Inelastic Neutron Scattering from Polycrystalline materials

MARI – Direct geometry chopper instrument

MARI (Multi-Angle Rotor Instrument) is a direct geometry chopper spectrometer. It uses a Fermi chopper to monochromate the incident neutron beam giving incident energies in the range 5 to 1000 meV. MARI has a bank of ^{3}He detectors that continuously covers a vertical angular range from -13° to 135° ($\Delta\Theta_V$ = 2.58 rad.) and a horizontal angular range of ±8° ($\Delta\Theta_H$ = 0.28 rad.). This makes a total solid angle of $\Delta\Omega = \Delta\Theta_V \times \Delta\Theta_H$ = 0.72 steradians. Unusually, the MARI detectors are arranged in a vertical scattering plane – *i.e.* with a sideways sample geometry. This contrasts with the MERLIN spectrometer, which has a horizontal scattering plane geometry, and a total detector solid angle of around π steradians, and therefore is able to map large regions of Q-E space in a single measurement. The distance from the sample to the MARI detector bank is 4 m, giving MARI an energy resolution of between 2-4% ΔE/E, depending on the rotation frequency of the Fermi chopper.

The detectors are 10 bar ^{3}He gas proportional counters, 30 cm long and 2.5 cm in diameter.

The core of the instrument is the Fermi chopper. This is a set of collimating slits (*Söller* collimator) that is magnetically suspended in a vacuum and able to rotate at frequencies of up to 600 Hz. The incident neutron energy is selected by phasing the opening time of the slit package with respect to the neutron pulse from the target station.

Three low efficiency scintillator detectors (called monitors) are placed in the main beam. The first is placed just after the background ("nimonic") chopper to monitor the incident flux for the purposes of normalisation. The second and third are placed just after the Fermi chopper and behind the sample respectively. These are used to accurately determine the incident energy of the neutrons. The beam size at the sample position is 50 mm by 50 mm, but motorized slits in the Fermi chopper pit can be used to reduce this size.

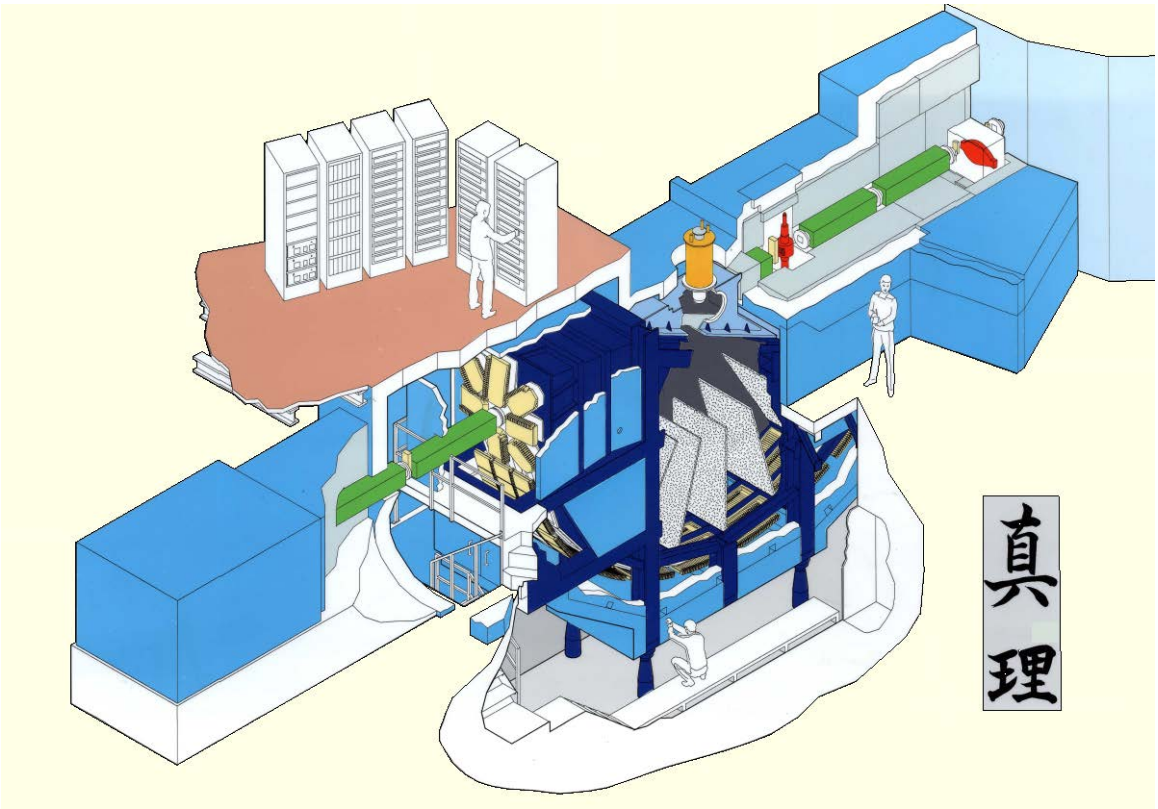


Figure 1, Schematic of MARI

TOSCA – An indirect geometry spectrometer

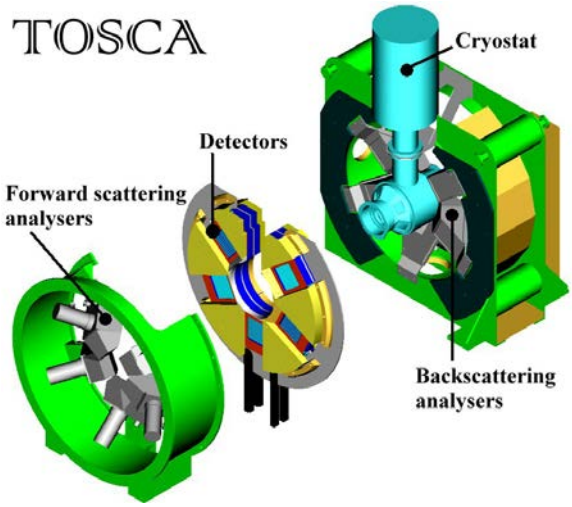


Figure 2: Schematic of TOSCA

TOSCA is an indirect geometry time-of-flight spectrometer at ISIS. It is optimal in the energy range 30 – 4000 cm^{-1} (4 – 500 meV) with the best results below 1600 cm^{-1}, (200 meV). However, data is always collected between 30 and 16000 cm^{-1} (4 – 2000 meV) and may be analysed across the entire range (for details of conversion between cm^{-1} and meV see appendix C). In the range 30 – 250 cm^{-1} (4 – 33 meV) the resolution is approximately constant at ~ 8 cm^{-1} (1 meV). At larger energy transfer, the resolution is ~1.5% of the energy transfer. Thus TOSCA provides a large energy range at the highest resolution available.

The source of neutrons on TOSCA is a white beam from the water moderator. A small fraction of the incident neutrons are inelastically scattered by the sample; those that are backscattered through an angle of 135° or forward scattered through an angle of 45° impinge on a graphite crystal. Bragg's law states:

$$n\lambda = 2d\sin\theta, \qquad (1)$$

where d (Å) is the interplanar distance in the crystal, λ (Å) is the wavelength of both the incident and scattered neutrons and θ is the angle of incidence on the crystal plane.

Since both d and θ are constant only one wavelength (plus its higher orders) will be Bragg scattered by the crystal, the remainder will pass through the graphite crystal to be absorbed by the shielding. The beryllium filter, which acts as a long wavelength pass filter, absorbs the neutrons at higher order wavelengths (λ/n), and the remaining neutrons are detected by ^3He filled detector tubes. The net effect of the combination of the graphite crystal and beryllium filter is to act as a narrow band-pass filter. A cut-away of an analyser module is shown in *Figure 3*.

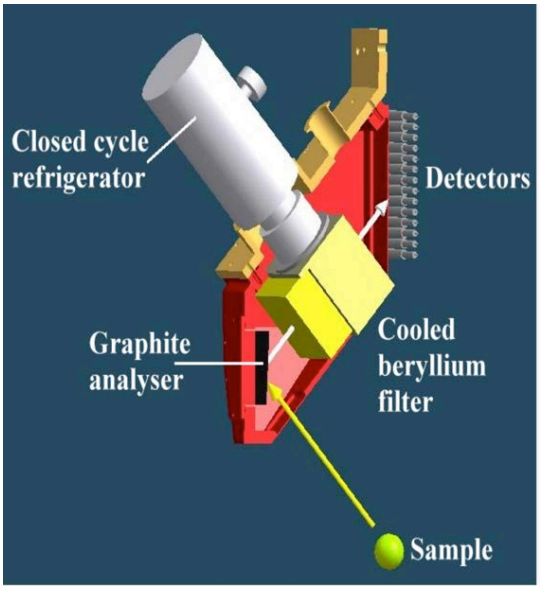


Figure 3: Schematic of an analyser module on TOSCA

A consequence of the indirect geometry is that for energy transfers > 100 cm^{-1}, the momentum transfer vector is essentially parallel to the incident beam. The significance is that for an INS transition to be observable there must be a component of motion parallel to the momentum transfer vector. This means that with oriented samples (such as single crystals or aligned polymers) measurements directly analogous to optical polarisation experiments are carried out.

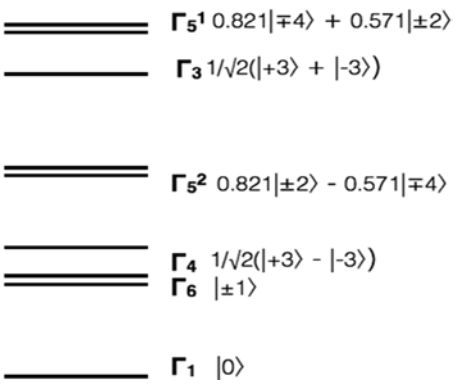
Worksheet

Data collection on $PrAl_3$ polycrystal:

The intermetallic compound $PrAl_3$ is a *Van Vleck paramagnet*. Pr interactions in $PrAl_3$ are dominated by single ion crystal field interactions. These are Coulomb interactions between the charge density at the rare-earth ion site and the symmetry of the local electric field produced by the neighbouring ions. These interactions generally lift the degeneracy of the 2J+1 states of a particular electronic state multiplet, such that different orientations of the charge distribution carry different energies. These orientations in space are characterised by the quantum numbers m_J representing the space quantisation of the electronic state.

Question:
Given that Pr ions in $PrAl_3$ are in the Pr^{3+} ground state, use Hunds rules to find L, S and J of Pr^{3+} and the expected degeneracy of the ground-state multiplet.

The ground state multiplet of the Pr^{+3} ion in $PrAl_3$ splits in the hexagonal crystal field into 6 levels with a singlet Γ_1 ground level and a doublet Γ_6 first excited level:



Question:
Given the neutron selection rule $\Delta m_J = \pm 1$ identify the allowed transitions in the level energy diagram. What do you expect to see at low temperature?

We want now to measure the crystal field excitations in $PrAl_3$ to better characterise the energy level diagram.

Setting up the instrument:

1) The first excited state is expected to be below 10 meV.
2) Set the energy on the instrument (see Appendix A).
3) Set the temperature to cool down the $PrAl_3$ sample and start to collect data while cooling.
4) When at 100 K end the measurement and start a new one when T is about 5K.

Exercise 1:

Assume that you are on MARI and require an incident energy of 15 meV, calculate (use the instrument parameters in Appendix B):

a) What phase will you need to set on the chopper? (the phase the opening time of the chopper with respect to the source)
b) When would expect the neutrons to arrive at monitor 2?
c) Calculate when the elastically scattered neutrons arrive at the detector
d) Calculate when neutrons that loose 5 meV arrive at the detector

Assume now that we are performing this experiment on TOSCA

e) Calculate when elastically scattered neutrons arrive at the detector. Why is this bad and suggest how it could be overcome?
f) Calculate when neutrons that loose 5 meV arrive at the detector

The sample size and geometry

It is always wise to spend some time thinking about the size and geometry of your sample when planning your experiment. This is for three main reasons:

a) To know roughly how long your measurement will be.
b) To minimise multiple scattering
c) To minimise self-shielding effects

There is always a trade-off between being able to collect sufficient statistics and multiple scattering. The larger the sample the quicker you will be able to make a measurement but the greater the

probability that the neutrons will be scattered more than once. The only way to calculate these things accurately is to use Monte-Carlo codes which simulates neutron scattering from various sample shapes, using tabulated cross-sections and instrumental parameters (detector angles, neutron energies). There are, however, very simple rules of thumb that can be used to calculate multiple scattering. Since elastic events generally dominate the scattering the most likely multiple scattering event is a two elastic event. But this will not change the energy of the neutron it will only smear the scattering in angle. The most likely double event in the inelastic region is one-elastic one-inelastic. As before this will not change the energy of the event, but it will smear it out in angle. Generally we aim to use a 10% scatterer – i.e. one from which 10% of the neutron beam is scattered by the sample. Given that the scattering is dominated by the elastic, the one-elastic/one-inelastic event is roughly 10% the intensity of the inelastic scattering. To a first approximation the multiple scattering does not have any angular dependence. Another problem in neutron scattering is self-shielding (attenuation of the neutron beam due to sample absorption). This distorts scattering as a function of angle. For simple geometries like that of the slab or a cylinder it is possible to write correction formula. But is also possible to minimise the correction by using an annular geometry.

Exercise 2:

a) Refer to Appendix D to calculate what is the transmission of the $PrAl_3$ sample.

b) Estimate the ratio between elastic scattering and inelastic scattering at low temperature.

c) Use the PyChop program to find the chopper resolution and flux for the energy of the experiment.

d) Given the incident flux from the PyChop program calculate:

- Number of neutrons scattered per second.
- Number of neutrons per second reaching each ^3He detector (2.5 cm diameter by 30 cm long).
- Assume that the inelastic scattering is evenly distributed from 0 to the maximum energy transfer. How long will it take to collect enough counts to give 5% errors in each 0.2 meV energy bin?

Look at the experimental data:

Using Mantid, plot the elastic scattering as a function of Q and compare the data above at 100K and 5K. What do you notice?

Data collection on Aluminium powder:

Place the Al can with Al pellets inside the CCR.

Choose your experimental configuration: considering that the maximum of the dispersion for Al phonons is about 40 meV, use PyChop to decide for an incident energy and chopper frequency. Start your data collection at room temperature.

Exercise 3:

a) Look at the data with Mantid and compare the low-Q data with the high-Q data: what do you notice?

b) Compare the Q-dependence of the Al and the $PrAl_3$ inelastic peaks. How do they compare?

Appendix A: Setting the incident energy

To set the incident energy use the command

>> set_ei <Ei(meV)> <frequency(Hz)>

This command will set the necessary phase and frequency of the Fermi chopper and disc chopper. It also calculates the time channel boundaries for this energy and writes them to the file, TCB.DAT. These will be loaded into the instrument control program (ICP) the next time a change or load command is issued.

The two dark green lights in the Fermi Chopper Control panel will become light green when the chopper will reach the nominal speed and the actual delay. Once a run has started, it is possible to check that the chopper has phased correctly to give the desired incident energy using the following commands in the Control window.

>> updatestore

and then running Mantid to look at the data.

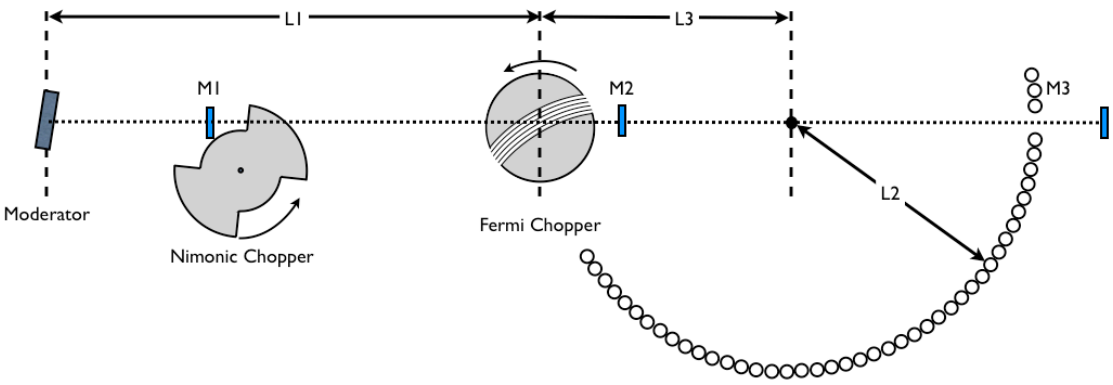
Data collection commands:

All the following instrument control commands may be abbreviated to three letters.

>> begin	Starts a run.
>> updatestore	Stores the data collected so far in the file MAR00000.raw
>> pause	Pauses data collection.
>> resume	Resumes data collection
>> abort	Aborts the current run without saving any data.
>> end	Ends the current run and stores the data in MAR<run no.>.raw
>> change title	Changes the title of the current run

Appendix B: MARI and TOSCA parameters

MARI flight paths



Flight paths:

Moderator to Fermi Chopper (L1)	10.05 m
Moderator to sample (L1 + L3)	11.74 m
Sample to detectors (L2)	4.02 m
Moderator to monitor 1	7 m
Moderator to monitor 2	10.30 m
Moderator to monitor 3	17.56 m

TOSCA flight paths

Moderator to sample	17.0 m
Sample to detectors	0.63 m
Analysing energy	3.35 meV

Appendix C: Useful Conversion Factors

Neutron energy conversion:

$$E = \frac{h^2k^2}{2m_n} = \frac{h^2}{2m_n\lambda^2} = h\nu = \tfrac{1}{2}m_n\left(\frac{L}{t}\right)^2 = k_BT$$

In neutron friendly units, we get

$$E = 2.072k^2 = \frac{81.81}{\lambda^2} = 4.136\nu = 5.227\times10^6\frac{L^2}{t^2} = \frac{T}{11.6}$$

where E is in meV, λ in Å, ν in THz, k in $Å^{-1}$, L in m, t in μsec and T in K.

Thermal neutrons:

The standard "thermal neutron" (for which absorption cross-sections are quoted in tables) has the following properties:

v = 2.2 m s^{-3} E = 25.3 meV λ = 1.798 Å

Energy to wavenumber:

For molecular spectroscopy measurements, the energy is often expressed in *wavenumber units* which allows comparison with light spectroscopy measurements.
NB, this is not the neutron wavenumber, but the "photon-equivalent" wavenumber:

$$E = hc\bar{\nu} = 0.124\bar{\nu}$$

where E is in meV and $\bar{\nu}$ is in cm^{-1}

Appendix D: Sample Quantity and Multiple Scattering

Inelastic neutron scattering is a scarce process because neutron sources are weak and the incoherent cross sections are small, 10^{-22} to ~ 10^{-24} cm^2. Thus the initial impulse might be to load as much sample as possible into the beam. Within limits, this is an excellent idea and multiple scattering sets these limits. Multiple scattering arises when a neutron is scattered twice (or more) within the body of the sample. The most likely process is two elastic scattering events since the elastic scattering generally dominates inelastic scattering contributions (although not in a liquid). This process does not, however, affect the inelastic scattering spectrum measured. An elastic scattering event followed by an inelastic event (or *vice versa*) is potentially more troublesome. Since the additional distance travelled by the neutron is small compared to the total flight path, the difference in time-of-flight is negligible, so the energy transfer, ΔE, is correct. However, the direction that the neutron was travelling in has changed, thus the measured Q-value will be incorrect. Less probable still is two inelastic events, which is fortunate, since both Q and ΔE will have shifted in this case

This simple analysis suggests that the double inelastic event is detrimental in all cases, whereas the elastic + inelastic case is detrimental with chopper instruments since the momentum transfer information is lost, but less serious for the beryllium filter and crystal analyser instruments that do not have good Q-resolution. Analysis of spectra recorded on TOSCA suggests that up to ~ 25% of the total scattering can be elastic + inelastic without degrading the spectrum.

This begs the question of how much sample should be used? Experience suggests that the multiple scattering from a sample that scatters 10% of the neutron beam (or less) is acceptable. The mass of sample that scatters this proportion of neutrons can be calculated from an equation that is directly analogous to the Beer's Law of absorption in optical spectroscopy.

$$T = \frac{I}{I_0} = \exp(-N\sigma t)$$

where I_o and I are the incident and scattered intensities respectively, N is the number density of formula units in atoms Å^{-3}, t is the sample thickness and σ is the total scattering cross-section. (i.e. the sum of the absorption cross-section and the scattering cross-section).

The number density is related to the mass density, ρ in g cm^{-3}, by

$$N = \frac{\rho N_A}{M_f} = \frac{\rho}{1.661 \times M_f}$$

where N_A is Avogadro's number (6.022×10^{23}).

As an example, for H_2O, ρ = 1.0 g cm^{-3} and M_f = 18.0

$$N\sigma = N\sum_n \sigma_n = N(2\sigma_H + \sigma_O)$$

$$= \frac{1}{1.661 \times 18}(2 \times 80 + 1 \times 0.0) = 5.35 \text{ cm}^{-1}$$

So the quantity required for a 10% scatterer (*i.e.* 90% transmission) is:

$$T = \exp(-N\sigma t) = 0.9$$

$$\Rightarrow t = -\frac{\ln(0.9)}{5.35} = 0.02\text{cm}$$

Assuming a beam size of 5 x 5 cm, as used on MARI, this gives a sample volume of 0.50 cm^3 and a sample mass of 0.50 gm. On an indirect geometry instrument, 2 – 3 gm would still give an acceptable spectrum.

Together with nuclear scattering, in $PrAl_3$ you have to consider also the magnetic scattering. For $PrAl_3$ at low temperatures, the magnetic scattering consists of only one narrow inelastic CF transition (no quasielasic and/or elastic magnetic scattering, sometimes hidden under the strong nuclear elastic peak) comprising the total magnetic cross-section of the free Pr^{+3} ion ($\sigma mag = 48.433 \times g_J^2 J(J+1)$ barns where g_J is the Lande factor. For Pr^{+3}, g_J = 0.8).