High Flux Diffractometers on Reactor Neutron Sources

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Abstract

Continuous neutron sources such as reactors can deliver a very high time-averaged flux to the sample using a relatively wide band of wavelengths, while still retaining good resolution. For example, the D20 diffractometer at ILL Grenoble, the world's highest flux neutron powder machine, can collect complete patterns at 100 millisecond intervals, and this has been important for the real time study of explosive SHS reactions. New very large 2D detectors, such as those recently installed on D2B and D19 at ILL, are up to an order of magnitude larger than previous designs, and will provide unmatched speed of data collection from very small samples, opening up new scientific perspectives for powder and single crystal diffraction. We will discuss future reactor based diffractometers designed for rapid data collection from small samples in special environments.

Keywords: DRACULA; large 2D detectors; fast diffractometers;

1. Simple measures of diffractometer performance

Jorgensen et al.[1] concluded that because neutrons are scattered isotropically, the relative merit of a powder diffractometer with a given resolution can be estimated from the product of just three parameters – the time averaged flux on the sample, the solid angle of the detector and of course the volume of the sample, which may be limited by resolution and other requirements.

This product rule appears to be supported by the current best high flux diffractometers, GEM on the ISIS pulsed source and D20 on the ILL reactor, which are roughly of equal merit, even though the time-averaged flux on D20 from the ILL reactor is more than an order of magnitude greater than on GEM (fig.1 in n.cm^{-2}.sec^{-1}).

	D20	**GEM**	**Dracula**	**SNS**
Time averaged flux	$5x10^7$	$2x10^6$	10^8	$2.5x10^7$
Solid angle (sr)	0.27	4.0	1.5	3.0
Sample volume	1	1	1	1
Merit product	18	8	150	75

Fig.1 The product of flux.angle.volume as a measure of efficiency.

The pulsed source machine GEM is unique in that its extremely large detector, which compensates for the relatively low flux on the sample, is not restricted to high resolution backscattering, but covers all scattering angles, with however correspondingly lower resolution.

2. High flux on the sample combined with big detectors

A recipe for a high flux neutron diffractometer is then:

- A wide band of wavelengths
- A very high flux on the sample
- A very large area detector

Quasi-Laue image plate detectors[2], such as LADI and VIVALDI at ILL and the similar machine at the Bragg Institute, are excellent examples of these principles; a white beam of neutrons is used, as on a TOF instrument, but this beam is continuous, so the time-averaged flux on the sample is normally much higher than with a pulsed beam from a spallation source. Neutron image plates allow a very large solid angle for the detector, and the sample volume can also be rather large, depending on the detector radius.

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Fig. 2 VIVALDI combines high flux on the sample using a continuous white beam with a very large image plate detector.

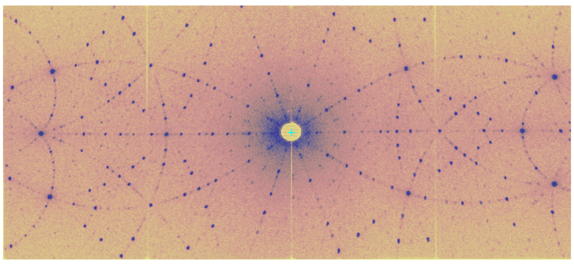

Fig. 3 The image-plate detector and high flux on the sample allow surveys of reciprocal space eg this quasi-crystal on LADI.

"Niimura special" image plate detectors can have an efficiency of 25% for thermal neutrons, but a neutron CCD camera such as the new Orient Express machine developed at ILL by B.Ouladdiaf [3)], can have higher efficiency and also provide real-time read-out of the diffraction pattern. Orient Express uses a pair of relatively small CCD detectors similar to those developed for X-rays, but using a gadolinium oxide neutron converter. Figure 4 shows the instrument set up for backscattering to give high angular resolution for crystal alignment. The neutron beam passes through a small hole between the image plates.

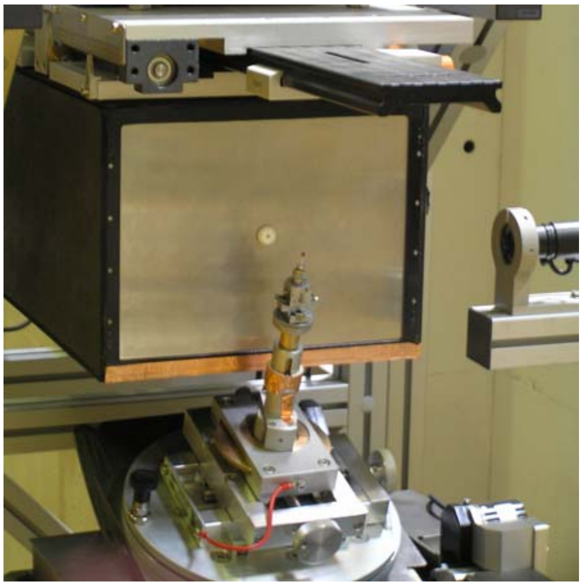

Fig. 4 Orient Express at ILL is a simple CCD detector on a continuous white neutron beam (Ouladdiaf, this conference).

Orient Express is located at a low flux position behind other machines on a long neutron guide, but is so fast that diffraction patterns that previously took minutes with photographic film can now be obtained in seconds.

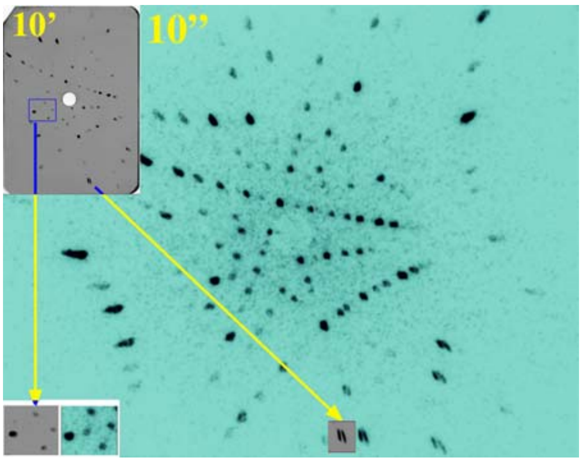

Fig. 5 Diffraction pattern from a small ruby crystal obtained on Orient Express in 10 seconds, instead of 10 minutes with film.

A white neutron beam, either continuous or pulsed, does have some disadvantages for the most precise measurements because of wavelength dependent corrections for intensity, absorption etc, and also because without TOF resolution, the background is integrated over all wavelengths while only specific wavelengths contribute to the peaks.

3. Big detectors with monochromatic neutron beams

Electronic detectors with monochromatic beams avoid these problems at the expense of reduced intensity, yet even then, the time averaged flux on the sample from a continuous source can, according to figure 1, be an order of magnitude greater than from a pulsed source. The challenge is to construct a large detector with real-time readout to match the big area detectors commonly used for TOF.

The first such large position sensitive detector (PSD) at ILL was the D20 microstrip detector[4], which is currently the world's fastest powder diffractometer. Yet the D20 detector still covers only 0.27 steradian (fig.1), and owes its speed to the high flux delivered to the sample using large vertically focusing monochromators (300 mm high).

With the option of using 120^o take-off angles, the resolution of D20 approaches that of D1A, except that D20 is very much faster. Figure 6 shows the diffraction pattern obtained from $Na_2Ca_3Al_2F_{14}$ in only 2 minutes !

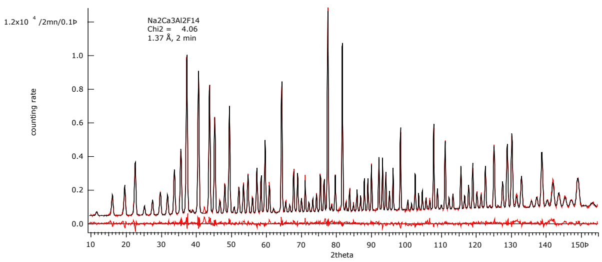

Fig. 6 The complete refined diffraction pattern obtained from $Na_2Ca_3Al_2F_{14}$ in only 2 minutes on D20 in high resolution mode.

The very high intensity and rapid read-out of the D20 PSD can be used for fast chemical reactions, such as the explosive SHS reaction forming the new ceramic Ti_3SiC_2 studied in time slices of 100 msec by Riley, Kisi et al [5].

Fig. 7 The explosive SHS reaction in Ti_3SiC_2 on D20. The intermediate phase (bright spot) lasts only ~1 second.

Large 2D position sensitive detectors can also be used for high resolution powder diffractometers such as D2B at ILL. The super-D2B Millennium project[6] resulted in a x6 gain in efficiency with almost no loss of resolution; indeed the higher intensity now allows higher resolution to be used for most experiments.

Super-D2B uses an array of 128 commercial linear wire detectors behind an array of 5' collimators. The detectors and collimators are 300mm high, so the curvature of the powder diffraction cones is clearly visible at low and high angles (fig.8)

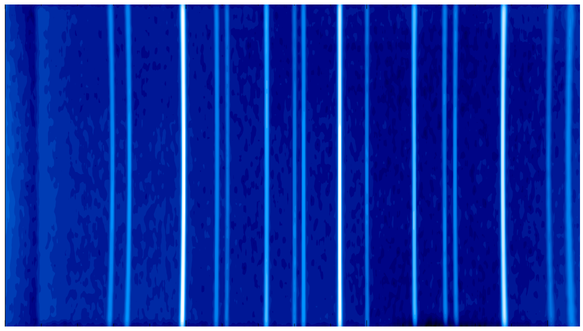

Fig. 8 A high resolution 2D detector array is needed to correct for the curvature of the diffraction cones on the new super-D2B.

The new super-D2B still covers a relatively small solid angle because of the use of fine collimators. For lower resolution machines it becomes attractive to use a true position sensitive detector, as on D20, but covering a much larger solid angle with 2D resolution.

Such a detector has already been constructed for the D19 Millennium project[7]. Again it consists of linear position sensitive wires defining the vertical resolution, but now all of the wires, together with electrodes deposited on glass plates, are within a single high pressure He^3 gas envelope (Guerard[8], this conference).

Fig. 9 A very large 2D PSD for D19, showing arrays of linear sensitive wires in front of electrodes deposited on glass (inset).

4. DRACULA, a very high flux neutron diffractometer

DRACULA will be a new **D**iffractometer for **R**apid **AC**quisition over **U**ltra **L**arge **A**ngles, and a natural extension of the ideas already tested on D2B, D19 and D20. It is the next step in the application of the Flux*Solid Angle principle, and will result in a machine where the distinction between "powder" and "single crystal" disappears.

As for D2B and D20, large focusing monochromators will be used, with even larger mosaic spread. As well as focusing in real space, focusing in reciprocal space means that a wide band of wavelengths $\Delta\lambda/\lambda$ can be used (fig.10). When this beam is scattered by the sample back into the direction of the beam from the source, all of the wavelengths enter the detector with the same incident angle; this means that the width of the Bragg peaks depends only on the size of the sample and detector elements, and the divergence of the beam from the reactor.

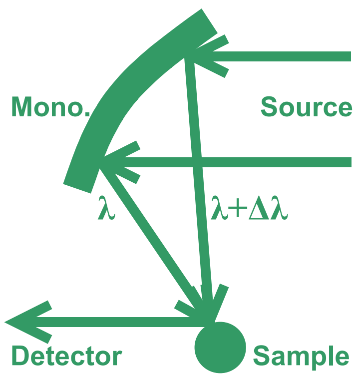

Fig. 10 Focusing of a large band of wavelengths still permits high resolution at high monochromator take-off angles.

Since very small samples (diameter d) would normally be used, and since a choice of Soller collimators can fix the horizontal divergence from the reactor, high resolution $\Delta d/d \sim 10^{-3}$ would be obtained even with a wavelength spread of ~1%. For angles near 90° with a radial collimator, scattering would be limited to a small volume of diameter D (fig.11).

A choice of fixed monochromator take-off angles would be available, probably 44°, 60°, 90° and 120°. The standard take-off would be 90°, but a low angle take-off to provide very high flux from a graphite monochromator would also be available, together with a high take-off of 120° for very high resolution. The main monochromators would be germanium [hhl] giving, for a take-off angle of 90°, a choice of wavelengths and a range of d-spacings (fig.12) for scattering within the restricted range 2Θ=60°-120°:

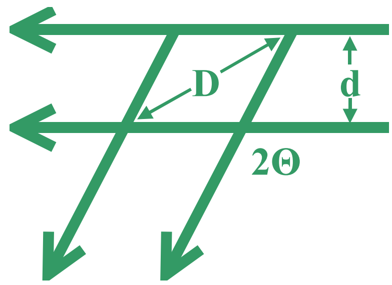

Fig. 11 For angles near 90° with a radial collimator, scattering would be limited to a small volume of diameter D.

Even if the scattering range is limited to 2Θ=60°-120°, which is attractive for reducing scattering from the sample environment with a radial collimator, a large range of d-spacings could be covered with just three different wavelengths, which would be obtained by simply rotating the Ge[hhl] monochromator about its vertical axis as on D1A/D2B. The most useful wavelength of 1.54Å would not require any filter, while a graphite filter would be used for 2.44Å and a beryllium filter for 4.61Å neutrons.

[115] -> 1.54Å		d= 0.889Å - 1.54Å
[113] -> 2.44Å	(graphite filter)	d= 1.39 Å - 2.44Å
[111] -> 4.61Å	(beryllium filter)	d= 2.66 Å - 4.61Å

Fig. 12 The large range of d-spacings available within the limited scattering range 2Θ=60°-120° using just three wavelengths from a focusing Ge[hhl] monochromator.

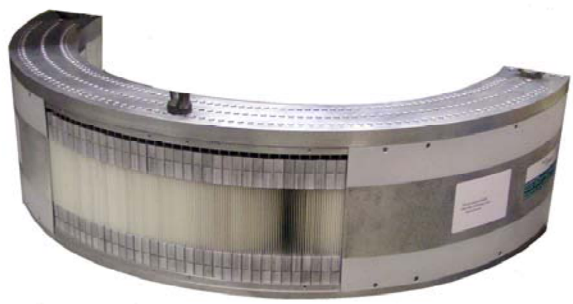

Fig 13. The Dracula radial collimator will cover a very large solid angle (160°x30° vertical) yet restrict scattering to a very small volume of diameter ~5mm around the sample. It will be similar to the new D20 radial collimator above (EuroCollimators, 2005).

5. The DRACULA Sample Environment

Because of its very high flux, Dracula will be particularly powerful for measuring very small samples, as in high pressure cells. Following the pioneering work at Saclay and ISIS, a new type of Paris-Edinburgh cell (VX5) has been constructed for ILL to operate at up to 100 kbar in a cryostat. This new pressure cell will be particularly suited to Dracula, with its high flux for small samples, and radial collimator to eliminate background scattering from the sample environment.

Fig. 14 The new 100 kbar pressure cell with its He cryostat.

One of the problems with the present ILL diffractometers D2B and D19 is that they are situated under the reactor transfer channel, which limits the height of the sample environment. Dracula will not be limited in this way, and will allow even large cryostats to be used, such as our 15 Tesla magnet, the new 7 Tesla diffraction group cryomagnet, and cryostats equipped with dilution refrigerator inserts.

Very high temperatures can already be obtained with mirror furnaces and microwave furnaces, and will also be available on Dracula.

6. The DRACULA Detector

This is the key element, and will provide Dracula with a detector x4 times as large as that of D20, which is already the fastest detector on a fixed-wavelength neutron powder diffractometer. Together with the extra flux on the sample, Dracula will then be an order of magnitude faster than D20 at the cost of slightly less resolution than available in D20's high resolution mode. Indeed, the solid angle of the Dracula detector will reach 50% of that of the fastest TOF machines, which can also measure at negative scattering angles without loss of resolution since monochromator focussing is not needed. The big difference will remain the very much higher flux on the sample due to the relatively wide wavelength band.

The Dracula detector will be almost identical to the new D19 detector, except that extra modules will extend coverage to 160^o, like D20 instead of 120^o as on D19. The vertical acceptance angle will remain at 30^o . The principle of using a large 2D detector for powders has already been proven on super-D2B, where it was shown that the diffraction cones could be integrated around their curved sections without substantial loss of resolution.

With a horizontal definition of at least 2.5mm, the Dracula detector will be resolution-matched to samples as small as 2.5 mm diameter. For even better definition of the powder profile, it will be possible to fine-step the Dracula detector on its tanzboden floor, as on D2B.

The complete neutron pattern in fig.6, which was obtained in just 2 minutes on D20 can be refined to give a high precision structure, as indicated by the red obs-calc difference pattern in the profile plot. On Dracula we might expect to obtain similar results in a matter of seconds, or a few 10's of milliseconds for large samples to study chemical kinetics.

For very small samples, such as those in high-pressure cells, we might expect to collect good quality high-resolution data from samples of a few 10's of milligrams. The sample volume in the new 100 kbar cell, at ~4 mm^3, is large enough to allow very short counting times; this would mean that data could be collected as a function of temperature even at very high pressure!

7. New Science on DRACULA

7.1. High Pressure and Extreme Sample Environments

High pressure is easier with X-ray diffraction because high fluxes, especially from synchrotrons, mean that very small samples can be used. Yet there are many problems where it would be useful to be able to use neutrons as well – for the same reasons that neutrons are needed for materials at zero pressure. Many electronic and magnetic properties depend on pressure, we need to understand why, and these are just the kind of problems where neutrons are most useful. Clearly, the maximum pressure that can be obtained with a cell still small enough to fit in a cryostat scales with the size of the sample, so high pressure means small samples and high flux diffractometers like Dracula. TOF diffractometers have some advantages for high pressure, but Dracula will also collect all d-spacings with different wavelengths over a limited scattering range.

7.2. New Materials and High Pressure Synthesis

New materials are usually only available as very small polycrystalline samples, and X-ray powder diffraction is often not sufficient to understand their structure. Examples are the high Tc superconductors, GMR and other magnetic materials. This is particularly true when new materials are synthesised under high pressure; yield volumes are small, and several samples must often be combined for neutron measurements, with the corresponding risk of inhomogeneity. A diffractometer with an order of magnitude increase in efficiency would be of great benefit in the search for new materials synthesised at high pressure.

7.3. Isotope replacement

Isotope replacement is a potentially powerful method for investigating the role of particular atoms in a structure, yet because of the cost of producing large samples, this technique is often restricted to deuteration. Yet isotope replacement has already demonstrated its interest for superconducting materials, where both the isotope effect predicted by BCS theory, and the effect of magnetism on specific atoms, has been investigated. Dracula would make isotope replacement feasible for a wider range of problems, since much smaller samples would be required.

7.4. Strongly aborbing elements

One of the big advantages of neutrons over X-rays is their low absorbtion for most materials. Yet neutrons are strongly absorbed by a small number of rare earth elements whose compounds are increasingly interesting. For example, it is difficult to study magnetism in these materials, absorbtion of hydrogen etc., and it is not always feasible to use sufficiently energetic neutrons. This problem can be addressed by using very thin samples, but again a highly efficient neutron diffractometer is needed.

7.5. In-situ chemical kinetics

Because they can penetrate relatively large chemical and electro-chemical cells, neutrons have long been of interest for the in-situ study of chemical reactions. For example, the chemical reactions that occur in a full-size Li-MH battery can be studied as the cell is discharged and recharged. Intercalation experiments, especially those involving hydrogen or other light elements, are ideally studied with neutron diffraction. Classical examples include hydration of minerals, hydrogen storage materials, zeolites and clathrates etc.

7.6. Very fast reactions

Many other chemical reactions are simply too fast for neutron diffraction. The order of magnitude increase in speed that would be possible with Dracula would open up many new areas of chemical kinetics that cannot adequately be studied with X-rays. The explosive SHS reaction[5], occuring on a time scale of 100's of ms is a good example.

7.7. Very weak magnetic order and polarised neutrons

Magnetic order can sometimes be missed because of very weak superstructure peaks, or very small changes to peak intensity for ferromagnetic materials. A very high intensity machine like Dracula will mean that such small changes could be more easily and quickly observed. A polarising filter option, already tested for powder diffraction, is planned for the study of magnetic density.

7.8. Texture

A large 2D detector is ideal for the study of the texture and preferred orientation of materials, such as mineral and geological samples, as well as industrial components.

7.9. Single crystal diffraction

Finally, the large 2D detector of Dracula will be equally powerful for single crystal studies, where many reflections might be obtained simply by spinning the crystal about an axis. This is the application foreseen for the D19 large structure diffractometer; a similar machine is needed for smaller structures.

8. Conclusions

The main disadvantage of neutron scattering is the low flux compared to X-ray diffraction. An order of magnitude gain in neutron flux would have a big impact on many problems in chemistry and physics, and open up whole new areas for neutron diffraction. Eventually we must build a very high flux neutron source like ESS. But it is clear that we could do more with the neutron sources we already have, which in the case of reactors provide high time averaged flux to the sample. Advanced detector technology has now made it possible to make far better use of already available neutrons for a relatively modest cost.

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