NEUTRON DIFFRACTION TO 10 GPa AND BEYOND : THE STATE OF THE ART OF THE PARIS-EDINBURGH CELL

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We review two versions of a low weight (50 kg) 250 tonne press that, for the first time, makes possible neutron-diffraction studies on powder samples of 40 to 100 mm^3 to 25 GPa. The assembly consists of a hydraulic ram compressing two opposed toroidal anvils, made of tungsten carbide (WC) or sintered-diamond dies, supported by steel binding rings and backed by tungsten carbide seats. An optimal signal-to-background has been achieved by an improved shielding geometry. Besides standard procedures for the studies of solid powders at ambient temperature, loading procedures for liquids and gases have been developed and represent an original characteristic of this device. The performance will be illustrated by recent results on D_2O ice VIII and B_4C to 10 GPa. We finally report on the first low temperature experiments to 100 K as well as recent developments towards a reduction in size (x0.8) and weight (x0.5) of the apparatus.

INTRODUCTION

Neutron diffraction experiments on powder samples require in general samples at least 50 mm^3 in volume in order to collect patterns on which full profile refinement can be performed in a reasonable amount of time. Since the development of the McWhan cell[1] in the late 1960's, however, little progress has been made in the construction of standard user devices for pressures beyond 3 GPa, although presses and multianvil assemblies for compression to 10-20 GPa are commercially available. The reason for that is evident: diffraction experiments impose rather severe restrictions on the geometry of the anvils and the weight (size) of the press, rendering standard devices either useless or extremely cumbersome. The Paris-Edinburgh cell is a high pressure device which combines a toroidal anvil assembly with an optimized low weight (50 kg) 250 tonnes hydraulic ram. The anvil geometry requires measurements of the diffracted beam at a fixed angle $2\theta \approx 90°$, which is advantagous since suppression of background from illuminated parts of the cell by proper collimation is relatively easy. Therefore, it suits only measurements on pulsed sources by time-of-flight spectroscopy. The cell has been designed specifically for use at the POLARIS-station at the U.K. pulsed source ISIS.

DESIGN AND PERFORMANCE

Description of the cell

Figure 1 shows two versions (V2 and V3) of the Paris-Edinburgh cell [2], which differ mainly in the shape of the hydraulic press: V2 is equipped with an axial bore at the back of the ram allowing transmission measurements, which is not present in V3. The thrust on the anvils (5) and seats (6) is generated by the piston-cylinder (7) assembly which is shown here with the piston fully recessed. With a 250 MPa (2500 bar) pressure in the hydraulic fluid which is fed in through

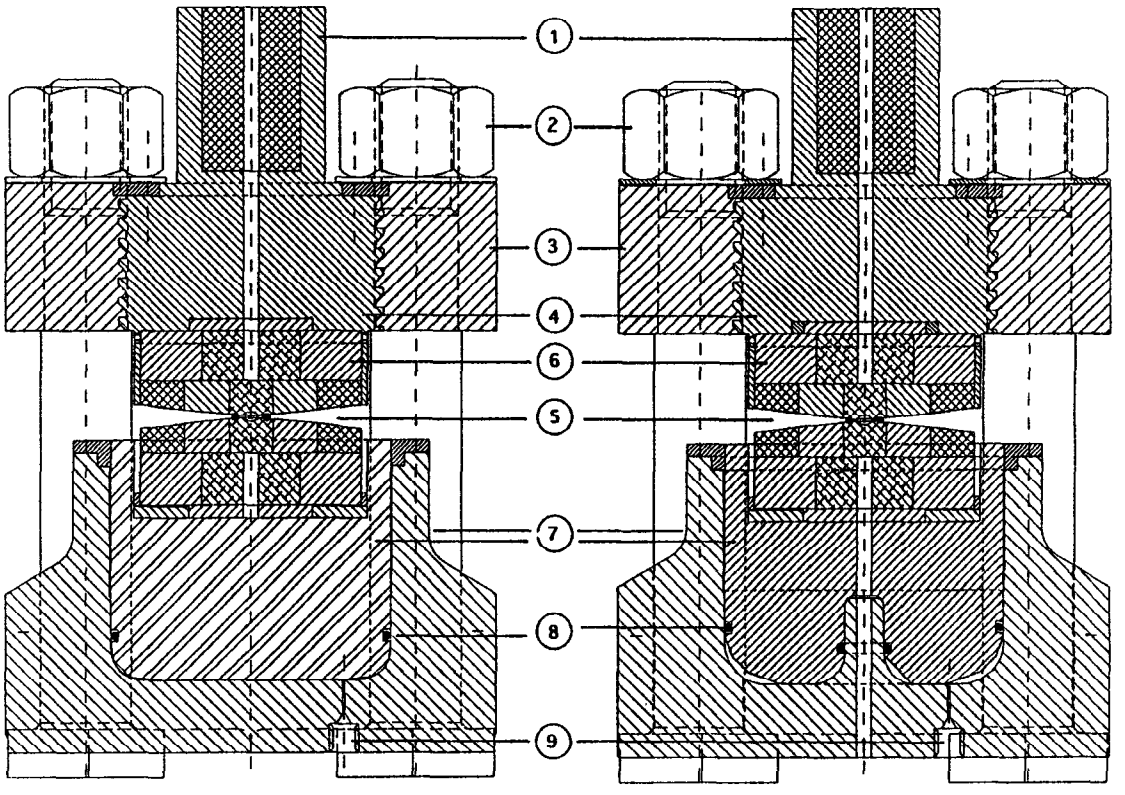

Figure 1: Cross cut of two versions of high pressure cells V3 (left) and V2 (right). (1) collimator, (2) nuts and tie rods, (3) top platen, (4) breech, (5) anvils, (6) anvil seats, (7) piston-cylinder assembly, (8) hydraulic fluid seal, (9) high pressure fluid inlet.

the inlet (9) a 250 tonnes (2.5 MN) thrust is generated by the 100 cm^2 piston. The tie rods with their corresponding nuts (2) connect the ram body to the top platen (3). The press is almost entirely made of high performance steel 819A by Aubert et Duval (35NCD16).

Finite element calculations were used in order to find the optimal shape and dimensions of the ram. This leads to the unusual shape shown in Fig. 1, where the deformations at the level of the O-ring seal as well as the centering ring are almost zero although some parts of the cylinder deform by 0.45 mm at 200 tonnes load. Maximum stresses of ca. 1 GPa occur at the bottom of the ram. The inlet for the hydraulic fluid was placed in a region of minimal stress.

Toroidal anvil and gasket assembly

Figure 2 shows an enlarged view of standard WC anvils including the gasket, consisting of a washer and a toroidal part. The high pressure chamber (sample volume V) is situated in the center of the drawing, limited laterally by the washer and vertically by the two spheroidal surfaces of the anvils.The washer is laterally supported by the toroidal gasket. High pressure is created by applying load onto the anvils which causes the sample volume to decrease both by the decrease of the gasket thickness as well as the intrusion of the washer into V. For such a profile the upper limit for the volume reduction V_o/V is roughly 2. This causes no restriction for experiments on solids and liquids, where V_o/V is between 1 (NaCl : 1.2) to 2 (NH_3, CH_4), between loading and ~ 10 GPa but excludes measurements on gaseous samples (H_2, He) if they are loaded at ambient pressure above the current low temperature limit of 100 K.

The standard anvils are made of slightly conical WC kernels (overall cone angle 3°) of 25 mm diameter and 14 mm height. They are supported by pressing them into a steel binding ring (819A by Aubert et Duval) at ambient temperature, producing a tangential stress of ca. 1 GPa. At the back they are provided with a recess of 6 mm depth and 5 mm diameter to reduce the attenuation of the incident neutron beam.

The compressive strength of WC is approximately 60 tonnes/cm^2, which means for

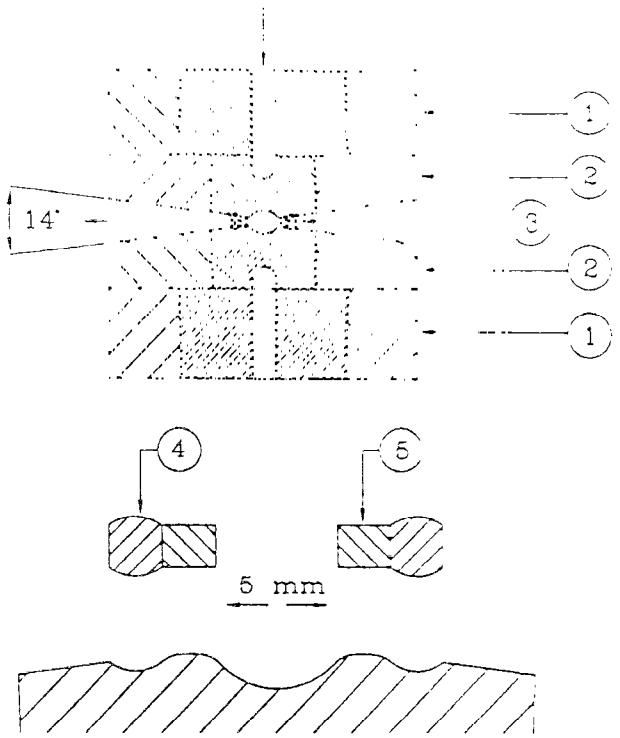

Figure 2: Toroidal anvil assembly (top) with enlarged view of the gasket and anvil profile (bottom). (1) Seats (CW), (2) anvils, (3) sealing assembly consisting of (4) toroidal gasket and (5) flat washer. Anvils are made of CW (standard) or diamond dies, supported by steel binding ring.

gaskets of 18 mm diameter a maximal load of ca. 150 tonnes. According to the empirical load/pressure characteristic of the cell (see below) this results in a maximal pressure of 12 GPa. For pressures beyond this limit, there seems at the moment to be only one feasible solution, namely compacted diamond dies. These are provided by General Electric under the commercial name COMPAX and have to be shaped to the specific anvil profile by spark erosion. Our experience at the present time is limited to a few experiments beyond 10 GPa, among them one on Ni above 20 GPa and another on D_2O (ice VIII) to 13 GPa.

Gasket materials

Pyrophyllite and Cu:Be, were initially used as gasket materials, but are now replaced by null-scattering TiZr (52% Ti, 48% Zr by weight) to eliminate wavelength dependent absorption due to Bragg edges. Despite a much lower yield strength (900 MPa) compared to 1300 MPa for hardened CuBe the performances of the two materials in a given configuration are very [illegible] that the performance [illegible] by the geometry rather than the mechanical properties of the gasket material.

Scattering geometry and shielding

Figure 3 shows schematically the cell in its measuring position within the POLARIS tank. The incident neutrons (beam diam. 5 mm) are directed along the axial bore of the cell and have to pass through ca. 6 mm of anvil material (WC or diamond) before they reach the sample. They are scattered and collected at $2\theta=90°\pm7°$ by ZnS-detectors[3] covering 65° in the equatorial plane at each side of the cell. Proper shielding of the detectors proved to be essential for "clean" spectra i.e. without spurious peaks from the anvil material and elevated background from stray neutrons of various parts of the cell. Systematic background measurements on the

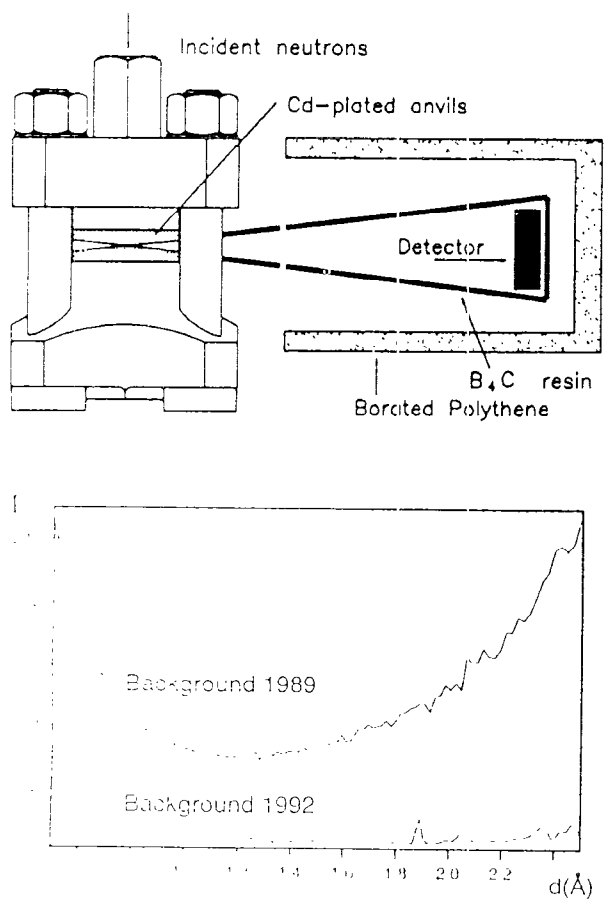

Figure 3: Top: Scattering geometry and shielding at the POLARIS station. Only half of the detectors are shown. Bottom: Background (1992) with improved shielding (see top) compared to former level (1989).

TEST-line lead finally to the set up shown in Fig. 3 (top). The detectors sit inside a conical box which comes right up to the tank. Two removable parts extend to the edge of the anvils which are plated with neutron absorbing cadmium up to 1 mm close to the gasket. The effect of such a shielding on the background is shown in Fig. 3 (bottom) in comparison with early measurements of 1989.

Load-pressure characteristic

After sealing the high pressure chamber under a load L of ca. 20 tonnes, P increases linearly with L to approximately 8 GPa and 90 tonnes, followed by a levelling off at 12 GPa and 130 tonnes. This holds for both solid and initially liquid samples, if the starting volume is chosen according to the specific elastic properties by using gaskets of different dimensions. The pressure/load characteristics for TiZr and CuBe gaskets are almost identical.

Loading procedures

To alleviate pressure broadening effects, which are commonly observed in solid powder samples at high pressures, the following procedure proved to be effective. As much as possible of the powder sample is placed into the bore of the gasket, glued to the bottom anvil. The sample is then soaked with Fluorinert and the pressure chamber is quickly sealed off by applying a load of ca. 20 tonnes.

Liquid samples are loaded directly in the cell, with no need for encapsulation: the cell is placed into its "measuring position", i.e. with its axis horizontally. Then a rubber ring is placed between the anvils, before applying a few hundred N onto them, which creates a sealed cavity around the gasket assembly. Then the sample is injected by a syringe, while a second one ensures that no air bubbles remain in the cavity. Again, 20 tonnes are applied to seal off the high pressure chamber before finally the rubber is cut off.

Gaseous samples are loaded by condensing them at sufficiently low temperatures into a loading chamber around the gaskets as in the previous case. This can be a rubber ring, or, for temperatures below 200 K a PTFE-ring, supported by a metal bracket. Such a set-up holds pressures to well beyond 50 bars, which means that some gases (Ar, CH_4) can be loaded close to their critical point at relatively elevated temperatures. This again is an original feature of this large volume cell. The time required for loading is mainly determined by the cooling and warming delay of the cell and thus between 1 and 6 hours.

Low temperature experiments

Being able to cool the cell down to moderately low temperatures (100 K) is important for structural studies (phase transitions, especially magnetic), but also for loading gaseous samples and for enabling improved structural information to be obtained because of the reduced thermal motion.

To vary the temperature, the cell and its support are placed into a thermally insulating container which fits into the existing POLARIS tank. By filling the bottom of the container with ca. 10 cm of liquid nitrogen, the cell cools down to 150 K within 2 1/2 hours and to 100 K in 5 hours. Data collection at low temperature has been successfully tested in an early experiment on .ice VIII to 110 K and recently on ammonia to 120 K.

RECENT RESULTS

D_2O (ice VIII)

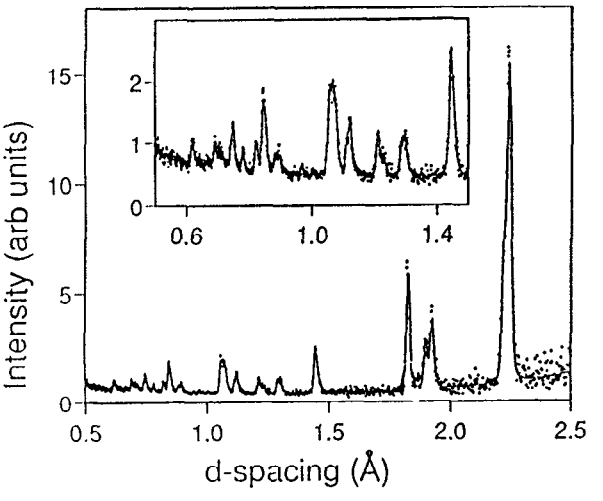

Figure 4: Spectrum of D_2O (ice VIII) at 10 GPa.

The aim of this experiment was to study structural changes of the ordered high pressure phase of water, ice VIII, in particular the variation of the intramolecular O-D distances to 10 GPa[4]. Fig. 4 shows a typical spectrum at 10.4 GPa obtained after 6 hours of

data collection with only one of the two detector banks. The profile refinement of the structure gives a precision of ± 3 x 10^{-4} nanometers on the intramolecular O-D bondlength - the same precision as at 2.5 GPa. This is the first time that variable atomic coordinates have been successfully refined up to 10 GPa from neutron diffraction data.

B_4C ($^{11}B_4C$)

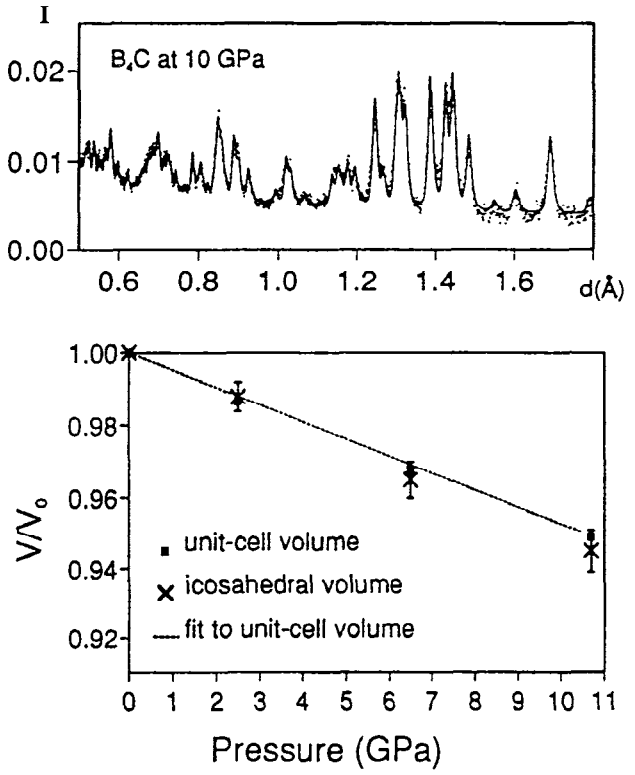

Figure 5: Spectrum of B_4C at 10 GPa (top) and relative volume changes as a function of pressure (bottom).

Boron carbide is an example of a low-z material with both interesting structural features as well as applications as high temperature electronic material. Similar to many other boron compounds, the structure of B_4C is made up of interconnected B_{12} icosahedra, with a three-atom chain along the rhombohedral axis. Conductivity occurs by hopping of small bipolarons between icosahedra and studies at elevated pressures have revealed the that the resistivity increases with pressure. This phenomenon has been explained by the idea that the icosahedra are more compressible than the overall structure. Figure 5 shows a spectrum collected at 10 GPa, along with the behaviour of the relative volumes of the unit-cell and the icosahedra. It is clear that the icosahedra compress at a rate close to that of the unit-cell. Hence, a new explanation must be sought for the behaviour of the resistivity[5].

Future developments

At the moment, development is focussed on two issues: first, development of smaller presses for standard use to 10 GPa and possibly for low temperature work. All dimensions can be scaled down by a factor 0.8, leaving the anvils as they are and leading to a cell with a mass of ca. 30 kg instead of 50 kg.

A second development concerns the extension of the standard pressure range beyond 10 GPa. This requires in general not only the use of COMPAX-anvils and hence more complicated absorption corrections due to Bragg edges of the diamonds, but also an improved anvil profile.

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REFERENCES

[1] D.B. McWhan, D. Bloch and G. Parisot, *Rev. Sci. Instrum.* **45**, 634 (1974).

[2] See also: J.M. Besson, R.J. Nelmes, G. Hamel, G. Weill, J.S. Loveday and S. Hull, Physica B 180+181, 907, (1992); J.M. Besson, R.J. Nelmes, G. Hamel, G. Weill, J.S. Loveday and S. Hull, High Pressure Research 9, 179, (1992); J.S. Loveday, R.J. Nelmes, J.M. Besson, G. Hamel and S. Hull, Adv. in Powder Diffr. II, Gaithersburg USA, abstracts in the Nat. Inst. of Standards and Technology (USA), Special Publ. 864, 223 (1993).

[3] funded by the European Community.

[4] R.J. Nelmes, J.S. Loveday, R.M. Wilson, J.M. Besson, P. Pruzan, S. Klotz, G. Hamel S. Hull, *Phys. Rev. Lett.* **71**, 1192 (1993).

[5] R.J. Nelmes, J.S. Loveday, R.M. Wilson, J.M. Besson, S. Klotz, G. Hamel and S.Hull, subm.to *Phys. Rev. B*, rapid comm.