The Future of ILL Diffraction Instruments

Current Scientific and Technical Scope of the Diffraction Group

ILL Diffraction instruments are *all those that study the structure of materials on an atomic scale using elastic neutron scattering*. They can be divided into 3 groups: **A: thermal single crystal** (D10, D19, VIVALDI), **B: powder diffractometers** (D1A, D2B, D20) and **C: hot source instruments** (D3, D4, D9). A unique instrument for strain scanning (SALSA) is nearing completion. Each instrument within these groups has quite different applications, as we shall see.

No ILL Diffraction Group instruments use cold neutrons. This is because the resolution in real space is limited by the neutron wavelength – for highest real space resolution we need hot neutrons, and even to obtain atomic resolution we need thermal neutrons. This is true whatever the complexity of the structure, and applies as well to our protein and biological fibre diffractometer D19 and the other single crystal machines, as well as to all the powder diffractometers. There is however one case where we would like in future to use cold neutrons – that is for the study of long-range magnetic structures. We will refer later to the possible upgrade of D16 with a large D19-type 2D-detector for this purpose, even though D16 is not a Diffraction Group instrument.

No ILL Diffraction Group instruments use TOF methods. This is because on a (Constant Wavelength (CW) neutron source the $\Delta\lambda/\lambda$ wavelength bandwidth can be made much greater than the $\Delta d/d$ resolution of the instrument so as to maximise flux on the sample. VIVALDI is an extreme example, where a quasi-white neutron beam is used. More commonly, focusing of wavelengths in reciprocal space means that the $\Delta d/d$ resolution can be matched to the resolution required to separate adjacent Bragg peaks by using relatively high take-off angles, together with the relatively large monochromator mosaics needed to maximise flux on the sample. Again there is a possible future exception to this rule in the case of a very high resolution cold neutron diffractometer using TOF backscattering; this was indeed proposed under the "3eme Souffle" programme.

It is only by making best use of our natural advantages, the "Build On Our Strengths" principle (BOOST), that we can compete with the new high flux pulsed sources – which have a natural advantage for TOF techniques, especially using thermal or hot neutrons.

The scientific areas where ILL Diffraction instruments will continue to have advantages are those where a high flux on the sample is important. For example, there is no way that new TOF instruments can compete for small samples with instruments like VIVALDI or LADI because of the exceptionally high continuous white beam flux on the sample coupled with very large 2D area detectors. The same will be true of D19 when it receives its large 2D area detector – this is comparable to the size of detectors used on pulsed sources, but the time averaged flux on the sample will again be up to an order of magnitude greater, at least until ESS is built.

The same is true for high flux powder diffraction. D20 is currently the world's fastest powder diffractometer, even in its new "high take-off – high resolution" mode. Yet the D20 design is 20 years old, and uses a detector an order of magnitude smaller than modern TOF instruments at ISIS. The new D19-type detector technology will mean that a more compact, medium resolution machine like the proposed DRACULA will surpass even US-SNS machines for intensity. However, for high resolution powder diffraction, TOF techniques on high flux spallation sources will be much more competitive with ILL; there we will retain an advantage only because of the clean line shape for Rietveld refinement, the relative simplicity of the CW data for analysis, and the reliability of the reactor source.

Many studies of phase transitions with single crystals require investigation of just a few Bragg reflections or a small region of reciprocal space as a function of an external influence, such as temperature, pressure or magnetic field. Here a wide wavelength band on a TOF machine is of no advantage. A particular strength of the ILL's monochromatic single-crystal diffractometers for such studies is that they offer high flux over a small wavelength band. This advantage is reflected both in the number of single-crystal diffractometers at the ILL and in the greater proportion of UK users, who do not have a national steady-state source, who perform single-crystal investigations of structural or magnetic phase transitions on D3, D9, D10 and the CRG instruments, D15 and D23.

For hot neutron instruments, the ILL reactor is a unique source, especially when instruments like D3 require polarised neutrons ; there are simply more ways of polarising neutrons on a CW diffractometer than on a TOF machine. Because low neutron flux is always a problem with hot neutrons, which are scattered by many more reflections, hot sources on medium flux reactors cannot really compete with ILL. Of course spallation neutron sources can provide good fluxes of hot neutrons, but then the problems are different. It is relatively difficult to correct for the wavelength dependence with short wavelength TOF neutrons, whether it is for attenuation or inelasticity. This is important because ILL's hot neutron instruments are used for very precise measurements, whether it is difference scattering on D4, fine structural details at high atomic resolution on D9, or weak magnetic scattering on D3.

Future Science and Technology in the ILL Diffraction Group

Future trends will be to *more complex problems, more detailed information and the smaller samples* that are common with new materials. The most important requirement is for higher intensity, since only then can statistics and resolution match the trend toward complexity, detail and new materials.

The ILL should concentrate on maximising the efficiency of instruments requiring a high flux CW source. In diffraction, this means copying the trend at pulsed sources towards very large 2D detectors and focussing neutron optics. We have seen that the natural advantage of a CW source like ILL is the high flux on the sample due to wavelength focussing. For comparison, the natural advantage of pulsed sources is for TOF in backscattering, when the peak flux becomes important rather than the integrated flux. But until we have ESS, pulsed sources will struggle to provide enough intensity at high resolution in backscattering alone, so current plans at ISIS and SNS call for low angle detector arrays as well. This is where the ILL can compete in both resolution and intensity.

Much of the impact will however, continue to come from the unique nature of neutron scattering itself. To be convinced of this, one only has to look at the continuing scientific impact of "obsolete" diffractometers like D1A or D1B. By any measure, whether it be number of publications, number of citations, number of articles in top journals, emulation at other neutron laboratories… the simplest ILL diffractometers come out well ahead of the most sophisticated. Of course, this might change in future, but none of these more complex machines look any more certain of winning a Nobel prize than they did when they were first imagined more than 20 years ago.

Diffractometers only measure "structure", but the understanding of structure has so far been the most important contribution to the understanding of the function of materials, whether it be protein structure or ice structure, magnetic structure or electronic structure, chemical structure or physical structure. Even if structure itself were not important, knowledge of structure is a necessary condition for the interpretation of all other measurements.

VIVALDI as a new machine is only now starting to produce exciting new science. Major changes cannot yet be foreseen, although of course we have to standardise the components and make it easier to maintain. More effort is also needed on sample environment, especially in the use of refrigerators and magnets. The most important future need on VIVALDI though has to be manpower; we don't have enough scientific effort on what is essentially a high throughput machine. D19 is also a new machine, and again further major changes cannot yet be foreseen. The role of water and hydrogen bonding in biological structures is a natural opportunity for D19 – and structure at atomic resolution is the ultimate objective. There are of course further improvements needed on D19, including larger focussing monochromators and better sample environment. D10, the third instrument in the group, will profit from the higher flux from the supermirror guide, but at the expense of resolution, which is one of D10's strengths. D10 will increasingly become the "physics" diffractometer, with the best resolution and lowest intrinsic background, the highest magnetic fields, the lowest temperatures and the greatest pressures. The unique four-circle dilution cryostat has already revealed several novel magnetic structures at temperatures below 1 K. A larger PSD detector will allow the measurement of “more than just Bragg peaks” and make D10 the quasi-elastic version of 3-axis spectrometers.

The powder machines will have to contend with smaller and smaller samples, typical of new materials produced for the first time. They will also increasingly be required to measure as a function of temperature, magnetic field, pressure, and chemical composition… not just a few points in the phase diagram. And of course chemical and electro-chemical kinetic measurements will be needed on shorter time scales. For all these reasons, the emphasis will be on higher efficiency with bigger detectors and monochromators, better sample environment, faster sample changes etc…

D2B has just received its new detector and better shielding; the emphasis now will be on greater flexibility to change conditions such as wavelength to better match the sample being studied. D20 has only recently been able to work at “high resolution”, which means that more complex materials can be studied with the exceptional flux available on that machine. In the longer term, a larger 2D detector will be needed, but for the present we want an opportunity to make intensive use of what is already the world’s fastest neutron powder machine. The third instrument D1A, like D1B is still doing good science, but probably it will become a CRG in the medium term. ILL will then have only 2 fully scheduled powder machines, far fewer than foreseen at the spallation sources. A third machine would take the form of a new, very fast diffractometer (DRACULA) that could not be matched until ESS is built.

Greater improvements are foreseen for the hot neutron diffractometers. Many materials are well ordered on the nano-scale, but not ordered on a crystal lattice over long distances. The study of such structures – gels, carbon tubes, layer structures etc – has been labelled “structure beyond crystallography”, and indeed it is an exciting area. High-resolution diffractometers are not so useful here, and instead we need measurements to very large Q with hot neutrons, much like we have on D4 for liquids and amorphous materials. Locally these structures are well ordered, but they do not give sharp Bragg peaks. Pair Distribution Function analysis (PDF) will be increasingly important for the study of such materials, but ILL does not yet have a suitable diffractometer. D4 really needs to become a full-time instrument with perhaps a single large 2D detector rather than a number of small 1D detectors. A large 2D detector, with a higher take-off angle made possible with cold monochromators, could also be seen as a desirable evolution for D9. Indeed the same kind of detector might be used for diffraction from nano-crystalline, quasi-crystalline and amorphous/liquid samples.

We have already said that polarised neutrons are very important for neutron diffraction on reactors. The development of D3 under the Millennium Program, and the power of new methods such as He3 filters and CryoPad for the understanding of complex magnetic structures illustrate that point. Apart from D3, polarised neutrons should become an option on other machines such as D10, D20 or the proposed DRACULA. Polarised neutrons will remain one of the strengths of ILL.

User Community of the Diffraction Group

Neutron diffraction attracts users from a very wide community, partly because neutron diffraction uses the same techniques familiar to chemists and physicists with X-ray machines, but also because it is often an essential complement to these other techniques. This is particularly true of powder diffraction and polarised neutrons. The number of different groups using the ILL’s powder diffractometers is probably only matched on the small angle scattering machines, and this is reflected in the large number of publications.

For similar reasons, diffraction tends to attract new groups to neutron scattering, some of whom then go on to use more complex neutron techniques. Indeed, without diffraction and small angle scattering, the use of neutrons would probably stagnate around a few specialist laboratories – already a potential problem for some of ILL’s more sophisticated instruments.

The growth of neutron scattering in a country such as Spain is an instructive example. Since joining in 1987, Spanish publications with ILL have increased ten-fold, and Spain has now one of the most dynamic neutron scattering communities. If ILL is to grow, we must reproduce the Spanish experience in other new member states – there is relatively little potential for ILL growth in the UK, Germany and France.

When we look at why neutron scattering “took off” in Spain, we find many of the new users in diffraction, and especially neutron powder diffraction. In fact Spain is the second largest user of D2B and D20, ahead of the UK and Germany, who have good national facilities. The older powder diffractometers D1A and D1B are important here, since they have been used by the Spanish and other new users as an introduction to neutron scattering. These “new” Spanish users are now publishing a significant part of ILL’s output in high impact journals, such as PRL.

New member countries are also a potential growth area for ILL income. Again we have seen that Spain has increased its contribution in line with the growth in its user community, and contributed to ILL projects as well as investing in a CRG (D1B). ILL needs to repeat this success by introducing other new member countries to the “simpler” neutron techniques in diffraction.

Education provided by the Diffraction Group

Just as diffraction instruments are important for introducing new member countries to neutron scattering, the same is true for the education of students from all countries. Again powder diffractometers have a major role to play, since relatively little beam time is needed to obtain results that can be analysed and published. D1B is rightly famous for the number of students it has introduced to neutron scattering, but on most diffractometers students are involved in most experiments. ILL would be wrong to concentrate in future on “unique-in-the-world” instruments, because this would severely limit access to new groups and students, who are the future clients of our best machines, and our strongest supporters.

Finally it should be mentioned that neutron diffraction has always been a strong component of the very successful “Hercules” courses, and it is no accident that Emmanuelle Suard now heads this training programme for ILL.

Budget and Resources of the Diffraction Group

The investment budget for Diffraction in 2004 amounted to 230 K€ for the 8 instruments, or 29 K€ per instrument. For comparison, a single instrument day of ILL beam time is evaluated at about 15 K€ ! The Diffraction group investment budget reached a maximum of 313 K€ in 1999 and since then has slowly decreased in real terms, with nominal stability over the past 3 years. For comparison, the total DS plus DPT investment budgets for new instruments and techniques more than doubled from 1999 to reach 4108 K€ in 2004. Fortunately because Diffraction has had a number of large instrument projects, usually financed with external money, investment in diffraction has been considerable in this period, even though the group itself does not control this investment. (IGL’s do not normally sit on either the Science Policy Board or the Millennium Projects Management Committee).

We have been asked to discuss the consequences of a possible flat budget (no inflation) for the next 5 years. Since our budget has effectively been flat for the past 5 years, the answer is easy – we would have to rely again on attracting money from external sources. If instead the group investment budget were to be increased by 25%, to almost the amount we had in 1999, then we would have new opportunities for additional small investments, which would be made essentially for improved sample environment. In particular we are trying finance the replacement of cryostats with refrigerators, the construction of a new medium field cryomagnet (DIFMAG), small 2D detectors and other neutron optical components such as radial collimators, and a crystal alignment machine that would save neutron beam time. The Diffraction budget has been finely balanced in this period, with neither over-spending nor under-spending, so there is some evidence that we would use more money responsibly.

Even more important though would be a small increase in scientific manpower. At present we have no additional scientists for the new VIVALDI diffractometer, which represents an important part of the future of single crystal neutron diffraction. We cannot further reduce the number of instrument technicians in exchange for more scientists, since we typically have only one technician for two instruments. We would however be prepared to reduce support in some technical services to obtain more scientists, but not at the expense of sample environment, detectors or monochromator production.

Alan Hewat, 27/9/2004

Individual Instrument Details

- Publications are the numbers for the last 5 years 1999-2003 from the ILL library database. For D3, D4, D9 numbers are lower because the hot source was HS between 2000-2003. Papers not in the ILL database (an extra 50-100% in some cases) have not been included.
- "Top Journals" were taken to mean: Physical Review Letters, Physical Review, JACS, Nature, Science, J.Molecular Biology, Macromolecules and Langmuir.

A: Thermal single crystal instruments (numbers for 1999-2003)

	D10	**D19**	**VIVALDI**
Applications	Magnetism/structure with energy resolution & special environments, phase transitions, diffuse scattering	Large molecules, fibres, polymers, in chemistry & biology.	Rapid reciprocal space surveys, phase transitions, very small crystals
Publications	**47**	**44**	**4 (3 in press)**
Papers in Top Journals	**19**	**9**	
Proposals/Topics	**200** submitted **104** accepted	**108** submitted **73** accepted	**64** submitted **67** accepted
Users/Countries	**49** groups **10** countries France **25%** Germany **18%** UK **33%** Spain **2%** Switzerland **4%** Czech. Rep. **4%** Russia **2%** Non-member **12%**	**64** groups **14** countries: Germany **17** UK **14** France **7** Italy **4** Switzerland **3** Spain **1** Non members **18**	**49** groups **12** countries France **25%** Germany **12%** UK **27%** Spain **4%** Italy **4%** Switzerland **4%** Czech. Rep. **4%** Russia **8%** Non-member **12%**
PhD Students, postdocs		~15	
Similar instruments	6T2 at LLB (No energy analysis, lower resolution, higher background)	None to match D19 at present. Eventual competition from SNS and ISIS-TS2.	A copy of VIVALDI is being built for ANSTO-RRR.
Future development	Full 15T magnetic field Flat cone detector, Polarised-neutron option	Sample environment, further large vertical PSD, Image-Plate detector	
Closure Consequences	Kills ILL for much physics and magnetism oriented diffraction, and high P, high/low T	Kills ILL for much chemistry, biology & fibre diffraction	Kill's a unique method of searching reciprocal space, very small samples & structure vs temp.

D10 Hot Papers

- *Magnetic ground state of pure and doped $CeFe_2$*. Paolasini L., Ouladdiaf B, Bernhoeft N, Sanchez J P, Vulliet P, Lander G H, Canfield P (2003). **Physical Review Letters 90**, 057201-1.
- *Enhanced stability of charge and orbital order in $La_{0.78}Sr_{2.22}Mn_2O_7$*. Campbell B. J., Argyriou D N, Mitchell J F, Osborn R, Ouladdiaf B, Ling C D (2004). **Physical Review B 69**, 104403-1.
- *Field-Induced magnetic and structural domain alignment in PrO_2*. Gardiner C. H., Boothroyd A T, Mckelvy M J, McIntyre G J, Prokes K (2004). **Physical Review B 70**, 024416-1.
- *Formation of a magnetic soliton lattice in copper metaborate*. Roessli B., Schefer J, Petrakovskii G A, Ouladdiaf B, Boehm M, Staub U, Vorotinov A, Bezmaternikh L (2001). **Physical Review Letters 86**, 1885.
- *Pressure-Enhanced 3D antiferromagnetic correlations in $La_{1.4}Sr_{1.6}Mn_2O_7$*. Kamenev K. V., McIntyre G J, Arnold Z, Kamarad J, Lees M R, Balakrishnan G, Chung E M L, Paul D McK (2001). **Physical Review Letters 87**, 167203-1.

D10 priorities for additional investment:

The instrument elements such as the sample table and shielding are being replaced with non-magnetic materials. This will allow high magnetic field (up to 15T) experiments on D10. The Flat-Cone project is in progress (the design is finished) and will further increase the range of research to be studied on D10. In-situ kinetic studies of phase transitions and chemical reactions on single crystals will be possible due to the simultaneous measurements of a set of reflections. The technique is also well adapted for the measurement of both atomic and magnetic diffuse scattering and for fast reciprocal space survey.

D10's Strengths

D10 is a four-circle triple-axis spectrometer, which has unique properties. In particular the Eulerian cradle can be equipped with a unique 4-circle dilution cryostat for temperatures down to 100 mK and with a mirror furnace for temperatures up to 1800K. Heavy sample-environment apparatus such as the bulky pressure cryostats, cryomagnets or other furnaces can also be mounted on an automated tilt goniometer. Substantial improvements have been made to D10 over recent years to increase the efficiency and to allow new types of experiments. The 80x80 mm^2 microstrip area detector eliminates most of the time-wasting centring scans, allows monitoring of lattice parameters though phase transitions, and aids rapid identification of twinning and incommensurate structures. The possibility of working in normal-beam geometry to increase the out-of-plane access in experiments with the tilt goniometer, has been available since January 2001. The lifting detector covers an angular range –8 to 32° out-of-plane.

The very low intrinsic background allows measurements of features over four orders of magnitude in intensity. Thanks to the high reciprocal-space resolution, various topics such as phase transitions, incommensurate structures, magnetism and critical, Huang or other weak diffuse scattering can be investigated. Inelastic scattering studies may be performed on large samples in both the four-circle and two-axis modes.

D19 Hot Papers:

- *New insights into the structure of poly(p-phenylene terephthalamide) from neutron fiber diffraction studies*. Gardner K H, English A, Forsyth V T, (2004) **Macromolecules** (in press).
- *Neutron Diffraction Study of a Phenol-Nitroxide Radical Adduct: A Structural Model for Hydrogen Atom Abstraction by Peroxyl Radicals from Vitamin E and related Phenolic Antioxidants*. Arhens B., Davidson M G, Forsyth V T, Mahon M, Johnson A L, Mason S A, Price R D and Raithby P R (2001) **Journal of the American Chemical Society 123**, 9164
- *Crystal structure and hydrogen bonding system in cellulose Ialpha from synchrotron X-Ray and neutron fiber diffraction*. Nishiyama , Y., Sugiyama ,J, Chanzy ,H, Langan ,P (2003). **Journal of the American Chemical Society 125**, 14300-14306.

- *New mode of coordination for the dinitrogen ligand: Formation, bonding, and reactivity of a tantalum complex with a bridging N2 unit that is both side-On and end-on*. Fryzuk , M. D., Johnson ,S A, Patrick ,B O, Albinati ,A, Mason ,S A, Koetzle ,T F (2001). **Journal of the American Chemical Society 123**, 3960-3973.
- *Valence-Shell Charge Concentrations and Electron Delocalization in Alkyllithium Complexes: Negative Hyperconjugation and Agostic Bonding*. Scherer W, Sirsch P, Shorokhov D, McGrady G S, Mason S A, Gardiner M G. (2002) **Chem. Europ. J. 8**, 2324-2334.

D19 priorities for additional investment:

As pointed out at numerous EPSRC Management Committee meetings over the period of the current D19 upgrade project, the detector solid angle for D19 can be further improved beyond the situation envisaged for the new (horizontal) detector that will be installed in 2005. Vertical detectors at high or low angle are possible. More radical modes of operation also exist for the instrument - the development of an advanced biological mode for even larger systems, with the possible implementation of a monochromatic image plate (IP) system (design to be easily interchangeable with the gas detector system) optimised for low gamma sensitivity. There is no doubt that MAJOR developments for sample environment are needed to fully exploit the advantages that will be realised with the advent of the new detector system.

D19's Future

The future scientific emphasis will be based around the new detector system that is currently being constructed with major grant funding from the UK EPSRC. This development will provide a gain of detector solid angle of ~20 and open completely new areas. For chemical crystallography and biological/polymer fibre diffraction this means larger and more challenging systems, parametric studies (eg as a function of temperature, pressure or humidity), and structural studies of chemical and biological systems exploiting sample deuteration.

In conjunction with current & future detector developments, ambitious and flexible developments for sample environment will be needed. Gas flow low-T systems will be essential, and facilities for high pressure. On the polymer/fibre side, facilities that will allow simulation of industrial processing conditions (eg extrusion) or of correlation of physical attributes with structural features (eg conductivity of biopolymers for future advanced materials) will be important.

VIVALDI Hot Papers (VIVALDI is a new instrument & so little work has yet been published):

- *Neutron diffraction study of [$H_4Co_4(C_5Me_4Et)_4$], a tetrahedral metal cluster complex with four face-Bridging hydride ligands*. Bau R., Ho N N, Schneider J J, Mason S A, McIntyre G J (2004). **Inorganic Chemistry 43**, 555-558.
- *Hydride encapsulation by a molecular main-group metal cluster: the single-crystal neutron-diffraction structure of {[$Ph(2-C_5H_4N)N]_6HLi_8$}*, Boss S R., Cole J M, Haigh R, McIntyre G J, Raithby P R, Snaith R and Wheatley A E H, **Organometallics** (in press)

VIVALDI priorities for additional investment:

- **Especially-adapted sample-environment:**

Since VIVALDI offers a gain of 10 to 100 in measurement efficiency over conventional monochromatic diffractometers much smaller samples can be used. This is especially advantageous for high-pressure work. A trial has already shown that a Moissonite-anvil pressure cell allows a large view of reciprocal space without undue degradation of the diffraction pattern by scattering from the anvils, and the transparent anvils would allow calibration of the pressure by ruby fluorescence. Such a cell should be acquired or developed for VIVALDI.

- **Automation of the optional band-pass filters:**

Additional shielding is needed to allow routine use of the band-pass filter(s). The positioning of the filter(s) and rotation of the detector as a whole should also be automated and integrated with the present control software.

- **Improved image plates:**

The present 'white' image plates are only about 25% efficient at the mean wavelength available on VIVALDI. Manpower could be devoted to local development of more-efficient image plates that are less sensitive to γ-rays.

The Future:

- **Improved detector geometry:**

The diffraction pattern is only recorded over 288° of the present detector cylinder due to the location and size of the fixed erasing lamps. Retractable or smaller lamps would allow nearly 360° to be accessed with a consequent increase in Q range for many experiments. With the present detector radius of 16 cm the spatial resolution of reflections is determined primarily by the crystal size. A larger radius detector would improve both the resolution and the local signal-to-background. A larger detector would also space for an oscillating radial collimator to shield the often considerable background from cryostat heat shields.

- **Optional end-of-guide optics:**

At present the sample is placed in the collimated, but unfocussed beam at the end of a thermal guide. A focussing trumpet should increase the flux on very small samples. Ideally this would be adjustable to match the spot size to the spatial resolution.

- **Manpower from external groups:**

Two long-term visitors have already assisted in day-to-day running on VIVALDI during its three years of operation, and several other groups have expressed an interest. As the data-analysis suite is improved and more users become familiar with VIVALDI, this should be a good means of relieving the staffing requirements.

B: Powder Diffractometers (numbers for 1999-2003)

	D1A (0.5)	D2B	D20
	Rietveld refinement of medium size structures	High resolution, high flux version of D1A	Chemical kinetics, simple magnetic structures
Publications	**121**	**274**	**117**
Papers in Top Journals	**6**	**63**	**21**
Proposals/Topics	**97 accepted**	**620 submitted**	**217 accepted**
Users/Countries	**60** groups **11** countries esp. new members France **15 groups** Germany **12 groups** Spain **12 groups** UK **8 groups** Italy **7 groups** Switzerland **3 groups** Austria **3 groups**	France **88** Spain **86** UK **44** Germany **24** Italy **11** Russia **7** Switzerland **4** Non members **10**	**483** users **24** countries. France **21%** Spain **17%** UK **14%** Germany **13%** Japan **6%** Switzerland **6%** USA **5%** Italy **4%** Russia **3%**

PhD Students, postdocs	2 ILL PhD students	Students involved in most experiments	About 60 PhD students About 12 Postdocs
Similar instruments	D2B, LLB	FRM2-SPODI, HRPD-ISIS	GEM-ISIS HRPT-PSI, D1B D20 is the fastest with the best resolution
Future development	CRG, super-mirror guide, large PSD	Choice of wavelengths, filters, 7T cryomagnet	Radial collimator, polarised neutrons, S.environment (HP,LT)
Closure Consequences	Left with only 2 powder machines for 25% of all proposals	Kills ILL for high res. powder diffraction	Kills ILL for fast powder diffraction, chemical kinetics, weak magnetic structures, v. absorbing materials

D1A-Powder Hot Papers

- *Direct observation of phase formation in Ag-Sheathed Bi,Pb(2223) monofilamentary tapes by neutron diffraction study*. Giannini , E., Bellingeri ,E, Passerini ,R, Fluekiger ,R (1999). **Physica C 315**, 185.
- *Magnetic ordering of $TbFe_4Al_8$ studied by neutron diffraction. I*. Schobinger-Papamantellos P., Buschow K H J, Hagmusa I H, De-Boer F R, Ritter C, Fauth F (1999). **Journal of Magnetism and Magnetic Materials 202**, 410-425.
- *Charge ordering in the layered Co-Based perovskite $HoBaCo_2O_5$*. Suard E., Fauth F, Caignaert V, Mirebeau I, Baldinozzi G (2000). **Physical Review B 61**, R11871-R11874.
- *Interplay of structural, magnetic and transport properties in the layered Co-Based perovskite $LnBaCo_2O_5$ (Ln=Tb, Dy, Ho)*. Fauth F., Suard E, Caignaert V, Domenges B, Mirebeau I, Keller L (2001). **European Physical Journal B 21**, 163-174.
- *The crystal structure and phase transitions of the magnetic shape memory compound Ni_2MnGa*. Brown P. J., Crangle J, Kanomata T, Matsumoto M, Neumann K U, Ouladdiaf B, Ziebeck K R A (2002). **Journal of Physics Condensed Matter 14**, 10159-10171.

D1A priorities for additional investment:

It is not primarily money that is needed on D1A but manpower. Once the stress option has been shifted to SALSA, the electronic bay must be reorganized and changed to the ILL standard, the monochromators mechanics must be renewed.

D1A's Future

The future of D1A depends crucially on the performance of the instrument once the guide H22 has been replaced by an m=2 supermirror guide. If the simulations are correct, D1A should gain a factor of about 3 in intensity while loosing between 10% and 30% in resolution above a scattering angle of 2Θ=90°. As the replacement of the H22 guide will call for a redesign of the D1A/D1B casemate the option of changing the take-off angle to 135° has to be envisaged in order to recuperate part of the lost resolution at high angles.
D1A has a resolution comparable to D2B in its high intensity mode; the lower neutron flux is partly compensated by the very low background. Its peak shape is unique in its simplicity. Phasing out of D1A would leave D2B as the only high-resolution powder diffractometer at the ILL. Proposals of new or less experienced groups would be rejected due to the high demand. Very often D1A has been in the past some kind of entrance door for new users to the ILL (e.g. see above the high numbers of Spanish, Italien or

Austrian users on D1A). Fast sample testing to avoid the waste of measuring time on other ILL machines will be impossible and the training of PhD students would disappear.

D1A-stress and SALSA (under construction)

Half of the beam time available on D1A has been used for the determination of residual stress. For this purpose a special set-up has been developed, which is put on top of the instrument. Unique is its capability to perform measurements with very high lateral resolution, down to 30µm. This option has been extensively used by an ILL thesis student and for interface and surface investigations in applied engineering applications. D1A has as well been used for industrial experiments, that is for purchased beam time. D1A-stress is the prototype for the design of the new strain scanner SALSA, which is nearing completion and will replace the stress option on D1A in 2005.

The neutron residual stress method is complementary to that with synchrotron X-rays. The advantages of neutrons for strain scanning are not only the high penetration depth but also the convenient scattering geometry, allowing access to all components of the stress tensor, and the beam-divergence, which makes it insensitive to microscopic effects.

Strain scanning attracts not only materials scientists, but also mechanical engineers and users from industry. The challenge in terms of sample handling is the variety in size, shape, weight and the mechanical precision with which specimens have to be positioned. SALSA has introduced a new technique for sample manipulation, which is a hydraulic driven hexapod (or Stewart platform). It allows sample manipulation in three directions in space and three angles with a precision of the order of 10µm for specimens up to 2m length and up to more than 500kg weight. This opens new possibilities for measurements in "real" engineering samples and will certainly increase the user community. We can expect an increasing number of applications for neutron strain scanning beam time sales.

D2B Hot Papers

- *Simultaneous metal-Insulator and structural transition in $YNiO_3$*. Alonso J. A., Garcia-Munoz J L, Fernandez-Diaz M T, Aranda M A G, Martinez-Lope M J, Casais M T (1999). **Physical Review Letters 82**, 3871-3874.
- *Magnetic properties of pure and diamagnetically doped jarosites: Model kagome antiferromagnets with variable coverage of the magnetic lattice.* Wills A. S., Harrison A, Ritter C, Smith R I (2000). **Physical Review B 61**, 6156-6169.
- *Room temperature magnetoresistance and cluster-Glass behavior in the $Tl_{2-x}Bi_xMn_2O_7$ ($0<=x<=0.5$) pyrochlore series.* Alonso J. A., Martinez J L, Martinez-Lope M J, Casais M T, Fernandez-Diaz M T (1999). **Physical Review Letters 82**, 189-192.
- *Charge ordering in the layered Co-Based perovskite $HoBaCo_2O_5$*. Suard E., Fauth F, Caignaert V, Mirebeau I, Baldinozzi G (2000). **Physical Review B 61**, R11871-R11874.
- *Structural and magnetic properties of double perovskites $AA'FeMoO_6$ (AA'= Ba2, BaSr, Sr2 and Ca2).* Ritter , C., Ibarra ,M R, Morellon ,L, Blasco ,J, Garcia ,J, De-Teresa ,J M (2000). **Journal of Physics Condensed Matter 12**, 8295-8308.

D2B priorities for additional investment:

On D2B demand for special sample environments is very high, and we are trying to improve the capabilities and flexibility of the instrument in this domain (pulse tube refrigerator, heating insert, new superconducting magnet etc…). We plan to continue our effort in this direction since the demand is continuing to grow.

D2B's Future

D2B's main domains are crystalline structure solution and refinement, study of phase transitions, and refinement of magnetic structures. The recent upgrade of D2B (Millennium project) with the installation of the new 2D detector means that it is now possible to follow very accurately a phase transition (either in temperature or magnetic field etc..), by measuring short patterns to get as much information as possible through the transition. But more important is the possibility that we can now offer to the users, to measure very small samples (as small as a few milligrams) This new possibility open the instrument to a new community of users, mainly chemists who synthesize very small samples (either new materials often only available in small amount, or high pressure synthesis). In a second step (2005) the primary spectrometer will be improved as well, giving to the users a larger choice of wavelength. This will give even more flexibility to the instrument and therefore allow the best configuration for each scientific problem.

D20 Hot Papers

- *Self-Propagating high-Temperature synthesis of Ti_3SiC_2: I, Ultra-High-speed neutron diffraction study of the reaction mechanism.* Riley D. P., Kisi E H, Hansen T C, Hewat A W (2002). **Journal of the American Ceramic Society 85**, 2417-2424.
- *Icosahedral short-Range order in deeply undercooled metallic melts.* Schenk T., Holland-Moritz D, Simonet V, Bellissent R, Herlach D M (2002). **Physical Review Letters 89**, 075507-1-075507-4.
- *High pressure magnetic transition in pyrrhotite and impact demagnetization on Mars*. Rochette P., Fillion G, Ballou R, Brunet F, Ouladdiaf B, Hood L (2003). **Geophysical Research Letters 30**, 16-1-16-4.
- *Kinetics of the high- to low-Density amorphous water transition*. Koza M. M., Schober H, Fischer H E, Hansen T, Fujara ,F (2003). **Journal of Physics Condensed Matter 15**, 321-332.
- *Formation of porous gas hydrates from ice powders: Diffraction experiments and multistage model*. Staykova D. K., Kuhs W F, Salamatin A N, Hansen T (2003). **Journal of Physical Chemistry B 107**, 10299-10311.

D20 priorities for additional investment:

- A radial oscillating collimator and beam shutter (underway)
- A new Data Acquisition System (underway)
- CRYOPOL, A ^{3}He polarisation unit upstream of the sample.
- New furnaces and cryostats with different vanadium-tail diameters (off-line cooling)
- Multiple radial oscillating collimators (different foci for high-pressure & chemical cells)
- Better automatisation of instrument control (slits, collimators) & take-off angle.
- A gas-stream-levitation/CO_2-laser heating device
- A larger 2D-PSD with vertical definition and better horizontal definition

D20's Future

A challenge for the future will be the realisation of so-called extreme conditions, e.g., for the investigation of molten metals and oxides, important for different interdisciplinary fields such as vulcanology. These conditions can be obtained most likely with container-free techniques such as levitation on a gas stream and CO_2 Laser heating. Small samples will be a consequence, but D20 is able to handle this. High-pressure cells following the Paris-Edinburgh design will provide a new dimension for in situ geochemistry; conditions approaching those in the earth's mantle and core will be approached. Polarized neutrons together with the radial oscillating collimator will provide exciting insights, e.g., in molecular magnetism in biological compounds.

C: Hot source instruments (numbers for 1999-2003; hot source H/S 2000-2003)

	D3	D4 (0.5)	D9
	Complex magnetic structures, magnetic distributions, polarised neutrons	Liquids & amorphous structures	High-resolution atomic structures, a necessary complement to D3

Publications	**48**	**56**	**57**
Papers in Top Journals	**8**	**10**	**7**
Proposals/Topics	Submitted: **117** Accepted: **65**		**190** H-determination, H-bonding Charge density analysis Precise structures Charge-ordering T/Ns Absorbing elements Anharmonic vibration H.Pressure experiments
Users/Countries	UK: 11 groups France: 6 groups Germany : 2 groups Italy : 2 groups Russia: 2 groups Switzerland : 2 groups Spain : 2 groups Czech : 2 groups Portugal: 1 group USA: 1 group	UK: 60% Germany: 18% France: 12% Others: 10%	10-F 12-UK 15-D 5-E 7-I 2-CH 6-RUS 4-CZ 2-AUT 12-Others
PhD Students, postdocs	2 PhD students	1 ILL PhD student 90% of D4 expts include a student	6 PhD students
Similar instruments	LLB-5C1, flux an order of magnitude lower D23, but thermal n.	D4 will remain world's best even post SNS 7C2 at LLB (low flux) SANDALS (stability ?) NOMAD-SNS GLAD-Argonne SLAD-Studsvick HIPPO-LANSCE	SXD:ISIS 5C2:LLB
Future development	Cryopol + ^{3}He filter – High Pressure	Better monochromator, sample environment, independent of IN1	New Cu monochrom. New cooled mono. Bigger detector
Closure Consequences	No more polarised neutrons on the ILL hot source!	Kills structural studies of liquids & amorphous materials at ILL	Kills ILL for high spatial resolution, Gd, Sm compounds

D3 Hot Papers:

- *Spin and orbital moments in itinerant magnets*. Hiess A., Bourdarot F, Coad S, Brown P J, Burlet P, Lander G H, Brooks M S S, Kaczorowski D, Czopnik A, Troc R (2001). **Europhysics Letters 55**, 267.
- *Magnetization distribution in the layered colossal magnetoresistance manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ from polarized neutron diffraction*. Argyriou D. N., Brown P J, Gardner J, Heffner R H (2002). **Physical Review B 65**, 214431-1.
- *Complex magnetic ground state of CuB_2O_4*. Boehm M., Roessli B, Schefer J, Wills A S, Ouladdiaf B, Lelievre-Berna E, Staub U, Petrakovskii G A (2003). **Physical Review B 68**, 024405-1.

- *Spherical neutron polarimetry of the magnetic structure in UNi_2Al_3*. Hiess A., Brown P J, Lelievre-Berna E, Roessli B, Bernhoeft N, Lander G H, Aso N, Sato N K (2001). **Physical Review B 64**, 134413-1.
- *Experimental and theoretical spin density in a ferromagnetic molecular complex presenting interheteromolecular hydrogen bonds*. Pontillon Y., Akita T, Grand A, Kobayashi K, Lelievre-Berna E, Pecaut J, Ressouche E, Schweizer J (1999). **Journal of the American Chemical Society 121**, 10126-10133.

D3 priorities for additional investment and Future:

- **Focusing monochromator and Cryopol (use of 3He as polariser):**

Because Heusler polarising crystals are flux limited and provide a poor energy resolution, we propose to decouple the neutron spin selection from the optical functions by using a focusing Cu monochromator combined with a ^{3}He neutron spin filter. For this, a new version of Cryopol, able to shield the inhomogeneous and large stray field produced by the 10 T cryomagnet, will be developed in collaboration with the CEA-Grenoble and within the frame of the Neutron Spin Filter activity of the NMI3.

The drawings of the focusing monochromator are now almost finished and crystals have been done. The first test of "local-filling" of the ^{3}He cells has been successfully achieved on the D17 instrument in July. The technical study and drawings of the new Cryopol can thus start.

An increase of the D3 resolution and flux is an important challenge to push continuously the limit of science (access to smaller crystals with smaller magnetisation, e.g. molecular magnets).

- **High-pressure dependence of the form factors:**

In collaboration with the Inst. for High Pressure Physics, Troitsk, Russia, a first experiment combining the D3 cryomagnet and a pressure clamp has been realised last July. The $CePd_2Si_2$ form factor has been determined under 10 T and both under 0 kbar and 30 kbar. The changes in the shape and in the amplitude of the form factor are significant and show that it is worth to investigate pressure dependencies. The use of pressure cells in form factor measurements will give new insight on the covalency effects and hybridisation which govern the magnetic behaviour of a wide range of materials. Further developments will be realised in order to provide reliable and easy-to-use equipment to the user community.

- **Very low temperature:**

A dilution refrigerator is being built at the Sample Environment laboratory of the ILL. It will be available by the end of next year. This will extend the temperature range accessible with the 10T cryomagnet to 40mK to 650K. Thanks to this refridgerator, it will be possible to measure a number of molecular systems that could not be investigated before. As regards the zero-field measurements (Cryopad), very low temperatures are already accessible, up to 300K.

- **Single crystal alignment in zero-field and at low temperature:**

The determinations of magnetic structures and antiferromagnetic distributions require the access to many Bragg peaks in reciprocal space. For these reasons, a Cryocradle is being developed. This is a compact cradle mounted inside a 4K-1W pulse-tube cryorefrigerator. A prototype has been built, and the first tests are planned in 2005.

D4 Hot Papers

- *First solvation shell of the Cu(II) aqua ion: Evidence for fivefold coordination*. Pasquarello , A., Petri ,I, Salmon ,P S, Parisel ,O, Car ,R, Toth ,E, Powell ,D H, Fischer ,H E, Helm ,L, Merbach ,A E (2001). **Science 291**, 856-859.
- *Identification of the relative distribution of rare-Earth ions in phosphate glasses*. Martin , R. A., Salmon ,P S, Fischer ,H E, Cuello ,G J (2003). **Physical Review Letters 90**, 185501-1.
- *Chemical isomerism as a key to explore free-Energy landscapes in disordered matter*. Talon C., Bermejo F J, Cabrillo C, Cuello G J, Gonzalez M A, Richardson J W, Criado A, Ramos M A, Vieira S, Cumbrera F L, Gonzalez L M (2002). **Physical Review Letters 88**, 115506-1.

- *Structural studies of multiwall carbon nanotubes by neutron diffraction*. Burian , A., Dore ,J C, Fischer ,H E, Sloan ,J (1999). **Physical Review B 59**, 1665-1668.
- *Structure of a metallic solution of lithium in ammonia*. Wasse , J. C., Hayama ,S, Skipper ,N T, Fischer ,H E (2000). **Physical Review B 61**, 11993-11997.

D4 fields of application:

- Fundamental fluids: quantum fluids (^{3}He,^{4}He mixtures), liquid hydrogen
- Molecular fluids and solutions: hydrogenous liquids, liquids under extremes conditions, supercritical solutions, environmentally benign chemistry, non-aqueous electrolyte solutions.
- Water and aqueous solutions: especially at extreme T/P conditions (supercooled, supercritical), structural similarities between supercooled and interfacial water.
- Liquid and amorphous polymers and polymer blends: local structure and motion, and effects of ions in electrolytes; local structure and its effect on electronic properties, including conducting polymers; amorphous fraction in semi-crystalline polymers.
- Crystalline/liquid hybrid materials: Intercalated liquids in e.g. graphite, clays; liquid crystals
- Glasses: definition of basic structural units in glasses and the effect of modifiers on the distribution of bond lengths and angles; fluctuations in chemical order in multicomponent glasses; the crystallization process, pre-melting effects; crystallization in production of glass ceramics; Fast ion conducting glasses
- Semi-crystalline materials: crystalline materials with significant disorder; non-crystalline materials with significant local order, e.g. graphite, clay-type materials, network silicas.
- Geologically relevant materials: liquids and glasses of mixtures/solutions of lanthanide, actinide, alkali and alkaline earth silicates, phosphates and borates; amorphisation of geological materials under extreme pressure.
- Metals and metallic alloys, semiconductors: liquid metals and alloys; metallic (amorphous) glasses; diffuse scattering from chemical and positional disorder in alloys; amorphous silicon fuel cells
- Molten salts

D4 priorities for additional investment:

D4 is a relatively new instrument with a very good performance in terms of recorded neutrons and stability. It is possible to identify three potential improvements concerning the instrument itself. First, more flux could be available using a better monochromator (a double focussing one, for example). Second, a 2D position sensitive detector located at longer distances in the direct beam could extend the available low-Q region. Third, the sample environment can be refurbished, mainly in what concerns the high-temperature furnaces. Another clear improvement for this instrument is the possibility of being a full-operating instrument, i.e., not sharing the beam-tube with IN1 and having the whole cycle for users. This implies the re-localisation of one or both instruments. Perhaps moving D4 is the best option, because only a small marble surface is required.

The immediate improvements necessary on D4 concern better sample environment for experiments under extreme P/T conditions, and also standardised data analysis routines. In the short term, the sample environment for high-temperatures should be improved. Our old F2 furnace is not operational anymore, and it should be rebuilt. There is a project of collaboration to have a laser furnace with a levitation system, but once under operation, it will work mostly in the framework of this collaboration rather than as standard environment. A low-cost and very important improvement (feedback from users) is a set of user-friendly routines for data treatment, which can be done with the help of dedicated students.

D4's Future

Future emphasis will be on earth and environmental sciences, where the study of the local order of aqua-ions and the hydrophobic interaction will have a strong impact. The structure of liquid metal alloys is also a field which will grow in the future, because of its application on earth and planetary sciences.

The field of liquids and disordered materials ranges widely from low-density fluids (supercritical state), through liquids, melts, solutions, glasses, amorphous materials, to semi-crystalline solids. The materials of interest can be characterized by some degree of ordering. It is precisely the short to intermediate range order that is the focus of this field of science, both of fundamental interest and from a practical point of view. The understanding of the structure of non-crystalline materials has lagged behind that of crystalline materials due to the limited order encountered in the former. Yet for many of the materials with technological applications its usefulness depends on the nature of disorder found in them (for example, polymers, amorphous semiconductors, chemical process systems, oil recovery, supercritical solvents in "green chemistry" applications, etc.). The materials of interest may be in the form of bulk samples, films, and materials in confined environments. The length scales covered include local, short-range atomic/molecular order on the few Å's scale, and intermediate range order (intermolecular correlations, networks in glasses, etc).

D9 Hot Papers

- *Zener polaron ordering in half-Doped manganites*. Daoud-Aladine A., Rodriguez-Carvajal J, Pinsard-Gaudart L, Fernandez-Diaz M T, Revcolevschi A (2002). **Physical Review Letters 89**, 097205-1.
- *Investigation of magnetic interaction pathways by experimental electron density measurements: Application to an organic free radical, p-(methylthio)phenyl nitronyl nitroxide*. Pillet S., Souhassou M, Pontillon Y, Caneschi A, Gatteschi D, Lecomte C (2001). **New Journal of Chemistry 25**, 131-143.
- *Direct observation of a band Jahn-Teller effect in the martensitic phase transition of Ni_2MnGa*. Brown P. J., Bargawi A Y, Crangle J, Neumann K U, Ziebeck K R A (1999). **Journal of Physics Condensed Matter 11**, 4715-4722.
- *Holographic imaging of atoms using thermal neutrons*. Cser L., Toeroek G, Krexner G, Sharkov I, Farago B (2002). **Physical Review Letters 89**, 175504-1.
- *Ferroelectric order of parallel bistable hydrogen bonds*. Szafranski M., Katrusiak A, Mcintyre G J (2002). **Physical Review Letters 89**, 215507-1.

D9 priorities for additional investment:

- a new monochromator to improve the flux on the sample
- a cooled monochromators for increased resolution & reduced loss at higher take-offs
- a very large two-dimensional detector, with high efficiency & low gamma background

D9's Future

D9 has been progressively updated since the reactor re-start in 1995. Its sample environment was upgraded with a 4-Cercle cryostat with a low temperature limit of 1.8K in 1997 and a Joule-Thompson Displex in 2002, which could also reach 1.8 K. Concerning the detection part, a lifting counter was installed in 1998, giving the possibility of using cryomagnets as well as pressure equipment, and finally, in 2004 a new 2D-detector has increased the detection efficiency by almost 50%. Of course since the beginning of 2004, D9 works with the new hot source and a new beam tube.

The logical next step would be to build a new monochromator to improve the flux on the sample in order to be able to study smaller samples, as desired by the user community. That can be particularly interesting for most of the organic compounds where science is rapidly evolving but for which the size of the available samples is a problem for neutron diffraction or experiments under high pressures, due to the correlation between the size of the sample and the attained pressure. In this sense in the near future, we would like to have a new Cu-monochromator with a fixed horizontal focusing.

The next step will consist of a cooled monochromator for D9. The expected gain for the instrument will be two-fold: i) a higher take-off angle on the monochromators giving an improvement of the reciprocal space resolution with short wavelengths, ii) the reduction of losses from the Debye Waller factor allowing a gain of flux at the sample.

These improvements being effective, we would like to envisage also in a more distant future the development on D9 of a very large two-dimensional detector, in order to continue to favour experiments on smaller and smaller samples. At that time its definition will depend on the last developments of PSD, taking also into account challenges such as “more efficient detection of hot neutrons”, reduction of the background (in particular due to local gamma background).

In conclusion, our project is to upgrade the instrument both on the side of the incident neutron beam (better resolution and higher flux) and on the side of the detection with a very wide detector for shorter data collections. That will allow to speed-up experiments on “normal” crystals (large enough) and to collect precise structural data for small crystals, which is up to now often quite impossible.