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2005 J. Phys.: Condens. Matter 17 S3009

(http://iopscience.iop.org/0953-8984/17/40/003)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) S3009–S3015 doi:10.1088/0953-8984/17/40/003

Gas pressure cells for elastic and inelastic neutron scattering

W F Kuhs[1], **E Hensel and H Bartels**

GZG, Abteilung Kristallographie, Universität Göttingen, Goldschmidtstrasse 1, 37077 Göttingen, Germany

E-mail: wkuhs1@gwdg.de

Received 8 July 2005
Published 23 September 2005
Online at stacks.iop.org/JPhysCM/17/S3009

Abstract

Gas pressure cells techniques are well adapted to neutron scattering applications. They can routinely be used at least up to pressures of 0.5 GPa in a wide temperature range, they allow for an accurate pressure control and also provide the chemical activity for the study of materials where the gas is not only the pressure transmitting medium but also a chemical constituent of the system. We present some of the gas pressure cells which were developed by us for specific needs and discuss their design and performance.

1. Introduction

Unsupported gas pressure cells are likely to be the most widely used cell type in neutron scattering experiments, both for powder and single-crystal work. Usually He is used as the pressure transmitting gas. The precision and accuracy of the pressure measurement, and the ease of changing pressure even at low temperatures, are not surpassed by any other type of cell. Most cells can be operated in continuous-flow He cryostats. All gas cells in use are of cylindrical symmetry with free access in the scattering plane perpendicular to the cell axis and with an access out-of-plane, which is usually restricted by the cryostat and not by the cell itself. Sample volumes are typically of the order of a few cm^3. Clearly, safety is a main concern when operating these cells. Safety specifications and extensive material testing is mandatory more than for any other type of high-pressure cell (Paauwe 1977, Dawson 1977a). Specifically, the materials used for construction need to be certified by the manufacturer with respect to composition, homogeneity (ultrasonic test) and strength (tension test). The wall thickness depends on the material used, on the square-root of the cell volume, a coefficient proportional to the stored energy at the maximum working pressure, and on the mass of the ejectable parts of the cell in case of a rupture (see e.g. Dawson 1977b). Most materials need to be treated after manufacturing by an autofrettage procedure (using liquids) before applying gas pressure.

[1] Author to whom any correspondence should be addressed.

For any operation at non-ambient temperature conditions more extensive testing needs to be performed, as material properties may considerably degrade in particular upon heating. For these reasons only very few well-established materials are presently used for gas pressure cells in neutron scattering applications: high-strength Al-alloys, Ti–Zr and Cu–Be alloys (listed here with increasing bursting pressures; see Bloch and Voiron 1984). Al-alloys have low absorption, an acceptable background between the main Bragg peaks, are cheap and usually easily machined. Different qualities of high-strength Al-alloys are available: Al7049 (Al with typically 0.40% Si, 0.50% Fe, 1.2–2.0% Cu, 0.20% Mn, 2.0–2.9% Mg, 0.10–0.22% Cr, 7.2–8.2% Zn) is used for highest performance at ambient temperature, Al7075 (Al with typically 0.25% Si, 0.35% Fe, 1.2–1.9% Cu, 0.30% Mn, 2.1–2.9% Mg, 0.18–0.28% Cr, 5.1–6.1% Zn) for low-temperature applications. Their use is limited to pressures in the 0.5 GPa range. The Ti–Zr zero matrix alloy is the other common choice; it has a tolerable and homogeneous background and safely covers the pressure range up to 1.0 GPa. Gas cell designs suitable for neutron diffraction were presented by Kleb and Copley (1975) and by Paureau and Vettier (1975). The latter came in use at ILL/Grenoble and was used for a large number of successful neutron scattering experiments. This cell had only one seal ('Paureau-seal') originally made of indium-plated copper. The cell has evolved over the years and has been replaced by several other cells, which mostly operated with a Paureau-seal or a combination of a Bridgman mushroom-type piston seal (see e.g. Sherman and Stadtmuller 1987) and a cone-type metal seal for the gas capillary (see e.g. Paauwe and Spain 1977). The gas pressure cells presented here are build on these principles too.

The experience of some limitations of existing neutron gas pressure cells and the need for in-house laboratory work led us to develop our own cells. Some pressure cells were also designed for the use of non-standard gases providing the necessary chemical activity for experiments where the pressure-transmitting gas is also a component of the material studied, in particular for filled ices and gas hydrates (Kuhs 2004). To avoid unnecessary background and to speed up temperature equilibration in cryostats we started to build a whole series of Al-alloy pressure cells with reduced wall thickness adapted for the envisaged pressure ranges. Likewise, at the expense of achievable maximum pressure, thinner-walled low-absorption cells were needed for hard synchrotron x-ray studies. To overcome the 0.5 GPa pressure limitations we also started to construct our own Ti–Zr cells. Some typical examples of our gas pressure cells will be described in the following.

2. Experimental details

For a well-controlled gas pressure experiment in He-flow cryostats ('orange cryostats') a number of precautions need to be taken. The temperature reading should be taken as close as possible to the sample. Moreover, as the gas pressure is read externally when the gas capillary is open to the supply system, one has to make sure that no blockages occur in the capillary. This can easily happen in orange cryostats as the capillary in the sample stick passes close to the liquid He and liquid N_2 reservoirs of the orange cryostat, in particular when volatile samples or gases close to condensation conditions are used. Therefore, the sample stick is generally equipped with a heating of the capillary. We use for this purpose a 104 Ω thermo-coax heater, which can be connected to an ILL temperature controller. The density of winding of the heater around the gas capillary was such that the temperature differences along the stick inserted into an orange cryostat were minimized. In this way, the temperature variation along the capillary was kept within 10°–20° from a preset value. It is often useful to survey the deformation of the pressure cells directly using a strain-gauge; thus, the proper functioning of the cell can be surveyed and blockages of the capillary can easily be detected. Figure 1 shows schematically

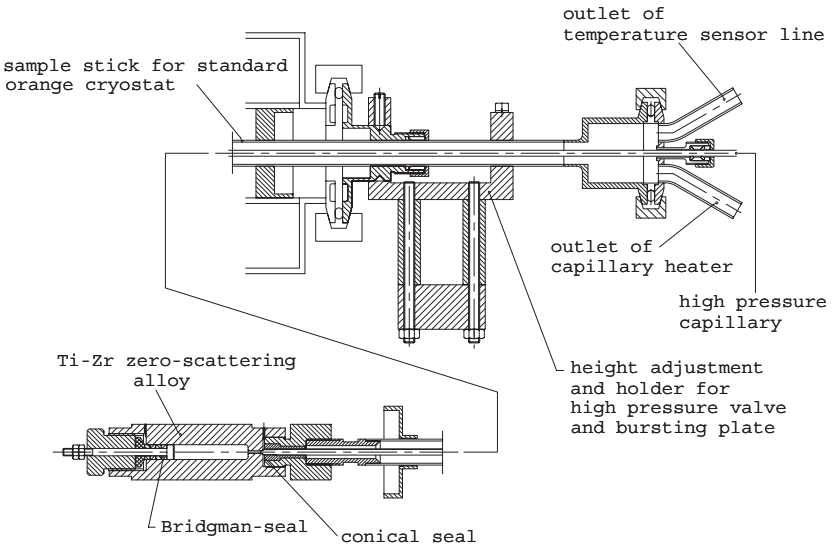

Figure 1. TiZr pressure cell with sample stick for the use in 'orange cryostats'.

one of our gas pressure cells mounted on a sample stick suitable for standard orange cryostats with 49 mm openings; the sticks are equipped with a (exchangeable) bursting disc. Figure 2 shows a cell for lower pressures which is in use for experiments on D20 with its narrow heat-exchanger part of the cryostat preventing the use of a large number of existing gas pressure cells.

A commercial gas compressor of the diaphragm-type is used for pressures up to 0.3 GPa. Further pressure increase is achieved by an intensifier stage (see e.g. Edmiston *et al* 1977) going up to 0.7 GPa. We also operate a mobile 0.1 GPa unit for the use at HASYLAB/Hamburg. In the construction of the pressure cells we have ensured to use conical seals compatible with high-pressure capillaries at neutron facilities so that cells and pressure generating systems can easily be interchanged. Recently, a pressure cell for the use on time-of-flight (TOF) neutron spectrometers was constructed and tested on IN10 at ILL/Grenoble. Working with hydrogenous materials with their high adsorption calls for very thin samples, typically 0.5 mm thick. Often a cylindrical geometry is ideal, which can be achieved by a thin double-walled cylinder for the sample can. The cell body and inserted sample can are shown in figure 3; the unused sample space can be filled with a pure Al rod to avoid scattering and adsorption by scattering from the gas. A similar sample container was also used successfully for kinetic powder diffraction experiments on hydrogenous materials performed on D20 at ILL/Grenoble (Staykova *et al* 2003).

All cells are autofrettaged and tested using a hand-driven screw-press (SITEC 750.1700) operated with polydimethylsiloxane (Baysilone M3) before using them with gas pressures.

The pressure reading is done using a piezoelectric sensor (Ashcroft Type KXD); several variants are used for different pressure ranges and the readings are registered via a RS232 interface on a laptop computer. The sensors are calibrated from time to time using a high-accuracy mechanical manometer (Heise CM series).

3. Results and discussion

The performance of a pressure cell in scattering experiments depends on the accuracy and stability of pressure and temperature as well as on the tractability of the data reduction, in

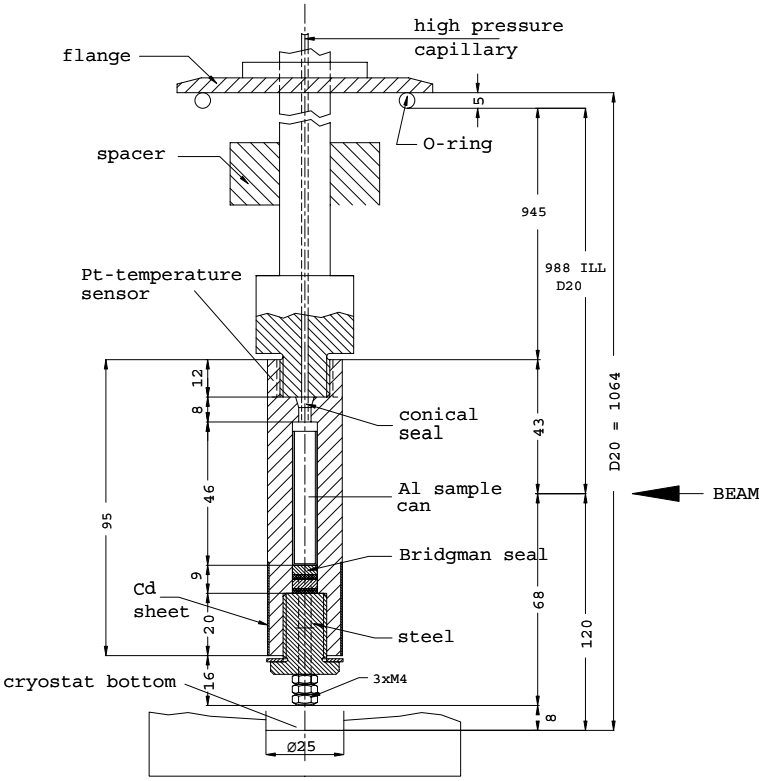

Figure 2. D20 gas pressure cell.

particular the background correction. For neutron applications the problem of activation by neutron capture should also be considered. Gas pressure cells are certainly well performing in terms of accuracy of pressure (and temperature); problems with the background treatments exist, however. High-strength Al-alloys contain various precipitates, which translate into large background variations as shown in figure 4. A major part of these problems can be circumvented using an empty-cell correction (at the same pressure and temperature conditions as the data collection); when the pressure and temperature are varied this may take an appreciable part of the beam-time. Some of the background features also exhibit texture, so the cell orientation must also be reproduced for the empty-cell run.

In addition, some of the alloying constituents (in particular Zn, Mn and Cu) contribute to a considerable activation in the neutron beam. This means that the pressure cells usually have to remain under the control of radioprotection after the experiment. The sample cans located inside the pressure cell may be made of normal Al, so that samples can be taken back after the end of the experiment—given that the sample is not activated itself.

Ti–Zr pressure cells have occasionally posed other types of problems. The incoherent background from these cells is so high that the available detector efficiency corrections based on a vanadium run became insufficient in quality for long data acquisitions. This may occur on scanning powder diffractometers like D2B. The problem was cured by running a calibration based on the incoherent scattering from the pressure cell itself for the detector efficiency correction.

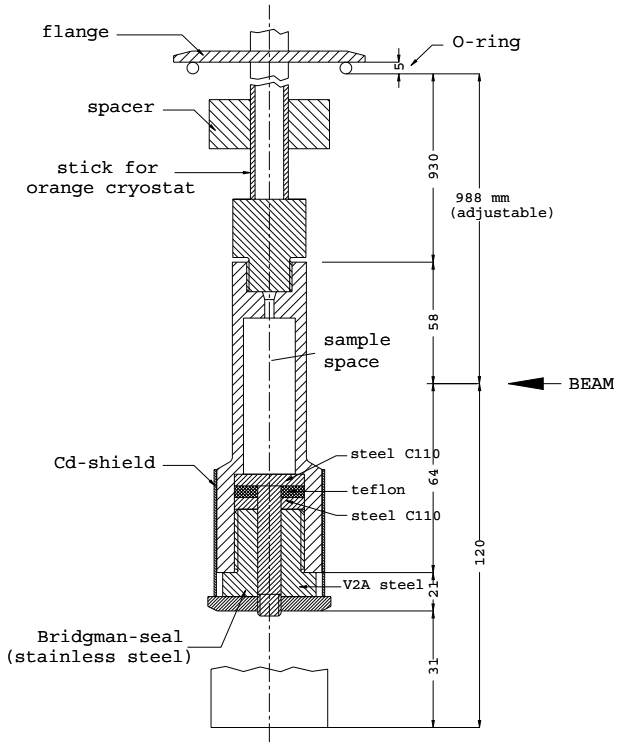

Figure 3. Cylindrical TOF gas pressure cell. The wall thickness is 5 mm and designed for pressures up to 0.01 GPa.

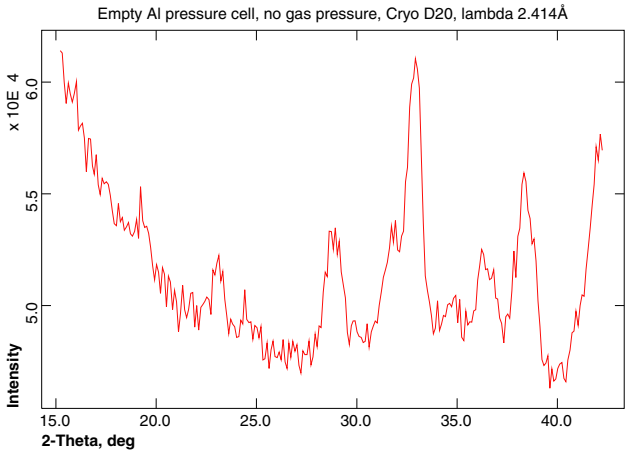

Figure 4. Background features of the Al7075 gas pressure cell originating from precipitates; 5 min data acquisition on the high-flux diffractometer D20/ILL (Grenoble).

(This figure is in colour only in the electronic version)

4. Applications

The gas pressure cells were developed for applications in essentially two fields: gas hydrates (clathrate hydrates) and high-pressure ices; an overview was recently given by Kuhs (2004).

Very few clathrate hydrates are stable at ambient conditions. Most need elevated gas pressures of the guest component for formation and stability. Therefore, experiments on gas hydrates can be done only at elevated gas pressures (*in situ*) or on samples recovered to ambient pressure at liquid nitrogen temperatures, where gas hydrates can be kept metastably for extended periods. Such recovered samples decompose upon heating typically at temperatures exceeding 160–190 K at ambient pressure. It should also be noted that it is not sufficient simply to maintain a high mechanical pressure. Rather, it is important to have the guest species available at some high activity which is generally obtained by using the guest phase as the compression medium. Working with certain inflammable or explosive gases can put severe restrictions on the experimental set-up and may render experiments very demanding for safety reasons, especially when working with larger sample volumes. This is true in particular for oxygen and we have used here special high-pressure equipment free of any organic material and a water-driven gas compressor.

A number of powder diffraction investigations were performed on gas hydrates over the years—mostly on D2B at ILL/Grenoble. The focus was on the pressure-dependent changes of structure and cage filling of various gas hydrates (e.g. Kuhs *et al* 1997, Chazallon and Kuhs 2002, Klapproth *et al* 2003). The precision and accuracy of this work turned out to be comparable to ambient pressure work after increasing the data acquisition times by a factor of 2–3. More recently, using the cell shown in figure 2 a series of kinetic diffraction experiments was performed on D20 at ILL/Grenoble to study the formation and decomposition kinetics of CH_4- and CO_2-hydrates (Staykova *et al* 2003, e.g., Genov *et al* 2004, e.g., Kuhs *et al* 2004, e.g.). Unique information, in particular on the initial stage of the reactions (e.g. existence of intermediate phases), was obtained from these *in situ* studies.

Likewise, various gas pressure cells were used to study the phase diagram of water. The transformation behaviour between different high-pressure phases of ice is known to depend on the gas used. Helium (and also to some extent neon) is found to enter into ice Ih and ice II (but not into ice III or V) leading to changes in the phase boundaries (Londono *et al* 1992, Gotthardt 2001, Lobban *et al* 2002). Using argon gas as a pressure medium apparently does not change the stability range and structure of the known high-pressure phases of ice (Lobban *et al* 2000). The highly accurate pressure control inherent in a gas pressure system allowed the formation of (metastable) high-pressure phases of ice (like ice IV and the new phase ice XII) both in the laboratory and in the neutron beam using TiZr cells like the one shown in figure 1 (Lobban *et al* 1998).

In conclusion, gas pressure cells for neutron scattering applications were used by our group in some 50 experiments over the last 15 years. They work very reliably, allow for an unsurpassed pressure control and can be operated in a large temperature range, in particular at low temperatures. They can be modified for special geometries and adapted for a wanted pressure range. Pressures can be adjusted remotely in-beam (of interest in high radiation environments) and may eventually become fully computer-controlled.

Acknowledgments

The contributions of Bertrand Chazallon (Göttingen, now at Lille), Colin Lobban and John L Finney (London), Alice Klapproth, Doroteya Staykova, Georgi Genov, Helmut Klein (all Göttingen) as well as Thomas Hansen, Louis Melesi and Jean-Luc Laborier (Grenoble) are gratefully acknowledged. We would also like to thank the ILL and ESRF (Grenoble) as well as the HASYLAB at DESY (Hamburg) for beam-time and support. The work was partly financed by the DFG (Grant KU920/3, Grant KU920/9, Grant KU920/11), BMBF (Grant 03GO553A) and EC (Grant ENV4-CT97-5048).

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