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A New Instrument for Neutron Time-of-flight Single Crystal Diffraction

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1. Background/Context

The aim of this project is to produce a world-leading single crystal diffractometer at ISIS with very large detector solid angle coverage to exploit emerging experimental methodologies in single crystal neutron diffraction. This instrument takes single crystal neutron diffraction beyond the, nonetheless important, field of hydrogen atom location and into new areas such as parametric studies of crystal structures (including variations with pressure) and phase transitions. In addition it extends the range of single crystal neutron diffraction to crystals with smaller physical size and larger structural complexity. The diffractometer is already having a large impact in many scientific areas (chemical crystallography, structural physics, mineralogy and in the exploitation of non-ambient diffraction) and a major impact on future designs of single crystal neutron diffractometers and methods of data collection.

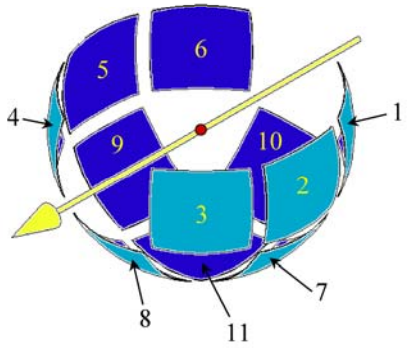

Figure 1. Schematic layout showing the solid angle coverage for each of the detector modules.

The project depends on the ability to collect diffraction data more quickly than any other single crystal neutron diffractometer worldwide. At the time of the proposal this meant a significant improvement on the SXD diffractometer at ISIS, the instrument that the new diffractometer has now replaced. The new instrument (hereinafter called the new SXD) uses the same 'time-sorted' Laue technique as SXD. A polychromatic beam of neutrons is diffracted by a single crystal sample and the resulting Bragg scattering is collected by large two-dimensional position-sensitive detectors (psd's), with the orders of a given reflection all incident on a single spot on the detector, but separated in neutron time-of-flight. Whereas SXD had two 4096 pixel psd's, each with 192x192mm^2 active area, the new SXD has 11, covering ~50% of the total scattering volume (see Figure 1). Very large detector solid angle coverage coupled with the time-of-flight neutron diffraction technique means that a very large number of Bragg reflections (reciprocal space volume) are measured for each crystal orientation simultaneously. A consequence of this is that very few crystal orientations are required for complete reciprocal space coverage. This further enhances the data collection rate, simplifies the required sample rotations and allows the use of more complex sample environment with more restricted scattering access. The advantages of this design, in terms of scientific opportunity, are summarised in Section 2.3 below.

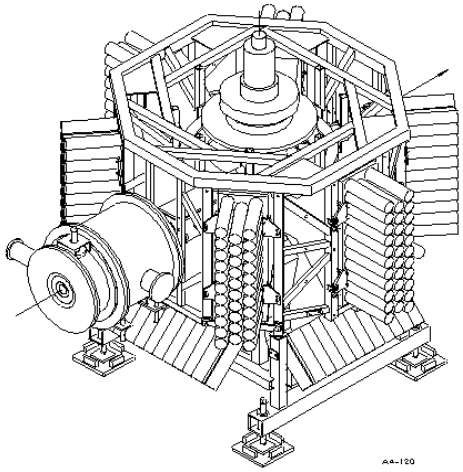

Figure 2. Drawing of the diffractometer, showing the arrangement of detectors about the sample tank. The incoming neutron beam is from the lower left.

2. Key Advances and Supporting Methodology

2.1. Instrumentation

• The diffractometer consists of an integrated sample tank and detector support assembly that is lowered onto surveyed kinematic mounts on beamline S3 at ISIS (see Figure 2). The 11 psd's are arranged around the sample tank as shown

schematically in Figure 1 with six modules in the equatorial plane of the diffractometer (modules 1-6), four at an angle of 45^o to the horizontal (modules 7-10) and one directly underneath the sample position (module 11). This gives almost continuous coverage for $15^o<2\theta<165^o$ either side of and beneath the sample, over 180^o coverage at $2\theta\sim90^o$ and 2π solid angle coverage in total. Figure 3 shows the completed assembly installed on the beamline. The fully cabled assembly may be lifted in and out of the beamline as a single item [operational May'01].

• In order to minimise backgrounds and to improve placement of the sample in the neutron beam, particularly for small samples, a number of modifications to the existing SXD beamline were made. These include a pair of computer controlled sintered boron carbide apertures upstream of the sample position [operational Oct'02] and a laser alignment option, whereby a laser passing along the line of the neutron beam may be observed at the sample position, either visually or using a CCD device [installed Oct'02 and being commissioned]. Further sample alignment is possible using offline devices that accurately reproduce the diffractometer geometry [available Oct'02, being commissioned].

• This project has also been able to support two initiatives to test further efficiency gains on the diffractometer. The first of these is neutron focussing. A small neutron m=3 supermirror 'trumpet' has been constructed which is designed to focus the beam in two dimensions to 2x2mm^2 at the sample position. Such devices are most effective at higher neutron wavelengths and initial results [Dec'02] are extremely promising, with flux gains of ~3 at λ=2Å, rising to ~10 at λ=3Å without loss of flux at shorter wavelengths. Further work is ongoing to optimise the alignment of the device. The second concerns detector efficiency. A 12th detector module has been purchased together with prototype Gd,B-based neutron scintillator materials. Tests are underway to investigate these new scintillator materials.

• Each frame of data (i.e. a measurement with a fixed crystal) consists of 11 detectors each of 4096 pixels, each using ~2000 time-of-flight channels, i.e. ~90million data events. New data acquisition electronics (dae-II) and computing were purchased to collect the large quantities of data [operational Sept'01]. Coupled with this, new software has been developed throughout the latter two year period of this project, using the IDL graphical programming package. This has been made possible through additional staff effort on the project as a result of Dr Keen's EPSRC Advanced Research Fellowship award.

• To maximise the efficiency of data collection, a number of sample environment items have been re-engineered to make them compatible with the new diffractometer. These include a refurbished closed cycle helium refrigerator for use with helium gas pressure cells, modified vanadium tails for a helium cryostat, an option for sample rotation about a non-vertical axis and initial work on the design of a new furnace.

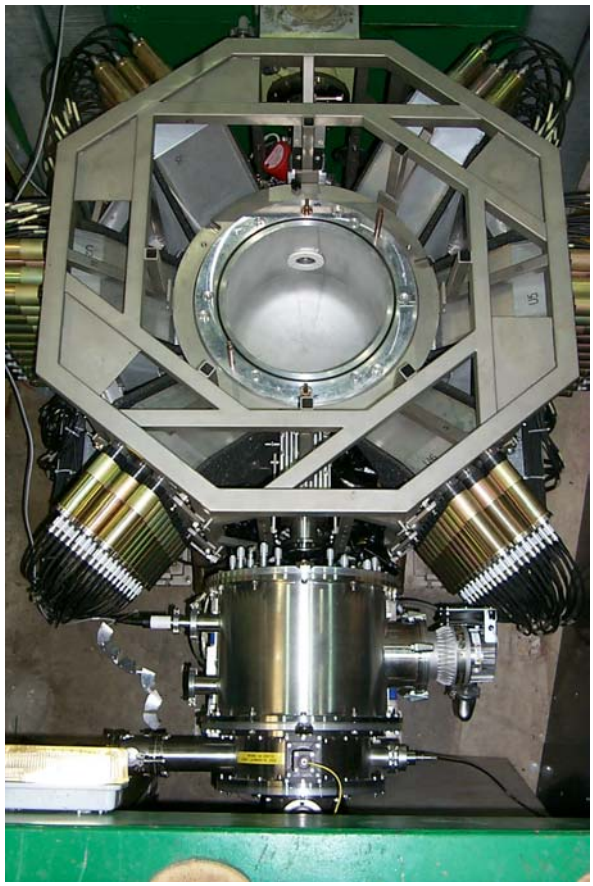

Figure 3. View from above of the completed diffractometer in position on S3 at ISIS. The incident beam is from the bottom of this picture.

2.2. Commissioning

The instrument commissioning was carried out in three phases. An initial 3-month period used the previously existing data acquisition electronics (dae) system, which allowed full simultaneous encoding of three detector modules. In this configuration the detector performance could be fully assessed and a limited scientific programme started. Immediately after this, the second phase used the newly installed dae-II, allowing all 11 detectors to be encoded simultaneously (producing individual data sets of around 250-300 Mbyte) and providing the single-

shot 2π solid angle detector coverage. After an initial 1-2 week commissioning/calibration phase with this configuration, the full scientific programme was launched. A third commissioning phase was undertaken towards the end of the grant period allowing for installation and optimisation of many of the optical components including collimating jaws, laser alignment and initial tests of the focusing device.

2.3. Scientific exploitation

A series of experiments have been carried out, designed to demonstrate the capabilities of the new diffractometer. These have centred on the scientific aims as outlined in the original proposal, namely:

2.3.1. Rapid data collection of full structure factor data sets. This is a major design goal of the new instrument (see Section 1). Some early examples of work in this area are given here.

The search for structural evidence for parity violation: Neutron diffraction investigations of L- and D-alanine at 295K and 60K [Johnson, Ghosh (Oxford), Wilson (ISIS), Wang (Beijing), Myles (ILL/EMBL); ref 9]

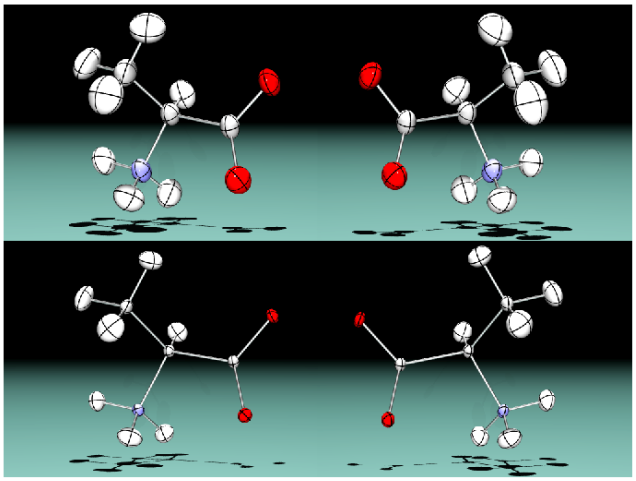

Figure 4. The structures of L- (left) and D- (right) alanine determined at 295K (top) and 60K (bottom) on the new SXD, showing their clear similarities.

The new SXD has been used to investigate the structures of the amino acids L- and D-alanine. The aim was to provide a structural basis for the proposed phase transitions around T_c ~ 270K, by obtaining accurate single crystal neutron diffraction data from both D- and L-crystals at temperatures above and below T_c. A total of 5 - 6 frames of data (each of ~2-12 hours duration) were collected from each sample at 295K and 60K over a period of ~5 days. The long exposure times provided data of the necessary high accuracy to look for possible subtle structural effects. The results of the precise determinations of both structures at 295K and 60K (the neutron structure of D-alanine being determined for the first time) show that the geometries of the L and D enantiomers are equivalent, as are their temperature-corrected geometries at 295K and 60K (Figure 4). Therefore there is no structural basis for the previously observed anomalies in DSC, Magnetisation and Raman measurements at 270K, and the results offer no structural support for other physical measurements which are indicative of the observable effect of parity violation of the electroweak force in these phase transitions. Subsequent to these measurements, the results for D-alanine were confirmed at several intermediate temperatures on the new VIVALDI instrument at the ILL.

Structural and Theoretical investigations of Short Hydrogen Bonds: Neutron Diffraction and Plane-wave DFT Calculations of Urea-Phosphoric Acid [Wilson (ISIS), Morrison (Edinburgh); ref 5]

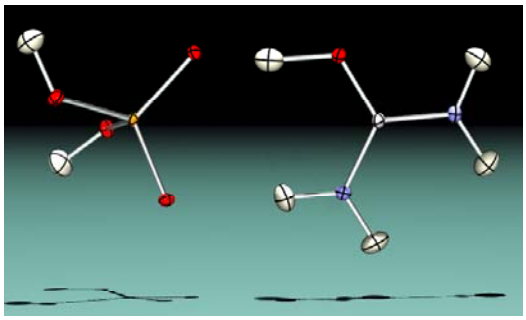

Figure 5. The low temperature (15K) structure of urea:phosphoric acid (1:1) from an overnight data collection on the new SXD.

Low temperature single crystal neutron diffraction data from the new SXD have been combined with high level computational methods to investigate the short hydrogen bond in urea-phosphoric acid (UPA). The data were collected in a rapid overnight experiment, hitherto almost unprecedented for neutron single crystal diffraction of materials of this nature, and resulted in a high quality refinement (Figure 5). This accurate re-determination of the structure of UPA at T=15K was used to initialise the detailed quantum chemical calculations. It was found (see Table 1) that isolated molecule calculations predict a 'normal' O-H···O hydrogen bond, completely contradicting the very short, three-centre, two-electron hydrogen bond found from the neutron diffraction. Extending these calculations into a periodic environment using plane-wave DFT methods give much improved agreement with

experiment, with a much shorter, stronger hydrogen bond, and significant elongation of the O-H 'covalent' bond. This is the first satisfactory description of a short, strong hydrogen bond in a periodic, crystalline environment. The work is being extended as a function of temperature to investigate the 'migratory' behaviour of the proton observed in related SXD experiments.

	O…O (Å)	O-H (Å)	H…O (Å)
Neutron 15K	2.41	1.158	1.267
Isolated Molecule	2.65	1.004	1.604
Plane-wave DFT	2.42	1.105	1.329

Table 1. Hydrogen bond lengths in UPA.

High data/parameter ratio in a rapid study of β-sulfanilamide: new SXD integration software in action [Coles, Hursthouse (Southampton)]

Data collected in a 2-day period from a large single crystal of the β-polymorph of sulfanilamide were used in the development of the new IDL-based SXD peak integration software. The improved nature of this software, particularly for determining the intensities of weaker peaks more reliably, has allowed a significant extension to the available data sets. A unique, merged data set of over 3500 reflections (to $\sin\theta/\lambda$ of 0.91Å^{-1}) was obtained, giving a data/parameter ratio of over 20 in this 172 parameter problem, and a high precision structural refinement.

2.3.2. Smaller samples, larger unit cell volumes. In the early commissioning of the new SXD, there has been a concentration on smaller samples, partly driven by the success of the high-pressure gas-cell programme. Preliminary measurements have, however, been made of large unit cell materials including volatile and air-sensitive organometallic complexes, vitamin B12 derivatives, carbohydrates and nucleosides.

The ability to study small samples at the 1-2mm^3 level is vital in the rapidly expanding high-pressure programme in the TiZr gas cell; pressure experiments now account for ~30% of the instrument usage. The sample volume is limited by the small internal diameter of the cell (~1.7mm) and the restricted ω-rotation geometry means that the large detector array is vital. There have been many successful high-pressure experiments carried out in the cell, including multi-parameter determinations of a range of materials containing short hydrogen bonds [Wilson (ISIS)], investigation of novel high pressure polymorphs [Howard (Durham)] and early attempts to grow single crystals *in situ* under pressure on the diffractometer [Pulham (Edinburgh)].

Potassium hydrogen maleate: A symmetric hydrogen bond revisited by variable temperature, variable pressure neutron diffraction and plane-wave DFT methods [Wilson, Thomas (ISIS), Morrison (Edinburgh); ref. 1]

Here data were collected in the range 30<T<295K and p<4kbar from three ~1.5mm^3 single crystals, all loaded inside a TiZr gas pressure cell mounted on a helium closed cycle refrigerator. High quality structures were obtained from each multi-crystal data-set consisting of only three data frames from all eleven detectors. The data collection time for each frame varied from ~1-3 hours. The crystallographically constrained symmetric disposition of the hydrogen atom in the short, strong hydrogen bond is confirmed for each of the eight sets of measured (p, T) conditions (Figure 6). The high quality of the data for the molecular structure under high pressure confirms that there is no asymmetry of the proton in the hydrogen bond.

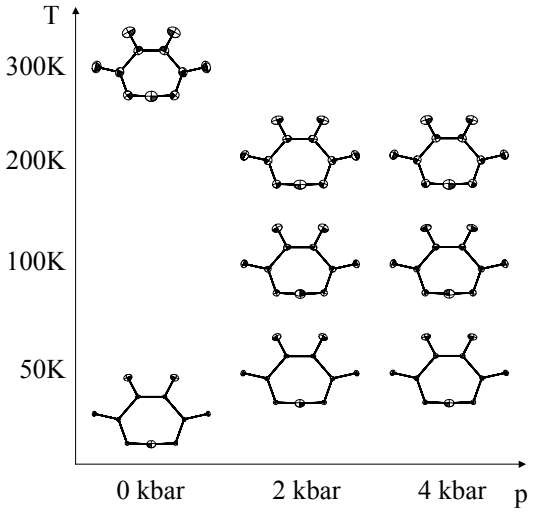

Figure 6. The effect of pressure and temperature on the hydrogen bond in the maleate ion in potassium hydrogen maleate. The large sampling of p,T space is highly novel for neutron single crystal diffraction.

2.3.3. Precise structural parameters from rapid measurements of fixed single crystals. Several experiments to date have utilised the large solid angle coverage to obtain data from samples whose geometry is restricted for various reasons. In addition to the complex pressure-cell environments discussed above, these have included measurements of low melting point and highly air-sensitive materials. Among these has been a successful refinement of the structure of hexafluorobenzene [Lehmann *et al* (MPI Muelheim)]. It is liquid at

room temperature and the only way to obtain reliable large single crystals for the SXD experiment was to grow these *in situ* on the beamline, leading to highly restricted rotation geometry. In spite of the fact that the crystal produced actually consisted of two fragments, the structural analysis was successful (using the SXD multiple crystal software) leading to a good quality refinement. The exploitation of 'single-shot' measurements, where only a single SXD data frame is required, has been demonstrated in principle but not yet exploited in a full scientific application on the new instrument.

2.3.4. Characterisation of phase transitions. Several examples of structural evolution in organic materials have been studied on the new SXD to date, each of which has benefited from the much increased data collection rates for such experiments. Examples here include the search for phase transitions in D- and L-alanine (see section 2.3.1.), in which it was possible to study both enantiomers at two temperatures in the available time rather than the single enantiomer originally anticipated. Another example of a phase transition search in a low symmetry material was the investigation of the putative migrating proton in zinc pyromellitate [Howard *et al* (Durham)]. Variable temperature X-ray data had indicated that the hydrogen atom in the short hydrogen bond in this material appeared to change position with temperature. However, a neutron experiment using the new SXD (and the multiple crystal data collection method) clearly showed this not to be the case, by locating the protons reliably and with good precision. In this experiment, the original plan was to examine the structure at 2 temperatures; the new SXD made it possible to obtain data at no fewer than 6 temperatures, confirming the findings.

2.3.5. Temperature dependent diffuse scattering. Reciprocal space surveying, including diffuse scattering and studies of superlattice reflections are routine on the new SXD. In one experiment, the low-temperature transformation between β-tin and α-tin was followed using a fixed crystal and taking diffraction data every 30minutes at 231K [Takahashi (Japan)]. During the transformation, superlattice reflections appeared as the Bragg reflections from β-tin broadened. After ~5hours both the β-tin and superlattice reflections reduced in intensity and scattering from α-tin was observed. Other more routine experiments have included measurements of the incommensurate reflections in $KCuF_3$ [Radaelli and Keen (ISIS)] (Figure 7) and the diffuse scattering from a number of doped fluorite-structured materials. These types of experiments benefit from the new data analysis software, which can display the scattering within any measured reciprocal lattice plane.

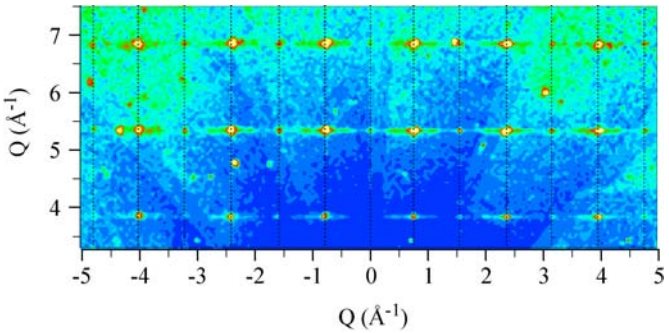

Figure 7. 0k0 reciprocal lattice of $KCuF_3$ showing weak superlattice reflections either side of the strong Bragg peaks.

3. Project Plan Review

Construction, installation and commissioning of the instrument assembly and 11 detectors were all carried out to full specification as proposed and following the timetable which had been revised in April'99 to take into account the additional work undertaken as part of the EPSRC-funded HRPD-90 and ENGIN-X projects. Full exploitation of the 11-detector array followed in Sept'01 after commissioning of the dae-II electronics. A normal user programme continued from SXD to the new diffractometer with only limited disruption. As a result of cost savings in the detector module manufacture (see section 5), the project scope was significantly extended to include additional beamline components (see section 2.1). This needed an additional installation and commissioning period in Oct'02 and held back some sample environment items until 2002. Full assessment of the diffractometer performance began after this second installation period and is still ongoing. Nevertheless, the opportunity to significantly improve the final diffractometer within the period of the original project had to be taken. It was managed effectively and without further interruption to the user programme.

The grant was run as a formal CCLRC project, and a project working group met monthly at RAL throughout the grant. At these meetings all aspects of the project were discussed, from design and procurement to installation and finances. The grant-holders met formally in mid-project to review progress and were kept informed regularly as to progress by the project team. Each of the grant-

holders has also participated in experiments on the new instrument.

4. Research Impact and Benefits to Society

The immediate research impact may be seen from the variety of topics and quality of results described in section 2.3. This is certain to continue and broaden with improvements to (for example) beam focusing, background reduction, software and sample environment. In line with other major instrument development grants, the publication rate will also increase with increased exploitation. The over-subscription on SXD (i.e. the ratio of requested experiment days to allocated experiment days) has increased steadily throughout this project from ~1.4 in 1999 to ~2.0 in 2003. This is due to the increased opportunities on the new instrument for single crystal diffraction and does not reflect an increase in the demand for 'routine' measurements. Prior to 2000, around 60% of experiments were 'routine' structure determinations; now the proportion of such experiments has reduced to ~40% as the number of more novel experiments (e.g. diffuse scattering, magnetic, variable temperature and variable pressure etc. measurements) has increased. This is particularly true for high-pressure experiments. Until 2000 there had only been sporadic high-pressure work on SXD whereas they now account for ~30% of all proposed experiments. These developments are all a direct consequence of this development project.

5. Explanation of Expenditure

The majority of the expenditure was as planned, although the competitive tendering for the detector modules, at a time when a number of different instruments were being constructed at ISIS, resulted in significant cost savings in the detector fabrication. The project was therefore able to design, build and install a number of additional items (e.g. computer controlled collimating jaws, a laser alignment facility and off-line alignment assembly) and fabricate an additional detector module. These offer significant benefits to the diffractometer and its users in terms of ease of use, improved instrument performance and increased flexibility. In spite of these additional items, the project was still within budget.

6. Further Research and Dissemination Activities

This project was envisaged as the beginning of a longer term development of single crystal neutron diffraction at ISIS. Further enhancements are possible by moving the instrument to a beamline with increased neutron flux at longer wavelengths, particularly for magnetic and larger molecular structures (including small biological systems). This is still the intention, although with changes to the funding mechanism for CCLRC and the possibilities for a second target station (TS-II) at ISIS, such proposals must now be folded into a wider development plan. The proposers will actively pursue these routes to further improve instrumentation for single crystal diffraction at ISIS. Options being considered include those outlined in the original proposal (i.e. taking advantage of the modular nature of the instrumentation and moving the diffractometer to a beamline which views the methane moderator), a new instrument on TS-II optimised for biological crystallography and more radical instrumentation for high resolution single crystal diffraction.

In the more immediate future, there will be a continued expansion of the user programme on the diffractometer in the areas specifically identified in the proposal. These will include the more 'exotic' experiments such as high-pressure molecular crystallography, rapid data collection studies, time-dependent measurements and in-situ crystal growth as well as 'routine' experiments which were previously impossible because of crystal size or complexity. Also, the promising results from the early tests of neutron beam focusing and new detector scintillator materials, made possible through the seed-corn funding from this project, will encourage further work in this area, funded through routine operational budgets.

The community has been kept informed of progress on a regular basis, through web sites, emails and ISIS annual reports. The proposers and others have presented the new diffractometer, or results from it, at ISIS crystallography user's meetings, and a range of national and international conferences. There has also been significant interest from the American user community, and following visits from US colleagues to ISIS, the new SXD has been used as the basis for a multi-million dollar proposal for a single crystal diffractometer at the Oak Ridge SNS source. There has also been a strong dissemination through the positive experiences of visitors using the diffractometer in their research programmes.