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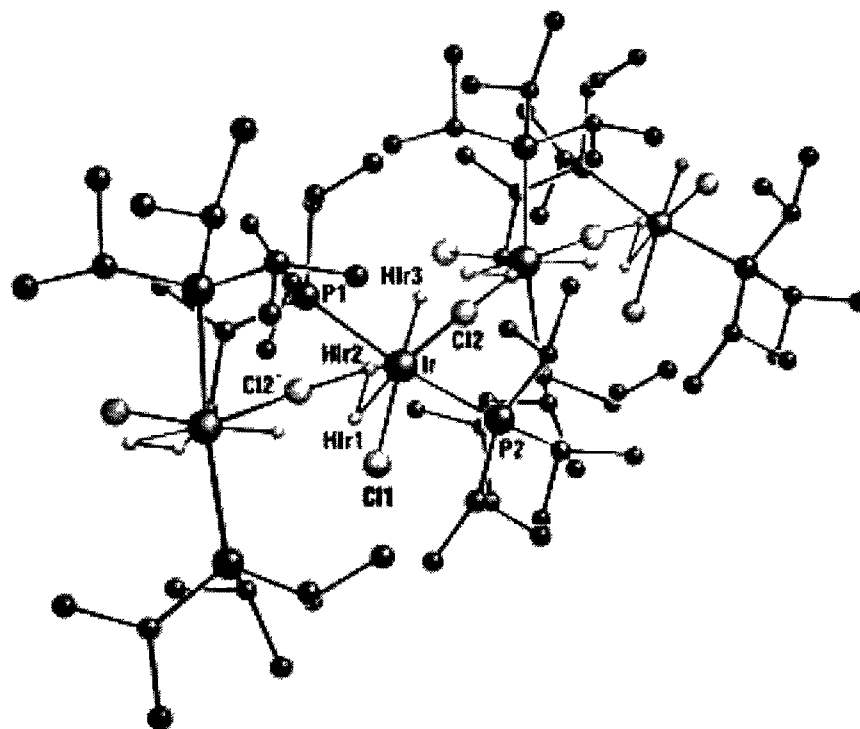
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# Single-Crystal Neutron Diffraction at the Australian Replacement Research Reactor

Report of the Single-Crystal Diffraction Workshop

ANSTO

11-12 December 2001



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Report prepared by the participants of the Single-Crystal Diffraction Workshop,  
held at ANSTO, 11-12 December 2001

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Figure front page: Structure of  $\text{IrH}(\text{H}_2)(\text{Cl})_2[\text{P}(\text{Pr})_3]_2$  (Albinati *et al.* JACS, 115, 7300-7312, 1993).

## **Executive Summary**

Australia has a diverse community of users of single-crystal neutron diffraction. A quasi-Laue image-plate diffractometer allows the fastest throughput by far, but would exclude an important number of experiments. Most of these could be covered by the additional possibility to locate the image-plate detector on a monochromatic beam. Therefore we recommend both a white thermal beam and a monochromatic beam for an image-plate detector. At little additional cost the existing 2TanA instrument could be located semi-permanently on the same monochromatic beam, thus offering three quite different types of single-crystal instruments. Small improvements could be made to the 2TanA instrument to cater for the remaining experiments not suited to an image-plate diffractometer.

A quasi-Laue diffractometer would need to be located at the end of a neutron guide. A bender may be technically possible, but estimated losses of 50-70% of the thermal neutron beam are too high.

The user community needs a variety of sample environments.

An Instrument Advisory Team will be assembled, and will help in specifying, designing and commissioning the instrument.



Model of the Replacement Research Reactor.

The workshop for the Replacement Research Reactor Project was held 11-12 December 2001 at ANSTO, Lucas Heights, NSW 2234, Australia.

The subject was single-crystal neutron diffraction.

The purpose of the workshop was to:

- identify the future needs and opportunities for single-crystal neutron diffraction, and
- specify instrument requirements

This document represents the accumulated views of the participants at the workshop.



Back Row (left to right): Jane Hanrahan, Erich Kisi, Trevor Finlayson, Darren Goossens, Colin Weeks, Appadurai Thiyakesan, Andrew Goodwin, Peter Turner , Steve Best

Middle Row (left to right): Dai Hibbs, Leonard Lindoy, Robert Burns, Linda Xiao, Geetha Rajaratnam, Ross Piltz, Brian Figgis, Jenny Forrester, Andreas Ostermann, Jeff Sellar, Mark Spackman, Suzanne Hughes, Greg Halder, Rob Robinson

Front Row (left to right): Richard Welberry, Sax Mason, Garry McIntyre, Christina Hoffmann, Tony Klein, Hans Freeman , Wim Klooster

The participants and their affiliations are listed in Appendix A. The workshop program is listed in Appendix B.

## **1. Introduction**

Single-crystal diffraction is a widely used technique to study structural properties of materials. This is mostly done using X-rays. Neutron single-crystal diffraction is less commonly used because of the special facilities needed. However, neutron single-crystal diffraction can be essential to study certain features, which can not be studied using other methods. The need for neutron single-crystal diffraction has been recognised and led the Beam Facility Consultative Group (BFCG) to recommend a new single-crystal diffractometer for the Australian Replacement Research Reactor Project.

This document outlines the scientific case for a single-crystal diffractometer, the desired specifications, and other issues associated with the operation.

## **2. Scientific Case**

### **2.1 Overview**

The proposal for single-crystal neutron diffraction at the Replacement Research Reactor (RRR) is relevant to the interests of chemists, physicists, materials scientists, geologists, biologists and others.

The availability of highly accurate structural data has revolutionised chemical and biological sciences. Data of this sort are predominantly obtained using X-ray and neutron diffraction techniques, where the information provided by these experiments is complementary.

The accurate determination of atomic positions in a wide variety of crystalline solids is a core activity of any neutron diffraction facility. This has been an important area of study by Australian based research groups and these activities have been conducted at a range of neutron sources including HIFAR, ISIS and ILL. It is anticipated that the demand for the structural information provided by these experiments will expand in the future.

The recent rapid expansion of topical areas of chemistry, such as supramolecular chemistry, crystal engineering and molecular modelling, requires accurate fundamental information concerning weak intermolecular interactions involving hydrogen atoms.

Neutron diffraction provides the means for full characterisation of such interactions in the solid state.

Important advantages of neutrons which are of particular relevance to structure determination, stem from the fact that neutrons are primarily scattered by the nucleus, rather than the electron cloud of an atom. Thus the neutron scattering length of an atom is not simply proportional to the atomic number and the form factor for neutrons falls off more slowly with scattering angle than occurs with X-rays. Moreover, the magnetic moment associated with the neutron gives rise to magnetic scattering, enabling more detailed characterisation of magnetic materials.

Neutrons play a critical role in the determination of hydrogen atom positions. This is essential for the characterisation of hydrogen bonding interactions in solids (biology, chemistry), metal hydrides (catalysis) and organic compounds (drugs, chemistry, biology). Light atoms such as hydrogen can be located as precisely as, and in the presence of, heavy atoms such as uranium or platinum.

Another limitation of X-ray techniques arises in instances where it is necessary to distinguish between elements of similar atomic number. In many cases the neutron scattering lengths differ markedly and provide a high level of contrast between such atom types. The contrast also applies for different isotopes of the same element.

Thus, neutron crystallography is capable of providing important structural information that can not be obtained by X-ray diffraction.

Types of materials to be studied by single-crystal neutron diffraction in the context of Australian research needs include:

- Organic compounds, including biologically important species
- Inorganic solids, organometallic complexes and coordination compounds
- Framework solids
- Metals and alloys
- Minerals
- Biological and synthetic polymer fibres
- Incommensurate solids
- Supramolecular structures

Other aspects of single-crystal neutron diffraction of particular interest to the Australian scientific community are:

- Charge density studies
- Phase transitions
- Hydrogen bonding
- Diffuse scattering
- Magnetic structures
- Diffraction physics
- The influence of temperature, pressure, electric and magnetic fields on materials

The above types of research will be carried out at the RRR single-crystal neutron facility from day 1.

## **2.2 Projected Development**

The RRR will provide the opportunity for Australian investigators to play a role in expanding the range of neutron diffraction applications. Areas in which the existing expertise and interests of the Australian scientific community may make significant contributions are:

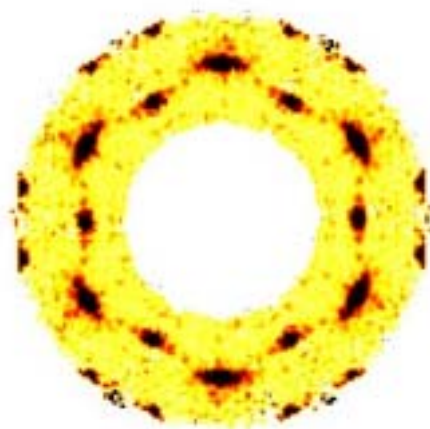
- The improvement of the sensitivity of the techniques, resulting in shorter measurement times and/or the ability to record data from smaller crystal specimens than are currently required.
- An extension of static neutron diffraction studies to time-resolved measurements.

If even one of these two advances were implemented, the application of neutron diffraction techniques (not just in Australia) would be greatly expanded.

## **2.3 Diffuse Scattering**

Diffuse scattering is the weak background scattering that occurs in the diffraction patterns of all real crystalline materials from the simplest, e.g. NaCl, to the most complex

macromolecule (e.g. protein). While the strong sharp diffraction peaks in the pattern are used by conventional crystallography to deduce the average repetitive arrangements of atoms in crystals, diffuse scattering contains information about the *deviations from the average*. Quite often it is just these deviations from the average, or types of *disorder*, rather than the average structure itself, that give materials their unique or novel properties. In particular there are numerous examples of technologically important materials whose unique properties are intimately associated with their intrinsic disorder (e.g. cubic stabilised zirconia). See Figure 1 for an example.



**Figure 1.** Diffuse neutron scattering pattern in benzil (courtesy of Darren Goossens, ANSTO).

The recent return to the use of 2-D detectors in diffraction experiments has meant that many scientists are seeing diffuse scattering for the first time. For almost a generation diffuse scattering has been overlooked entirely due to the use of single point detectors. Enormous improvements in measuring power (sources and detectors) and computing power have made and will continue to make the collection and analysis of diffuse scattering data more commonplace, and it is desirable to be in a position to capitalise on this.

Because diffuse scattering is very weak compared to Bragg scattering there is a need for:

- large samples 10×10×10 mm would be required
- multi-detector (as large a solid angle as possible)
- low background such as air scattering, stray scattering from other experiments etc.



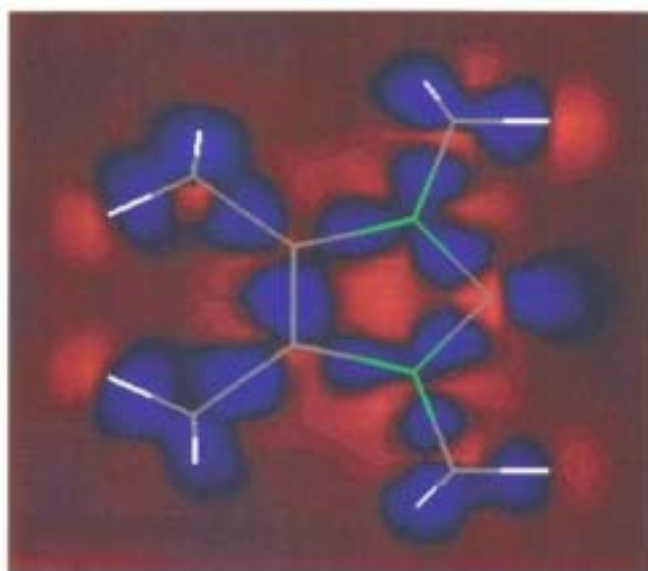
(Note: what Bragg scatterers call background might be the signal. Because of low counting statistics, subtracting background is problematical.)

For a reactor source it is necessary to have a monochromatic beam with low  $\Delta\lambda/\lambda$  and beam divergence, ideally giving the possibility of resolving features in the diffraction pattern corresponding to spacings of  $\sim 100$  Å in the sample. For instance, for a 10 Å cell we need to sample at intervals of 0.1 in the reciprocal cell.

There is also a need to record a wide range of diffraction angles ( $d$ -spacings) in order to be able to determine disorder effects due to displacements.

#### 2.4 Charge density studies

Another area of particular interest is that of charge density studies, where X-ray and neutron data are combined to obtain the electron distribution and derived properties. See Figure 2 for an example. The data need to be as accurate as possible, with esd's for bond lengths of order 0.001 Å. This necessitates good quality crystals, and a diffractometer like 2TanA, preferably with single counter detector. Image plates may be an option for the future if the accuracy improves sufficiently. The data must be collected at low temperature, but that will pose no problems.



**Figure 2.** Charge density in a carbene (Arduengo *et al.* JACS, 116, 6812-6822, 1994).

## 2.5 Time-dependent studies

To study time-dependent phenomena one requires study of a particular feature of the scattering from the crystal (either the intensity of a particular set of diffraction peaks or the diffuse scattering) as a function of time (on the scale of hours). An image plate diffractometer is well suited for that.

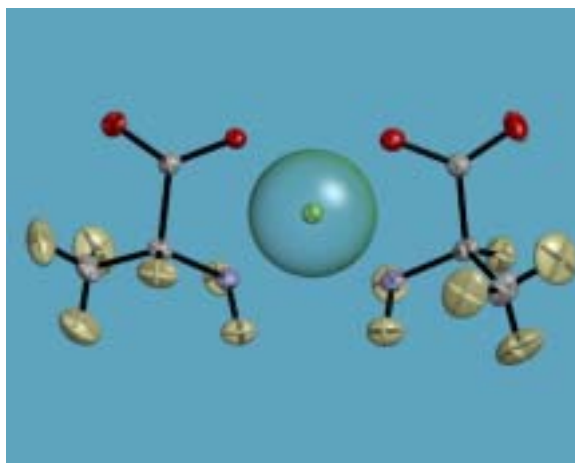
## 2.6 Magnetism

A magnetic field is of interest specifically to the class of materials which exhibit strong magnetostrictive components and offer the possibility of having a response in an applied magnetic field. The experimental requirements for this will be to apply the magnetic field (typically from an electromagnet) to the sample being held at a particular temperature in the Displex cryostat.

Magnetism could be served by other instruments quite well (polarisation analysis, TAS, HIPD, HRPD). However, it would still be possible to do 3-dimensional magnetic structures on the new single-crystal diffractometer.

## 2.7 Biology

A workshop on Neutrons in Biology was held 10-11 July in Melbourne, (<http://home.ansto.gov.au/ansto/neut/bio.pdf>) and one of the recommendations was that there be *no* specific effort to provide high-resolution protein-crystallography facilities at the RRR, but that a watching brief be kept on instrumentation and sample-preparation technologies elsewhere.



**Figure 3.** Cu-Alanine complex (courtesy of Ross Piltz, ANSTO).

### 3. Instrument Requirements

#### 3.1 To build a 4-circle diffractometer or quasi-Laue diffractometer?

This is an important question. Different types of studies can be done with different types of diffractometer (Table 1).

**Table 1.** List of fields with the most suited type of diffractometer.

	<i>4-circle</i>	<i>quasi-Laue</i>
High throughput chemistry "routine structural"		X
H-bonding	X	X
Diffuse scattering	X	
Small biological molecules	X	X
Low temperatures and highly accurate structures	X	
Small molecules	X	X
Charge density studies	X	
Kinetic studies	X	
Small crystals		X
Fibre Diffraction	X	
Liquid Crystal	X	
Bio(macro)molecules	X	X
Geology		X
Phase transitions	X	possibly
Magnetic structures	X	
Multilayers	X	
Thin films	X	
Esd 0.001 Å on a bond length	X	possibly
3-d peak shape studies	X	
Incommensurates and quasi-crystals		X
Diffraction physics	X	
Highly accurate cell dimensions vs environmental parameters	X	
Texture studies	X	
High pressures and temperatures	X	

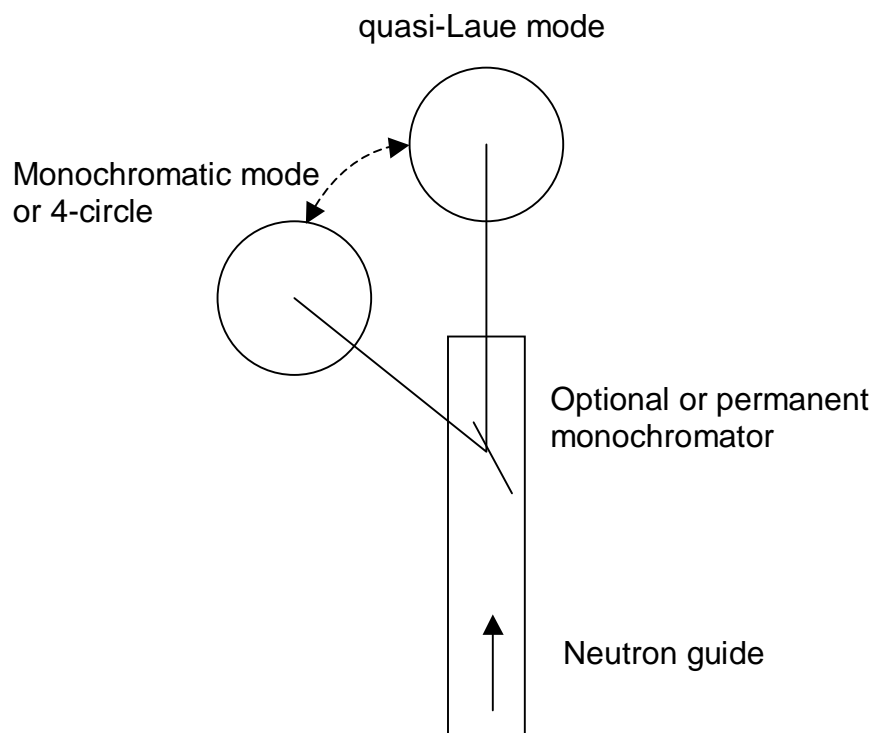
Note that a monochromatic image plate machine could do a lot of these things. It would be slower than a quasi-Laue diffractometer, but faster than a 4-circle diffractometer.

A quasi-Laue diffractometer is more like a workhorse machine. Faster and cheaper, but less flexible. Accuracy is not quite the same as for 4-circle diffractometer, but is still improving and esd's on bond lengths of  $\sim 0.002$  Å are possible. The extra data from a quasi-Laue diffractometer may make up for lower precision in some ways. A 4-circle diffractometer can be reconfigured in many ways, and is flexible, which require more user input. Australia has a small but diverse user community, which suggests a flexible option.

There are several possible visions:

- 4-circle diffractometer only
- quasi-Laue image-plate diffractometer only
- quasi-Laue + monochromatic image plate diffractometer
- quasi-Laue image-plate diffractometer + 4-circle diffractometer
- quasi-Laue + monochromatic image plate diffractometer + 4-circle diffractometer

There is a trichotomy in the choice of instrument to satisfy all scientific interests of the single-crystal community. A (quasi)-Laue image-plate diffractometer allows the fastest throughput by far, but would exclude an important number of experiments. Most of these could be covered by the additional possibility to locate the image-plate detector on a monochromatic beam. Therefore we recommend both a white beam and a monochromatic beam ( $\lambda = 1$  to  $2.4 \text{ \AA}$ ) for the image-plate detector (see Figure 4).



**Figure 4.** Possible layout for an image-plate diffractometer.

At little additional cost the existing 2TanA instrument (Figure 5 and <http://www.ansto.gov.au/ansto/neut/2tana.html>) could be located semi-permanently on the same monochromatic beam, thus offering three quite different types of single-crystal instruments.

Small improvements could be made to the 2TanA instrument to cater for the remaining experiments not suited to an image-plate diffractometer: exchange of the Eulerian cradle for an automated tilt goniometer for extremely bulky sample environment (cryomagnets, large pressure cells), optional larger area detector, analyser crystal. Although this option would provide all scientific opportunities and may be reasonably cheap, this would probably require at least two scientists for which there is currently no funding.



**Figure 5.** 2TanA at HIFAR.

One could use a quasi-Laue diffractometer for survey of reciprocal space, the 4-circle diffractometer for detailed examinations, and the monochromatic image-plate diffractometer for diffuse scattering studies and work between the Bragg points.

### **3.1.1 The case for an image-plate diffractometer**

A detector employing neutron-sensitive image plates is comparatively cheap and capable of high spatial resolution, has good homogeneity, a large dynamic range, extended linearity and no dead-time, and can be constructed to subtend very large angles at the sample. Dramatic gains in data-collection rate have been realised using cylindrical ( $2\pi$  sterad) image-plate detectors and the quasi-Laue technique at the ILL [1] and on a monochromatic beam at JAERI [2] (Appendix C).

### **3.1.2 Advantages of the (quasi)-Laue image-plate diffractometer**

- Uses all or most of the intensity of the beam
- At least 82% of unique data to the diffraction limit are observed without overlap
- No monochromator
- Smaller crystals and/or faster data collection

- Simple experiments (as easy as powder diffraction)
- One axis, thus simplifying sample environment
- Pretty, educational, patterns

### 3.1.3 Disadvantages of the (quasi)-Laue diffractometer

- Higher background
- Indexing can occasionally be difficult
- Harmonic overlap, especially of small-Q data
- Not at all suitable for diffuse scattering
- Wavelength-dependent corrections e.g. absorption, extinction

### 3.1.4 Applications already demonstrated at the ILL [3]:

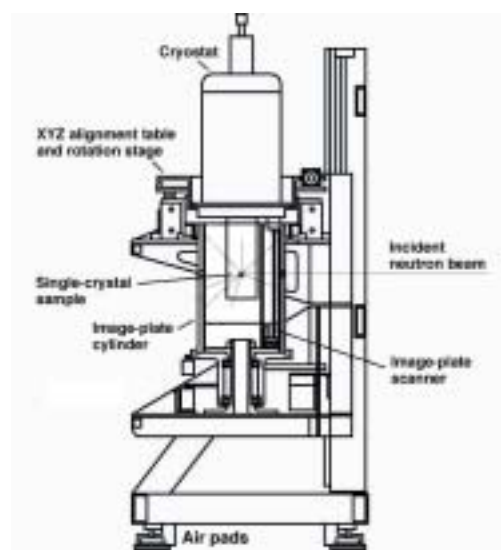
- **Rapid structural studies:** Gains in efficiency between one and two orders of magnitude compared with monochromatic experiments on the same or similar compounds have been achieved, with only modest loss of precision in bond lengths and angles. Often the precision in a rapid experiment is sufficient to allow physically meaningful conclusions to be drawn concerning chemical or physical properties [4].
- **Compounds containing hydrogen:** Even compounds with a hydrogen content of 50% or more give clear interpretable diffraction patterns despite the large inherent incoherent background [4,5].
- **Reciprocal-space surveys:** The large detector surface combined with the white beam allows rapid survey of large continuous regions of reciprocal space, and facilitates identification of complex features due to incommensurability and twinning [6,7].
- **Very small samples:** Crystal volumes of 0.1 mm<sup>3</sup> or less are now feasible because of the gain in efficiency over monochromatic experiments. This is particularly attractive for high-pressure experiments, or for first investigations of topical new materials when the crystals initially produced are small.
- **Phase transitions:** Complete data collections are possible in just an hour or so, which allows the nuclear or magnetic structures to be followed in detail with temperature, (magnetic or) electric field or pressure, for example, through phase transitions [8].

This is particularly relevant to crystal structures where individual reflections are not directly related to the order parameter.

- **Maximum-entropy reconstruction:** About 18% of the unique data, mostly at low Q, are absent from or harmonically overlapped in the Laue diffraction pattern. Maximum-entropy reconstruction was successful in circumventing this problem to obtain a model-free density distribution of rotationally disordered molecules [9]. Similar techniques might make possible *ab-initio* structure solution from Laue data.

### 3.1.5 Construction details

The image-plate detector should be very similar to that of VIVALDI (Very-Intense Vertical-Axis Laue Diffractometer; for more information see <http://www.ill.fr/YellowBook/VIVALDI/>) at the ILL. The axis of the detector should be vertical to facilitate the use of heavy cryostats, furnaces and pressure cells, and the cryostats and furnaces should be top loading to minimise loss of beam-time between samples or experiments, and quick exchange of the entire cryostat or furnace should be possible.



**Figure 6.** VIVALDI at ILL.

A neutron beam with low  $\gamma$ -ray background is essential since (present) image plates are  $\gamma$ -ray sensitive and would otherwise need extensive protection;  $\gamma$ -rays in the beam itself are simply transmitted. With present bender technology an end position is essential. A free path length of about 2 m should be allowed before the detector for insertion of optional wavelength band-pass filters [10] for exclusion of longer wavelengths that contribute little to the reflections, or for selection of longer wavelengths for experiments on reflections at small Q that would otherwise be harmonically overlapped.

The height of the instrument must be variable to allow the detector to be moved to other beams, e.g. to a cold-neutron guide for experiments at much longer wavelengths.

One can allow the possibility for either replacing the four-circle diffractometer with the image-plate detector or for placing the image-plate detector behind the four-circle diffractometer for monochromatic image-plate experiments e.g. of diffuse scattering. The beams should therefore be close enough to permit this by movement on air-pads and

without breaking electrical connections. Positioning the instrument on either beam should be reproducible.

## 3.2 Location

### 3.2.1 Thermal or Cold Neutrons

At the Neutrons in Biology workshop, 10-11 July 2001 in Melbourne, (<http://home.ansto.gov.au/ansto/neut/bio.pdf>) it was decided that there is no current need for a dedicated protein crystallography single-crystal diffractometer. In addition, at the present single-crystal workshop no significant case was made for cold neutrons. Thus, the single-crystal diffractometer should be at a thermal beam port. However, even at a thermal beam it may be possible to collect protein data using a monochromatic beam, like the BIX machines at JAERI. Also, if the diffractometer is easily movable, it may be possible to use cold neutrons if user demand changes and an appropriate beam port is available.

### 3.2.2 Reactor Face or Neutron Guide

Low noise is important, but a high neutron flux is needed to give the best possible counting statistics. The number of neutrons is considerably higher at the reactor face (Table 2). However, the wide divergence of the beam at the reactor face (Table 2) will not be very useful, since a monochromator cannot accept this full divergence, and will only add to the background. It would be better to be in the guide hall, where the number of neutrons in the desired bandwidth with the right divergence is of the same order of magnitude as at the reactor face, but with considerably lower background. The wavelength is slightly longer at the neutron guide, due to energy losses. This might be a consideration in favour of a reactor face position.

**Table 2.** Calculated neutron flux (Kennedy *et al.* Applied Physics A, submitted).

<i>Beamline</i>	<i>distance (m)</i>	<i>flux (<math>n.cm^{-2}.s^{-1}</math>)</i>	<i>Wavelength peak (Å)</i>	<i>Divergence(°)</i>
TG3 (neutron guide)	49	$\sim 1.6 \times 10^9$	1.3	2.0
TG4 (reactor face)	6	$\sim 1.6 \times 10^{10}$	1.1	3.8

\* Calculated divergence for beam CG1 at reactor face and neutron guide distances



The location at the neutron guide is not so important for a 4-circle or monochromatic image-plate diffractometer, since they will need a monochromator to extract the right wavelength neutrons from the beam. However, a quasi-Laue diffractometer should be at the end of a neutron guide. It might also be possible to locate it elsewhere using a bender. A bender could give a clean spectrum, but the estimated intensity losses of 50-70% for a thermal neutron beam are too high, especially if Australia wants to be competitive.

### 3.3 Monochromator / Velocity Selector

To obtain a monochromatic beam there is a variety of options available.

About half the physics experiments at D10 (ILL) are done using pyrolytic graphite (PG,  $\lambda = 2.35 \text{ \AA}$ ) because of good Q-resolution, good access to magnetic form factor, and good PG reflectivity.

Chemistry experiments typically use wavelengths in the range  $\lambda = 0.9\text{-}1.5 \text{ \AA}$ , but the low end is limited by the neutron guides. 3 Monochromators are suggested: Cu(220) at  $1.235 \text{ \AA}$ , PG and Ge(11n),  $n=1,3$ . BIX (JAERI) uses a bent perfect Si monochromator, but that is a compromise. Si can be focussed to a tiny spot. The new monochromator at IN8 at ILL is very good, but very expensive (Figure 7).



**Figure 7.** The new 3-face monochromator for the IN8 3-axis spectrometer at ILL.

For a quasi-Laue diffractometer multiple different supermirror benders can select the appropriate wavelength range. Wavelength filters are relatively inexpensive.

For short wavelengths one really needs to be at the reactor face, or even better, at a hot source. Keep this in mind for the future.

### 3.4 Type of Detector

The neutron flux at RRR will be better than at HIFAR, 2TanA has  $6 \times 10^5$  n.cm<sup>-2</sup>.s<sup>-1</sup> at sample, but the best opportunities for improvement are the detectors.

#### 3.4.1 Image Plates

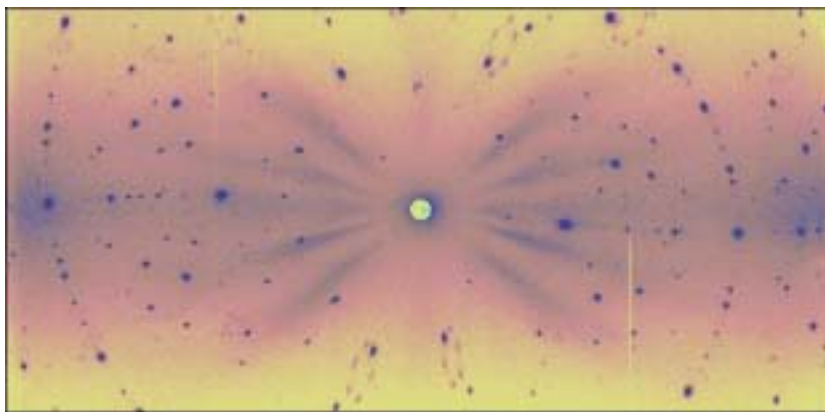
Overall, an image plates are the most bang for the bucks (see 3.1 and Figure 8).

A disadvantage of image plates is the readout time, which is currently around 3 minutes (plus 1 minute to clear the image and 1 minute for movements). This is not so bad when the exposure time is an hour or more, but if the exposure time is only 5 minutes, the readout time is too long. People are working on faster readout times. 10 seconds was mentioned, but these are not commercially available yet.

Another solution might be to read the image plate while another is used to collect a new set of data, as is done at some synchrotrons. However, this is not easily done because of the shape and large area needed at a neutron single-crystal diffractometer. The shielding may also be a problem.

Another disadvantage is the  $\gamma$ -ray sensitivity of image plates. The commercially available image plates (from Fuji) have iron in the material on the back which gets irradiated and can cause background images. Iron-free image plates are available, but are more expensive.

Another advantage of image plates is the simplicity of the system, and when better image plates are available, they can easily be replaced.



**Figure 8.** A test image taken by VIVALDI (courtesy of Garry McIntyre, ILL).

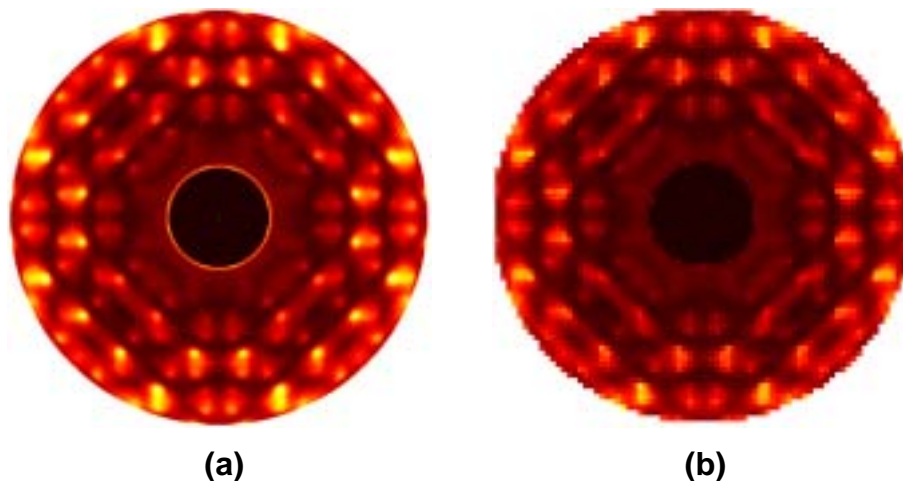
### 3.4.2 Other detectors

A 4-circle diffractometer should aim for an area detector for at least 10 x 10 degrees, with detector resolution of 1 mm at 50 cm.

Other detector types are possible. For example,  $^3\text{He}$  gas detectors, multiwire detectors etc. These are expensive, but could be a future option.

### 3.4.3 Resolution

The resolution of image plates is nowadays around 200  $\mu\text{m}$  or better, and for gas detectors about 2 mm. For diffuse scattering experiments the resolution needs to be good. See Figure 9 for an example of a high and low resolution diffuse scattering pattern.



**Figure 9.** Example X-ray pattern showing effect of resolution (courtesy of Darren Goossens, ANSTO).

Ytria stabilised cubic zirconia, 0.5 $\mu\text{m}$  section, Cu K $\alpha$ . radiation.

(a) resolution of  $\sim 0.1$  degrees in 2-theta (b) resolution of  $\sim 0.5$  degrees in 2-theta

### 3.4.4 Efficiency

Single counter detectors are very efficient, but slow for data collection, since they have to scan through a peak and are limited by the speed of the various drives.

An area detector efficiency is around 35% ( $2\tan A$ ). These can collect more data at once, including the peak profile, and incommensurate peaks and diffuse scattering and so.

Image plates have an efficiency around 80% (BIX). These can collect whole sections of reciprocal space in one run.

Multiwire detectors are 50-100 % efficient (ILL). These type of electronic detectors are being developed, and can be very good, but are still very expensive.

### 3.4.5 Background

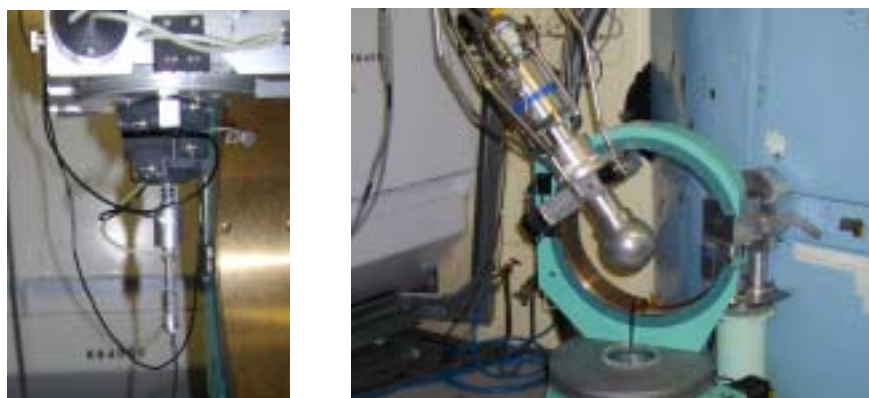
The general consensus was that the background should be as low as possible. This is crucial for experiments like diffuse scattering, since the signal is 1000 to 10000 times less than that of the Bragg peak. A low background is also important for superlattice reflections. If hydrogen is present in material, it will create its own background. Other instruments can also cause background. This would strongly suggest a location at the neutron guide, not at the reactor face.

### 3.5 Types of ancillaries

Flexibility for various sample environments is desired. In order to facilitate special environments, a  $\kappa$ -geometry may be necessary.

- **Temperature:** Displexes down to 1.5 K and furnaces up to 2000 K. Temperature precision and control of cooling and heating rates is important. In-house support staff is crucial. A quasi-Laue diffractometer shows considerable background due to cryostat. If using an image-plate diffractometer, a cryostream as is used in X-ray diffraction would allow low temperature data to be collected without getting an unwanted signal from a cryostat or cryorefrigerator. This is particularly useful when looking for weak or diffuse features and is strongly recommended if a quasi-Laue type machine is built. Equipment for temperatures less than 1 K (special cryostat) is desirable.
- **Pressure:** A high pressure cell is desirable, to 1GPa, possibly higher. Also of interest are particular stress fields (e.g. uniaxial or biaxial). The stress fields can be achieved through the use of small aluminium clamps. Such clamps need only be of the order of a centimeter in size, so could easily be accommodated within the sample space of a Displex cryostat. Such clamps would be constructed by the experimenter, compatible with the particular crystal.
- **Electric Field:** An electric field in the order of  $50 \text{ kV.cm}^{-1}$  can be applied easily and cheaply.

- **Magnetic Field:** A magnetic field is more difficult to apply due to the size of the equipment. No cryomagnet in a quasi-Laue diffractometer due to physical size and background. For the 4-circle diffractometer a magnetic field of around 10 T could be an option.
- **Chemistry Laboratories:** The chemistry laboratories should contain oxygen free, humidity controlled, gloveboxes. Need the ability to (re-)mount samples on-site. Should not be a long path (no doors) between glovebox and instrument. Snap freezing of hydrated crystals (< 1 mm on a side) good for attracting chemists.
- **Mounting Crystal:** It should be possible to mount and align the crystal off-line, so a minimum of time is spend putting the crystal on the diffractometer.



**Figure 10.** High voltage cell and cryostat for 2TanA (courtesy of Ross Piltz, ANSTO).

There will be a “standard” suite of ancillaries, which can be used at various instruments. This would include cryogenics (5-300 K), cryofurnaces (10-600 K), furnaces (300-2000 K), pressure cells (0-1 GPa), cryomagnets (0-14 T), and sample platform (xy translations).

### 3.6 Shielding

Shielding is an issue whatever diffractometer will be build. If it will be build at the reactor face, it will be more expensive.

### 3.7 Software

The data-collection program should be a graphical user-friendly application with optional command-line operation and the possibility for a series of batch commands. Users of LADI and VIVALDI are usually autonomous within a quarter of an hour, and thus little time

is demanded of the instrument scientist. Analysis of the diffraction patterns at ILL will mostly be performed with user-friendly software based on the CCP4 Laue suite [11]. Little assistance is needed for conventional structures. All sorts of users will be using the software!

GUI, user friendly, data interchange should be easy, consistency across facility. HMI is held up as excellent example of integrated, consistent and yet flexible software, C.A.R.E.S.S.

Will there be the opportunity for remote data collection? It is technically possible. This is a policy decision. People should really come and see for themselves, not necessarily for the whole experiment if it takes a long time.

#### 4. Desired Performance Specifications

- Versatility
- Speed for a quasi-Laue diffractometer should be roughly one structure per day
- Small sample  $\sim 0.1 \text{ mm}^3$  should be possible
- Experiment turnaround about 10% of experiment time
- Temperature of 1-2000 K, 10-400 K in a cryofurnace
- Solid angle for image-plate diffractometer at least  $2\pi$ . 4-circle should aim for at least  $10 \times 10$  degrees, with detector resolution of 1 mm at 50 cm
- Dynamic range of detector of at least 1000
- At  $\lambda \sim 1.2 \text{ \AA}$ ,  $\Delta\lambda/\lambda$  of about 1-3%,  $\Delta d/d \sim 0.0001$
- All angles, positioning precision should be 0.01 degree
- Handle  $d$ -spacings up to  $40 \text{ \AA}$
- Time stability:  $< 1\%$  decay per week
- Q-range of about 10 ( $\sin\theta/\lambda \sim 0.85 \text{ \AA}^{-1}$ )
- Low background (1 count per hour per pixel)
- Support services: controlled atmospheres (non-oxidising, wet, dry... all close to instrument)

Other:

- Access is very important: there is a clear need for efficient and unobtrusive security arrangements, and to ensure the shortest possible time between visitor arrival and access to instrument.
- User friendly, easy access, remote monitoring, internet connections in rooms in guesthouse, good food (available on weekends and in evenings), friendly software, night and weekend ancillary support

## **5. Other Discussions**

- Build a user community. Some attendees had no idea there is a 4-circle diffractometer at HIFAR. It is important to get many people involved in experiments. This can start by doing experiments at HIFAR, possibly at other places, and go around the community to spread the word. Neutron diffraction is still perceived as exotic, whereas in reality it is as easy as X-ray diffraction.
- Defuse anti-nuclear sentiments through education. Some students should come to ANSTO to get familiar with neutrons (prepwork for 1 week for example). Possibly single-crystal diffraction, and simple structures for advanced students. Possibly via the internet. For a case for educational use of equipment, see Appendix D.
- As much of the hardware as possible should be compatible with the other machines being developed. This is important for exchangeability of ancillaries. Also, as much of the software as possible should be compatible with the other machines being developed.
- All data should be deposited.

## 6. Summary

Australia has a diverse community of users of single-crystal neutron diffraction. A (quasi)-Laue image-plate diffractometer allows the fastest throughput by far, but would exclude an important number of experiments. Most of these could be covered by the additional possibility to locate the image-plate detector on a monochromatic beam. Therefore we recommend both a white thermal beam and a monochromatic beam ( $\lambda = 1$  to  $2.4 \text{ \AA}$ ) for an image-plate detector. At little additional cost the existing 2TanA instrument could be located semi-permanently on the same monochromatic beam, thus offering three quite different types of single-crystal instruments. Small improvements could be made to the 2TanA instrument to cater for the remaining experiments not suited to an image-plate diffractometer: exchange of the Eulerian cradle for an automated tilt goniometer for extremely bulky sample environment (cryomagnets, large pressure cells), optional larger area detector, analyser crystal.

A quasi-Laue diffractometer would need to be located at the end of a neutron guide. A bender may be technically possible, but estimated losses of 50-70% of the thermal neutron beam are too high.

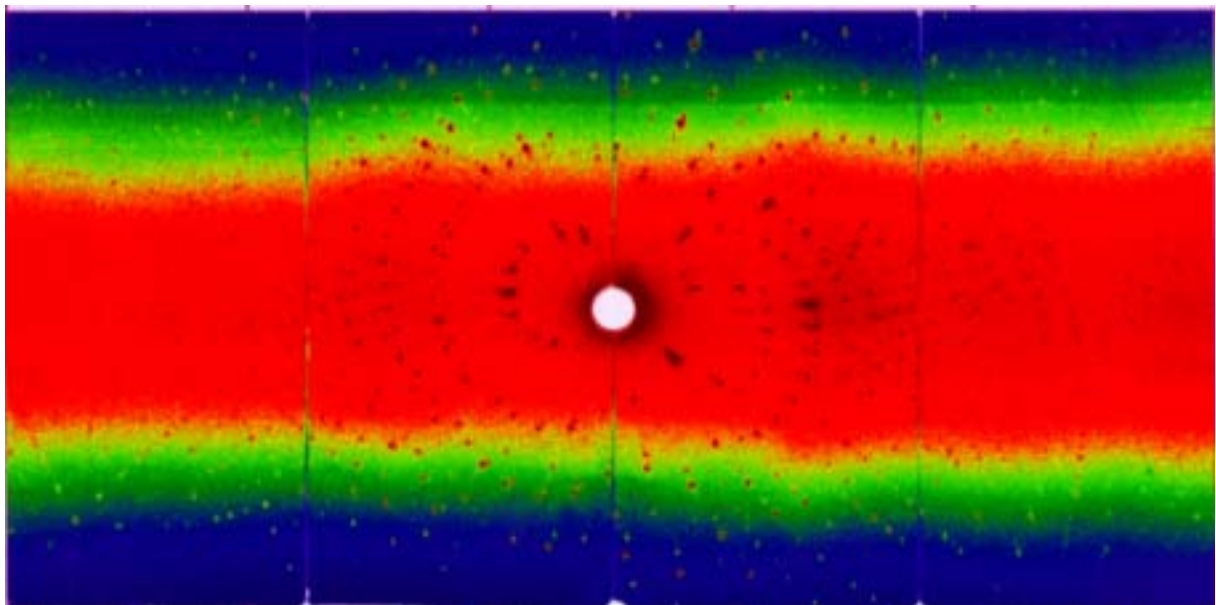
The user community needs a variety of sample environments.

An Instrument Advisory Team will be assembled, and will help in specifying, designing and commissioning the instrument.



## 7. References

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**Figure 11.** False-colour image of a typical scanned Laue pattern from lysozyme (Niimura *et al.*, Nature Structural Biology, 4, 909 (1997)).

## Appendix A: Participants List

### *Participants :*

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## Appendix B: Workshop Program

### Program for Workshop on Single-Crystal Diffraction

11-12<sup>th</sup> December 2001

Conference Room, Building 55, ANSTO, New Illawarra Road, Menai, NSW 2234

#### *Tuesday, 11<sup>th</sup> December 2001*

**Purpose:**

**Morning:** to outline scientific opportunities, technique and state-of-the-art instrumentation at overseas facilities.

**Afternoon:** to discuss background issues associated with instrument design specifications.

Time	Presentation	Presenter	Chair
8:30	Arrival at ANSTO		
9:00	Opening and Welcome	H. Garnett, ANSTO	H. Freeman
9:05	An overview of Instrument Opportunities at the Australian Replacement Research Reactor	R.A. Robinson, ANSTO (U. Sydney)	
9:30	Charge to the Workshop	R.A. Robinson, ANSTO	
9:35	Introduction to Single-Crystal Neutron Diffraction	W.T. Klooster, ANSTO	
10:20	Coffee		
10:35	Single-Crystal Diffraction Facilities and Science at the ILL	G. McIntyre, ILL	R. Welberry (ANU)
11:20	Single-Crystal Diffraction in the Australian Context	R. Piltz, ANSTO	
12:05	Scientific and Technical Visions	5 minutes for each interested attendee	R.A. Robinson (ANSTO)
12:30	Lunch		
13:30	Macromolecular Crystallography with Monochromized Neutrons: Recent Results from the Single-Crystal Neutron Diffractometer BIX-3	A. Ostermann, JAERI	S. Best (U. Melbourne)
14:00	D19: a fast monochromatic diffractometer for single-crystal and fibre diffraction studies in chemistry, physics and the bio-sciences	S. Mason, ILL	
14:45	The case for a neutron scattering instrument dedicated to educational use	A. Klein, Melbourne	
15:00	Workshop Photo		
15:15	Afternoon Tea		

15:30	Discussion of Scientific Opportunities	Forum for discussion	L. Lindoy
17:30	Move to Dinner		(U. Sydney)
18:00	Workshop Dinner		

## Wednesday, 12<sup>th</sup> December 2001

**Purpose:** to draft *Report on the Scientific and Technical Requirements for Single-Crystal Diffraction at Australia's Replacement Research Reactor.*

9:00	Welcome Back	W.T. Klooster, ANSTO	
9:05	Characteristics of the Cold, Thermal and Hot Source and Neutron Guides at the Australian Replacement Research Reactor	S.J. Kennedy, ANSTO	B. Figgis (UWA)
9:45	An Overview of the Elastic Scattering Instruments at SNS with Emphasis on the Single Crystal Instrument	C. Hoffmann, SNS	
10:15	Coffee		
10:30	Discussion of Single-Crystal Instrument Type	Forum for discussion	S.J. Kennedy/
11:15	Discussion of Single-Crystal Instrument Design	Forum for discussion	W.T. Klooster
12:15	Charge for writing Workshop Report	R.A. Robinson, ANSTO	
12:30	Lunch		
13:30	Report writing		
16:30	Workshop Summary and Close	W.T. Klooster, ANSTO	

## Appendix C: Characteristics of Image-Plate Detectors (Data from ILL, JAERI).

		<i>VIVALDI</i>	<i>LADI</i>	<i>BIX-3</i>
<b>monochromators</b>	Laue	white thermal beam	white thermal beam	monochromatic
		$0.8 < \lambda < 4.5 \text{ \AA}$	$3 < \lambda < 4 \text{ \AA}$	2.35 / 1.23 $\text{\AA}$
	filtered, position 1	$0.8 < \lambda < 3 \text{ \AA}$	multi-layer (Ti and Ni)	elastically bent perfect
	filtered, position 2	$3 < \lambda < 4.5 \text{ \AA}$		Si (111 / 311)
<b>collimation sample</b>	pinholes beam size	0.5 to 10 mm up to 10 x 10 mm <sup>2</sup>		
	flux (unfiltered)	$> 10^9 \text{ n cm}^{-2} \text{ s}^{-1}$	$3 \times 10^7 \text{ n cm}^{-2} \text{ s}^{-1}$	$3 \times 10^6 \text{ n cm}^{-2} \text{ s}^{-1}$
	sample space	122 mm in diameter		
<b>detector</b>	neutron image plate	Gd <sub>2</sub> O <sub>3</sub> doped BaFBr:Eu <sup>2+</sup> same		same
	configuration vertical cylinder			
	- radius	159.7 mm	159 mm	200 mm
	- active area	800 x 400 mm <sup>2</sup>	200 x 400 mm <sup>2</sup>	500 x 450 mm <sup>2</sup>
			4 plates	2 plates
	- angle subtended	144°	144°	143°
	pixel size	200 x 200 $\mu\text{m}^2$	200 x 200 $\mu\text{m}^2$	200 x 200 $\mu\text{m}^2$
readout time	3 min	3 min	3 min	

## **Appendix D: Education**

### **The case for a neutron scattering instrument dedicated to educational use.**

Report to the ANSTO Beam Facilities Consultative group Workshop  
by  
A.G. Klein, School of Physics, The University of Melbourne

#### 1. Introduction.

Since a new research reactor facility is a major national investment, it is important to maximise its benefits for the largest number of citizens. Beyond its scientific, utilitarian, and political benefits there are educational benefits which can be achieved by involving students in practical, hands-on experimental work using reactor neutrons. The educational benefits are two-fold: sociological and scientific.

#### 2. The sociological benefits of an educational facility.

These revolve around demonstrating that reactors, radiation, nuclear power etc. are not evil and dangerous but when suitably controlled and intelligently handled are a natural extension of physical technology not unlike electricity or, for that matter, fire. Ignorance and adverse propaganda have poisoned the minds of a whole generation into attitudes of anti-nuclear hysteria and this may have cost our nation dearly (vis-a-vis its Uranium-mining and nuclear-powered economic competitors). This state of affairs must not be allowed to continue or to recur if nuclear power is to gain a foothold in Australia in the 21st Century, as it undoubtedly must. Education to recognise the potential of "clean, safe, nuclear power" must begin at its source. The largest number of students must be exposed to a modicum of practical learning on the subject, in particular future scientists, future science teachers and future leaders with a scientific education. It is important to note that these sociological benefits are automatic concomitants of the scientific activities described below.

#### 3. The scientific benefits of an educational facility.

These are concerned with concrete contributions to the education of physical scientists and engineers. I have in mind senior undergraduate students of physics (and possibly chemistry and materials science) coming to Lucas Heights for "practical work" as part of their degree course, possibly in a system administered by an "undergraduate arm" of AINSE.

Exposure to the environment of a research reactor (even just the guide-hall) contributes (even if tangentially) to students' knowledge about radiation,

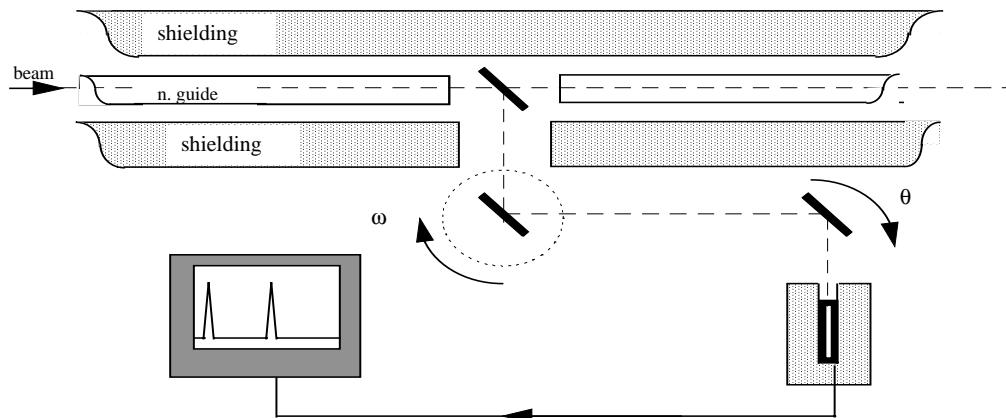
including reliable information about safety aspects, shielding, detection and monitoring, neutrons, fission, beams, etc.

#### 4. Suggested Experiments

In more direct terms, I envisage one or more set projects as "practical work" for, say, 3rd year students as a result of which they become acquainted with many concrete aspects of the nuclear field while, at the same time gaining valuable knowledge and skills.

I have in mind an experiment in which a monochromatic beam of thermal neutrons is Bragg diffracted by a large crystal of Sodium Chloride (Silicon is probably too "perfect", therefore diffracting too narrow a range of wavelengths). Knowing Avogadro's number and the density of NaCl, (hence the lattice spacing), the neutron deBroglie wavelength can be calculated.

A more interesting variant diffracts the neutrons from a *rotating* NaCl crystal, with the diffracted beam intercepted by a crystal of the same material, in the parallel (non-dispersive) configuration, situated at a distance of the order of a metre away. With timed detection, recorded in a PC connected as a multi-scaler, this is effectively a time-of-flight measurement, which allows the measurement of the neutron velocity. Thus, with the experimental determination of wavelength as well velocity, one can find Planck's constant (knowing the mass of the neutron) or vice-versa.



While the above is a fairly straightforward laboratory exercise, I hope that its collateral educational content is obvious. It contains a lot of fundamental physics as well as a number of valuable laboratory techniques. Furthermore, it can support variants, which would make it accessible to a very wide spectrum of students. Ideally, I would like to see every physics major in Australia exposed to it or its equivalent.

More advanced exercises can be envisaged using other available beam instruments, eg. simple structure analysis with a diffractometer; the observation of an anti-ferromagnetic material structure; a small angle scattering exercise, etc.

I would also recommend one or more similar laboratory exercises involving irradiation facilities, for example:

- \* a life-time measurement;
- \* an elementary exercise in activation analysis;
- \* a (non-radioactive) isotope dilution analysis exercise with Indium (might appeal to environmental science students !);
- \* an  $(n,\gamma)$  on Nitrogen protein assay on a food sample (might appeal to biological science students).

## 5. Conclusion

In conclusion, I feel that direct involvement with laboratory exercises in a research environment is a powerful educational opportunity which leads to acquaintance with and de-mystification of reactor, radiation, neutron and nuclear apparatus and concepts.

3 December, 1997