

CHEMISTRY AND MATERIALS MODULE

Powder Diffraction Practical

1. Indexing of Powder Diffraction Data, and Instrument Calibration

The condition for Bragg reflection to occur is given by Bragg's law:

$$\lambda = 2 d \sin \theta$$

where λ is the wavelength of the incident radiation, d is the interplanar d -spacing and 2θ is the angle between the transmitted (straight through) and scattered neutron beams.

Practical Exercise

1. Collect diffraction data from a nickel powder sample. Whilst the data collection is in progress convert the data to d -spacing. Use the cursor to determine approximate positions of the first few (at least half a dozen or so) peaks, starting at highest d -spacing (you may want to think about **where** the peak position actually is). You can now use these peak positions to index the pattern.

For a cubic crystal the interplanar d -spacings are given by:

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

where h , k and l are integers (0,1,2,3...), and a is the lattice parameter. It follows from this that taking the square of the ratio of the d -spacing of two Bragg peaks will yield the ratio of two integers.

$$\frac{d_1^2}{d_2^2} = \frac{(h_2^2 + k_2^2 + l_2^2)}{(h_1^2 + k_1^2 + l_1^2)}$$

Using the highest d -spacing Bragg peak (d_1) as a reference, apply this operation to your measured Bragg peak positions (d_2 , d_3 , d_4 etc.) to identify $(h^2+k^2+l^2)$ and, hence, hkl for the first few peaks of highest d -spacing (nickel is cubic). Finally, determine an approximate value of the nickel lattice parameter a . From the selection rules for systematic absences given in Appendix A4, determine the structure type of nickel.

(It may help to prepare a table containing a listing of integers, n , and those combinations of $(h^2+k^2+l^2)$ which add up to n)

This procedure is known as indexing and it can be extremely useful, for example in identifying unknown peaks in an experimental diffraction pattern, or alternatively as a first stage in determining the structure of a material.

Practical Exercise

2. Measure the powder patterns of two 'mystery' materials for long enough to identify the Bragg peak positions.

Given that these samples are either cubic (*P*, *I*-centred or *F*-centred) or hexagonal, use the information in Appendix 4 to identify their structure type and calculate their lattice parameters. Given that these samples are pure elements use the information in Appendix 5 to identify these samples.

Time-of-flight, *d*-spacing, and wavelength

Questions

1. Use the formulae given in Appendix 3 to write a relationship between neutron wavelength, λ , flight path, L , and time-of-flight, t . An important feature of the time-of-flight technique is that the wavelength of a neutron is proportional to its time-of-flight over a given flight path.
2. Now take your answer and use Bragg's law to obtain a relationship between *d*-spacing and time-of-flight. You will find that *d*-spacing is also proportional to time-of-flight, but it is also important to note that the constant of proportionality depends on the product $L \sin \theta$, rather than on the flight path, L , alone.

The Bragg peaks from a crystal of known lattice parameter may thus be used to calibrate $L \sin \theta$ for a diffractometer, but cannot give a value for the total flight path L . In order to perform a complete calibration of a diffractometer it is necessary first to obtain an independent value for L .

3. Determine as accurately as you can the time-of-flight for one of the nickel Bragg peaks which you have identified. Given that the lattice parameter of nickel at 20°C is $a = 3.52387 \pm 0.00008 \text{ \AA}$, calculate an experimental value for $L \sin \theta$.

Structure factors and Intensity

The intensity of the (hkl) reflection is proportional to the square modulus of the structure factor F_{hkl} defined by

$$F_{hkl} = \sum_j b_j \exp(2\pi i(hx_j + ky_j + lz_j)) \exp(-B_j s^2)$$

where the summation is over all the atoms in the cell. (x_j, y_j, z_j) is the position of the j^{th} atom in unit cell coordinates (i.e. in fractions of the lattice parameters), b_j is its scattering power, B_j its isotropic temperature factor and $s = \sin\theta / \lambda$ for the reflection hkl .

- In a *body centred lattice*, for every atom having coordinates (x, y, z) there will be a symmetry-related atom at $(x+1/2, y+1/2, z+1/2)$.
- In a *face centred lattice* the atomic positions related by symmetry are (x, y, z) , $(x+1/2, y+1/2, z)$, $(x+1/2, y, z+1/2)$ and $(x, y+1/2, z+1/2)$.

Exercise

For both of these lattice types, substitute the sets of symmetry-related atomic coordinates into the structure factor equation above and rearrange it to get expressions that explain the selection rules for systematic absences.

you will need to use the following relationships:

$$e^{i\theta} = \cos\theta + i \sin\theta,$$

$$\cos(A+B) = \cos A \cos B - \sin A \sin B,$$

$$\sin(A+B) = \sin A \cos B + \cos A \sin B$$

Make sure that you understand how the selection rules for systematic absences arise from the expression for the structure factor.

2. Powder Diffractometer Resolution and Powder Peak Shape

The shape and width of a Bragg peak measured on a time-of-flight diffractometer (and hence the resolution of the diffractometer) are due to a number of factors which can be divided into two types:

1. Time

- *Histogramming*. The fact that the data are collected in histogram form has a broadening effect. However, provided that the histogram bins are sufficiently narrow that an individual Bragg peak is covered by a reasonable number of bins (say 10 as a rule of thumb) this effect will not be significant.
- *Moderation time*. In converting the data to a d -spacing scale (for example) the data are treated as though all neutrons leave the source at the same instant in time. However, in practice the neutrons leave the source over a range of times, due mainly to the moderation process. Hence, whereas it is assumed that neutrons arriving at the detector at a given time have a precise velocity according to $v=L/t$, in reality they have a range of velocities in the region of this value.

2. Geometry

- *Angle uncertainty*. The moderator, sample and detector all have finite sizes with the result that there is a spread, $\Delta 2\theta$, in the scattering angles of those neutrons that reach the detector after being scattered from the sample.
- *Flight path uncertainty*. Due to the finite sizes of the moderator, sample and detector there is also a spread, ΔL , in total neutron flight paths from source to sample to detector.

Generally the angle uncertainty makes the dominant contribution to the resolution of a powder diffractometer.

Questions

1. Differentiate Bragg's Law to obtain an expression relating peak width (in d -spacing) and detector angle. Extend this to show that $\Delta d/d = \Delta t/t = \Delta Q/Q$.
2. How does the resolution vary with scattering angle 2θ ? For a fixed set of flight paths L_1 and L_2 , what two steps can be taken to achieve the highest resolution (i.e. minimise $\Delta d/d$) ?
3. Estimate the angular width $\Delta\theta$ arising from the finite detector width for your experimental setup. Using your formula, calculate the d -spacing width, in the form $\Delta d/d$, for the detectors you have used to measure the powder diffraction pattern of nickel. Compare this width with what you measure experimentally.

The shape of a Bragg peak measured on a time-of-flight powder diffractometer is well described by the convolution of a Gaussian and an exponential decay. The peak broadening due to geometry is modelled by the Gaussian, whilst the exponential contribution comes from the shape of the pulse from the moderator. For your high scattering angle data measured on Polaris you can fit this function to each of the non-overlapping peaks using the GEC function in GENIE.

>> GEC (note that the workspace MUST be in time-of-flight units)

If the fitting is successful then you will have two width parameters for each peak: σ the Gaussian width (standard deviation) and τ the constant in the exponential decay. τ is actually the mean time spent in the moderator by a neutron. Record these values along with the position of the peak. You should perform the fit for as many Bragg peaks as you can, being sure to have data over as wide a range of time-of-flight as achievable (be sure to have results extending to both sides of the Maxwellian peak in the flux shape).

Eventually you will not be able to fit the peaks at the low time-of-flight end of the spectrum because they will start to overlap and also become less intense. With the large dynamic range (i.e. wide range of neutron wavelengths) available on a pulsed source, and in particular the rich flux of very short λ neutrons, it is inevitable that there will be overlapping peaks at the low time-of-flight (i.e. low d -spacing) end of the spectrum. The experimental situation which can be achieved within the scope of this course is somewhat limited in terms of count rate and counting time, and thus you will need to be quite careful to get good fits over as wide a range of time-of-flight as possible, and even then the results may tend to be somewhat noisy. However, with care they should be good enough to illustrate the points that we wish to convey here.

Using the cursor in GENIE, measure the full width at half maximum, Δt , of as many reflections as you can.

Exercises

Plot $\Delta t/t$, σ , τ , σ/t and τ/t versus time-of-flight t . You should find that...

- $\Delta t/t$ ($=\Delta d/d$) tends to decrease somewhat with increasing time-of-flight t , with a slight maximum at the Maxwellian (i.e. the diffractometer resolution is slightly better at longer times of flight than at shorter times).
- The mean time spent in the moderator, τ , increases steadily with increasing t , starting from a very low value. This is reasonable because neutrons detected at a larger time-of-flight have a lower energy and must, on average, have spent a longer time in the moderator to achieve this lower energy. At high time-of-flight τ tends to a constant value. What is this value for the water moderator from which the POLARIS beamline obtains its neutrons? In fact this time contribution may be minimised by using very long flight paths (as in the high resolution powder diffractometer HRPD at ISIS); because the time uncertainty Δt is a constant for a particular neutron wavelength the effect of increasing the flight path (and hence the time-of-flight, t) is to reduce $\Delta t/t$.
- The geometrical contribution to the resolution width σ/t is essentially constant, independent of t . (i.e. the curve of σ versus t is a straight line passing through the origin). What is this constant value of σ/t ? The FWHM of a Gaussian is given by $\sqrt{8 \log e} \times \sigma = 2.355 \sigma$ so you should multiply the constant value for σ/t by 2.355 to

obtain the geometric contribution to the FWHM for the resolution function. Using the relation obtained earlier by differentiating Bragg's law, calculate the value of $\Delta\theta$ which this corresponds to. Supposing that this $\Delta\theta$ were due only to detector width, w , what value of w does your $\Delta\theta$ value correspond to? Compare this with the physical width of the detector.

- On your plot of $\Delta t/t$ versus t draw a horizontal line corresponding to the geometric contribution to the FWHM for the resolution function, showing the relative magnitudes of the two contributions to $\Delta t/t$ as a function of t .

4. Magnetic Neutron Diffraction

The final practical section of the powder diffraction course will introduce magnetic neutron diffraction. Because the neutron possesses spin it can interact with electron spins and induced orbital moments, as well as nuclei, during the scattering process. In ferromagnetic materials where the magnetic moments are aligned, the "nuclear" and "magnetic" unit cells are identical and the magnetic scattering appears in the same Bragg reflections as the nuclear scattering. However, in materials where the magnetic moments are not aligned, e.g. in an antiferromagnet, the "nuclear" and "magnetic" unit cells are different and the magnetic scattering gives rise to additional reflections. One important aspect of magnetic neutron diffraction is that the magnetic scattering by an atom or ion is non-zero only when there is a component of the magnetic moment perpendicular to the scattering vector.

The magnetic properties of a material change with temperature, thus the magnetic scattering intensity may vary as a sample is heated or cooled. To illustrate this effect, diffraction patterns will be collected from the inorganic compounds manganese oxide and manganese fluoride at a series of different temperatures.

Manganese oxide, MnO, has the rock salt structure, with Mn at (0,0,0) and O at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (and equivalent positions due to face centring), and is paramagnetic above 120K. Below $T_N=120K$ the moments align antiferromagnetically.

Manganese fluoride, MnF₂, has the rutile structure, which is tetragonal, and is paramagnetic above 75K. Below 75K, as in MnO, the manganese moments align antiferromagnetically, however due to the two distinct structure types the effect on the diffraction pattern is quite different.

Practical Exercise

Load a sample of MnO or MnF₂ powder into a cryostat, cool from room temperature to a temperature below the Neel temperature and collect a diffraction pattern. Heat the cryostat and collect diffraction patterns at a series of temperatures (the diffractometer will be set up to collect data overnight automatically) below and above T_N .

MnO, Space Group $Fm\bar{3}m$

Shull (Nobel Prize in physics 1994) and Smart did the first magnetic structure determination using neutron scattering on MnO in 1949. MnO crystallises in the rock salt type structure and is paramagnetic above 120 K. the magnetic moments of the Mn sublattice order antiferromagnetically below the Neel point.

| | |
|-----------------------|---|
| a [Å] | 4.43 |
| Mn | (0, 0, 0) |
| O | ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) |
| Extinction conditions | h k ℓ all even or all odd |

Measurements and exercises

1. Collect a diffraction pattern at RT and index the pattern. Determine the lattice constant and verify the conditions for reflections to be observed.
2. Collect a diffraction pattern well below 120 K. Again, index the cell and determine the lattice constants.
3. Measure at exactly 120 K. One will see diffuse scattering at the magnetic Bragg peak positions due to short range magnetic order.

Or: Measure a whole set of diffraction patterns from say 50-150K. One should see the magnetic intensity drop + appearance of short range order.

4. Try to figure out a model of the magnetic structure keeping in mind that two Mn-moments coupled via a 180° oxygen-bond are antiparallel. (180° Mn-O-Mn super exchange is antiferromagnetic)

In theory one could now try to refine the structure (but it is probably much easier to do that for MnF₂)

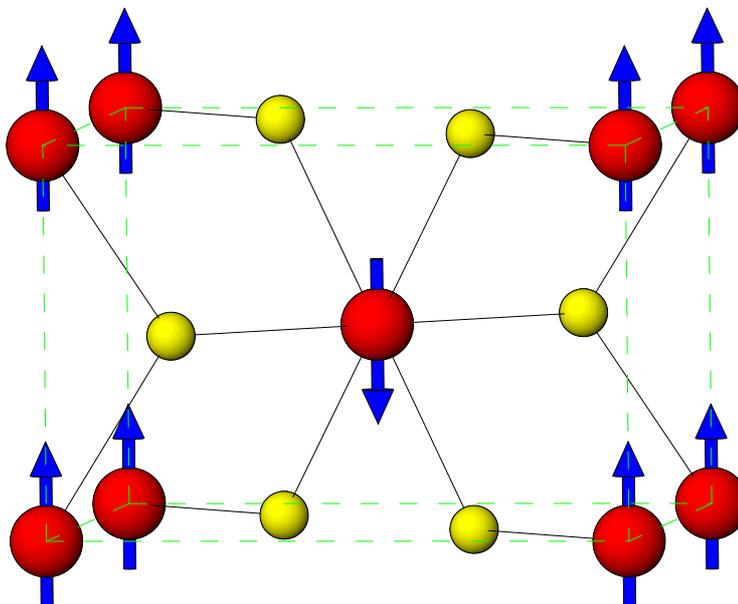
MnF₂, Space Group P4₂/mnm

| | |
|-------|------------------|
| a [Å] | 4.87 |
| c [Å] | 3.31 |
| Mn | (0, 0, 0) |
| F | (x, x, 0) x=0.31 |

Measurements and exercises

1. Collect a diffraction pattern from MnF₂ above and below T_N=75K.
2. Index the pattern keeping in mind that the nuclear cell is tetragonal (the magnetic cell is the same as the nuclear one).
3. Again one can come up with a simple magnetic model, based on the extinction conditions of the magnetic and nuclear peaks. Below the Neel point new (100) and (201) reflections appear, while other magnetic peaks are superimposed on nuclear ones like (111) or (210).

Although the cell is primitive the Mn atoms occupy body centred positions (000 and ½,½,½) and only contribute intensity to the nuclear reflections having h+k+l=2n. The appearance of 100 and 111 magnetic reflections violates that, implying antiferromagnetic ordering. Because only the 100 reflection is seen and not the 001 means that the magnetic moments are aligned along the c-axis (only the moment component perpendicular to the scattering vector gives magnetic intensity).



CHEMISTRY AND MATERIALS MODULE

Powder Diffraction Tutorial

1. Profile Refinement

It is possible to analyse powder diffraction data by measuring integrated peak intensities and relating these to the structure factors F_{hkl} defined above, in a manner analogous to a single crystal structure determination. However, due to overlapping of reflections (either partial or total) in a powder diffraction pattern, a large amount of intensity information is lost.

Nevertheless, some of this lost information can be recovered, and a very efficient way to do this is to perform a least-squares fit to the whole diffraction pattern, a procedure known as a profile refinement. This has the advantage that it can extract information from the positions, widths and intensities of all the peaks in the diffraction pattern, including those that are so close together as to be completely overlapping. With the large dynamic range available on a pulsed source it is inevitable that the data will have overlapping peaks at the low d -spacing end of the pattern.

Profile refinement is a very powerful technique, which can yield a large amount of physical information about a polycrystalline sample, and it would require a separate course to explain fully how to perform a profile refinement. Within the scope of the present course it is only possible to give an introductory demonstration of the technique.

In order to calculate an expected diffraction pattern, two sets of information are required:

1. Crystal structure data (unit cell dimensions, space group and atomic positions) enables the d -spacings and intensities of the allowed Bragg reflections, hkl , to be calculated.
2. Diffractometer information (detector flight paths and scattering angles, peak shape parameters) enables the time-of-flight positions of the peaks to be calculated along with the variation in full width at half maximum (FWHM) with time-of-flight.

The values of the diffractometer parameters are determined by Rietveld refinement using data collected from a standard sample, whose crystal structure and unit cell dimensions are well known and which gives a well defined peak shape. In most cases when you carry out a neutron scattering experiment, these parameters will have been determined previously, during the instrument calibration, and will be provided for you.

However, for the purposes of this exercise you will prepare your own **Instrument Parameter File** that contains the diffractometer information required by the program **GSAS**. You will be given a data file containing the diffraction pattern collected from a silicon standard sample (NBS SRM 640b). The data were collected in the Polaris backscattering detectors (C bank).

Silicon is cubic and crystallises in the space group $Fd-3m$, with silicon atoms in the (x, x, x) position with $x=0.125$. The unit cell parameter of this sample at room temperature is certified to be $a = 5.43094\text{\AA}$. Because the crystal structure of silicon is known you will keep these structural parameters fixed (except for the thermal vibration parameter) and refine the diffractometer parameters.

Peak Position Parameters

The theoretical time-of-flight at which a particular Bragg reflection will appear in a detector of known scattering angle, 2θ , and flight path, L , can be calculated using the equation you

derived in Section 2 (Question 1 in Time-of-flight, d -spacing and wavelength). However, in practice the relationship between time-of-flight and d -spacing is slightly more complex, requiring two additional parameters. The first of these is a simple zero point error, which accounts for timing delays in the detector electronics.

The second additional parameter arises as a consequence of the absorption of neutrons in the 'white' incident beam by the sample. Because absorption is energy dependent, lower energy (i.e. longer wavelength / longer tof) neutrons will experience greater absorption than higher energy (i.e. shorter wavelength / shorter tof) neutrons. This means that the average depth to which the neutrons penetrate into the sample before being scattered to the detector will vary with wavelength, resulting in an apparent small variation in total flight path with time-of-flight. This effect can be parameterised with a simple quadratic function in d .

The full equation in GSAS, giving the parameter names, is:

$$t = \text{DIFC } d + \text{DIFA } d^2 + \text{ZERO} \quad (\text{where } t \text{ is in } \mu\text{s} \text{ and } d \text{ is in } \text{\AA}).$$

Initially you will set both DIFA and ZERO to 0.

Question

1. To what number should you set DIFC?

During *instrument calibration*, DIFC, DIFA and ZERO can be refined. During *structure refinement*, DIFC and ZERO MUST be kept fixed. However, because DIFA is sample dependent it may be refined.

Peak Width Parameters

The peak shape observed on Polaris can be described by the convolution of a pseudo-Voigt function with two exponentials. The Pseudo-Voigt function is a linear combination of Gaussian and Lorentzian functions, whose full widths at half maximum are parameterised in GSAS as follows.

Gaussian width:

$$\sigma^2 = \sigma_0^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4$$

in GSAS these parameters are called sig-0, sig-1 and sig-2 respectively.

Lorentzian width:

$$\gamma = \gamma_0 + \gamma_1 d + \gamma_2 d^2 \quad (+ \text{ other terms associated with strain broadening})$$

in GSAS these first three terms are called gam-0, gam-1 and gam-2.

Because the variation in peak width with d -spacing in a pulsed neutron diffraction experiment is closely approximated by $\Delta d/d = \text{constant}$, initially you can set sig-0, sig-2, gam-0 and gam-2 to 0 and refine sig-1 and gam-1. During instrument calibration, sig-0, sig-1, sig-2 and gam-2 can be refined. In any subsequent structure refinement sig-1, sig-2, gam-1 and gam-2 may be refined, but their behaviour may not always be stable.

Neutron Training Course

The rise and decay coefficients for the two exponential functions are described by the parameters α , β_0 and β_1 . During *instrument calibration*, these parameters can be refined with care. During any further *structure refinement* they must be kept fixed.

The starting instrument parameter file can be found in:

\\Olympic\Babylon5\Public\Neutron training course_MnF2 and Si data\trainer.ipf

(note: you will need to replace DIFC from this file with the value you calculated in Question 1, above)

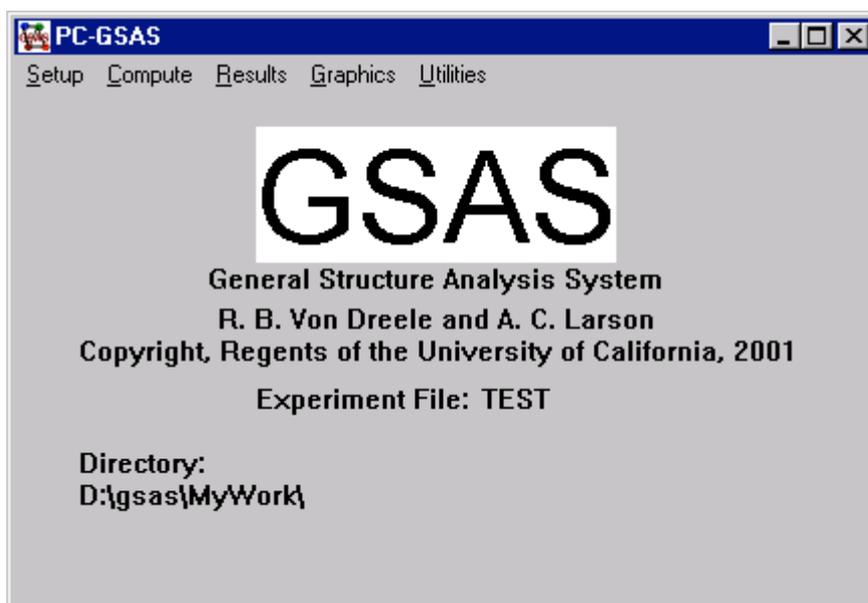
The silicon powder data file can be found in:

\\Olympic\Babylon5\Public\Neutron training course_MnF2 and Si data\silicon_train.gss

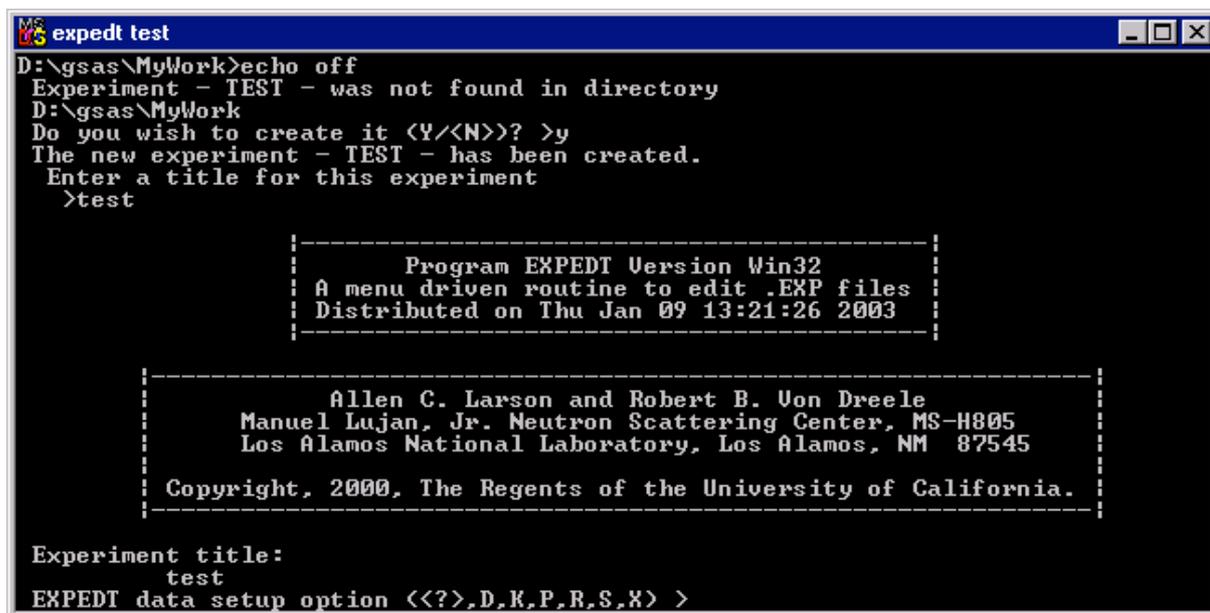
These two files should be copied to the folder C:\GSAS\MyWork

2. The Rietveld Method - Profile Refinement Using GSAS.

There are two ways that GSAS can be run. The first runs PC-GSAS directly and operates in an identical menu-driven manner to GSAS running on a terminal-based operating system such as VMS. After the experiment has been given a name (e.g. *TEST*) using the *Expname* option from the Setup pull-down menu, the various routines within GSAS are run by selecting them from the appropriate pull-down menu (*S*etup, *C*ompute, *R*esults, *G*raphics or *U*tilities - note that only the Setup and Utilities menus are displayed until the experiment name has been entered).

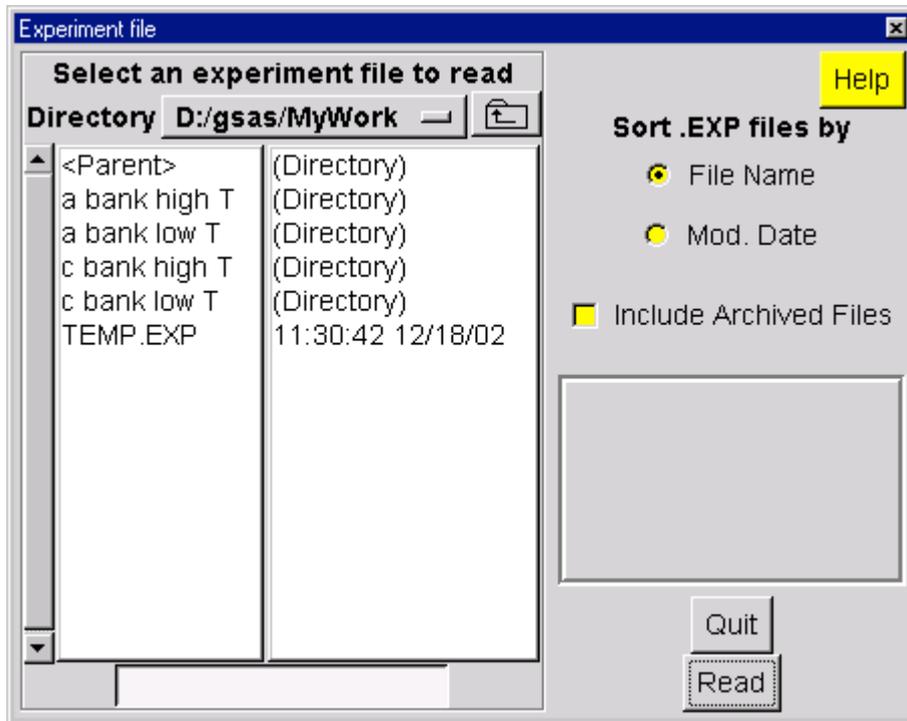


Thereafter the individual routines within GSAS will run in separate MS-DOS windows:

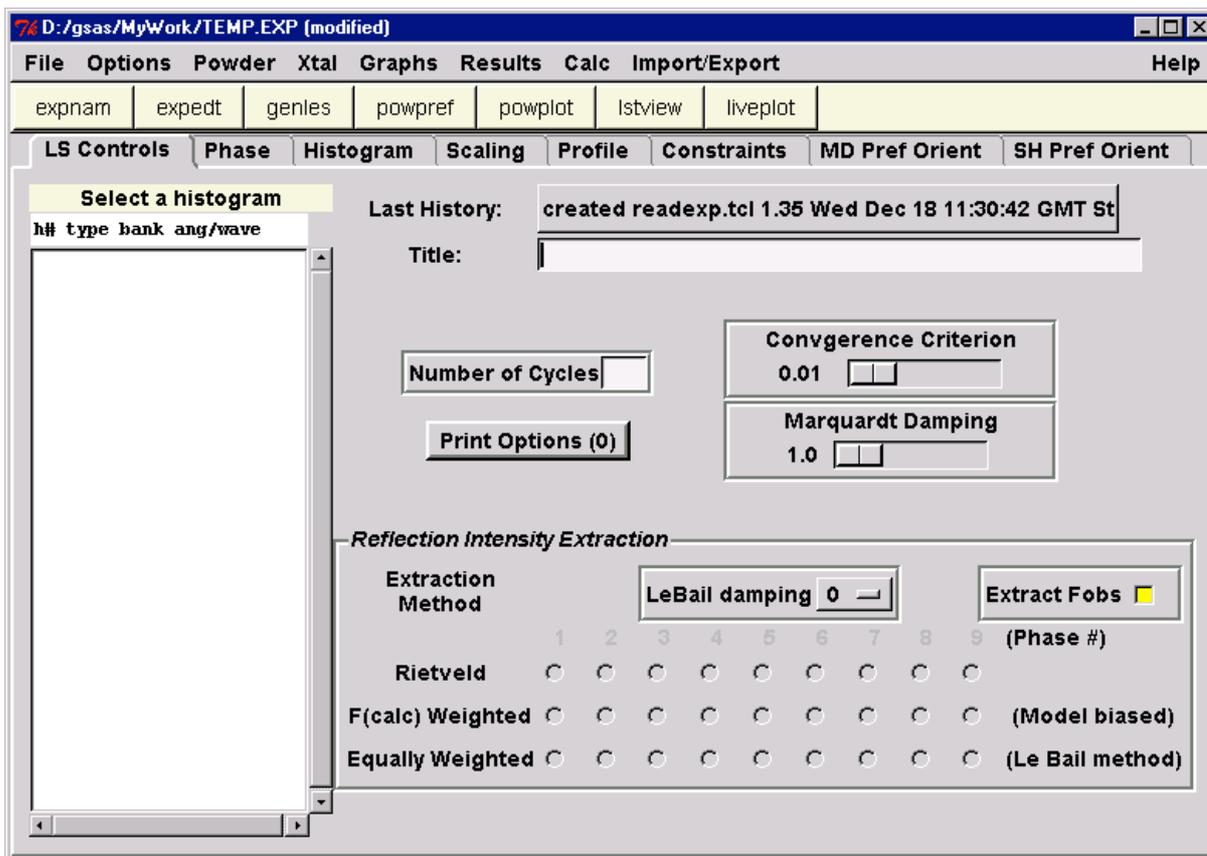


A table of selected menu commands, and the GSAS routines from which they are run, is given in Appendix 6.

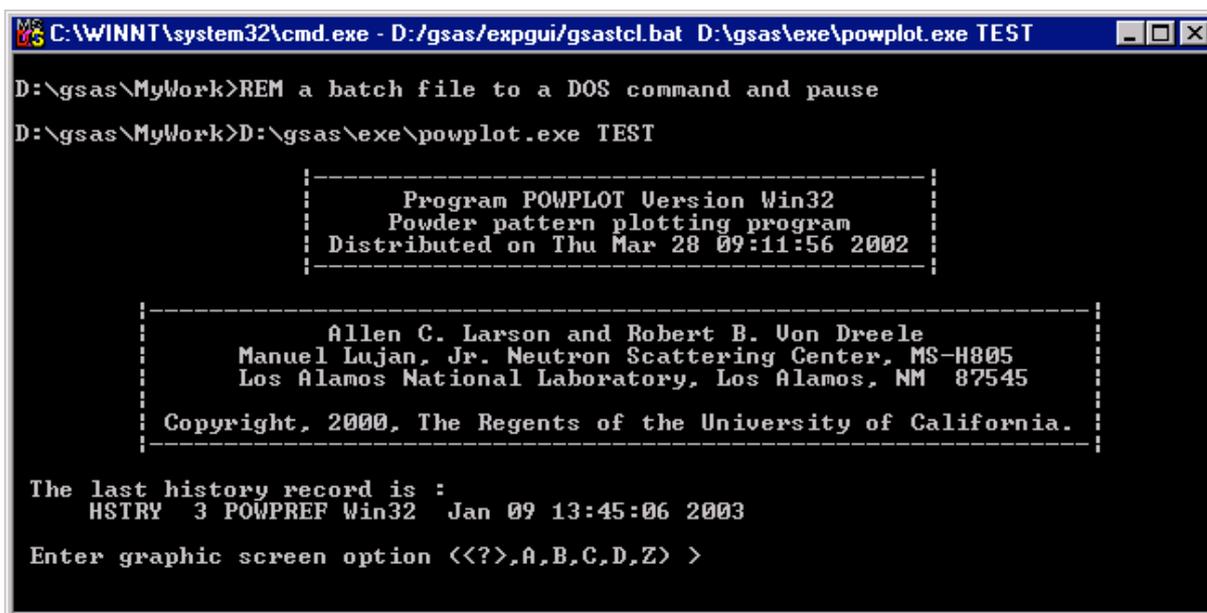
Alternatively on a PC, a graphical interface called EXPGUI is also available. First, the experiment name is selected from a list of available titles or a new name is entered in the field at the bottom of the Experiment File window.



Once the experiment name has been selected the EXPGUI interface is opened. The sample, instrument and least squares parameters can be inspected and modified by selecting the appropriate tab (LS Controls, Phase, Histogram, etc.). Specific GSAS routines are executed by clicking on the buff coloured buttons immediately above these tabs (expnam, expedt, genles, etc.), or from the pull-down menus (File, Options, Powder, etc.)



Most routines will open a new MS-DOS window in which to display the results of the calculation, and which may ask you to enter or confirm some details before the routine is executed (in an identical manner to the running of PC-GSAS itself), e.g. clicking on "powplot" in EXPGUI opens the window shown below.



Typing a carriage return in response to a GSAS prompt will produce a help listing of the actions carried out by each of the options:

```
C:\WINNT\system32\cmd.exe - D:/gsas/expgui/gsastcl.bat D:\gsas\exe\expedt.exe TEST
Manuel Lujan, Jr. Neutron Scattering Center, MS-H805
Los Alamos National Laboratory, Los Alamos, NM 87545
Copyright, 2000, The Regents of the University of California.

The last history record is :
HSTRY 4 EXPEDT Win32 Jan 10 11:20:47 2003 File cleanup only

Is this the file you wish to use? (<?>,D,K,Q,R,Y) >y
Experiment title:
test
The last history record is :
HSTRY 4 EXPEDT Win32 Jan 10 11:20:47 2003 File cleanup only

EXPEDT data setup option (<?>,D,K,P,R,S,X) >
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
K n - Delete all but the last n history records
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,K,P,R,S,X) >
```

Appendices

Appendix 3 Useful Conversion Factors

Density: $\rho(\text{g cm}^{-3}) = A(\text{amu}) \times \rho(\text{atoms } \text{Å}^{-3}) \times 1.66057$ where A is atomic mass and ρ is density.

Neutron energy:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2} = h\nu = \frac{m L^2}{2 t^2} = k_B T$$

$$E = 2.0717k^2 = \frac{81.787}{\lambda^2} = 4.1354\nu = 5.2276 \times 10^6 \frac{L^2}{t^2} = 0.086165T$$

$E[\text{meV}], \lambda[\text{Å}], \nu[\text{THz}], k[\text{Å}^{-1}], L[\text{m}], t[\mu\text{sec}], T[\text{K}].$

Appendix 4 d-spacings and selection rules for simple crystal systems

E1. Simple Cubic (sc)

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + \ell^2)}} \quad \text{all reflections allowed}$$

E2. Face Centred Cubic (fcc)

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + \ell^2)}} \quad h, k \text{ and } \ell \text{ must be all even or all odd}$$

E3. Body Centred Cubic (bcc)

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + \ell^2)}} \quad (h+k+\ell) \text{ must be even}$$

E4. Hexagonal Close Packed (hcp)

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{\ell^2}{c^2} \quad \text{allowed reflections must satisfy:}$$

$hk\ell$ all reflections allowed, 00ℓ : $\ell=2n$ or $hk0$: $h-k-1=3n$
or $hk0$: $h-k-2=3n$, where n is an integer.

Appendix 5 Crystal structures of some metallic elements

| | | | | | |
|------------|----|---------------|---------|-----------|------------------------|
| Scandium | Sc | hexagonal | a=3.31Å | c/a=1.594 | |
| Titanium | Ti | hexagonal | a=2.95Å | c/a=1.588 | |
| Vanadium | V | bcc | a=3.02Å | | |
| Chromium | Cr | bcc | a=2.88Å | | |
| Manganese | Mn | cubic | a=8.89Å | | |
| Iron | Fe | bcc | a=2.87Å | | |
| Cobalt | Co | hexagonal | a=2.51Å | c/a=1.622 | |
| Nickel | Ni | fcc | a=3.52Å | | |
| Copper | Cu | fcc | a=3.61Å | | |
| Zinc | Zn | hexagonal | a=2.66Å | c/a=1.856 | |
| Yttrium | Y | hexagonal | a=3.65Å | c/a=1.571 | |
| Zirconium | Zr | hexagonal | a=3.23Å | c/a=1.593 | |
| Niobium | Nb | bcc | a=3.30Å | | |
| Molybdenum | Mo | bcc | a=3.15Å | | |
| Technetium | Tc | hexagonal | a=2.74Å | c/a=1.604 | |
| Ruthenium | Ru | hexagonal | a=2.70Å | c/a=1.584 | |
| Rhodium | Rh | fcc | a=3.80Å | | |
| Palladium | Pd | fcc | a=3.88 | | |
| Silver | Ag | fcc | a=4.09Å | | |
| Cadmium | Cd | hexagonal | a=2.98Å | c/a=1.886 | |
| Lanthanum | La | hexagonal | a=3.75Å | c/a=1.619 | |
| Hafnium | Hf | hexagonal | a=3.20Å | c/a=1.582 | |
| Tantalum | Ta | bcc | a=3.31Å | | |
| Tungsten | W | bcc | a=3.16Å | | |
| Rhenium | Re | hexagonal | a=2.76Å | c/a=1.615 | |
| Osmium | Os | hexagonal | a=2.74Å | c/a=1.579 | |
| Iridium | Ir | fcc | a=3.84Å | | |
| Platinum | Pt | fcc | a=3.92 | | |
| Gold | Au | fcc | a=4.08Å | | |
| Mercury | Hg | (rhombohedral | | a=2.99Å | $\alpha=70.45^\circ$) |

Appendix 6 Menu commands for selected actions in GSAS

| | Program | Command | Action |
|-------------------|---------|------------------------------|--|
| experiment name | GSAS | EXPNAM string | name your problem <i>string</i> |
| powder data | EXPEDT | P H I | insert powder histogram into GSAS |
| phase information | | P P I | insert crystalline phase information (space group and unit cell data) |
| atom parameters | | L A I 1 | atom parameters menu insert atom |
| | | L A V 1 U V 1 -U | atom parameters menu set UIISO refinement flag ON set UIISO refinement flag OFF |
| | | L A C | change individual parameters |
| least squares | | L L C 6 | maximum 6 cycles of Least Squares |
| background | | L O B C 1 8 / | background parameters menu use background function 1 8 parameters accept default values |
| difc, difa, zero | | L O C C DIFC 2345 | diffractometer constants menu change a diffractometer constant select constant (must be upper case) enter new value |
| | | L O C V CAZ CZ | diffractometer constants menu set refinement flags refine all three (no spaces) refine only DIFC and ZERO |
| peak width | | L O P V | set refinement flags |
| | | L O P C | change individual parameters |
| | POWPLOT | G H 1 D T M P 2.5 10 A | select large X display (on VMS) read and display histogram display from 2.5 to 10 ms, autoscaled |
| | POWPREF | | profile pre-processing |
| refinement | GENLES | | perform Least Squares refinement |

To accept existing (or default) parameter values type a slash ("/").