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A review of sample environments in neutron scattering

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Abstract. Sample environment equipment, cryostats, furnaces, pressure cells etc. are an essential adjunct to most neutron scattering experiments to induce the sample being studied into a phase or state of particular interest. He we give a brief overview of the diverse range of Sample Environment equipment that is currently in use, a background to its development and also some recent trends.

Introduction

Of the many hundreds of neutron scattering experiments which are carried out each year in the major neutron research centres across the world, most will require additional equipment to apply special physical or chemical "conditions or environments" to induce the sample into a phase or state of particular interest. In this context Sample Environment equipment and facilities are not simply accessories to the experiment but are an essential and integral part of it.

Most commonly the "conditioning" will be cryogenic, high temperature, high pressure, a magnetic field, viscous flow, gas flow, chemical preparation or sometimes a simultaneous combination of two or more together. In addition there may be the requirement to physically manipulate, reorient or re-position the sample, and to know its position to a high degree of accuracy, during the course of the experiment. In all cases the researcher will, against the contrary instincts and wishes of the designer, want to restrict any neutron attenuation, scattering or shadowing effects of the Sample Environment equipment to an absolute minimum. In all such cases the designer needs to know both the mechanical and the neutron characteristics of the materials that he intends to use. These two constraints have often tested the ingenuity of the design engineers to their limit.

Probably the most wide ranging review of Neutron Sample Environments was the report of a Workshop, Sample Environments in Neutron and X-ray Experiments, [1], held at the ILL in 1984.

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1. Neutron properties

As an investigative probe of condensed matter the neutron has very convenient and useful properties;

- no electric charge; so is very penetrating and is scattered by the nucleus,
- a magnetic moment; so is sensitive to the magnetic field of the atom,
- an intrinsic energy comparable to; and therefore readily modulated by inter-atomic vibrations,
- both scattering and absorption properties which are isotopically dependent. For example the neutron scattering properties of hydrogen is dramatically different to that of deuterium. Isotopic labelling, or contrast variation, within a sample can be very useful in identifying the active site of a particular element in a molecule.

2. Materials

For many purposes aluminium and its alloys often combine the best compromise of mechanical and neutron characteristics for mechanical structures in the proximity of the sample. Thus vacuum chambers which are a fundamental part of both cryostats, furnaces and many other items of SE kit are almost without exception made of aluminium. Other commonly used materials, particularly for sample containers used in diffraction experiments, are Vanadium and a null-matrix alloy of Ti and Zr. These two materials exhibit almost no structural scattering, ie. are isotropic, so do not contribute to the structure being studied.

In the correct relative proportions, $Ti_{66}:Zr_{34}$, the negative scattering amplitude of Ti cancels the positive scattering amplitude of Zr. This alloy is usually made to order from specialist metal founders or home-made in laboratory quantities.

However, for experiments requiring extremes of temperature or pressure the prime consideration in choosing a suitable material must be its practicality rather than absolute neutron compatibility. Hence the use of Be–Cu alloy and Maraging steel for pressure cells at pressures greater than $\sim$0.7 GPa, while for temperatures above 1000 °C sapphire and super-alloys such as Inconel have been used.

Because no material is entirely "neutron friendly", it is probably true to say that the choice of material is always a compromise and will depend on the degree of "neutron unfriendliness" that can be tolerated.

3. Cryogenics

It is probably no exaggeration to say that by far the largest proportion of all experiments or measurements are performed under cryogenic conditions. The principal reason for this being that the thermal motions of the atoms, vibrations, rotations etc. are reduced, but also that under cryogenic conditions phase transitions of particular interest may be initiated and explored.

The range of temperatures commonly referred to as cryogenic temperatures can be conveniently divided into 4 sub-ranges corresponding closely to off-the-shelf commercial or proprietary cryogenic systems:

- 300 K to 10 K, Helium Closed Cycle Refrigerators, (CCRs),
- 300 K to 1.5 K, Liquid helium bath cryostats
- 3 K to 300 mK; 3 Helium sorption systems
- 0.8 K to 10 mK. He^3/He^4 dilution refrigerator systems.

3.1 Closed Cycle Refrigerators, CCRs

Typical CCR-based cryostat systems are either "direct-cooling", in which the sample is attached directly to the cold-head, or "indirect cooling", more often called "cryogen-free" in which the sample is held in a helium exchange-gas chamber which is cooled by the second-stage of the cold-head. In both configurations the CCR's first stage is used to cool an intermediate temperature heat shield. On some CCRs the first stage heat shield may achieve temperatures as low as 40 K.

While direct cooling provides a very rapid sample cooling, of the order 40 minutes, it has the disadvantage that sample changing requires that the entire CCR unit is removed from the instrument vacuum chamber with the probability of air and water condensing on both cold head and sample. To reduce temperature gradients in the sample an additional thermal shield, also attached to the second stage cold head, may be introduced to surround the sample.

Until relatively recently the base temperature of commercially available CCR units was restricted to $\sim$10 K. However developments by Balzer Ltd. in the US and Sumitomo in Japan using improved materials and manufacturing techniques has led to the introduction of CCRs with a base temperature of $<$4 Kelvin and a usable cooling power of $\sim$1 Watt at 4 Kelvin.

Cryogen-free CCR cryostats are in use at most major neutron centres and although having the same basic principals of operation and function the concept has generated many individual designs. These systems have the advantage that samples being physically isolated from the CCR can be changed without stopping and warming up the CCR. The second, coldest stage of the CCR is mechanically and thermally attached to the sample volume at a point a few centimetres above the sample position. This point then functions both as the heat exchanger, cooling the helium exchange gas and sample, and also as temperature monitoring and control.

The various designs differ from one another only in their degree of sophistication and customisation. The system shown here, Fig. 1 is that in use at Dubna; [2], the design principles of which strongly influenced a 4 K version recently built at ISIS.

In both direct-cooling and cryogen-free CCRs systems it has been relatively straightforward to introduce and integrate external Omega rotation motors, gearboxes, vacuum seals, and angular encoders for their adaption as cryostats for single crystal use.

3.1.1 Extended temperature range CCR systems

The ILL's Cryogenics Group have recently built two innovative prototype 10 K CCR-based systems which incorporate a Joule-Thomson stage. This CCR and Joule-Thomson combination can achieve a base temperature of 1.8 K, [3].

To increase the maximum temperature up to which CCRs can be used the non-linear thermal conductivity of sapphire can be exploited to function as a thermal switch. Below 50 K it is superior to copper while at $T > 300$ K it is inferior to stainless steel. Sapphire rods are used as stand-offs between the sample and cold-head so that the sample may be heated to 800 K without affecting the performance of, or damaging the cold-head. Practical hot-stage CCRs of this type have been developed at Argonne, [4].

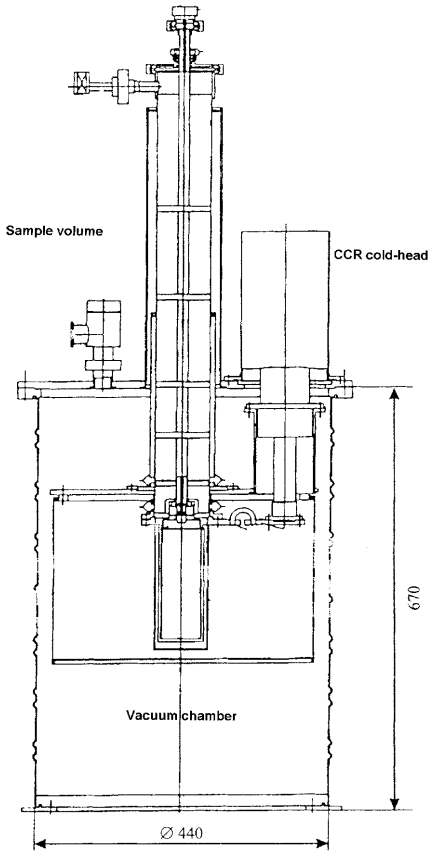

Fig. 1. Schematic of Top loading CCR system in use at Dubna.

3.1.2 Pulse tube refrigerators

These are relatively new devices; which have only recently become commercially available; the cooling process being the result of pulsed compression and expansion of a closed volume of helium gas. A pulse tube refrigerator will be used to cool the new CRYOPAD 3 device, (q.v.), at ILL.

3.2 Liquid helium bath cryostats

Until the late-1970s there was no single design of cryostat for neutron scattering experiments – each centre had its own preference, often from a national or local supplier. That situation changed when Brochier at the ILL designed a liquid helium bath cryostat specifically for use in neutron scattering experiments [5]. That design of cryostat has now been adopted by many neutron scattering centres world wide. It is now regarded as the international standard with variations built which differ either in sample access diameter, tail geometry or even having superconducting coils incorporated. The standard Inner Vacuum Chamber, IVC, diameters are 50, 70 and 100 mm. From the earliest prototype these cryostats have always been externally painted Orange, hence their popular name "Orange Cryostat". Their particular advantage being that the sample is suspended in low pressure, ~10 mbar, helium exchange gas inside the IVC, and liquid helium exhausts through a heat exchanger integral with the IVC. The exhausting cold helium gas passes through annular space around the IVC so cooling the it along its entire length.

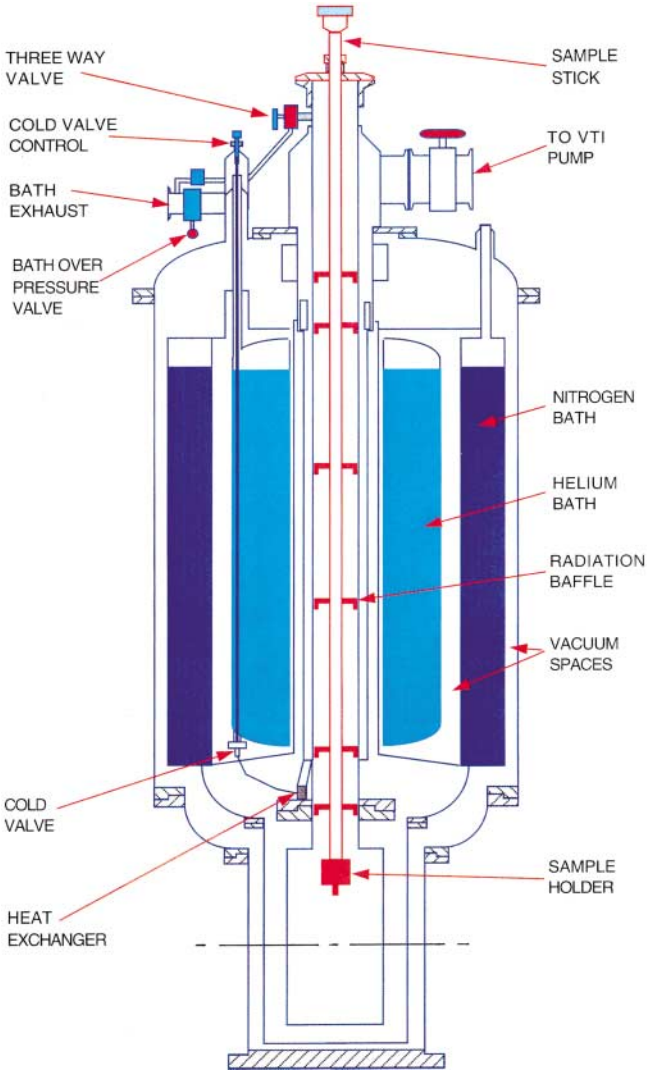

Fig. 2. Schematic of Orange Cryostat.

At ISIS OC tail variations incorporate thin, 0.1 mm, 70 mm × 70 mm aluminium foil windows, domed tails, and vanadium windows throughout. And to enable laser alignment of horizontal samples on the reflectometer instrument, CRISP, sapphire windows are fitted This tail-set is rectangular in cross-section to fit between the poles-pieces of an external 1.5 Tesla electro-magnet.

In an early version of a 70 mm IVC Orange cryostat built for use with high-pressure cells, liquid helium flowed directly into the sample space so allowing the massive cell to be at least partially immersed in liquid Helium.

A Cryofurnace version developed in the mid-1980 s has substantially more powerful heaters than the standard cryostat, and an all-welded 70 mm dia. IVC which allows the cryostat to be operate up to 300 °C.

Since the OC's inception a number of attempts have been made to refine and automate the helium cold valve operation. Amongst these was a novel electro-magnetically operated ball valve version. The current version of the automated cold valve, devised by M de Palma at the ILL, has the standard micrometer adjustment replaced by automatic compressed air operation coupled to a pressure transducer which monitors the exhausting helium gas pressure. An in-house developed stepping–motor controlled cold-valve is currently being evaluated at ISIS.

In the mid-1990 s Oxford Instruments Ltd, OI, marketed their own range of Variox^{BL} cryostats for neutron scattering. Its particular novel feature is the incorporation of a motorised cold valve. With their ITC5® temperature controller it constitutes an integrated automatic cryogenic system in which the liquid helium flow, and therefore consumption, is linked to the user-demanded set temperature value of the ITC5.

3.2.1 Cryostat enhancements

In parallel with the acceptance of the Orange Cryostat so have there been developments, mostly by individual users, of complementary equipment to extend its range of use and versatility. These have chiefly taken the form of special centre-sticks and low temperature inserts.

Amongst the list of special-purpose cryostat centre-sticks are: Omega rotating (for single crystals), high-pressure, gas handling (for in-situ chemical reactions), and at the ILL a purpose-built trans-Uranic element handling centre-stick. The Orange Cryostat's performance envelope has been further enhanced by the development of ultra-low temperature inserts such as Karl Neumaier's "Charlie" dilution insert [6], Fig. 3.

More recently at the ILL a continuously circulating Helium3 refrigerator insert, [7] having a 400 mK base temperature has been developed. In addition the "single shot" Heliox® Helium3 Sorption Inserts built by Oxford Instruments can conveniently be used in a standard 50 mm Orange Cryostat.

Fig. 3. "Charlie" Dilution Fridge Insert for 50 mm Orange Cryostats.

At ISIS a Sample Changing centre-stick for the CRISP Reflectometer has been built, Fig. 4, which holds 4 planar samples stacked one above the other. Samples may be tilted through $\pm 2^\circ$, from the horizontal plane by a 0.01° resolution high-precision mechanical movement. The centre-stick fits inside the sapphire-windowed rectangular tail set described earlier.

Fig. 4. CRISP 4 position cryogenic sample changer.

3.3 Cryomagnets

Many laboratories have super-conducting cryomagnets both of symmetric-pair and asymmetric-pair geometry; and in both horizontal and vertical field configurations. Currently the most comprehensive suite of cryo-magnets available to the neutron user community is that at the Hahn-Meitner Institut's Berlin Neutron Scattering Center, BENSC, which comprises 4 vertical field magnets and 2 horizontal field magnets covering the maximum field range 4 Tesla to 17 Tesla. They are described in more detail by Michael Meissner and Peter Smeibidl in [8].

The mechanical structure and the neutron "windows" of cryomagnets are usually determined by the detector geometry of the instrument suite on which the cryomagnet will be used and the field intensity at the sample position. The magnet supports may be either a number of discrete rings, or one or more angular or "wedge" shaped pillars which may allow 340° of uninterrupted neutron access to the sample. Again, field intensity will dictate their size and placement.

3.3.1 Dysprosium field boosters

In their review, [8], Meissner and Smeibidl describe having successfully used the field concentrating properties of magnetically aligned polycrystalline Dysprosium pole-pieces as proposed by Stepankin, [9], to boost the magnetic field on small volume samples by up to 4 Tesla in super-conducting cryomagnets.

In practical terms BENSC's standard 14.5 Tesla magnet can, over the small sample volume limited by the pole-pieces' 6 mm diameter and 4 mm gap, be boosted to $\sim$17 Tesla.

3.4 Flow-through cryostats

The extremely demanding spatial and geometric constraints imposed by the Eulerian-cradle arrangement has frequently tested the ingenuity of cryogenic engineers when called upon to build cryostats for 4-circle instruments. One highly successful solution to this problem is a novel flow-through cryostat, [10], used on the D10 instrument at the ILL, Fig. 6. Designed in the late 1970 s, it incorporated helium transfer lines with rotating joints which allow a full 360° rotation of the cryostat within the Chi, X, circle.

About a decade later its performance was enhanced by the addition of a 200 mK dilution fridge stage, [11], whose performance depends on techniques developed for space technology.

3.5 CRYOPAD

A novel and elegant exploitation of superconductivity has been in the construction of the ILL's CRYOPAD, (Cryogenic Polarization Analysis Device), [12]. The Cryopad incorporates two internal cylindrical super-conducting Meissner-screens made of Niobium. The screens together with additional internal and external magnets then define three co-axial but magnetically-independent annular volumes. One of the two magnetic volumes in-

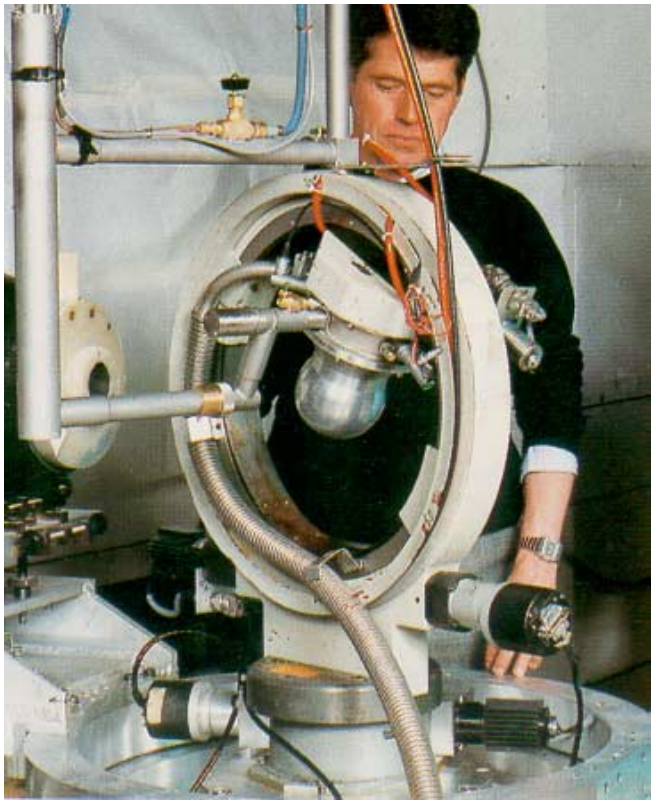

Fig. 5. D10 Flow-through cryostat being put through its paces off-line by R. Chagnon.

side the cryostat one is the zero-field sample volume. Each magnetic annulus traversed by the neutron beam is used to control and analyse the three spherical components and coordinates of the incident and scattered neutron polarization.

A description of the third generation CRYOPAD device was published in a recent review of the ILL's D3 project, [13].

3.6 Multiple cryogenic environments

As pointed out previously, the range of cryogenic facilities has been widened, giving researchers access to previously inaccessible regions of thermodynamic space. Not only have there been upgrades to enable cryostats to operate at more extreme temperatures but also to combine other environments together under cryogenic conditions. Recent examples of this have been the use of cryomagnets with dilution refrigerator inserts, cryomagnets with high-pressure cells, qv. [40], and recently a dilution refrigerator with a 1 GPa high-pressure cell, [14].

4. Furnaces

4.1 Metal foil element furnaces

Unlike the case of the Orange cryostats there has been no standardisation of high-temperature furnace designs. However the process of "parallel evolution" has required most neutron furnaces to conform to a similar design.

The typical furnace configuration is a cylindrical metal foil heating element, typically 40 μ thick, surrounded by three or more concentric heat shields. The sample is inserted into the centre of this assembly. The choice of heating element material, usually V, Nb, Ta, Mo or W, is primarily determined by the working temperature range but also by whether the experiment is elastic or inelastic scattering. Although vanadium has many desirable neutron properties for diffraction experiments, its tendency to undergo a brittle recrystalliization at ∼900 °C restricts its long-term upper working temperature to ∼1100 °C. Above this temperature, and particularly for inelastic scattering experiments, the next best choice is Niobium which may be used up to 1800 °C. For higher temperatures the preferred option is usually Ta, Mo or W.

The power requirement for this type of furnace will be of the order 150–200 Amps at ∼9 Volts which may be generated either from a transformer and thyristor combination firing in phase-angle mode, a variable reactor unit, or a solid state PSU.

In the late 1970s a furnace built for use at AERE Harwell had a temperature range of up to ∼3000 °C, [15]. At about the same time a furnace, reported in [1], development by Aldebert for the study of kinetic processes in ceramics had a Molybdenum heating element giving a maximum operating temperature of 2500 °C.

4.2 Closed shell furnaces

Instrument configuration, ie. 4-circle, sample type or the characteristics of the expected sample, also pose severe constraints on furnace design. Again, as in the case of cryostats on 4-circle instruments, there have been many attempts to design and build furnaces that retain the instrument's maximum flexibility of operation. Parallel evolution has defined that these furnaces have developed along similar lines; often using proprietary mineral-insulated heating elements coiled around the sample pedestal away from the primary neutron beam. The heater and sample sub-assembly, together with its heat shields is enclosed in a small vacuum chamber and this is then attached to the Phi motion of the Eulerian cradle. A closed-shell furnace of this type having an upper working temperature of 1023 K at 50 W input power, [16], was in use on the D9 single-crystal instrument at ILL in 1992.

4.3 Mirror furnace

Mirror, or imaging furnaces which utilise high power quartz-halogen bulbs and double ellipsoidal reflectors of the type developed for crystal growth in the Space-lab project have also been developed for neutron use, [17] see Fig. 6 below.

The Mirror furnace's particular advantage being that it can be operated in air and requires no heat shields, thus eliminating the sources of parasitic scattering. Because both reflectors focus the thermal energy at a relatively small volume in space the use of this type of furnace has been confined almost exclusively to single crystal samples.

A recent development at ISIS has been the use of proprietary linear reflector heaters on the strain scanning

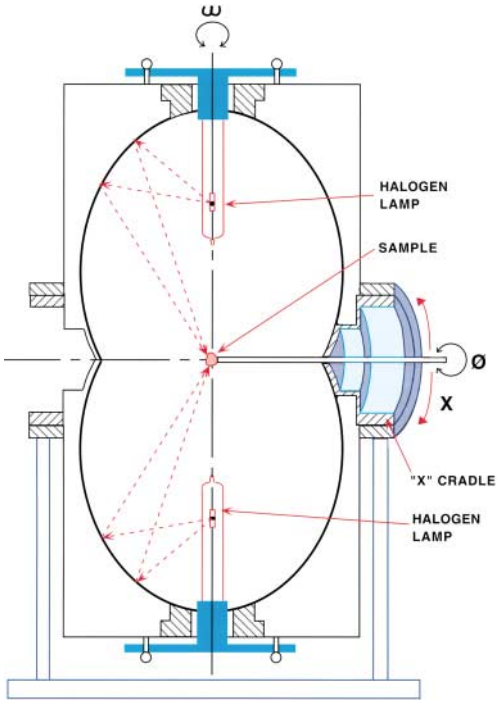

Fig. 6. Mirror furnace developed at the Institut für Mineralogie, L-MU Munich.

facility ENGIN. In this design four heaters are placed; two on each side of the sample with a common line of focus along the "surface" of the sample. This configuration is capable of achieving sample temperatures of up to 1000 °C. A further development of this furnace has been the addition of a quartz tube between the sample and heaters through which a stream of gas can be passed. This allows the sample to be studied in the stressed state, up to 50 kN tensile load, heated to 800 °C in an inert or non-oxidising environment.

4.4 Laser heating

A recent development in high temperature sample environments has been the use of a 100 Watt CO laser to heat a small, ∼ 3 mm dia. spherical sample, [18]. By the use of mirrors and lenses to guide and focus the laser beam it is capable of heating the sample to >2000 °C. The sample is insulated from its surroundings by levitation at the sample position on a fine jet of Argon gas.

5. High pressure

Pressure is a very powerful variable since it can be applied over a four-decade range of values, 0.1 MPa–30 GPa, to directly induce both structural and magnetic phase transitions. A comprehensive review of this area by Carlile & Salter, [19], was published in 1978, while the proceedings of International Seminar on Neutron Scattering at High Pressure held in 1996 at JINR Dubna, [20], gives the most recent overview of techniques. These techniques are now finding increasing application in the solution of a range of mineralogical problems as the report of a Neutron scattering techniques in Mineral and Earth Sciences attests [21].

Currently the largest range of pressure systems routinely available to users is that at ISIS. With a suite of helium intensifier cells, ILL-type Be-Cu clamped cell, McWhan clamped cells, a SANS 0.16 GPa cell, Paris-Edinburgh cell and the Kurchatov clamped cell, users can access pressures up to 25 GPa. Some of these pressure devices can be used at cryogenic and elevated temperatures.

The Pressure : Temperature working ranges of these cells are illustrated in Fig. 7, and described in detail below.

Although the first neutron experiments at high-pressure were performed in the mid-1960 s they have only become commonplace since the mid-1970 s. Early proponents and pioneers in this challenging field being Lechner, [22], Vettier & Paureau, [23], Kleb & Copley, [24] and McWhan, Bloch & Parisot, [25].

The requirement to induce high-pressure related transitions in a sample has probably generated the greatest variety of equipment and cell design to access any of the ther-

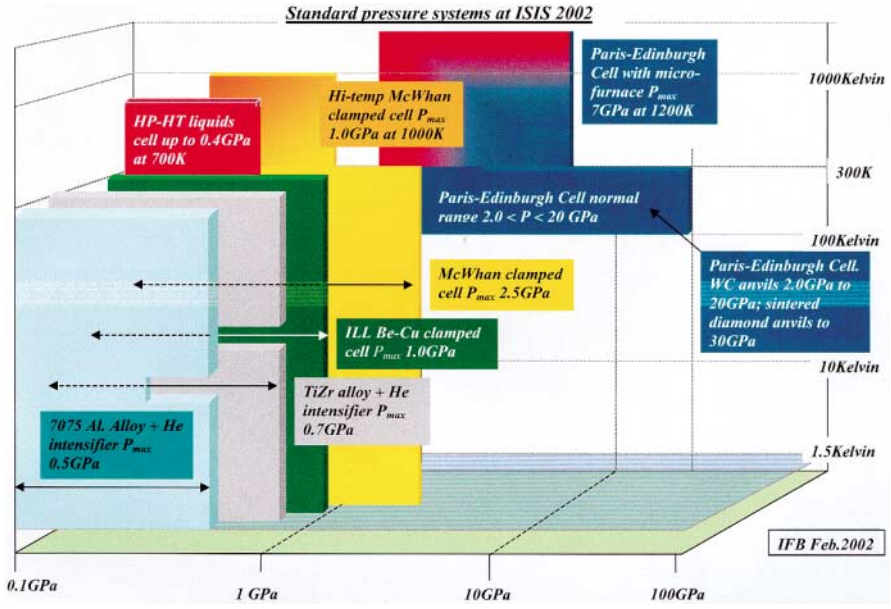

Fig. 7. Pressure facilities currently available at ISIS.

mo-physical variables. The variability in cell design has arisen to optimise each high-pressure cell design for a specific application, area of study or pressure range. Consequently there has been no standardisation of cell design, particularly for a given material, its internal: external diameter ratio, the maximum permissible working pressure, or of sealing mechanisms. However one design constraint common to all pressure cells is to achieve the optimum maximum working pressure for least mass – which by inference is unwanted material in the beam.

For the purposes of this review I have divided neutron high pressure techniques and cells into 3 main types: high-pressure gas, piston-in-cylinder and opposed-anvil clamped cells.

5.1 Continuously variable – high pressure gas

This technique covers the pressure range up to ∼0.7 GPa, (7 kbar), and typically uses compressed helium gas as the pressure medium. Cells designed for this technique are typically thick cylinders of perhaps 2 cm^3 internal volume of either type 7075 or 7049 aluminium alloy, or Ti−Zr null-matrix alloy. The cell attaches to the cryostat centre-stick with a capillary line linking it directly to a high-pressure intensifier. Pressure is applied to the cell and sample at a temperature at which helium is in its gaseous phase. The cell's temperature is then reduced freezing the helium at the applied pressure. Further changes of pressure can only be made by bringing the temperature of cell and sample back above the freezing-temperature of the pressurised helium. The helium pressure can then be changed and the cell re-cooled.

The preferred seal types are either, the classic unsupported area "Bridgman seal", [26] or the patented "Paureau seal", [27] the latter type being used for many years in the ILL's high pressure helium cells. For comparison Fig. 8 illustrates the components which make up the 2 seal types. The Paureau seal has fewer components but requires closer tolerances in their manufacture.

Although built for experimental purposes, these pressure cells are often required to conform to national Safety Codes because of the potential hazard of their stored energy. A typical 5 kbar Helium pressure cell at ISIS may have a stored energy of 6.7 kJoules – the equivalent of ∼1.5 gm of TNT.

To improve the neutron efficiency of high-pressure gas cells, i.e. pressure rating to wall thickness, several techniques may be employed. One such method is to auto-frettage the cell; a mechanical overstraining process described by Blaschko & Ernst [28], which simultaneously generates extreme tension in the outer "skin" of the cell and simultaneously forces the inner layers into compression. Early pressure cells, such as Lechner's [22], was made of several close-fitting Al. alloy cylinders shrunk on to one another. This construction is similar to the auto-frettaging process but requires close machining and manufacturing tolerances. At the IPNS, at Argonne National Laboratory, a compound 3-part Al. alloy shrunk-fit auto-frettaged pressure cell cleverly incorporates four Gadolinium-epoxy collimating foils between two of the component shells, [29].

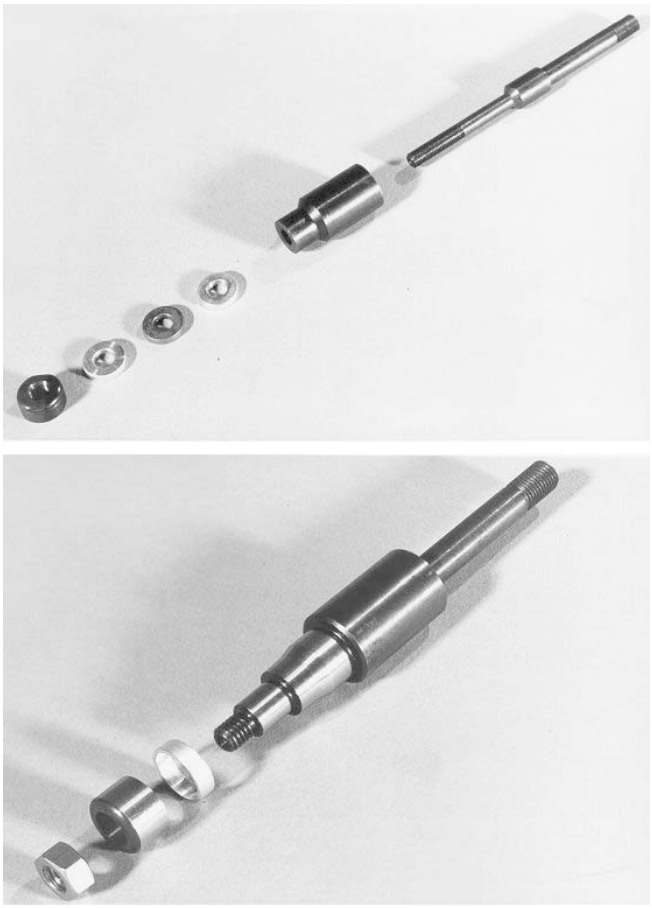

Fig. 8. Comparison of Bridgman, (top), and Paureau seal components.

While it is possible to generate pressures up to 15 kbar using helium, the common "neutron friendly" materials, Al alloys and Ti−Zr alloy, have only moderate ultimate tensile strengths; ∼500 MPa and ∼700 MPa respectively. The stored energy problem of compressed helium adds a further complication prohibiting its use at pressures above ∼0.7 GPa at non-specialist user facilities.

5.2 Piston-in cylinder clamped cells

To exceed the 0.7 GPa pressure limit imposed by the mechanical properties of Aluminium and TiZr alloys, requires

Fig. 9. A selection of Ti−Zr alloy and Al. alloy ISIS High Pressure Intensifier cells with Bridgman seals.

the exploitation of extreme mechanical forces to generate high pressures. Where the use of large samples ($\sim$100 mm^3), has dictated that the size of ultra-high pressure, >1 GPa, equipment becomes large and massive, practical solutions have been examples of complex engineering. The first of these piston-in cylinder "clamped cells", exploiting mechanical pressure generating techniques date from the early-70 s, the McWhan clamped cell, [25]; see Fig. 10, also described in detail below.

Piston-in-cylinder clamped-cells commonly have at their cores a radially compressed barrel-shaped alumina (Al_2O_3) cylinder at the centre of which a small aluminium sample capsule is placed. The pressure on the sample capsule is generated by externally loading, up to 10 tonnes, a pair of tungsten carbide, (WC) pistons which fit in the bore of the alumina cylinder. The load on the pistons is locked in place by tightening clamp rings. Hydrostatic pressure is assured by immersing the sample in Fluorinert, a non-hydrogenous fluid, or a 4 : 1 mixture of d-methanol : d-ethanol. The actual pressure is obtained from the diffraction pattern of a small quantity of NaCl included with the sample. Both the pre-compression forces on the alumina cylinder, and also those which lock in the pressure, are taken in the walls of an external steel or aluminium alloy outer shell of the device which holds the assembly together.

For simplicity of design and use, piston-in-cylinder strain-hardened Be−Cu alloy clamped cells, [30], using Fluorinert as the pressure medium has few rivals for pressures up to $\sim$1.5 GPa [31].

5.3 Opposed anvil pressure cells – Diamond anvil cells

With the increasing sophistication of neutron instrumentation, particularly in detectors and neutron flux, the size of samples that can now be routinely studied has considerably reduced. The early type of piston-in-cylinder high-pressure cell requiring sample volumes of $\sim$200 mm^3 have been complemented by opposed anvil cells having much smaller sample volumes. The anvils are commonly diamond, sapphire, or most recently synthetic moissanite, (hexagonal silicon carbide).

A diamond anvil cell, (DAC), developed by the Kurchatov Institute in Moscow has a sample size $\sim$1 mm^3 at $\sim$7 GPa, [32] & [33]. Similarly the Paris-Edinburgh Cell, (P-EC), with sintered diamond anvils has a sample size of $\sim$100 mm^3 at 25GPa [34]. These cells are illustrated in Fig. 11, and Fig. 12 respectively.

The Kurchatov Institute's DAC design is optimised for magnetic studies; both in its geometry, to minimise the parasitic background, and constructed of beryllium-copper a non-magnetic material. Its size allows it to be readily used in a standard Orange cryostat.

At LLB Saclay, a Kurtchatov diamond-anvil cell was used for neutron diffraction studies up to 43 GPa at low temperature, – the highest neutron pressure experiment yet performed [35].

The advantage of the P-EC is that it has an integral 250 tonne hydraulic press which permits *in situ* pressure changes and additionally can be used for powders, single crystals and simple fluids such as water, ammonia and H_2S. Although built primarily for diffraction work the Paris Edinburgh cell has also been successfully used for inelastic experiments.

In conjunction with a specially built nitrogen cryostat the P-EC working envelope is currently down to 100 K, or with an *in situ* micro-furnace to 1500 K, [35].

It has recently been demonstrated, [36], that using paired hemispherical Ti−Zr alloy soft metal gaskets with d-methanol : d-ethanol as pressurising medium almost perfect hydrostatic pressure can be maintained up to 9 GPa.

Other developments of high-pressure cells have concentrated on extending both upper and lower working temperature ranges, and their use in high magnetic fields.

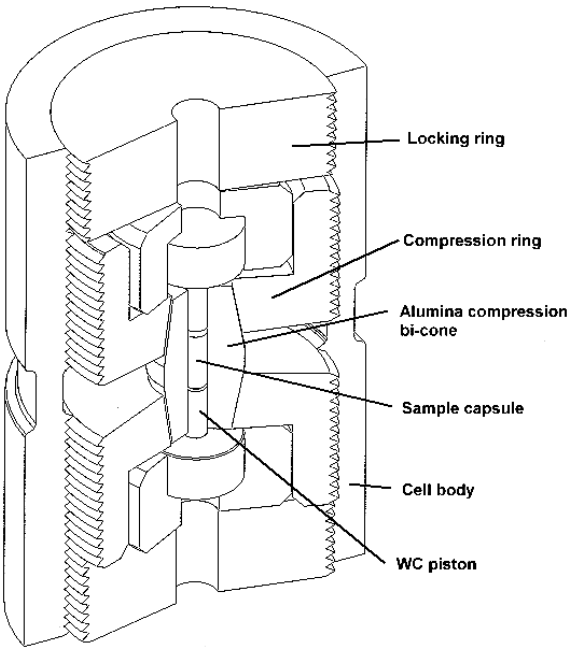

Fig. 10. Schematic of 25 kbar McWhan clamped high-pressure cell.

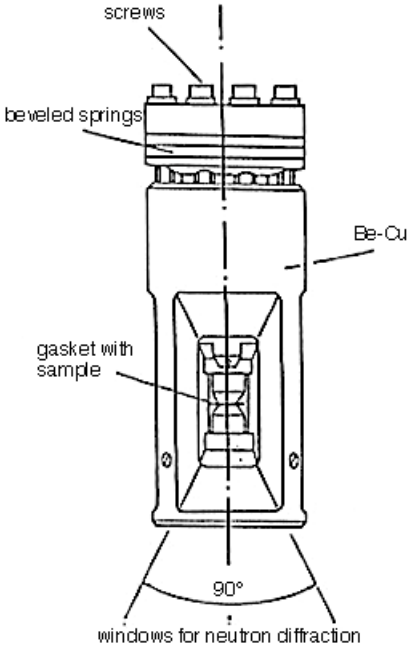

Fig. 11. Kurchatov Institute Diamond Anvil Cell.

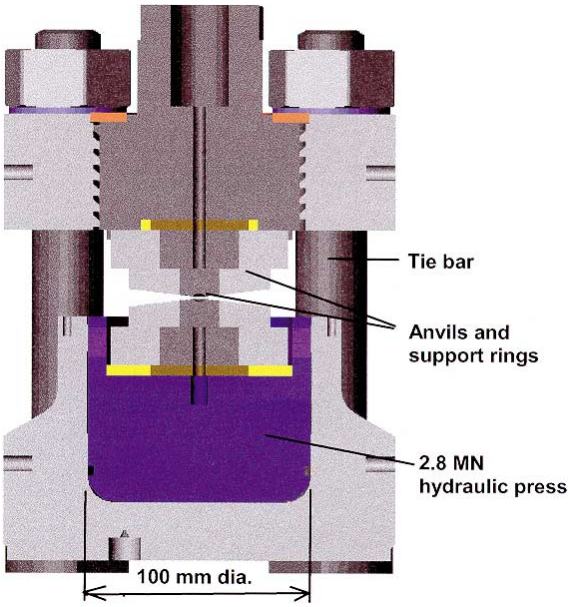

Fig. 12. Schematic of Paris-Edinburgh Cell.

Particular high temperature & high pressure cells are those by Hull & Keen, a McWhan-type cell with an integral graphite heating element; [37], up to 1.2 GPa & 1100 K, and the Kiel-Berlin Cell II; 1.2 GPa & 800 K, [38], and for high magnetic fields and low temperature the Osaka-Kyoto cell [39].

Synthetic moissanite hexagonal silicon carbide, having properties superior to those of diamond at high temperatures – resistant to oxidation and burning, has been reported [40], as a possible alternative to diamond in high temperature opposed-anvil cells.

Pressure measurement in both diamond and moissanite anvil cells utilise the ruby fluorescence technique.

5.4 Small angle neutron scattering high pressure cells

While many high-pressure developments have been principally beneficial to crystallographers there have also been significant advances in the HP facilities for small angle neutron scattering, SANS. Here a particular difficulty is the conflict between on the non-ideal "flat" sample geometry and the force generated on large neutron-transparent windows. For this type of cell the most favoured window material is sapphire. A recently built SANS HP-cell at ISIS, Fig. 13, has design parameters of 160 MPa (1.6 kbar) at 120 °C. At this pressure the 40 mm diameter sapphire-window assemblies carry a force of 200 kN. This cell has been tested to 1.6 kbar at 100 °C and first experimental use has been on super-critical CO_2 at 600 bar and 60 °C.

Similarly a SANS cell built at LLB Saclay, [41], has been used at up to 750 bar at 90 °C for studies of super-critical water and has been tested to 300 bar at 400 °C. The chemical reactivity of samples in this temperature and pressure regime also imposes strict constraints on the choice of materials from which such cells may be built.

Neutron high pressure studies have not been confined to solids but have also been made on liquids such as water in its many phases, and on many condensed gases; particularly on hydrogen and Helium 3 and Helium 4.

Fig. 13. SANS 1.6 kbar 400 K cell at ISIS.

While in most instances a cylindrical geometry is preferred for pressure cells there may occasionally be the need to construct pressure cells which have a flat or quasi-flat geometry. These specific requirements of pressure cell geometry are imposed by both the type of experiment and by the instrument on which it will be undertaken.

In several instances flat cells have been approximated by an array of discrete tubes with a manifold at each end, [42] and [43], or by a flat-plate with a matrix of parallel holes. The latter design has been adopted particularly when suitable tubes are unavailable; ie in the construction of Ti–Zr alloy sample cell used in the study of super-critical water, [44].

These types of experiments often not only require a special sample cell but also a local manually-operated pressurising system, see Fig. 14.

6. Time resolved methods

The versatile nature of neutron scattering techniques, not only as a probe of fundamental molecular and atomic structures but also as an investigative tool, has broadened its appeal to disciplines where it can be used to directly observe the real-time evolution of physical and chemical phenomena and processes.

Fig. 14. Hand operated pressure generator.

6.1 Neutron stroboscopic methods

Neutron stroboscopic techniques, first proposed by Windsor, [45], and pioneered, ca. 1975, at IPNS by Nimura and Moto, [46], and further described by Eckold for triple-axis spectroscopy, [47], have been used to make time-resolved studies of transient physical phenomena such as phase transitions having relaxation times in the milliseconds to seconds range. The phase transition may be induced by an externally applied cyclic perturbation such as electric fields or mechanical stress, [48] & [49]. Cyclic magnetic fields or thermal shock have also been proposed. A unique feature of the technique is that it can be pulsed in-phase with a chopped or pulsed neutron beam so that the time-varying response of the sample can be observed at different time intervals and at various stages of its evolution. The data is collected over several timed frames then added together to create a "super-frame".

6.2 Physical chemistry

Physical-chemistry is another area in which time resolution has been exploited to study both chemical and catalytic reactions in real-time. For the study of catalysts this technique has been pioneered at ISIS by Turner et al., [50].

This work required a sophisticated gas-handling system which permitted the pre-mixing of up to 4 different gases, at pressures up to 5 bar, feeding to a custom-built flow-through sample cell which could be heated in a standard furnace. The catalytic reactions between sample material and gas were observed as function of both temperature and pressure.

In a similar vein a hydro-thermal cell to study the real-time crystallisation of zeolites and similar micro-porous materials from their solid and liquid precursors has been developed by Walton, Smith & O'Hare, [51] & [52].

7. Large scale structures

While much of the review has described SE equipment to access the extremes of temperature and pressure for diffraction or inelastic studies the SE requirements for Large Scale Structures studies are generally much more modest, most experiments being at, or close to ambient temperatures. Most commonly the experiment will require fluid circulating baths, heaters to 200 °C or occasionally cryostats, but because of their high sample throughput sample changers, are often an essential adjunct to the instrument. A typical ambient temperature Sampl-Changer thermostatted with a fluid bath may take 5 or 6 flat-plate samples at a single loading: these will then be sequentially scanned across the neutron beam.

7.1 Rheometry

SANS experiments are also undertaken to investigate the 4 types of shear to which liquids can be subjected: Couette, and the closely related Searle-type shear, Poiseulle and Extensional shear. However only Poiseulle, the forced flow of the liquid through narrow channels or apertures, and Couette and Searle shear, to which many lubricants are subjected, are easily studied. Couette and Searle shear can be induced in a liquid "trapped" in a 0.5 mm annulus between two cylinders, one of which may be rotated at up to 3000 rpm, [53]. Extensional shear can only be easily induced in very small spatial volumes so is unfeasible with the present day neutron intensities on low Q instruments.

7.2 Reflectometry instruments

The Sample Environment requirementss on reflectometers, where the studies are of thin film structures and surface interfaces, has prompted the development of special cryostats and cells in which such films can be supported.

Since the neutron beam access to the sample is at a low grazing angle the facility to accurately tilt the sample holder is essential and often in-built into the instrument. In a typical set up the liquid interfaces are frequently formed against the surface of an optically polished silicon block. Frequently the assembly will be temperature controlled to enable monitoring the sample's response to temperature change, see Fig. 15.

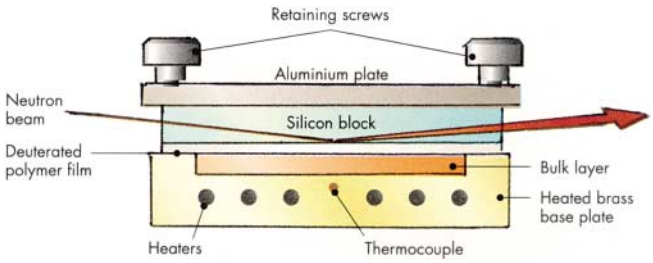

Fig. 15. Reflectometry thin film apparatus.

8. Sample changers

In those instances where the study is of a number of generically similar samples, or where the instrument is capable of a high sample throughput, Sample-Changers can be essential. Their geometric configuration is likely to be instrument specific. At ISIS 6 different instruments, CRISP, POLARIS, LOQ, GEM, SANDALS, and TOSCA all have Sample-Changers. In all cases the multiple samples are simultaneously loaded into a frame or a rack, which is then automatically positioned; rotated or scanned across the beam, and from which a sample is selected and mechanically placed in the neutron beam.

Summary

In a short review it is only possible to describe and highlight what can only be a snapshot of all the SE equipment in use world-wide. Similarly in a short review it is inevitable that some methods, such as strain scanning and sample changers, are mentioned only in passing.

The ubiquitous nature of neutron scattering, which serves an increasingly diverse range of disciplines, from magnetism to mineralogy and surfactants to strain scanning requires it to encompasses many different techniques. It is also a demanding field often testing the ingenuity of the most accomplished engineers and scientists. I have also shown that it is a area of active development which is driven primarily by the needs of science to progress, both as instrumentation techniques are refined and also as new phenomena are encountered. In addition there will always be a desire to push at the limits of whatever today's technology allows, be it of temperature, pressure, magnetic field or other physical variable. Together these influences continue to ensure that it is a challenging and dynamic discipline.

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