.7 Å, the unit cell parameters, atom positions, or bond length can be determined to the precision of $10^5$ Å. Does this make any sense?*

c) Please perform a polycrystalline XRD diffraction with the Panalytical Empyrean system and perform a search-matching with Match! and COD, see if the sample is pure or not.