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Determination of Unit Cell Constants from the Powder X-ray Diffraction Pattern  
( Windows95/98/2000/NT )

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If a reasonable set of the unit cell constants could be obtained by using the programs introduced below, you may perform the peak fitting procedures by use of GSAS. If this could be successfully performed, it means that you have a set of intensity data to be used to solve and refine the structure in a conventional manner, as the single crystal X-ray crystallographers perform. This is one method I know. And this sounds easier! However, in the actual refinement, we also need to evaluate the peak shapes. In the modern Rietveld analysis, several important factors must be taken into consideration in performing the deconvolution procedure and structure refinement simultaneously. One is that the unit cell constants, and the positional/thermal parameters can be refined at the same time during the same least-squares minimization processes. Second, we can also suppress the background data within the same least-squares analysis. It also involves a component evaluating the preferential orientation term (this is the term how the needle-like crystals prefer to lie down on their sides when they are located on a sample container). It also involves a set of parameters defining the peak function. Since I am not well familiar with the Rietveld method, I should stop here to give you the suggestions about it. Anyway, this time, I send these data to you, together with the cell determination programs. And you should try how they work. All we need to do first is to get to an appropriate guess about the unit cell constants. This is the main entrance to the Rietveld method. In the following, I will mention some instructions about how you should use the programs one by one! The larger the molecular volume is, the smaller the peak-to-peak separation is. This makes it more and more difficult to carry out the Rietveld analysis. But at the same time it sounds somewhat challenging!!

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<<What programs do we need to install before starting? And what we do?>>

- (1) XRDCConv.EXE This is a file converter for the diffraction data.  
It reads the data collected in either Rigaku or Mac Science system. And saves a data file having an extension of \*.DAT.
- (2) XFIT.EXE This reads \*.DAT.  
In this program peaks are graphically, but in a sense manually, selected so as to prepare a file for the subsequent cell determination runs in CRYSFIRE. The peak file should be saved as a file named as 'XFIT.TXT'
- (3) XF2CRY.S.EXE This is a converter to generate a file to be read by the CRYSFIRE program. With this converter, XFIT.TXT will be saved as a file having an extension of \*.CDT.
- (5) CRYSFIRE.EXE This program reads the CDT file (\*.CDT) and performs 5 or 6 automatic cell determination programs called (1) ITO12, (2) DICVOL91, (3) TREOR90 (this

seems nice), (4) TAUP, (5) KOHL, and (6) FJZN6. There are two more programs installed in this system, but they do not work with some reasons. I don't know why so, but we can just forget about them because 1-6 tests seem enough!

- (6) CHECKCELL.EXE This first reads the peak listing (XFIT.TXT) and also reads the results of tests done by CRYSFIRE (\*.SUM). Then we can visually check the matching between the observed peak positions and the calculated peak positions for each unit cell. If you find any good result, save the cell from File/Save/cell. The file will be saved as \*.CRY (this will be read by the CELREF.EXE for further cell refinement in which systematic absences due to the difference in space group will also be taken into consideration).
- (7) CELREF.EXE This first reads the peak listing (XFIT.TXT) and also reads one of the results of tests done by CRYSFIRE (\*.CRY; save by CHECKCELL.EXE).
- (8) POUDRIX.EXE This reads \*.DAT generated above at procedure (1), and you should manually input the cell constants. In this program, you may also perform a simulation of the powder pattern by locating atoms by defining the actual atomic coordinates under a certain space group. This is not the actual Rietveld analysis. Nevertheless, if you have any idea with regard to the positions of major heavier atoms involved in the asymmetric unit, you might be able to get a reasonable simulation pattern only with use of this program. If you could get to a good goal, the results can be, for sure, refined by the Rietveld method.

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<<Installation of the programs>>

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**XRDCnv.EXE (download from <http://www.scc.kyushu-u.ac.jp/Sakutai/>)**

A standalone program developed by Sakai. It reads the X-ray data from the Rigaku and Mac Science instruments, and saves a \*.DAT file to be read by XFIT.EXE and POUDRIX.EXE.

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**XFIT.EXE**

Involved in a folder named **KOALARIE**

This folder should be located right below C:¥ (this is suggested by the developer of this program).

Where you get the program?

From the Web site listed below, download a zip file 'k-inst8.zip' and unzip the file.

Then you will find a folder named KOALARIE.

<http://www.ccp14.ac.uk/index.html>

<http://www.ccp14.ac.uk/ccp/web-mirrors/xfit-koalariet/k-inst8.zip>

<http://ccp14.sims.nrc.ca/ccp/web-mirrors/xfit-koalariet/k-inst8.zip>

<ftp://ftp.minerals.csiro.au/pub/xtallography/ccp14/ccp/web-mirrors/xfit-koalariet/k-inst8.zip>

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**CRYSFIRE.EXE**

**XF2CRYS.EXE**

These are involved in a folder named CRYSFIRE.

This folder should also be located just below C:¥ as C:¥CRYSFIRE.

The folder will be given by unzipping crysinst.zip obtained from the CCP14 sites below.

There is a crysinst.exe file to get this folder.

<http://www.ccp14.ac.uk/tutorial/crys/obtain.htm>  
<http://www.ccp14.ac.uk/ccp/web-mirrors/crys-r-shirley/>  
<http://ccp14.sims.nrc.ca/ccp/web-mirrors/crys-r-shirley/>  
<http://ccp14.semo.edu/ccp/web-mirrors/crys-r-shirley/>

Two important settings should be carried out as follows.

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Step 1.

One is to make your environment space larger so as not to receive an error message from the CRYSFIRE programs. If this is not set, you will see a message, 'out of environment space'. To avoid having this problem, you should set your SHELL larger as summarized below.

When you are working on Windows95/98, a c:\config.sys file should be edited by a certain text editor. Make a copy of one of the following three lines, and paste it into the file, save it, and exit.

```
SHELL=C:\WINDOWS\COMMAND\COMMAND.COM C:\WINDOWS\COMMAND\ /E:1024 /P  
SHELL=C:\WINDOWS\COMMAND\COMMAND.COM C:\WINDOWS\COMMAND\ /E:2048 /P  
SHELL=C:\WINDOWS\COMMAND\COMMAND.COM C:\WINDOWS\COMMAND\ /E:4096 /P
```

The values after E: correspond to the size of memory for the task done by CRYSFIRE. The last one would be good enough!

When you are working on Windows2000/NT, this could be defined as an environment variable. Environment variable named 'shell' should be defined as follows.

```
C:\WINNT\SYSTEM32\COMMAND.COM c:\WINNT\SYSTEM32 /e:4096 /p
```

If you are working on XP, input the following term instead of the above one:

```
C:\WINDOWS\COMMAND\COMMAND.COM C:\WINDOWS\COMMAND\ /E:4096 /P
```

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Step 2.

Finally, set the path for C:\CRYSFIRE.

For the Windows95/98 users:

Edit a file named 'c:\autoexec.bat'.

Add ';c:\crysfire' at the end of the line like follows:

```
Set Path=c:\windows;c:\...;c:\????;.....;c:\windows\command
```

The paths are separated by semicolons in this command line. So, you will the final line should appear as follows:

```
Set Path=c:\windows;c:\...;c:\????;.....;c:\windows\command;c:\crysfire
```

Windows2000/NT Users:

'c:\crysfire' should similarly added as an environment variable like 'SHELL' above.

In this case, 'shell' is already defined as your environment variable in you computer. So, add 'c:\crysfire' as the final path defined in the list.

Now you can run both CRYSFIRE.EXE and XF2CRYS from any DOS prompt at any directory!!  
Congratulations.

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**CHECKCELL.EXE**  
**CELREF.EXE**  
**POUDRIX.EXE**

These can be given by decompressing zip files: celref.zip, checkcell.zip, and poudrix.zip.  
All of them can be obtained from the CCP14 site as in the case mentioned above for the CRYSFIRE and KOALARIE programs.

<http://www.ccp14.ac.uk/tutorial/lmgp/index.html#chekcell>  
<http://www.ccp14.ac.uk/ccp/web-mirrors/lmgp-laugier-bochu/>  
<http://ccp14.sims.nrc.ca/ccp/web-mirrors/lmgp-laugier-bochu/>  
<http://ccp14.semo.edu/ccp/web-mirrors/lmgp-laugier-bochu/>

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\*\*\*\*\* About the LMGP Suite \*\*\*\*\*

There are many good facilities available from this site. The developer is Dr. Jean Laugier. The details are explained below.

<http://www.ccp14.ac.uk/index.html> ( there is some explanations on it )

- \*CELREF.zip      Estimation of Cells and Performing the least-squares refinement on them  
(this is one of programs introduced above)
  
- \*chekcell.zip    This is a modified version of CELREF.EXE. It seems that it has an automatic routine to determinethe cell constants, but I still do not know exactly how it works. But I think this can be a powerful tool for the estimation of the cell constants. One merit is that it reads the results of CRYSFIRE (\*.SUM) directly.  
(This is another program I explained this time above)
  
- \*poudrix.zip    This reads the peak position file (\*.DAT). By defining the unit cell constants as well as the atomic coordinates of possible atoms located in the asymmetric unit of the crystal of interest, a simulated X-ray diffraction pattern will be generated by this program. This is nice!
  
- descript.txt     I don't know what it is.
  
- dispano.zip      Visualization tool to view the anomalous scattering factors.
  
- equiv.zip        This shows you the symmetry operations of all the space groups. This could be used as a replacement tool for the Internatioal Tables for X-ray Crystallography.
  
- getdll.zip
  
- getspgr.zip      It reads shelxl.ins from SHELXL97 and let us know about the space group for it. I am not sure, right now. I once tried before, but now I have totally forgotten what it is.

gretep.zip gretep.txt	You can view the ORTEP view with this program.
indx.zip	Simple tool to generate a list of angle for each hkl by defining the unit cell constants and the space group.
lepage.zip	This is related with the program shown below named truecell. It give you the details on the appropriate unit-cell conversion matrix. It helps you think of the matrix for the appropriate transformation of the unit cell constants. For example, you may have to transform your cell to satisfy the standard settings for your cell.
orientex.zip	This visualizes the data from the so-called photograph method.
scatfac.zip	Perhaps, it helps you think about the atomic scattering factors of each element at a certain angle. I don't know the details of it.
truecell.zip	This reads the results of CRYSFIRE (*.SUM), and help you determine the true Bravais lattice constants. This routine seems to be involved in CHECKCELL, and should be done at the final stage in any case!! So, we have to do it to get to the correct setting of the cell.
wgetspec.zip	This also reads *.ins files from SHELXL97 and inform you the details about the space group.
wulff.zip	Perhaps, this is a program for the photograph method. I don't know the details.

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Unit cell determination using CRYSFIRE (one possible route is given below!)

- (1) If it is a file from a Mac Science instrument, and the file is an EXCEL file (sample.xls), open it by EXCEL and save it as a text file.  
If it is a file from a Rigaku diffractometer, and the file has an extension of 'ASC', which means that it is an ASCII file. Remember that the extensions for these files can be whatever.  
Let's suppose we now have a file named as 'sample.ASC'.
- (2) Open the file 'sample.ASC' by XRDCnv.EXE (developed by K.S.). Open it from File/Open if it is the file from the Mac Science one. Open it using File/OpenRigaku if it is a file from the Rigaku one. If the file is correctly read without any error, numerical data will be filled into the cells within the program window. Then save the file from File/Save\_XFIT\_DATA. Then the file should be saved as 'sample.DAT'. There is no strict requirement about the file name here again.
- (3) Run the XFIT.EXE program, and load the data (sample.DAT) from File/Load\_Data. However, I also gave some instructions below. Please learn the details at [http://www.ccp14.ac.uk/tutorial/xfit-95/peak\\_result\\_file.html](http://www.ccp14.ac.uk/tutorial/xfit-95/peak_result_file.html), if necessary.
- (4) Maximize the window size to better look at your powder pattern, first.
- (5) We now want to determine the position of peaks. Since there is no automatic peak picking routine available in this program. We do that manually and graphically. But this is the safer way to make a convincing list of peak positions. We only need 20 or 30 peak positions in the subsequent analysis. But remember that this routine might affect the result. So, if you do not get a good result in the subsequent analysis in CRYSFIRE and CHECKCELL. You should think about re-making the list of

peaks to be processed in CRYSFIRE. In the default routine, CRYSFIRE uses the first 19 peaks or so. Therefore, you should think of making a new list by skipping some of the peaks in lower angles.

- (6) Now I explain how to use the program:
  - >>If you give a right click on the signal window, the position will be set as a maximum point of your view.
  - >>If you give a left click on the signal window, the position will be set as as minimum point of your view.
  - >>Using these you will be able to zoom up with regard to the angle axis.
  - >>If you want to initialize the view, press the key 'l' (it's not 'one' but is 'L').
  - >>If you want to make a shift with regard to the angle axis, use the blue arrow button at the let top corner (in the right end of them). If you give a right click, the peak will move in the left direction, and vise versus.
- (7) If you are ready to select you peak positions, select the 'Ins/Del\_Peaks' button in the 'OPTION' window.
- (8) Let you cursor overlapped onto one of your signal TOP, and give a left click to actually make a selection of it. If your selected angle position seems wrong and you want to retry the selection, you can release the selection by giving a right click on the selection line. Do this process as carefully as possible because it should, for sure, affect the results.
- (9) Please be careful not to select a peak which is too weak. After you once finished your selecting task, you may initialize the view window by pressing 'l' to re-evaluate if you are really successful. If there is a doubtful one, please deselect it!
- (10) Now, to save the list of peak, you should select the 'File Details' item at the 'OPTION' window. Then, you should have a new window. There you should select 'Peaks', and then 'Two Theta, All Pk types'. Finally, click 'Creat TXT Reports'.
- (11) Now, you have another window which shows you the list of peaks in a file format which can be read by the CRYSFIRE program. To save this file there seems several routines at File/Save or File/Save\_As. But these do not correctly work when working along with Windows 2000 and XP. So, what I am doing is to select the whole part of the text codes displayed within that window, and press 'Cntrl' + 'C' to make a copy of the content. Then paste it directly onto a blank text file, and then save it under a name of 'XFIT.TXT'. In this case, the name should be exactly same with 'XFIT.TXT'. You can save it as 'xfit.txt' because MS-DOS doesn't care whether it is named by small letters or capital letters. UNIX does care, but MS-DOS doesn't!
- (12) You should now have an MS-DOS prompt cell to work up on the data using the CRYSFIRE program. If you are not familiar with this, then go to 'START'/'PROGRAM'/'ACCESSORY'/. Somewhere around there you should find 'Command Prompt' or something similar to this. Then launch it, and type in as follows:

Let's suppose that your data is located within d:\data\test  
Type the following codes.

```
> d:[return]
> cd \_[return] (where _ means that you should type in a single space)
> cd_data\test
> us[return] (if you are working on a Japanese system) (US and Canadian people can skip this)
>XF2CRY[return] (this launch the program XF2CRY.S.EXE, which converts XFIT.DAT into a file
to be read by the CRYSFIRE program)
```

>Repeat typing the [return] key to process the file conversion all in a default way. If all the tasks have completed successfully, you should have a resultant file named 'sample.CDT'. The extension name CDT means that this is a Crysfile DaTa. The name before the extension can be whatever you want. To tell the truth, XFIT.TXT could be in a different name, but in order to make it easier, I explained that the name should be exactly same with this.

In the following, I gave some minimum explanations about the MS-DOS commands necessary to work up under the MS-DOS operating system (The younger people should be unfamiliar with this, even though it's quite similar to that in UNIX in a sense).

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MS-DOS commands often used:

c:[return] or d:[return] (This is to get into a folder below the folder where you are now in access.)

cd folder[return]      cd folder¥folder2¥folder3[return]    ( change directory )

cd ..[return] (this is to go to the upper directory.    If you do this when you are in c:¥folder¥folder2, you can go back to c:¥folder)

dir[return] or dir /p[return] (shows you the content of the directory where you are in access. The option '/p' means that you can show them page by page, by pressing [return] )

dir .dat[return]    (you will be able to look at the file having an extension name of 'dat', if there is any. '\*' means whatever.)

del name[return]    (deleting a file)

copy name name2[return] (make a copy of file, where file 'name' will be overwritten into file 'name2'.)

copy name c:¥folder¥folder2 (the file 'name' will be copied into the folder assigned at the end)

copy name c:¥folder¥folder2¥name2 (the file 'name' will be copied as 'name2' into the folder assigned)

md folder[return] (make a directory below the access folder)

rd folder[return] (this remove the folder, if it is an empty folder)

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(13)Launch the CRYSFIRE suite. (This can be run either in Japanese or in US mode) by typing as follows:

C:¥data¥test > crysfire [return]

(just type in crysfire and then return at the folder where you are working)

(14)LO [return]

(15)Sample[return] (you should not enter the extension term for this query)

(16)SA [return]

(17)Q[return]

(18)IT[return] (Instead of IT, DV, TR, TP, KL, FJ and LZ can also be selected for this. Repeat the same procedure from (13) to (20) seven times.)

(19) All the queries can be merely answered as a single [return] to perform the calculation by default. If you get used to the program and you know how you should determine the detailed conditions for the calculations, you may have to think about giving your own choice at each query. However, I do not know well about these routines. I will stop here in giving further messages in this regard.

(20) At the next query about the CRYSFIRE command, please enter as follows:

QU [return]

[return] (upon the second return the calculation will start!)

Repeat giving [return] for the subsequent queries until you get a MS-DOS command prompt.

(21) Go to (13) if you have not finished performing all the seven possible tests (IT, DV, TR, TP, KL, FJ and LZ).

(22) The results of calculation will be stored in a file named 'sample.SUM'. In this file, the second value in each line (I/I20) corresponds to the number of peaks which gave a good match with the corresponding observed peak position. Therefore the larger this value is, the more the validity of the assignment becomes high.

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Evaluation of the results from CRYSFIRE using CELREF (The routine using CHECKCELL described below would be easier, so I rather recommend the method using CHECKCELL)

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- (1) Launch the CELREF program.
- (2) From the Measured reflections window, open the 'XFIT.TXT' file involving the list of peak positions. Open it from 'File' under the XFIT.TXT format.
- (3) Activate the sheet for the Initial cell parameters, and click the Keyboard button.
- (4) If a window handling the unit cell parameters appear, select an appropriate crystal system for it, assign your space group (just guess what it is!), and then input your cell constants, and finally press the 'Calc.' Button. If an error message appears, it often means you forget to assign either of cell constants, crystal system, or space group for your trial. If it works, you will see multiple green lines appeared at the bottom of the window. It shows you the calculated peak positions for your assumption. All you need to do is to check if the observed and calculated positions of peaks are consistent to each other.

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Evaluation of the results from CRYSFIRE using CHECKCELL (this program read the list of results generated by CRYSFIRE, and that's the merit of using this! And this one seems easier.)

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- (1) Launch the CHECKCELL program.
  - (2) At the Measured reflections sheet, open your peak listing file (XFIT.TXT) from File under the appropriate file format.
  - (3) Open up the Cell parameters sheet, and click the 'Crysfire File' button. Select the file 'sample.SUM' which involves all the results given by the automatic cell determination procedures implemented in CRYSFIRE.

**<<<< Treatment at the cell parameters window >>>>**

- (4) Search your best choice of unit cell, by evaluating the matching in the positions between the observed and calculated peak sets. However, it is often difficult to evaluate the results only from the apparent view of them.
- (5) In order to obtain a good solution, you should try the 'Best Group', the 'Best Solution', and the 'TrueCell' procedures. If you are able to obtain a good guess, then select the line you have chosen as a result of extensive analysis by use of the above mentioned routines available at this stage.

**<<<< Treatment at the Refl. Selection window >>>>**

- (6) Next, you should open up the Refl. Selection sheet to decide which one should be actually used in the subsequent least-squares analysis. It is recommended that a peak which largely deviates from the calculated position should be deleted at this stage. It is recommended that you first deselect all the yellow flags that should be used in the subsequent least-squares calculations. All the peaks flagged by the yellow numbers have their own theoretical hkl indexes. These information is to be used in the least-squares analysis. If the assignment of hkl is inappropriate, the result will be inappropriate, of course. Therefore, it is preferable that doubtful assignment should be deleted before the least-squares calculations. You should zoom up each peak one by one, and think whether the OBSERVED peak has a reliable correspondence which can be used in the least-squares analysis. You can just graphically select the part where you want to magnify by mouse. If you decide that you would use that peak, you should click the black peak in the upper window which corresponds to the observed peak position from the XFIT.TXT file. If you want to re-zoom to view the initial peak range, press the 'Z-' button. In this way, you should select 20 or 30 peaks to be used in the subsequent refinement.

**<<<< Treatment at Cell Refinement window >>>>**

- (7) Just press the Calculator button to launch the least-squares refinement of the unit cell constants. It immediately ends upon pressing the button, and you will see the results. After obtaining the results, you can save it as a file from 'File/Save/Cell'. The file will be saved in a file format which should be read by the poudrix program. But remember that the file does not involve the estimated standard deviations calculated in this analysis. So, the details should be write down on your note. Otherwise, a hard copy of the window should be saved as a file, or should be printed out by use of any graphical software.

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Simulation of X-ray powder diffraction data using POUDRIX

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- (1) Start up the POUDRIX program.
- (2) Within the lower 'Diffraction diagram' window, read your diffraction data in a Rietveld format (\*.dat which you first prepared at the first stage right after the measurement). Now, we can compare our prediction with the actual observed pattern in this program.

- (3) In the upper window, open the Cell file saved by using the CHECKCELL program (\*.CRY). After that, by pressing 'Select Space Group', input your selection about the crystal system and the space group. Finally, input possible atomic coordinates for the major heavier atoms. Then perform the calculation to see how it works. You will see what happens. If reasonable matching is seen between the observed and simulated patterns, you should and, perhaps, you CAN perform the Rietveld analysis for the system.

An example of results is shown below. This is a simple test case for one of the samples received from Dr. Danny Leznoff. It involves a gold complex. We were trying to solve the structure by use of the Rietveld method.

