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Final

UNIVERSITY OF CALIFORNIA, SANTA BARBARA
Department of Physics

Physics 128

X-RAY DIFFRACTION CRYSTALLOGRAPHY

Purpose: To investigate the lattice parameters of various materials using the technique of x-ray powder diffraction.

Overview: Powder diffraction is a modern technique that has become nearly ubiquitous in scientific and industrial research. Using x-rays of a specific wavelength, one can use the scattering patterns of x-rays incident on a material to reconstruct a picture of a substance's atomic structure. It is a quick and effective technique for classifying materials, and allows the user to find the particular crystal lattice parameters that enable more advanced calculations. In this lab, we will begin with a general discussion of x-ray safety and techniques, as well as an introduction to the theory behind crystallography. After that, we will move on to performing several powder diffraction experiments using the professional facilities available in the Materials Research Laboratory, and perform data analysis to calculate the intermolecular spacing for each sample.

Part I: Safety and Training

"With great power comes great responsibility." –Uncle Ben

X-ray sources produce a tremendous amount of radiation, and can cause very serious injuries if used incorrectly. While there are many safety features in place to prevent such problems from occurring, these features may still fail, and a good scientist should be prepared for anything to happen. Before beginning your project, please watch *The Double-Edged Sword*, a radiation safety training video designed to scare small children away from ever receiving a chest x-ray. It is about 20 minutes long, and may be obtained at the UCSB Learning Labs (Kerr Hall, 2nd floor), or through an online stream at:

http://www.msg.ucsf.edu/local/XRayLab/DoubleEdgedSword.html

The online stream requires Apple's QuickTime software to be installed locally, and the video is about twenty minutes long. It is, in parts, a bit outdated, but the dangers it communicates are still very real. In fact, the x-ray diffractometer you will be using in the coming weeks are of much higher intensity than the ones in the video, and, as such, can cause much more serious burns upon unintentional exposure.

Much advancement in x-ray instrumentation has been made since the taping of the video, and there are now many safety mechanisms in place to prevent the user from accidental exposure. Most x-ray apparatuses are now completely contained whenever the

shutter is open, and have a switch to close the shutter if the seal is broken. Typically, the entire beam line (from source to detector) is enclosed in a radiation-proof housing, which can be made from any material of reasonably high density. It may also have a viewing window, which can be made out of lead-infused glass or a high-density polymer (typically made by doping with heavy metals). Additionally, it is usually impossible to open the shutter when the doors are open. This is made possible by the use of an Interlock system, which consists of several contact switches between the doors and housing that keep the shutter closed while the circuit is open. The safety features on x-ray equipment are numerous, but one should nonetheless exercise care whenever using a radiation source.

(a)

(b)

Fig. 1: (a) Photograph of interlock system for a standard Philips machine.
(b) Interlocks on a custom housing.

Part II: Introduction to X-Ray Diffraction

Historical Background

The existence of x-rays was discovered quite by accident, but their applications were clear from the beginning. In November 1895, Wilhelm Conrad Röntgen was working on an early cathode ray tube when he noticed that the faint green light that the tube produced passed straight through all objects in its path. When he started adding more materials to block the beam, he saw an image of the bones in his hand projected on the wall opposite the CRT. Röntgen summarized these findings in a paper, in which he called the radiation "X," and received the first Nobel Prize for his discovery. Upon hearing of this radiation, Thomas Edison immediately began experimenting with different filament materials, and, within four months, developed the first standard fluoroscope for medical imaging. Further experimentation in subsequent years led to the understanding of this radiation, yet the name stuck (despite some suggestions of calling them Röntgen rays).

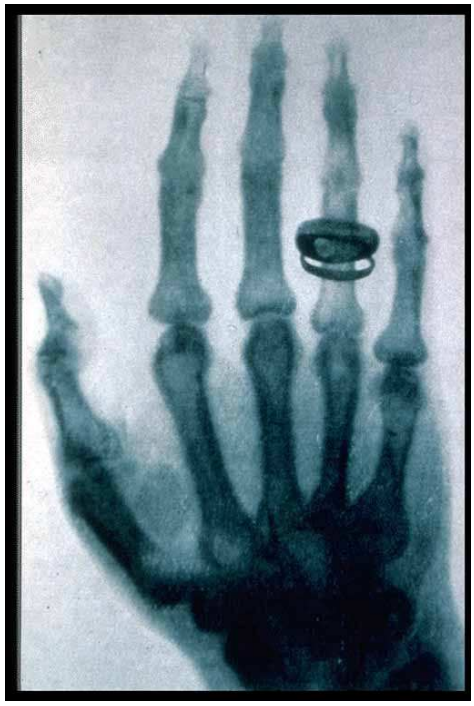


Fig. 2: X-ray photograph taken by Röntgen of his wife's hand, showcasing her wedding ring.

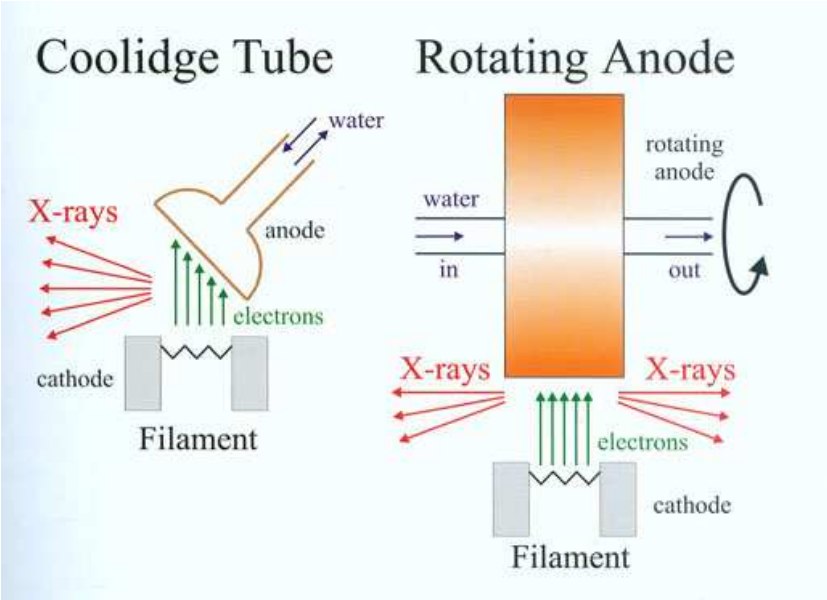
X-rays are still used extensively in medical imaging, but also now have physical applications ranging from astrophysics to condensed matter. In this lab, we will perform x-ray diffraction experiments, in which we will look at the scattering patterns produced when the radiation is incident on a crystalline material. By doing this, we will then be able to reconstruct an image of the crystal structure without disturbing the material. There are several types of laboratory x-ray generators used for diffraction, including sealed-tube *rotating anode sources* and those designed for special applications. Sealed-tube x-ray

tubes, similar to a traditional vacuum tube, were the first ones developed, and remain in high popularity due to their compact size and low cost. Rotating anode sources produce higher flux due to increased heat capacity of the spinning target, and are a reasonable addition to any diffraction laboratory. By contrast, there are also synchrotron sources, which provide a very high beam intensity, but come with an equally high cost. The X'PERT machines, which you will use in this lab, are of a third class, and serve as a happy medium between the two previous systems. All three techniques are discussed in detail below.

Instrumentation

Sealed-tube and Rotating Anode

In 1912, W.D. Coolidge of GE Research proposed an x-ray generator for diffraction experiments, which he called the *Coolidge tube*. It consisted of a stationary metal anode enclosed in vacuum, which was bombarded with an electron beam that had been accelerated across a high voltage electromagnetic field. When the beam collided with the anode, the electrons slowed down, and a continuous spectrum of x-rays were emitted, called *bremsstrahlung radiation*. Though cooling water was constantly run through the anode, there was still an immense amount of heat generated by this process, and the power was limited to 1 kW.



(a) **(b)**

Fig. 3: Diagram of (a) Coolidge tube and (b) rotating anode x-ray generators (reproduced from Als-Nielsen, p. 31, fig 2.1).

To solve the power issue, a technique was uncovered to improve heat dissipation in the anode. By spinning it around a central axis, the electron beam was exposed to a greater volume of metal, and any heat generated could be quickly dissipated to the surrounding cooling water. Though Coolidge was well aware of this fact, it was not immediately possible to create such a machine, due to vacuum and water sealing issues.

By 1960, these problems were finally resolved, and the first *rotating-anode* x-ray generator was made commercially available.

Fig. 4: Photograph of copper target for rotating anode system

The rotating-anode generators are still in wide use today, and currently afford power settings several orders of magnitude higher than the Coolidge tube. A typical anode is made out of copper or molybdenum, which emit x-rays with characteristic energies of 8 keV and 14 keV, respectively. Recalling the formula:

$$E = \frac{hc}{\lambda}$$

these correspond to wavelengths of 1.54 Å and 0.8 Å, which is of conveniently similar order to the spacing between atoms in a molecule. In most laboratories, copper is the metal of choice, and the UCSB Materials Research Laboratory is no exception. Its wavelength is close to the size of a typical atom, and it allows for many different types of measurements as well as a wide range of scattering angles. The MRL uses rotating-anode generators for small- and wide-angle x-ray scattering, popular with those needing a specialized set of equipment for their experiments. In this lab, we will use another, more modern generator, which is discussed briefly after a more in-depth discussion of the first two methods.

Synchrotron

Even with the relatively high intensity provided by the rotating-anode generator, there are certain applications for which a higher intensity is necessary. The development of the *synchrotron* increased x-ray production by several orders of magnitude, and quickly became the standard mechanism for high-profile laboratories.

In a synchrotron, a beam of either electrons or positrons is initially accelerated in a small linear accelerator to near the speed of light. The beam then moves through a small booster ring to an outer storage ring, where the electrons are kept circulating at roughly constant energy. The beam is held in a closed orbit by bending magnets or wigglers and undulators, which produce the x-ray radiation. In a wiggler, the beam is forced to follow oscillating paths rather than move in a straight line. The oscillations are of high amplitude, causing the signals to add incoherently. In an undulator, however, the amplitude for oscillation is much smaller, which causes the radiation to add coherently. It

is interesting to note that the synchrotron method of x-ray production is commonly witnessed in nature, as in plasmas around stellar nebula.

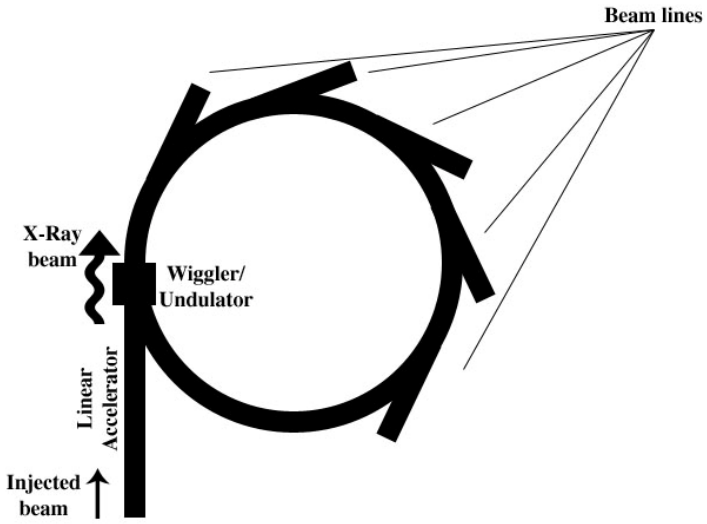


Fig. 5: Simplified diagram of a typical synchrotron facility. The beam is initially accelerated in a linear accelerator, and then held in constant circular orbit by magnets placed around the perimeter of the evacuated beam path. Tangents placed around this circle are usable beam lines, in which experiments such as diffraction may be performed.

The only major drawback to synchrotron radiation is the high cost to build and maintain a facility. Though this is indeed a major concern, there are still many laboratories that have been developed around such equipment. Synchrotrons are available, for example, at Stanford University (California), Argonne National Laboratory (Illinois), the European Synchrotron Radiation Facility (France), and Lawrence Berkeley National Laboratory (California). Most published data with x-ray diffraction is taken at one of those major laboratories, after initial testing with a table-top rotating-anode machine.

Sealed-Tube Sources

While rotating-anodes and synchrotrons are very popular x-ray sources, there are many other techniques that work well in modern special cases. For the machine used in this lab, for example, x-rays are produced by a *ceramic sealed tube*, similar in principle to the Coolidge tube. A tungsten filament, located in the negatively charged cathode, produces electrons that are drawn toward the copper anode. Upon colliding with its surface, the copper produces radiation at its characteristic wavelengths, which are collimated and sent down a beam line. This process is similar to the production of visible light in a light bulb, but the anode material causes it to instead produce photons in the x-ray spectrum. Machines that utilize this principle are now very small, and are a desirable choice for many companies and universities to whom size is a concern. The beam intensity produced is comparable to that of a rotating-anode generator, but come with a slightly higher initial cost. Modern techniques of x-ray production are continuously developing, as materials become available to shrink the size of the equipment.

Part III: Introduction to Crystallography

When a substance forms into its solid state, there are two different methods in which the process may occur. For many materials, the atoms do not bond in a regular pattern, leading the arrangement to a state of disorder. These materials are called amorphous, because they lack any sort of ordered arrangement in their fundamental structure. They bear many similarities to substances in their liquid form, and common examples include glass and wood. For other substances, however, the molecules form into a regular arrangement, called a crystalline state. B.D. Cullity defines a crystal as "a solid composed of atoms arranged in a pattern periodic in three dimensions" (Cullity, 32). All of the atoms are regularly spaced from each other to form a crystal lattice, which is repeated throughout the structure in an ordered fashion. The figure below shows an example of a simple point lattice, in which all atoms are represented by dots.

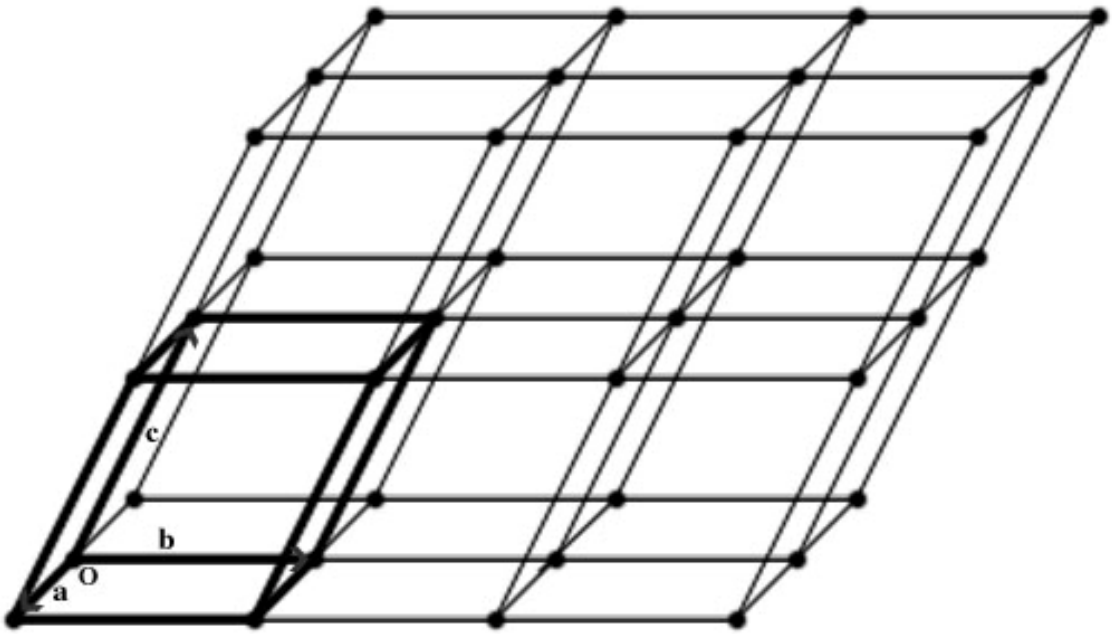


Fig. 6: A point lattice with the unit cell heavily outlined and lattice vectors noted.

Because the pattern is repetitious, one must only consider a small set of points in the structure to be able to predict the location of any other point. This initial set forms a *unit cell*, an example of which is outlined in bold in the figure above. By defining the unit cell, one may then label axes for the crystal in terms of the atom locations that fall along and inside of it. This is done by assigning vectors to each of the directions of translation, in terms of an origin (usually defined as a corner point). These vectors are usually written as **a**, **b**, and **c**, and they form the *crystallographic axes* of the unit cell. Using these vectors, one may then reach any other point in the lattice from the origin by a vector **r** that is a linear combination of the three vectors:

$$\mathbf{r} = a\mathbf{a} + b\mathbf{b} + c\mathbf{c}$$

One may also think of the unit cell in terms of the *repeat distances* a, b, and c between points (atoms), or even the angles α, β, and γ between the lattice vectors. After the unit cell has

been defined, it becomes possible to locate any point in the lattice from any other point by means of a *translation vector* **T**:

$$\mathbf{T} = P\mathbf{a} + Q\mathbf{b} + R\mathbf{c}$$

so that the location **r'** of the new point is:

$$\mathbf{r'} = \mathbf{r} + \mathbf{T}$$

There are many different systems associated with different repeat distances and vector angles. In this lab, we will deal primarily with cubic lattices, in which $a = b = c$, and $\alpha = \beta = \gamma = 90°$. Cubic lattices have very high symmetry, meaning that they may be rotated in almost any direction without changing the definition of the lattice vectors. Within the cubic system, there are different crystal orientations that are possible, the set of which is called the *Bravais lattices*. Several examples of these are pictured in the figure below.

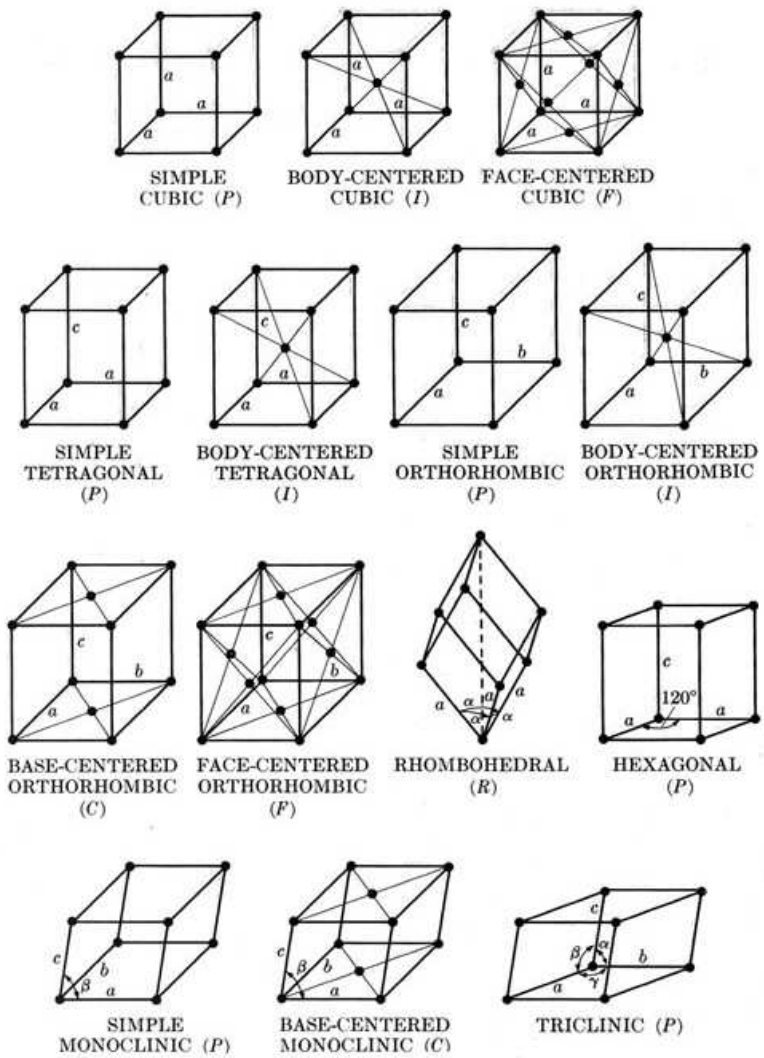


Fig. 7: The fourteen Bravais lattices (Reproduced from: B.D. Cullity, p. 36, fig 2-3).

The lattice vectors **a**, **b**, and **c** are useful for mathematical computations, but are rarely directly observable in the laboratory. As you will see in a minute, crystals may be probed with x-rays, and the lattice vectors may not be at all aligned with the x-rays' plane of incidence. Crystals have many different planes within themselves, and the x-rays will report all that are detectable with constructive interference. So, in an effort to describe the crystal in terms of each possible plane of incidence, one defines the system in terms of the intercepts of each plane with each lattice vector. Then, the reciprocal is taken of each intercept, forming an integer description of the relative locations of each crystal plane. These new numbers are called *Miller indices*, and are usually labeled *h*, *k*, and *l*. It is necessary to take the reciprocal in case the plane of incidence is parallel to a lattice vector; for such a system, the intercept is ∞, and so the corresponding Miller index is 0. In standard notation, the indices are always written as (hkl), with negative numbers represented as a bar on top of the index.

As an example, suppose we are looking at a plane that intersects the lattice vectors at (1/2)a, (1/3)a, and a. This plane would then give Miller indices of h=2, l=3, and k=1, and thus may be referred to as (231). If, instead, the plane intersected the lattice vectors at (1/2)a, ∞, and ∞, the Miller indices would be written as (200). Such an index corresponds to a plane parallel to both the **b** and **c** vectors, which intersects the **a** vector at half its repeat distance.

Through the use of x-ray diffraction, it is possible to determine the lattice constants a, b, and c for a particular system in question. When a beam of x-rays is incident on the surface of a crystal, the photons collide with individual atoms in the material, and then scatter off at the same angle as which they were incident. This collision is completely elastic, meaning that momentum alone is transferred in the scattering process, which is called *Thompson scattering*. Through iterative attempts at varying angles, one begins to notice that certain angles scatter a higher percentage of the beam than others, giving some insight into the actual composition of the material surface. The figure below illustrates this process of incidence and scattering off of the different planes in a point lattice.

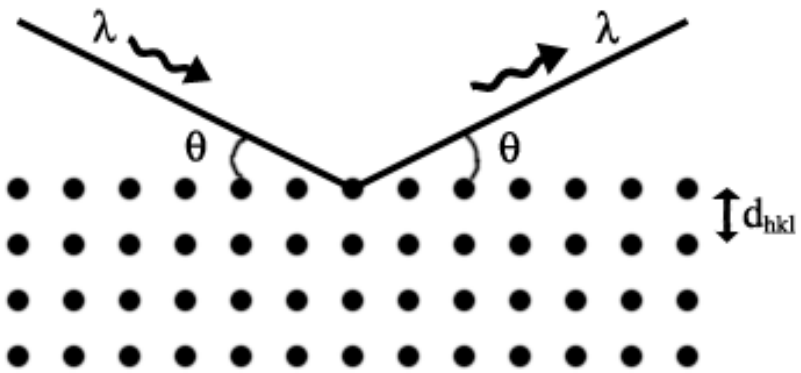


Fig. 8: Thompson scattering of photons with wavelength λ incident at an angle θ to the surface of a point lattice with interplanar spacing d_{hkl}.

By using an x-ray beam of known wavelength λ, one may find the separation distance d_{hkl} between planes through the Bragg law:

$$\lambda = 2d_{hkl}\sin(\theta)$$

This separation distance can then be used to compute values of *h*, *k*, and *l*, based on certain known formulas for different systems and Bravais lattices. In the face-centered cubic system (FCC), for example, each d_{hkl} must satisfy:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Recall that, for cubic systems, $a = b = c$; that is, each atom in the molecular structure is equally spaced from the others. Measurements at several different angles will give multiple values of d_{hkl}, and each of them has only one combination of integers *h*, *k*, and *l* that satisfy the above relationship. If the crystal repeat distance is known, one is then able to decipher which planes were detected by the XRD experiment through application of the formula.

In addition to the interplanar spacing formulae, there are also certain selection rules unique to each system, which each set of Miller indices must obey. As you have seen in Fig. 7, there are several possible orientations for each crystal geometry, and each of these has its own set of selection rules. By taking ratios of d_{hkl} for each angular measurement, these restrictions begin to emerge, and they allow formulas like the one above to be applied. They all may be derived mathematically, by considering the meaning of the Miller indices along with the requirements for constructive interference of the beam. Consider the question below:

<u>Exercise:</u>

If a face-centered cubic (FCC) lattice has $k = l = 0$, the selection rules require *h* to be even; that is, a peak may exist at (200) or (400), but not at (100) or (300). Why must this be true? What other selection rules can you derive for the FCC system? To check your answer, refer to Charles Kittel's *Introduction to Solid State Physics*, cited in the bibliography.

Part IV: X'PERT Powder Diffraction

In the experiment that follows, you will be walked through determining the Miller indices of various powdered materials. For the first series of experiments, try running the experiment with the suggested compounds, all of which are FCC. When you have a good handle on the measurement and analysis processes, try something more complicated, such as a tetragonal or orthorhombic geometry. A table of common crystals and their lattice constants may be found in Appendix B.

At this point, it will be assumed that the reader has already obtained access to the Materials Research Laboratory's XRD facility, as well as the login and password information for the computer control terminal. If such is not the case, then please discuss the issue(s) with your lab manager.

<u>The Experiment</u>

To begin, acquire a few different powdered samples (available in senior lab), as well as a sample holder (available from the MRL staff). Good sample choices for this experiment include Fluorite (CaF_2), Barium Fluoride (BaF_2), and Sodium Chloride (NaCl), to name a few. Head down to the MRL, and locate the X'PERT powder diffractometer. If you have any questions, please ask your lab manager or a member of the MRL staff.

Place the sample holder on the X'PERT stage, flip down the pin located immediately above, and pry up the stage to just barely meet the pin. This will put the sample at the optimal height for the beam, and ensure that x-rays are incident at the appropriate angle to the surface. Then, flip the pin back up to remove it from the beam path, and remove the sample holder to the outside of the machine to prepare your samples.

Next, fill the holder, pictured below in Fig. 9, with a small amount of the first sample. Pack the crystals down with a metal spatula, but try to use as little as possible for the measurement. The depth of sample should be only about one crystal (why?), not exceeding the top of the holder ridges, and it should be packed in the approximate middle of the well. Once packed, place the holder back on the stage, making sure that the sample holder is facing the proper direction with respect to the beam line. The silicon sample holders are cut a few degrees off-axis so that the material's own scattering angles do not interfere with the user's data. It must be oriented so this cut is facing the windows of the machine, and not directly down the beam path; the proper direction will be indicated somewhere on the holder. If everything looks ok, close the leaded doors of the machine (left one first, then right), and walk over to the computer control terminal.

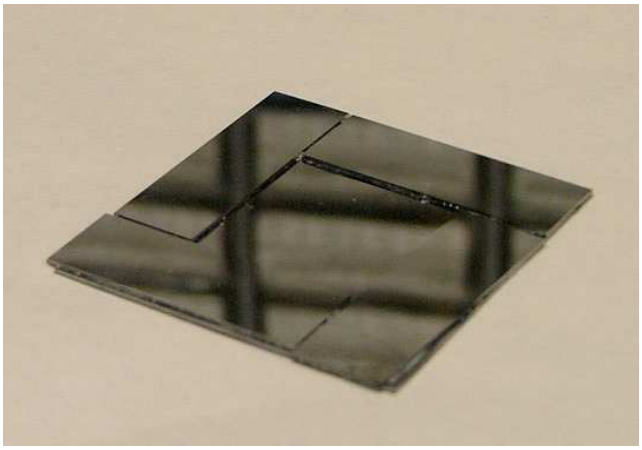


Fig. 9: The sample holder.

Immediately to the left of the computer monitor, there should be a list of instructions for initializing and operating the PANalytical Data Collector software. In case this is missing, a copy is included in the appendix to this document. Be sure to use the proper login name and password for the Physics 128 class, which may be obtained from the lab manager, instructor, or MRL staff.

Once the software has been initialized, click the INSTRUMENT SETTINGS tab on the left side of the screen, and then double-click POSITIONS to open position settings window, as pictured in the figure below. Set the 2theta angle to 45°, and then click OK to close the pop up window. At the top of the screen, click the MEASURE drop-down menu, and select MANUAL SCAN. This will allow you to set the parameters for the scan, which will be performed over the “gonio” axis. Change RANGE to 80°, and set TIME/STEP to a low enough value that the total scan time is 1-2 minutes. DO NOT CHANGE STEP SIZE (0.0083556) OR SCAN SPEED! Finally, click OK to begin the scan.

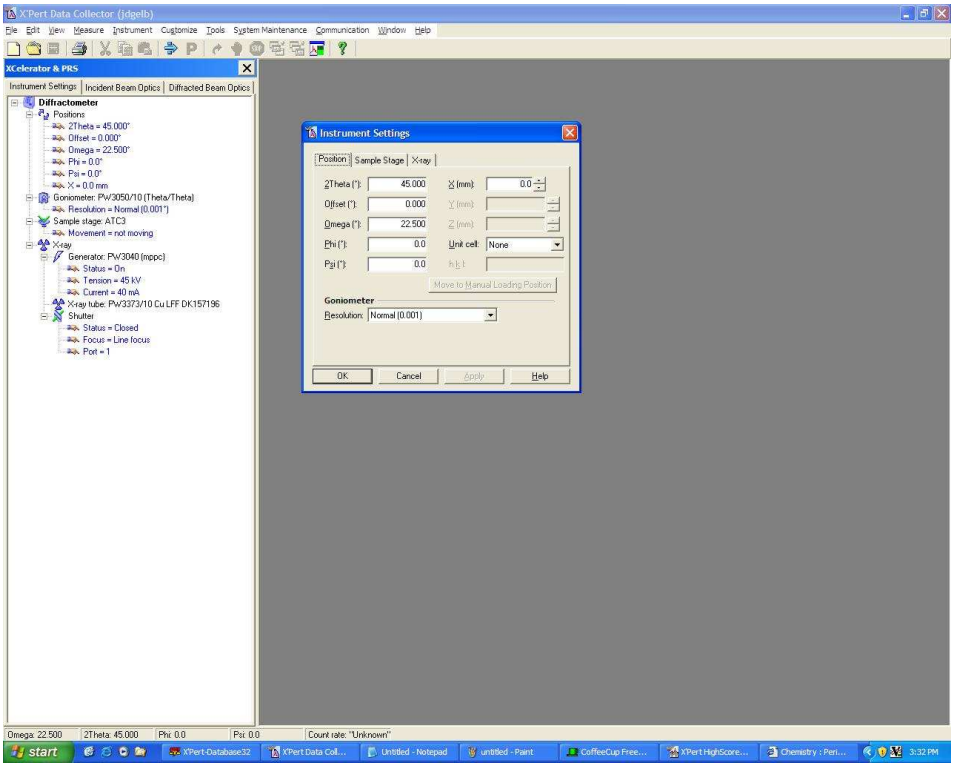


Fig. 10: Example of Data Collector interface and "Instrument Settings" dialog.

As soon as the scan begins, you will hear a click as the doors lock and then the orange LED on the arm of the x-ray source will light up. At this point, the machine is completely sealed off, and the user cannot open the doors (the author urges you to trust him on this, and not to attempt to prove it to yourself). The orange LED is to signal that the shutter is open, and x-rays are actively leaving the source.

When the scan has completed, a green, vertical line should appear on the graph displayed on the computer screen. Save the data by choosing FILE->SAVE AS from the menu bar, navigate to the Physics 128 folder under C:\XPERT data\, and provide a filename that contains the material name, current date, and your initials. Then, close the graph by clicking the X in the upper right-hand corner of the graph window; you will hear another click as the doors unlock and the shutter closes, and the orange LED should turn off. Replace your first powdered sample with the next, and repeat the process of data collection until all samples have been exposed.

Once you have run all of your samples, close the Data Collector program by clicking the X in the upper right-hand corner of the screen, and selecting OK when the confirmation dialog appears. Then, open the XPERT Data Viewer application, and use it to view your first data file (select FILE->OPEN and navigate to your directory). Select FILE->PRINT to get a copy of the graph, and then select FILE->CONVERT to convert the data into a comma-separated values file (.CSV). Save the .csv file to the Physics 128 directory on the hard disk, and open it with Microsoft Excel. Note the values for K-Alpha 1 and K-Alpha 2 wavelengths (in Angstroms), as well as the location of each peak; you

will need this information to perform your data analysis. It may even be a good idea to email this file to yourself, or save it to a removable disk, so that you have a personal copy for reference.

Repeat the procedure for all remaining samples. When you have finished with Data Viewer, close the program and clean up all your samples. Take them, along with your printouts, back to Senior Lab for further analysis.

Data Analysis

1. Using the graph and data table printouts from the experiment, note the 2theta angles that produced peaks of intensity.
2. The copper target used by the X'PERT produced three distinct lines of radiation. The primary line is called $K_{\alpha 1}$ and is the most intense wavelength associated with the target. It also produces $K_{\alpha 2}$ and K_{β} radiation, but the K_{β} line is filtered out and $K_{\alpha 2}$ is only about half the intensity of $K_{\alpha 1}$; in other words, $K_{\alpha 1}$ is the dominant wavelength for the copper target. Locate this wavelength on the printout and note its value – it will be listed in Angstroms.
3. Use Bragg's law to calculate the interplanar spacing d_{hkl} for each 2theta peak. Bear in mind that the angles reported by Data Collector are the sum of the incident and reflected angles, with respect to the plane of the crystal's surface. In other words, use
$$\theta = \frac{2theta}{2}$$
in your calculations of d_{hkl}.
4. Look up and note the lattice constant(s) in Appendix B or the MRL's structural database.
5. Locate the formula for the interplanar spacing in terms of the lattice constant(s) and Miller indices for the system's geometry in Appendix C. CaF_2 is a face-centered cubic lattice with a = 5.450, and so, by Cullity, it must satisfy the relationship:
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
6. For each value of d_{hkl}, calculate the whole numbers h, k, and l that give the appropriate value of a. Use these to label each peak on the graph with its Miller index.
7. Repeat the analysis procedure for each of your samples.
8. Look closely at the high scattering angles on your graphs. Do you see the existence of any doublets? If so, note the intensity of the second peak with respect to the first. What do you think is the cause of this phenomenon? Prove your theory.
9. Go back to the MRL and use the database on X'PERT High Score to look up your samples. How do your results compare with the published values? If you guessed the correct h, k, and l for each d_{hkl}, give yourself a pat on the back – you deserve it.

Further Analysis

1. Analyze a couple of different FCC lattices, and look at their Miller indices. What selection rules for *h*, *k*, and *l* can you determine for this system? Do they agree with the ones you derived analytically?
2. Do all of your samples obey the selection rules you calculated? Explain any discrepancies.
3. Suppose you did not know the lattice constant(s) for a particular system. How would you find it/them, assuming you have already classified the system's geometry?
4. Try repeating this experiment with a hexagonal, tetragonal, or orthorhombic structure. How might you determine the lattice constants for these systems if you did not have Appendix B?

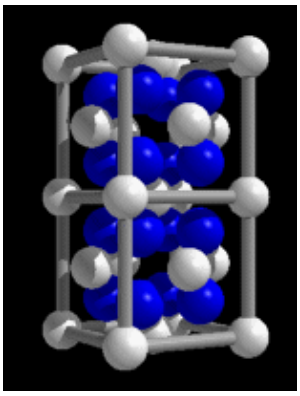


Fig. 11: Model of CaF_2. The outer points represent the Calcium ions, and the inner ones are Fluorine. Note that the FCC lattice is formed by the Calcium ions alone, and Fluorine only exists in the tetrahedral holes (reproduced from McClure).

Analysis with HighScore

In most realistic situations, data analysis is performed done on the computer rather than strictly by hand. Many times, a sample's composition is unknown, and powder diffraction is used to gain the information necessary to identify the material. On the terminal connected to the X'PERT, there is a very powerful analysis program called HighScore, which greatly aids in this effort. It contains a database with all diffraction data that has ever been published, and can compare the user's data to each entry, producing a list of possible candidates. As an exercise, work through the steps below to see how well HighScore can guess the composition of your samples, and compare your results to those that have been published.

1. Open the program by double-clicking on the icon labeled "X'Pert HighScore," which is located on the desktop.
2. Select FILE->OPEN, navigate to the Physics 128 directory, and open the .xrdml file from your experiment. A graph of the data should open on the upper-left of the screen.

3. In order for HighScore to discern the peaks, you must first specify the background radiation (i.e., the photon count intensity between peaks). Select TREATMENT->DETERMINE BACKGROUD, which will open up a control window. Keeping your eye on the green line at the bottom of the graph, drag the slider up or down so that it lines up with the background. Once finished, select “Subtract,” and then “Replace.” What are the sources of the background radiation?

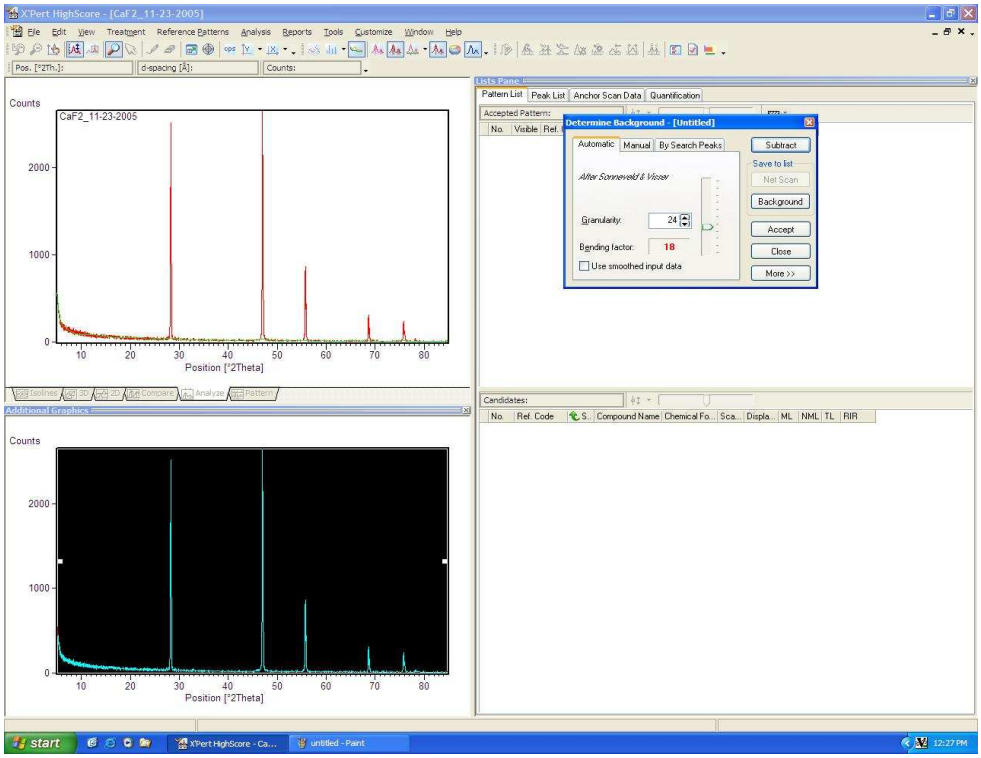


Fig. 12: Background determination in HighScore.

4. As you saw before, the data provided by the X’PERT contains peaks from both the K-Alpha 1 and K-Alpha 2 lines. This can be very confusing for HighScore, and can cause it to mistakenly identify peaks. To remove the excess lines, select TREATMENT->STRIP K-ALPHA 2. In the new window that pops up, select “Strip K-Alpha 2,” then “Replace.”
5. Next, we need to have HighScore determine the peak locations that it will compare with the database. To do this, select TREATMENT->SEARCH PEAKS, which will draw red tick marks at all possible peak locations. If it guesses peaks that aren’t there, increase the value of “Minimum significance” and click “Search peaks” again; if it doesn’t find all of the peaks, then reduce “Minimum significance” and click “Search peaks” until it does. When you are satisfied with the results, click “Replace.”

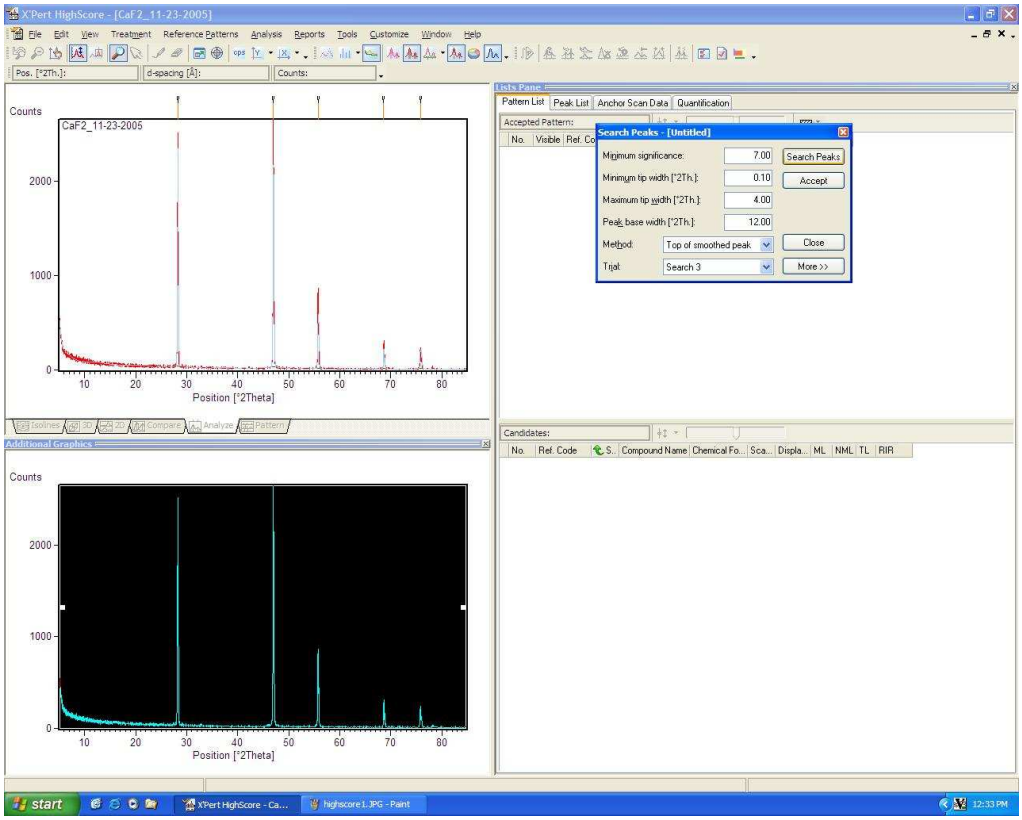


Fig. 13: Peak determination in HighScore.

6. Now, we can ask the program to compare the results with the database maintained by the International Center for Diffraction Data (ICDD). Select ANALYSIS->SEARCH & MATCH->EXECUTE SEARCH & MATCH. In the new window, click on the “Restrictions” tab, and select “None.” Then, click the “Parameters” tab, and set the data source to “Peak & Profile Data.” Finally, click “Search.”
7. At this point, HighScore will give a list of candidates on the right side of the screen, along with a ranking of how well each matches your experiment. By clicking on each search result, the corresponding stick diagram appears in the bottom left window, above that of your data. This indicates only the angles that exactly satisfy Bragg’s Law, and shows their relative intensity with respect to each other. Did HighScore guess correctly? If not, what might have gone awry?

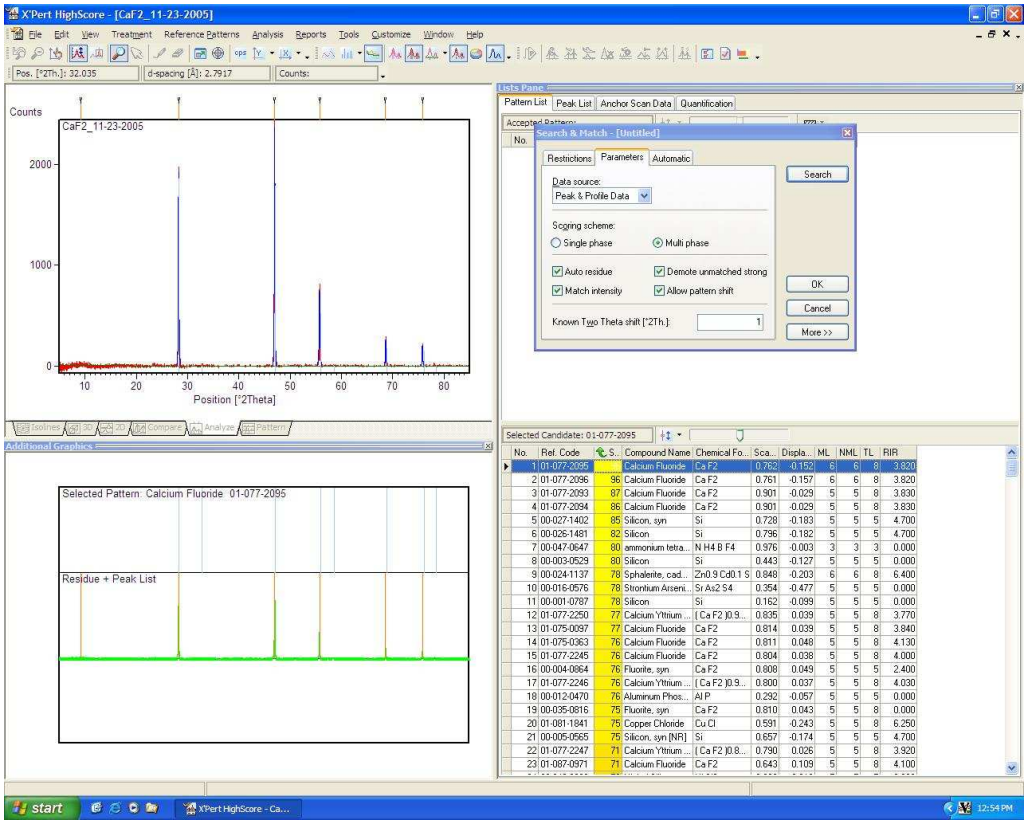


Fig. 14: Results of searching ICDD.

8. For comparison, select REFERENCE PATTERNS->RETRIEVE PATTERN BY->TEXT SEARCH. In the field labeled "Search for String," type in the chemical formula for the sample with a space between each element (e.g. CaF_2 is entered as Ca F2), and select the bubble labeled "Formula." Then, click "Load," followed by "Close." This will bring up a list of search results in the upper right window – double-click any of them to retrieve the published data. You may make a printout of each reference page by copy and pasting into Microsoft Word, or any other text editor on the computer.
    a. How well does your experiment match the published one? What about your calculations for the Miller indices?
    b. Are there any peaks missing from your experiment? What might account for this?

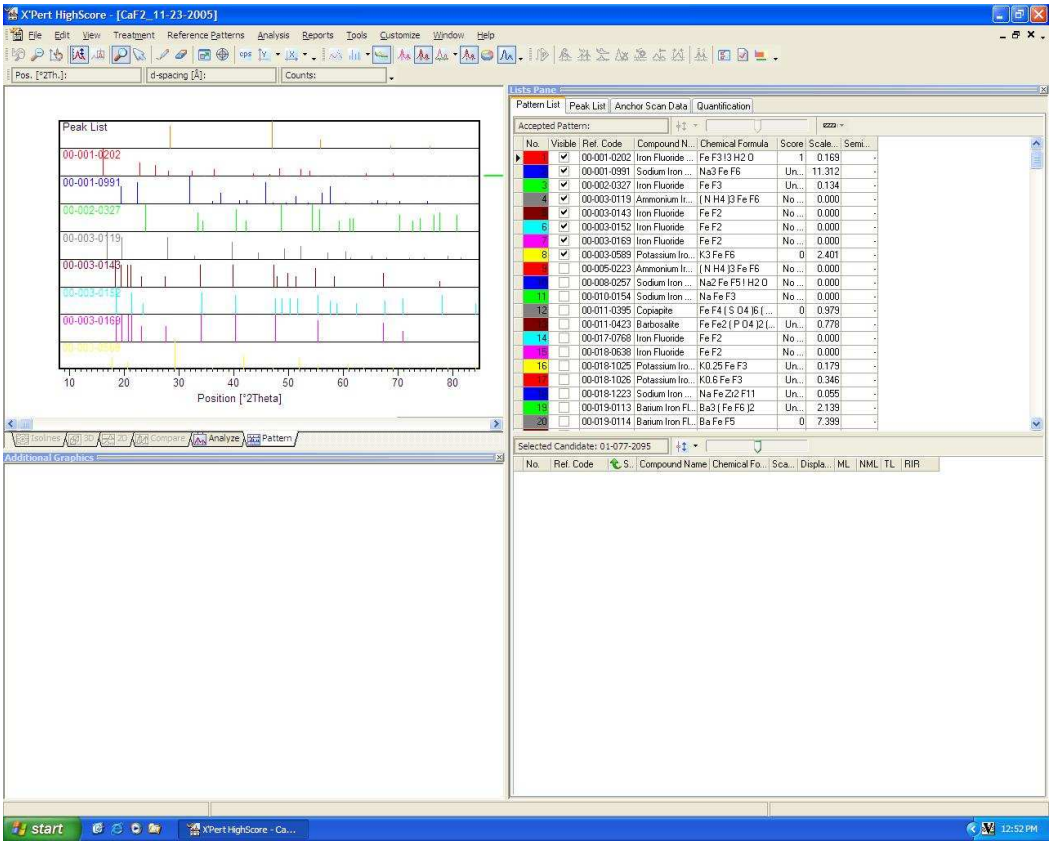


Fig. 15: Results of searching reference patterns for fluorite.

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Appendix

A. Data Collection on XPERT XRD with new X'celerator Detector

Initialization

1. Start DATA COLLECTOR program and log in
2. Click 'INSTRUMENT' ->'CONNECT'
3. In list of configurations, choose 'X'celerator & PRS', and click 'OK"
4. Click 'OK' in pop up information window. Once instrument is online, control panel is located on the left of the window.
5. From the menu on the top, choose 'CUSTOMIZE -> OPTIONS', and in the pop up window, click on 'POWDER' and choose configuration to be 'X'celerator & PRS'. THIS STEP IS NECESSARY ONLY FOR THE FIRST TIME YOU LOG IN.
6. In control window, click on 'INCIDENT BEAM OPTICS' tab
7. Click on 'Divergence Slit' (Slit #1 in instrument) and 'Anti-scatter Slit' (Slit #2) and change to the values of slits used in the instrument. (Recommended: 1 deg for Divergence Slit and 2 deg for Anti-scatter slit). DO NOT CHANGE OTHER SETTINGS.
8. Click on the tab 'Diffracted Beam Optics' and click on 'Detector..'. In the pop up window, choose

   Type: X'celerator[2]
   Usage: Scanning
   Active Length (2 Theta): 2.122

   Click 'OK' to close window

Manual Scan

1. In control window, click on 'INSTRUMENT SETTINGS', then 'POSITIONS' to open up a pop up window showing current positions of the instrument. Type in desired position and click 'APPLY' or 'OK' to move the instrument
2. Choose 'MEASURE' = > 'MANUAL SCAN'
3. In the parameter window, change 'Range' and 'Time/Step' to set up the scan. DO NOT CHANGE 'STEP SIZE (0.0083556)' AND 'SCAN SPEED'
4. Click 'OK' to start the scan. Data will be displayed in a graphics window. A green line representing the resting position of the instrument once the scan is finished.
5. Right click in the graphics window to choose 'ZOOM', 'PEAK', 'FWHM' modes for the display
6. Choose, 'FILE' =>'Save As' to save data to your own folder
7. Click 'OK' to close manual scan window

Program Scan

1. On the file menu, choose 'NEW PROGRAM'. Choose program type and click 'OK'

2. In the program set up window, choose scan type (Gonio for default), type in ‘START ANGLE’ and ‘END ANGLE’. DO NOT MODIFY STEP SIZE AND TIME
3. Click on ‘SETTINGS’ to open another window with list of all the instrument parameters. Most of them will show ‘ACTUAL’. From the list, click on ‘Detector’, on the window below, choose

   Type: X’celerator[2]
   Usage: Scanning
   Active Length (2 Theta): 2.122

4. Click ‘OK’ to return to the main program window, which will show a step size of 0.0167113. DO NOT MODIFY STEP SIZE AND SCAN SPEED. Change ‘TIME/STEP’ to set total scan time.
5. Click on ‘x’ to close and save the program
6. On the menu, choose ‘MEASURE -> PROGRAM’. Select correct folder and type in dataset name. Click ‘OK’ to start data collection. Data will be saved automatically.

Data Printing

Use the program DATA VIEWER to display and print data

Data Processing

Use the program HI-SCORE to display, treat, index, and match the diffraction data to known phases contained in PDF 2 database. Refer to quick start manual for HI-SCORE located on the desktop for details.

Slit Settings

Only two slits are used for the new detector. A divergence slit (S1) and an anti-scatter slit (S2). Because the resolution is determined mostly by the pixel size of the detector, using smaller slit does not necessarily improve the resolution. Several settings with typical applications are listed below

S1	**S2**	**Intensity (%)**	**Resolution (Deg)**	**Comments**
1	2	100	0.10	Recommended for most powder & thin film samples
½	1	55	0.08	Use this only if resolution is important
¼	½	28	0.08	Do not use this!
1/16	1/8	N/A	N/A	Use this only for SAXS measurements. Mininum 2Theta is 0.5 deg.

B. Crystal Structure of Selected Compounds

Substance (Mineral Name)	**Structure Geometry**	**Lattice parameters (Å)**
NaCl (Halite)	FCC	a = 5.6280
KCl (Sylvite)	FCC	a = 3.1380
CaF_2 (Fluorite)	FCC	a = 5.45
PbS (Galena)	FCC	a = 5.93
PbTe (Altaite)	FCC	a = 6.4390
PbSe (Clausthalite)	FCC	a = 6.1620
FeF_2	Tetragonal	a = b = 4.7000, c = 3.3100
BaF_2	FCC	a = 6.1870
PbF_2	Orthorhombic	a = 3.800, b = 6.4100, c = 7.61
GeAs	Tetragonal	a = b = 3.7150, c = 5.8320
Ge	FCC	a = 5.62
$KMnF_3$	Cubic	a = 4.1890
InSb (Antimony Indium)	FCC	a = 6.4782
CdS (Greenockite)	Hexagonal	a = b = 4.1420, c = 6.7240 $\alpha = \beta = 90°$, $\gamma = 120°$
KBr	FCC	a = 6.5780
$Cu(BrO_3)\cdot 6H_2O$	Orthorhombic	a = 6.6840, b = 9.2230, c = 11.9190
Al	FCC	a = 4.0406

($\alpha = \beta = \gamma = 90°$ unless otherwise noted)

Source: International Center for Diffraction Data

C. Plane Spacing Formulae

Cubic: $\frac{1}{d_{hkl}^{\ 2}} = \frac{h^2 + k^2 + l^2}{a^2}$

Tetragonal: $\frac{1}{d_{hkl}^{\ 2}} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$

Hexagonal: $\frac{1}{d_{hkl}^{\ 2}} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$

Rhombohedral: $\frac{1}{d_{hkl}^{\ 2}} = \frac{\left(h^2 + k^2 + l^2\right)\sin^2\alpha + 2\left(hk + kl + hl\right)\left(\cos^2\alpha - \cos\alpha\right)}{a^2\left(1 - 3\cos^2\alpha + 2\cos^3\alpha\right)}$

Orthorhombic: $\frac{1}{d_{hkl}^{\ 2}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

Source: Cullity, 501.