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Future ISIS single crystal instruments

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ABSTRACT
The designs of two proposed new single crystal instruments for ISIS are described. The biological structures instrument DIBS will allow the study of large unit cell materials in reasonable counting times. HRED, the high resolution elastic diffractometer, will provide a single crystal instrument of resolution $\Delta Q/Q \sim 10^{-3}$, increasing the available resolution for reciprocal space surveying by some 10-fold over that currently obtainable on SXD.

I. INTRODUCTION

The single crystal programme established at ISIS has now begun to illustrate the potential of the time-of-flight Laue technique at a pulsed neutron source. It is clear that the existing SXD is limited in its exploitation of the wide range of crystallographic science available at ISIS. For reasons both of limited unit cell size and limited resolution, there are parts of the programme which are effectively precluded from study by SXD.

To extend the size of structure amenable to study into the large molecule biological and organic chemical regime, the instrument DIBS (Diffraction Instrument for Biological Structures) is proposed. The development of neutron diffractometers for biological applications is hampered by the fact that biology is difficult for neutron crystallography, involving as it does very large unit cells and small crystals. However, there are many biological problems requiring neutron diffraction input, and with the expansion of the biological sciences it is becoming increasingly important that the potential exploitation of neutrons in biology is exploited. The main thrust of DIBS is towards maximising both useful flux on the sample and data accumulation rate, and it is hoped that this would allow such structures to be studied in a reasonable counting time. It is clear that for such an instrument, significant improvements in both hardware and software are required to give optimal performance. The somewhat mutually incompatible required mix of obtaining high flux on the sample, implying a short beamline, while retaining sufficient resolution for the separation of reflections from a large unit cell material, is tackled in the DIBS design.

One of the most successful ISIS instruments to date has been the high resolution powder diffractometer (HRPD). By exploiting the excellent resolution ($\Delta d/d \sim 5\ 10^{-4}$) available on a long flight path instrument at a pulsed neutron source, HRPD has opened new areas of science within the field of powder diffraction and has allowed a much deeper understanding of the detailed physics accessible by the technique. Experience on HRPD has shown that not only can an order of magnitude improvement in resolution lead to a greater understanding of effects previously suspected and partially measured, but can also yield hitherto unsuspected details. The development of single crystal diffraction at ISIS, on the other hand, has concentrated more on rapid reciprocal space surveying at modest resolution. The results obtained to date on SXD have shown the wealth of information available by this technique and have yielded promising results in both near and off Bragg peak diffuse scattering among others. However, the data obtained on SXD are at times tantalising - there is obviously a great deal of information available, much of which is masked by the low instrument resolution. Time-of-flight reciprocal space surveying has reached in some senses the stage reached by neutron powder diffraction before the advent of HRPD. A similar ten-fold improvement in resolution should have the same impact in this aspect of the single crystal field, allowing a greater understanding of that information at present only partially available and also yielding new information at present beyond the limits of SXD. The design of HRED, the High Resolution Elastic Diffractometer, should allow the opening of these new areas.

II. DIBS - SCIENTIFIC CASE AND GENERAL PRINCIPLES

Crystallography underpins all of the solid state sciences and has made a major impact in areas as diverse as high T_c superconductors and in the determination of the structure of DNA. Neutron diffraction, on the other hand, has made a major impact in physics and chemistry but much less in the biological sciences field. The impact of neutron diffraction methods in the latter has been modest to say the least, when compared with the impressive list of discoveries achieved using X-rays.

Neutrons do, however, have an extremely important role to play in the study of biological structures. Many of the mechanisms for biological activity in proteins, nucleic acids and other large scale biological systems, are associated with hydrogen bonding, solvent water structure and other forces depending crucially on a knowledge of the locations of hydrogen atoms within the structure. In the location of these vital hydrogen atoms, neutron diffraction has a significant advantage over all other techniques. In particular, these hydrogen atoms are virtually unlocatable by X-ray methods. In addition, the ability to perform isotopic substitution - exchanging deuterium for hydrogen - further enhances the potential of the neutron as a biological probe.

There are two principal problems with neutron diffraction from large unit cell samples: low neutron flux and small crystal size lead to prohibitively long counting times; the very large incoherent scattering of hydrogen gives a high background, prejudicing the peak/background ratio attained and thus leading to reduced precision. Designed to overcome these problems, DIBS was conceived in part as a result of ideas put forward by Lehmann and Wilkinson (1989) for a quasi-Laue diffractometer (LADI) at the ILL, and by extrapolation (Wilson, 1988) of earlier calculations of requirements for biological crystallography at a pulsed source presented by Jauch and Dachs (1984).

The current single crystal diffractometer (SXD) at ISIS is a time-of-flight Laue instrument, but is designed and optimised for the study of fairly small molecule structures, and is thus primarily a physics/chemistry instrument. With a largest cell edge amenable to study on SXD of some 30-35 Å with current hardware and software, and a largest unit cell volume of some 3000-5000 $Å^3$, much of organic, organometallic and biological crystallography is inaccessible. In addition, SXD is situated on a hot (ambient water) moderator, and the flux distribution peaks at a much shorter wavelength than would be ideal for large structural work. A cold moderator is much more suitable (see below). The aim in designing an instrument such as DIBS is to reach the specifications required in much of contemporary biological crystallography:

(i) Unit cell edges of up to 100 Å;

(ii) Cell volumes > 10^5 $Å^3$;

(iii) d_{min} in the range 1.2-1.5 Å dependent on crystal diffraction characteristics;

(iv) Reasonable data collection times (days/weeks rather than months);

(v) Crystals usually limited to V ~ 1 mm^3 even in favourable cases;

The Laue method, the most obvious data collection technique on a pulsed source, permits the simultaneous measurement of many Bragg peaks and is thus efficient for the rapid collection of many data (> 10^5 reflections for a moderately large protein). A single crystal instrument on a pulsed source has very significant advantages in using the Laue method, related to the fact that time-of-flight allows the separation of different reflection orders, but more importantly "stretches" the incoherent background from hydrogen. This latter scattering is of necessity integrated into the detector on a steady state Laue diffractometer. This factor has a significant effect on the peak/background ratios achieved. With such data, collected on position-sensitive detectors, excellent spatial resolution is necessary to resolve the many Bragg peaks, whose centres are typically closer than 1% in $\Delta Q/Q$.

II.1 Calculations and Assumptions.

Wilson (1988) proposed the following modifications to improve the prospects for biological structural studies on SXD:

(i) Profile fitting for the extraction of integrated intensities (see below) - the limiting resolution (in time) is given by $\Delta Q/Q \sim 0.017$ (assuming peaks separated by $\pm 2.5\sigma$) for SXD at 8 m, ~0.006 at 20 m. The required resolution for 1.2 Å d_{min} along a 100Å cell edge is ~0.006. Profile fitting can reduce peak separation to $< \pm 1\sigma$, reducing the required $\Delta Q/Q$ to some 0.015 or more. An ~8 m instrument would then become tractable in terms of time resolution;

(ii) Angular resolution requirements can also be reduced by using profile extraction of intensities. The assumption of 3 mm resolution detectors at L_2 = 1 m used in one of the earlier extrapolations (see below) is then unnecessarily strict. Placing 3 mm resolution detectors (current technology) at $L_2 = 0.3$ m is sufficient, if the anticipated resolution in the profile fit is obtained;

(iii) Flux improvements can be gained by using a large wavelength range ($\Delta\lambda$ of > 4 Å for short instrument, ~2-3 Å for a 20 m instrument) and a colder moderator to increase the useful flux of colder neutrons (where the λ^4 reflectivity term in the intensity equation becomes very favourable). A tight pulse is still required, however, for a short instrument to be viable and it may be necessary to sacrifice some flux to poisoning. It should be noted again that to first order the inclusion of a larger λ window does not prejudice the accuracy of the reflections which would be accessible in the short window, due to the favourable aspects of the time-of-flight technique. This is because in time-of-flight the background is time-sorted in a way unique to pulsed sources, allowing one to increase the range of data collection without penalty;

(iv) The detector array can be increased (see below), in light of recent advances in easy to construct ZnS scintillator PSD technology. Pursuing fibre-optic encoding designs for large area PSDs, better than 3 mm resolution is achievable over large (>300×300 mm²) areas. We can assume a variety of detector arrays, depending on cost and availability of profile fitting for intensity extraction;

(v) The use of a focusing guide extending into the insert shielding can further increase the flux on the sample;

(vi) Data processing would involve the extensive use of front-end transputer-based number crunching, to automate the bulk of the work of integrated intensity extraction. Coupled with the provision of a fast modern-day minicomputer such as VAXstation-3200, this set-up should be able to cope with the rapid data rates expected.

Under various scenarios, the following very approximate extrapolations can be made. These are based on the original estimates (Jauch and Dachs, 1984) of some 10 weeks data collection time for a 20 m instrument with a guide. The assumptions used are of a factor two increase in flux from both pulse exploitation and provision of more cold neutrons, a factor of three in detector coverage in designs (ii) and (iii) below and a factor of some five from the use of a focusing guide on the short beamline. In addition in all these calculations 100% detector efficiency has been assumed (this is not yet realised).

(i) High resolution, SXD-20, guide, 10 PSDs at $L_2 = 1$ m :
t_{est} ~ 20/2 = 10 weeks for 1.25×10^5 Å^3 cell (10w/25 = 3 days for lysozyme).

(ii) Moderate resolution, SXD-20, guide, 10 PSDs at 0.3 m :
t_{est} ~ 20/2/3 = 3 weeks for 1.25×10^5 Å^3 cell (3w/25 = 1 day for lysozyme).

(iii) Low resolution, SXD-8, focusing guide, 10 PSDs at 0.3 m :
t_{est} ~ 20/2/3/5 = 5 days for 1.25×10^5 Å^3 cell (5d/25 = 5 hours for lysozyme).

Given that software advances allow the 3D profile fitting intensity extraction method to be successfully exploited (and there is already evidence that this is the case), then obviously the most rapid data collection design should be chosen for biological studies. *DIBS would then resemble the ~8m instrument described above.*

The latter design begins to appear very similar to that proposed by Lehmann and Wilkinson (1989) for a protein Laue instrument at the ILL, where they assumed $L_1 = 7$ m, $L_2 = 0.1$ m, angular coverage of PSDs equivalent to 10 modules at 0.3 m, $\Delta\lambda = 2$ Å (achieved through velocity selectors), in which they estimated some three hours for the study of lysozyme, very similar to the data collection time given for DIBS above. Given the approximate nature of some of these estimates, the difference in these numbers (three versus five hours) is probably not significant. The reasons for this favourable comparison of count rate between LADI and DIBS, in spite of the probable order of magnitude greater flux on sample of the former, are two-fold: LADI requires 2–3 wavelength bands in its "quasi"-Laue approach, whereas DIBS time sorts the whole range in a single data set; poor peak/background (1:10) on LADI resulting from the integration of the hydrogen incoherent scattering compares unfavourably with that predicted for DIBS (1:1), giving a further factor of three in required counting time. Thus, in the present very rough approximation, the counting times on the two instruments appear roughly equivalent.

II.2 Software Improvements

In the context of DIBS, these are essentially geared towards the d_{min} for which reliable intensity information may be extracted for a large structure. The resolution limits quoted above are based on the assumption that reliable intensity extraction is only possible for peaks whose centroids are $> 5\sigma$ apart (σ being the FWHM of the peak profile). However, by adopting a strategy analagous to the Pawley (1981) peak fitting method (itself an adaptation of the Rietveld method) one can fit an overall "envelope" or profile to the entire observed pattern. Use of the Pawley method (in one dimension) has been shown to vastly improve the apparent resolution of peaks, i.e. to allow extraction of useful intensity information for peaks separated by considerably less than 5σ . By adopting a three-dimensional extension of this profile fitting technique it should be possible to resolve reflections separated by, say, 1σ ($\pm 0.5\sigma$), improving the apparent resolution by a factor of some five.

Initial work on this profile intensity extraction technique has begun, using data sets collected on the existing SXD. As an example, intensities were extracted from the (00l) row of reflections (Figure 1) from a W-hexaferrite sample with $c = 32.9$ Å. It was found possible in this case to extract intensities for reflections up to (0,0,80), $d = 0.4$ Å, in a region well beyond the normal "resolution" limit (in terms of overlapped peaks) of the instrument. This test bodes well for the implementation of the full 3D profile software.

II.3 Hardware Improvements

As mentioned above, in order to maximise count rate, it is necessary to have a very large array of position-sensitive detectors around the sample, subtending as large an angle as possible. The ILL proposal for LADI uses 100% efficient PSDs with 1 mm resolution situated at 0.1 m from the sample – technology as yet unproven in either aspect but which obviously reduces the area coverage requirements and hence the diffractometer costing. The area detectors proposed for DIBS are envisaged to be based on the fibre-optic encoded ZnS scintillator PSDs recently successfully installed and tested on SXD (Davidson, Mott, Rhodes and Johnson, 1989). The prototype module for this type of area detector has performed very satisfactorily and the extrapolation to the desired properties is being pursued at present. The specified properties for DIBS modules are:

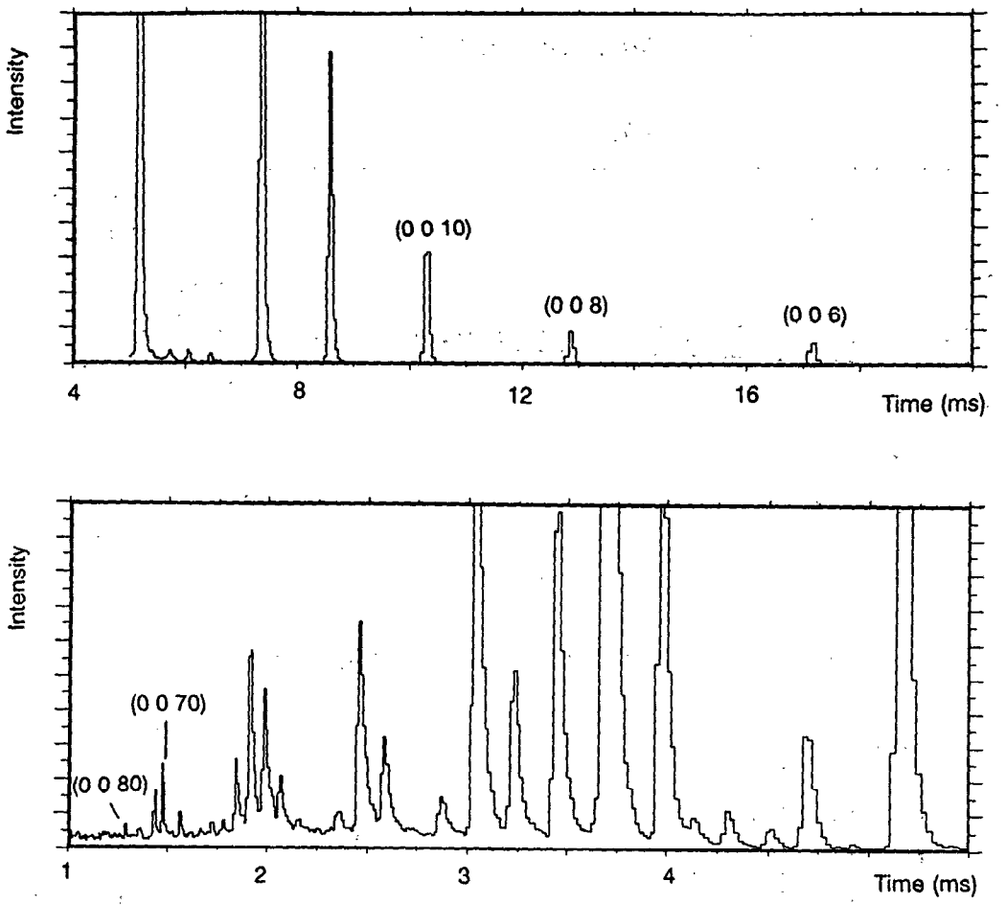


Figure 1 - Time-of-flight spectrum of the (00l) row of the W-hexaferrite, measured on SXD.

(i) 3 mm pixel resolution, possibly reducing to 1.5 mm by interpolation;

(ii) 2–3 μs dead time per module will be adequate for DIBS data collection rates;

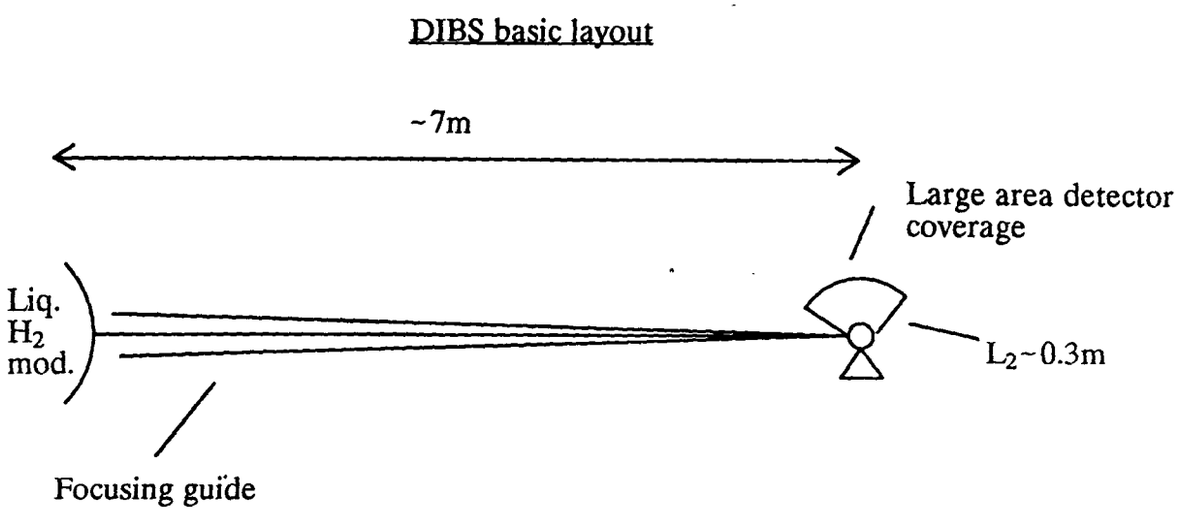
(iii) Efficiency > 50% for 1 Å neutrons, approaching 100% for longer λ – significant development is required to realise this for ZnS scintillator modules;

(iv) Ease and speed of construction - 300 × 300 mm^2 modules should be built on a timescale of 1–2 months when this becomes routine. The economical nature of the construction also allows large spatial coverage to be achieved without enormous expense;

(v) The modules could be constructed in a curved array, forming part of a spherical surface surrounding the sample;

(vi) Around 10 of these modules would form the basic DIBS array, situated at L_2 ~ 0.3 m.

The data acquisition and processing capability required for such an extensive data processing array and the data rates anticipated for DIBS would be substantial. The data collection is envisaged to use the proposed ISIS DAE–II and would rely on extensive use of transputers to push many of the number–crunching aspects of data collection and reduction into the hardware at the front–end, including the extraction of integrated intensities from the raw data. The removal of this taxing task from the computing system would allow the use of the extensive CPU for further processing.



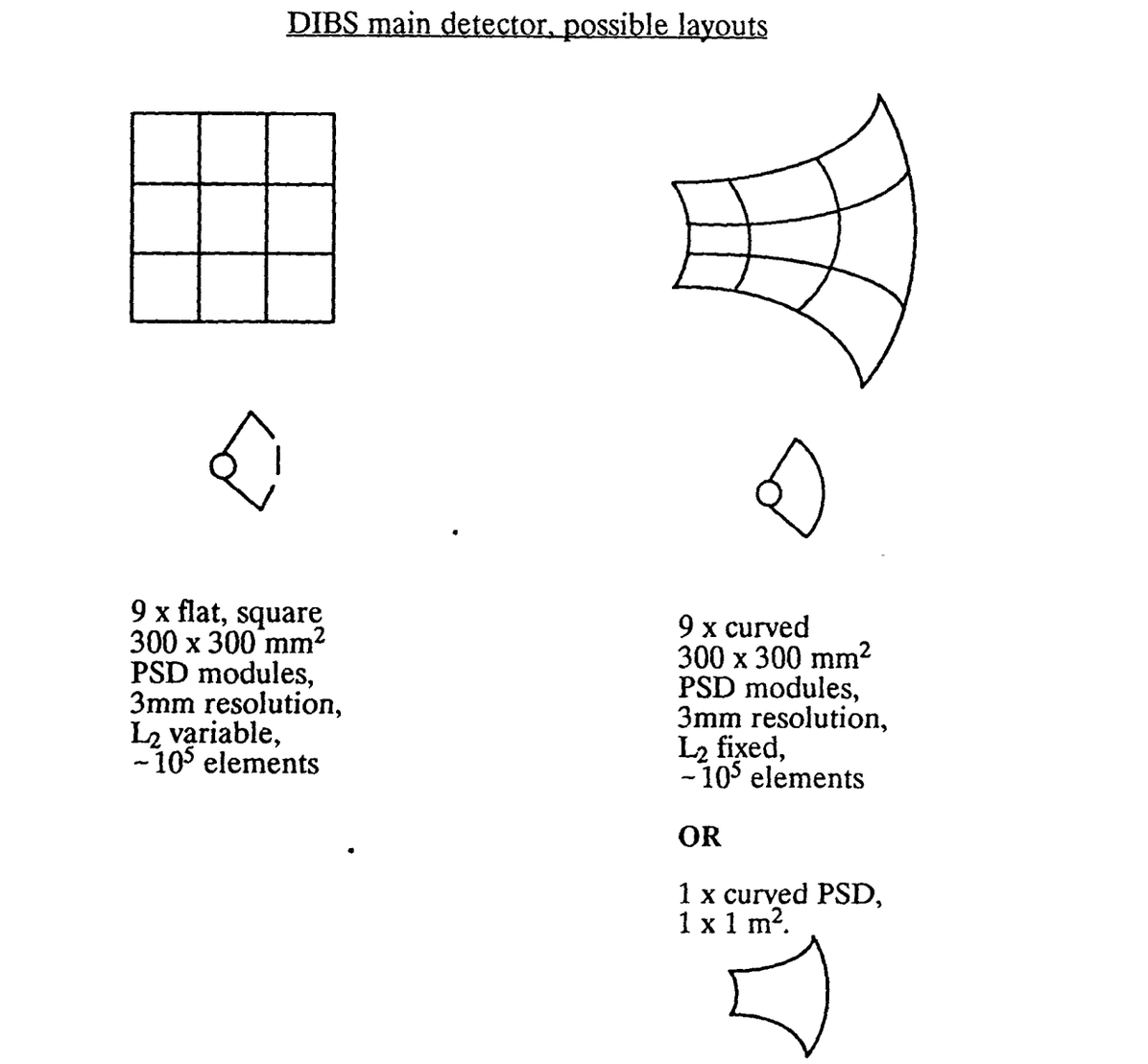


Figure 2 – Schematic DIBS design and detector layout (not to scale).

II.4 DIBS – a provisional design

The essentials of the DIBS instrument design (Figure 2) are therefore :

L_1 ~ 7–8 m;
L_2 ~ 0.1–0.3 m, depending on detector technology;
Cold moderator (liquid CH_4 or liquid H_2) – possibly on S4 or S5 at ISIS (see Figure 6);
Focusing guide;
Large area detector coverage (10 modules of 300 × 300 mm^2 active area, 3 mm resolution at 0.3 m L_2);
Restricted 4-circle geometry as for SXD;
Profile fitting intensity extraction in three dimensions;
Transputer based data treatment.

II.5 Prospects

It is hoped that testing of the DIBS principle can begin shortly on ISIS, with tests on a cold beam using the present ZnS fibre-optic encoded PSD with a moderately large unit cell material such as lysosyme or a large organic material. A larger version of the ZnS module is in construction and is intended to be installed on SXD early in 1991. This module will have most of the desired detector characteristics outlined above for DIBS and will represent a proving of the detector technology required. Further developments of the profile software are in hand, with extension to full 3D processing expected shortly. Given that these developments can proceed with some alacrity, it is hoped that a fully detailed and costed proposal for DIBS will be made in the near future. A working panel has been set up at RAL to further facilitate both this and more general developments in biological crystallography at ISIS.

III. HRED – SCIENTIFIC CASE AND GENERAL PRINCIPLES

The intrinsically high resolution available at pulsed neutron sources offers significant advantages in the study of crystal structures, with resolutions of $\Delta d/d \sim 10^{-3}$ easily achieved using primary flight paths of > 50 m. In addition, the constancy of this resolution function on a time-of-flight instrument implies that multiple orders of a Bragg reflection can be studied simultaneously with equal reciprocal space precision. This can be a great advantage, particularly if there is significant structural detail, such as twinning, satellite reflections and diffuse scattering, in the vicinity of Bragg peaks.

There are several fields in which an ultra-high resolution single crystal instrument such as HRED would obviously make a significant impact, although as stated above, it would be expected that still newer fields would open up in practice as a fully operational instrument of this type to some extent sets its own agenda. Those fields which HRED would obviously benefit are:

(i) High resolution near-Bragg peak scanning in all three reciprocal space dimensions
Twinning topology, incommensurate satellite reflections (intensities, q values, broadening), phase transitions, diffuse and quasielastic scattering, one phonon and magnon scattering;

(ii) Measurement of equivalent Q positions at different 2θ
Thermal diffuse scattering (TDS) and soft phonon studies, critical scattering and central peak measurements, magnetic diffuse scattering (2D and 3D spin correlation studies), extinction and absorption models;

(iii) Reciprocal space topology of diffuse scattering
Defect structures, orientational disorder;

(iv) Quasicrystals

III.1 Resolution considerations in the design of HRED

The resolution of a single crystal diffractometer can be highly anisotropic, with contributions from both time and angular uncertainties. In order to match the time-of-flight resolution, $\Delta t/t \sim 5.10^{-4}$, small detector pixels and long secondary flight paths are required in all but high backscattering angle positions. The proposed main detector for HRED is a quasi-one dimensional 'ribbon' array, using ZnS scintillator and fibre-optic encoding, with 2 mm x 2 mm pixels in an array 10 cm high, subtending angles in the range 60 to 175° at an average L_2 of 2 m. This will result in a FWHM reciprocal space resolution of some 10^{-3} in all reciprocal space directions. Additional 10 cm high ribbon detectors at $\pm$(20-60°) with L_2 of 1.5 m (for long d-spacing information) and a 300 x 300 mm^2 moderate resolution 2D PSD at 90° (primarily for orientation information) would complete the detector array. The overall detector array would thus consist of > 10^5 pixels, which with the large number of time channels required to match the resolution, would preclude the decoupled use of all pixels and all time channels. Selective sampling of reciprocal space would be software controlled and tailored to the experiment.

III.2 The scientific scope of HRED

One phonon TDS

One phonon thermal diffuse scattering (TDS) can already be examined in some detail using SXD, with early measurements (Wilson, 1990; Willis, Carlile, Keen and Wilson, 1990) showing considerable changes in the phonon spectrum as the scattering geometry changes. However, to date the quantification of these effects (Figure 3) has been made difficult by the relatively poor instrumental resolution and by the limited angular range accessible in a single measurement. A full understanding of the TDS close to Bragg peaks is essential in highly precise structural analysis, and the provision of ultra-high resolution and large angular coverage on HRED will make the instrument ideally suited for investigations of the effect.

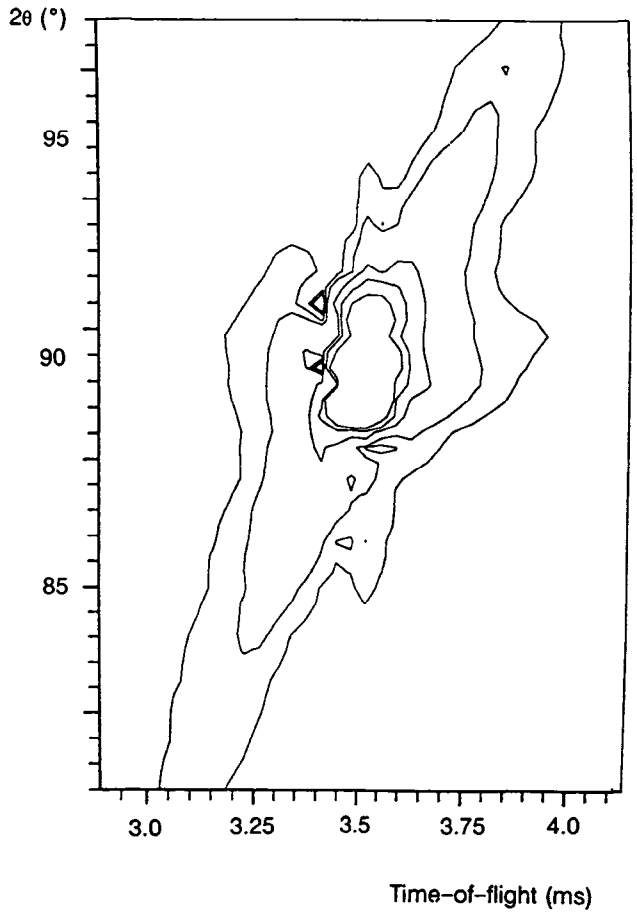


Figure 3 - Thermal diffuse scattering around the (224) reflection of SrF_2, measured on SXD. The features on this plot are seriously instrument resolution limited. The full study of scattering effects of this complexity requires the resolution offered by HRED.

Twinning in $LaNbO_4$

To investigate the potential of the HRED technique, single crystal pilot studies have been performed on HRPD (David, Kamiyama and Ibberson, 1990). By locating an Anger camera area detector at $2\theta \sim 90°$ on HRPD, with its 96 m flight path, fractional resolutions of 0.1% can be achieved, matching the projected performance of HRED. A test experiment was carried out on a single crystal of $LaNbO_4$, which undergoes a monoclinic–tetragonal ferroelastic phase transition at 495°C. This material is often twinned in the low temperature monoclinic phase and previous powder diffraction measurements had indicated unusual peak broadening in the vicinity of the phase transition.

Data were collected in four runs at 360, 430, 470 and 500°C, with the variation of the diffraction pattern close to the (220) reflection illustrated in Figure 4 The twinned nature of the crystal is clearly indicated at 360°C, in which the (220) and ($\bar{2}20$) reflections can clearly be seen. The separation of these two peaks, some 1%, is clearly resolved and can be seen to reduce as the temperature is increased towards the phase transition and the tetragonal phase. At 470°C, however, an additional reflection is seen, corresponding to the formation of a new type of twin which is only possible with small distortions and involves pinning to crystal imperfections such as dislocations. Above the phase transition at 500°C, the distortion has clearly collapsed and a single (220) Bragg peak is observed. At this temperature, however, the presence of diffuse scattering resulting from very soft acoustic modes can also be observed, further illustrating the wealth of information available at high resolution from single crystal neutron diffraction.

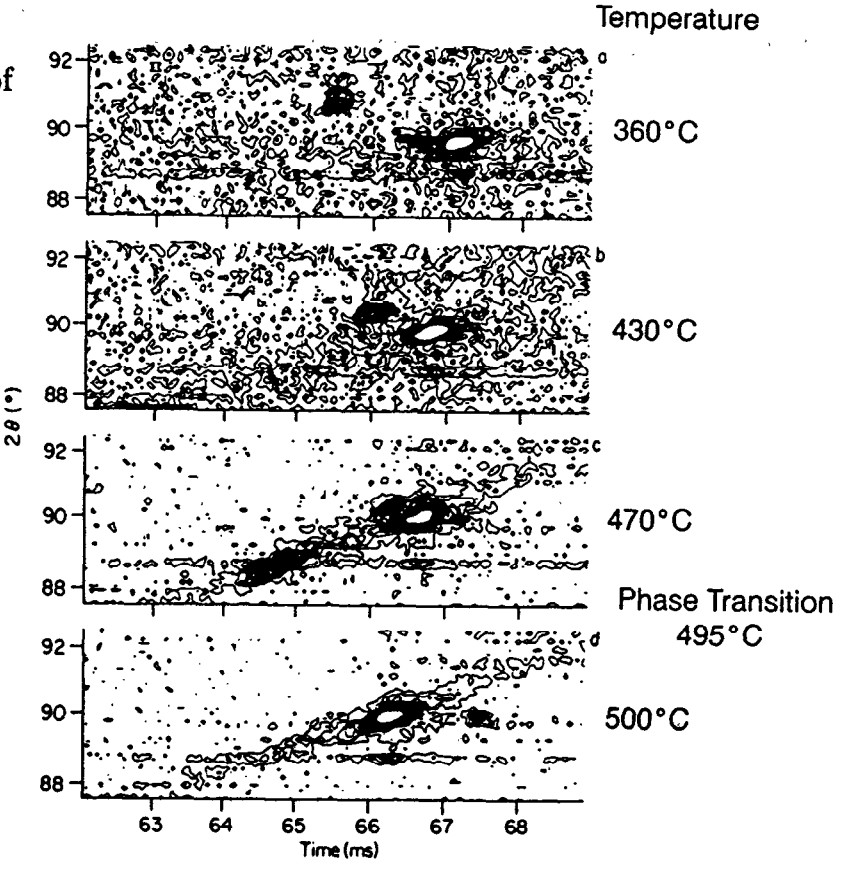


Figure 4 – The evolution of twinning in a single crystal of $LaNbO_4$. These data, measured on HRPD using an Anger camera area detector, are representative of the data available in a single crystal experiment at the resolution of the proposed HRED.

III.3 HRED – a provisional design

The instrument (Figure 5) has essentially the following features:

L_1 ~ 60 m;

Beamline S8, straight guide, CH_4 moderator (see Figure 6);

L_2 ~ 2 m (high angle), 1.5 m (low angle);

2D 'ribbon' PSD, $60° < 2\theta < 175°$, 10 cm high, 2 mm square pixels;

and 2D 'ribbon' PSD, $2\theta = \pm 20\text{–}60°$, as above;

and 2D PSD, $2\theta = 90°$, 300 × 300 mm^2, 3–5 mm pixel resolution, L_2 = 300 mm;

Resolution $\Delta Q/Q \sim 10^{-3}$;

Selective sampling of reciprocal space volumes.

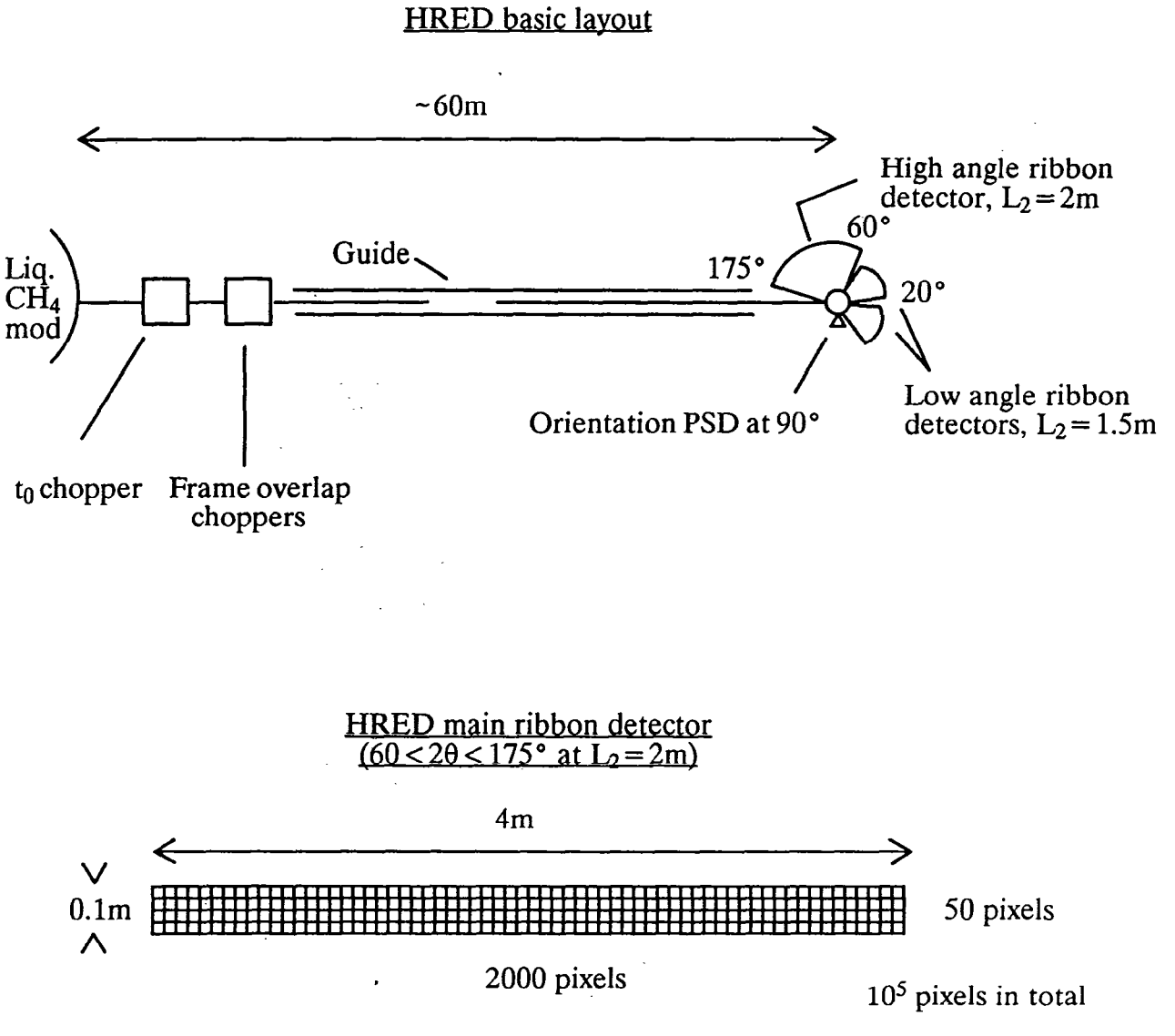


Figure 5 – HRED, basic schematic layout and detector design (not to scale).

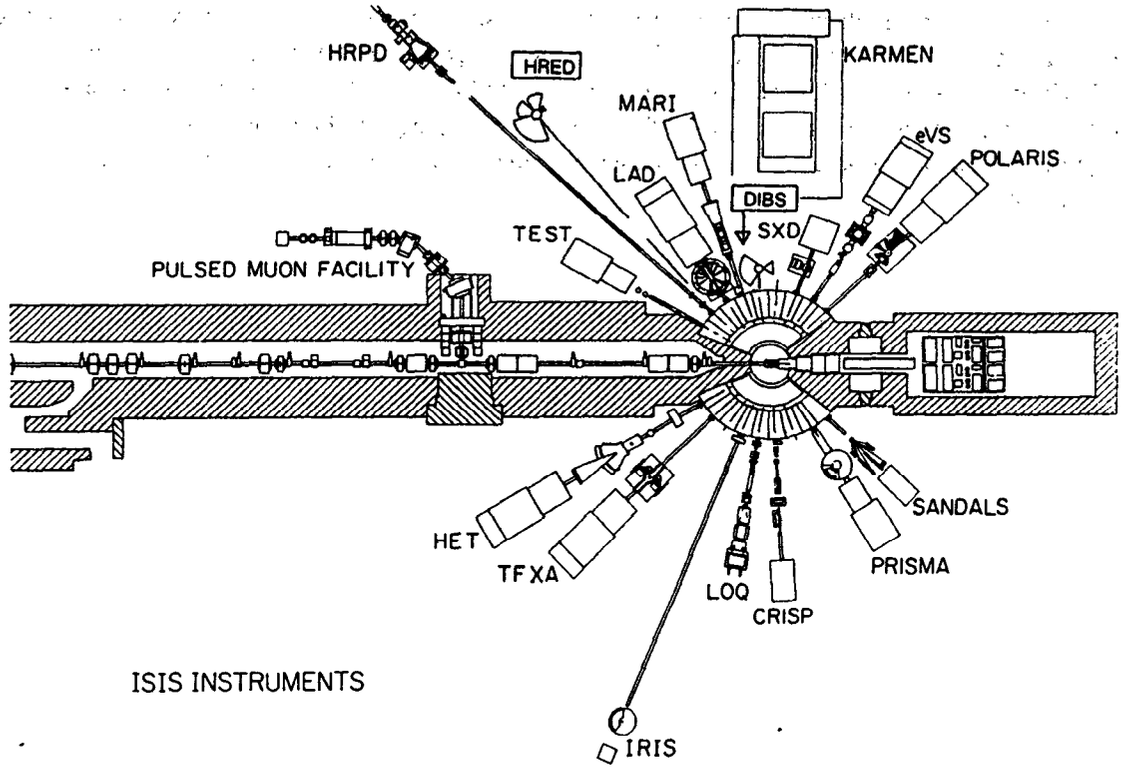


Figure 6 – Layout of the ISIS Experimental Hall, showing the possible locations of the two planned new instruments DIBS and HRED.

III.4 Prospects

Testing of the HRED concept will continue from both the high resolution (HRPD) and low resolution (SXD) limits, as part of the single crystal programme at ISIS. Results obtained from these will further indicate the scope of HRED for exploring new science and will enable, for example, detailed data collection and processing strategies to be examined. In addition, a small prototype fibre-optic encoded ZnS detector is planned, at the 2 mm resolution required for the instrument. In the light of these tests, a fully detailed and costed HRED instrument will be designed in the near future.

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C(N.Niimura): In single crystal diffractometer of TOF type, large area detector is essential. But if we want to measure several Bragg reflections with the $\lambda \approx 1$ Å neutrons, the observed number of reflections is limited. We must think about it. The larger detector is the better, but it depends on the kind of an experiment.

A(C.C.Wilson): TOF is ideal for measuring reflections at different λ - allowing for correction of λ dependent terms. We must also, of course, retain diffractometer flexibility to allow the measurement of what you suggest, but the advantages of the pulsed source / time-of-flight technique is not so apparent in such an experiment.