Cell refinement using computer programs

Experiment No:

Date:

1 Aim

To refine and calculate the refinement parameters of given crystallographic data file.

2 Motivation

Crystals are the important arena of condensed matter physics and materials science. The properties of the materials are often described based on their crystalline structure. Ideally, crystals are formed by the repeating basic units called 'unit cells', over the three dimensional space. Which means, if you look into a crystal from any direction, it resembles same over the space. This is only in the case of ideal crystals. But practically, due to the experimental limitations, crystals have some defects in their structure. Analysing such a defects are important, especially when we consider the crystal for applications. There are many methods and programs are available to estimate the defects and to refine the crystal structure in literature. Here we use two of such programs to demonstrate the cell refinement process.

3 Basics

3.1 X-ray diffraction

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern. The dominant effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of those X-rays from atoms within the tar-

get material. In materials with regular structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is described by Bragg's Law, $n(\lambda) = 2d.sin(\theta)$. The directions of possible diffractions depend on the size and shape of the unit cell of the material. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure.

3.2 Single crystal XRD

Single-crystal X-ray Diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering. Directly related is single-crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure.

3.3 Powder XRD

PXRD is primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

3.4 Crystal structure refinement

The electron density map generated by solution of the phase problem from the single crystal XRD can be seen as a basic structure map. However, the assignment of atoms to different intensity centers is key to understanding the structure. The step of atom assignment is referred to as solving the crystal structure and these resolved structures are given in a 'crystal information file' (cif) for further reference.

4 Method

Eventhough the cif files carries good quality data, they may have slight deviation from the ideal crystals. To analyse such a deviations, crytal refinement programs are used. Here we use two programs for the analysis of anthracene single crystal data. The

data file can be downloaded from the crystallographic open database (COD) with information card number 5000168. To analyse this structure we need 'Mercury program' - to visualize the crytal structure and to simulate the PXRD data, and 'checkcell package' - for cell refinement.

4.1 Procedure

1. Download the cif file from this page:
   `http://www.crystallography.net/cod/5000168.html`

2. Open the structure in Mercury program and note down its crystall cell parameters.

3. Now from the calculation options, simulate the PXRD data of the given file and save it into a desired folder.

4. Open checkcell program, assign source wavelength and fix 2theta values and enter your simulated data in the given space.

5. Then in the parameter selection page choose the parameters corresponding to your data and proceed to calculation area.

6. Here match your simulated data with theoretical data and calculate the refinement parameters.

5 Observations

5.1 Crystallographic parameters

Identifier		
Formula		
Compound name		
Space group		
Cell lengths	a	
	b	
	c	
Cell angles	α	
	β	
	γ	
Cell volume		

5.2 Simulated PXRD data

2θ	Intensity

5.3   Refinement Data

	Intial	Refined	Sigma
a			
b			
c			
α			
β			
γ			
Volume			

Mean square deviation of cell parameters = _____

6 Results

The given crystallagraphic data file was refined and the mean square deviation of cell parameters is about _____

Instructor comments:

Signature

7 Assignments

1. Compare the simulated PXRD pattern with experimental (reported) data.

2. Why real crystals are (slightly) defective?

3. How theoretical crystalline structures are derived?

4. Do the experimental PXRD reduce/increase cell parameters?

8 References

8.1 Basics

1. Introduction of Solid State Physics, by C. Kittel

2. https://www.youtube.com/watch?v=B99Sd1MQPkY

3. https://www.youtube.com/watch?v=suVNYD1nCm4

4. https://www.youtube.com/watch?v=C1cYJthlBZY

8.2 Experiment

1. http://pd.chem.ucl.ac.uk/pdnn/unit1/refcel1.htm

2. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.460.8439&rep=rep1&type=pdf