7C2, the new neutron diffractometer for liquids and disordered materials at LLB

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Abstract.

The disordered-materials diffractometer 7C2 at the Laboratoire Léon Brillouin (LLB), Saclay, France has been upgraded through the replacement of its detector. The old one, a banana like BF\textsubscript{3} detector, has been replaced by a new ensemble of \textsuperscript{3}He tubes arranged on a cylindrical surface concentric with the sample position, covering an angular range of 133°, with an angular step of 0.52°. At the shortest wavelength, 0.57 Å, this represents a maximum momentum transfer of 20 Å\textsuperscript{-1}. The gas pressure in the \textsuperscript{3}He tubes is 30 bars, which increases the efficiency to 80% for 0.72 Å neutrons, compared to 17% for the previous detector. A larger solid angle of detection and an improved efficiency have increased the total counting rate by a factor of 22, thereby reducing random error in the diffraction measurements. The banana-like multidetector gives to 7C2 the possibility of registering a complete diffractogram over the whole angular range in one shot, which is a comparative advantage with respect to other hot-neutrons two-axis diffractometers.

1. Introduction

The pair distribution function (PDF) for liquids and amorphous systems (or more generally, systems with no long-range order: nanoparticles, poorly crystallised materials, etc.) is the Fourier transform of the structure factor determined from diffraction experiments, giving detailed information on the short to intermediate length scales. This Fourier transform is an integral over the momentum transfer $Q$, which should extend up to infinity \cite{1}. This is the reason why the accurate determination of structure factors for disordered materials requires the precise determination of the scattered intensity over a wide range of momentum transfer. This momentum transfer is usually approximated by that corresponding to elastic scattering and given by the Bragg’s law ($Q = 4\pi/\lambda \sin \theta$, where $\lambda$ is the neutron wavelength and $2\theta$ is the scattering angle).

In the case of X-ray diffraction, because the interaction happens with the electronic cloud and can not be considered as punctual, the atomic form factor (strongly decreasing with $Q$) produces structural information only in a limited $Q$-range. On the other hand, neutron diffraction is a very well suited technique because the scattering power of a given nucleus is independent of
the momentum transfer, as consequence of the short range interaction between the neutron and the nucleus [2]. This scattering power is proportional to the square of the tabulated scattering lengths [3, 4].

Considering again the Bragg’s law, for a given scattering angle, the shorter is the wavelength the larger is the corresponding $Q$-value. Thermal neutrons (with energies around 25 meV) will produce diffractograms with a maximum momentum transfer of about $7$ to $10 \, \text{Å}^{-1}$, which is rather small for a good Fourier transformation. But using neutrons of wavelengths shorter than $1 \, \text{Å}$, i.e., with some hundreds of meV, the momentum transfer range can be increased up to $25$ or even $30 \, \text{Å}^{-1}$. In reactor sources, like Orphée reactor at Laboratoire Léon Brillouin (LLB), this is achieved using a hot source kept at high temperature ($1400 \, \text{K}$), where neutrons are thermalised at about $120 \, \text{meV}$. The High Flux Reactor at ILL (Institut Laue Langevin) has a hot source at $2400 \, \text{K}$, where neutrons are thermalised at about $170 \, \text{meV}$. In spallation sources, like ISIS in UK or SNS in USA, the attainable $Q$-range extents even up to $50 \, \text{Å}^{-1}$ [5, 6, 7].

![Figure 1. Sketch of the 7C2 instrument before changing the detector. A white beam of hot neutrons comes from the reactor’s hot source and is monochromatised by one of the three available monochromators. Then the beam pass the monochromator shielding through a collimation tube, before being transmitted by a filter which removes the harmonic wavelengths. An almost transparent monitor register the beam intensity for normalisation purposes. A diaphragm defines the beam geometry and size on the sample, which is located in the centre of a cylindrical vacuum chamber. Finally, the diffracted beam is registered by the banana-like multidetector.](image-url)
The main advantages of the reactor-based instruments (when compared to spallation-based ones) are the simplicity of the corrections and the counting stability (extremely important for isotopic substitution experiments). The two-axis diffractometers dedicated to liquids and amorphous systems in Europe are D4 at ILL [13] and 7C2 (Fig. 1) at LLB [8], and the former is considered as a reference in the field of disordered matter. In spite of its lower intensity (25 times smaller that D4), 7C2 had (and still has) the advantage of its banana-like multidetector and its sample changer. The upgrade of the instrument was then justified by the need of keeping it competitive with other available instruments.

2. The instrument
The 7C2 instrument is located on one of the two beam-tubes looking at the hot source of the Orphée reactor at Saclay [8]. A system of three monochromators (Ge 111, Cu 111 and Ge 311) on a rotating table allows changing the wavelength among three standard values (1.1, 0.72 and 0.57 Å), which are determined by the availability of suitable $\lambda/2$ filters.

After the monochromator, the beam is filtered in order to remove the harmonics of the main wavelength $\lambda$ ($\lambda/2$, $\lambda/3$, etc.), then it passes through an almost transparent detector serving as monitor for normalisation purposes. The final flux on the sample is $10^6$-$10^7$ neutrons/cm$^2$/s.

Finally, a diaphragm defines the size and geometry of the beam at the sample position, which is at the centre of a cylindrical vacuum chamber (Fig. 1). In addition to the standard room temperature experiments, the big vacuum chamber allows several sample environments, like cryostats, furnaces or pressure cells. The instrument has the possibility of using a 5-positions sample changer (Fig. 2), but only for room temperature experiments.

Thanks to the multidetector, a diffractogram can be registered in one shot allowing in situ experiments, like thermodiffractometry. This is a possibility that other dedicated reactor instruments for liquids and amorphous systems can not offer.

![Figure 2. Left: a view of the cylindrical vacuum chamber; the sample is located at the center of this cylinder. Right: the 5-positions sample changer, with a shielding to reduce the contribution from the other 4 samples; on the right we see the diaphragm defining the size and shape of the beam.](image-url)

3. The detector
The previous detector was a banana like multidetector, i.e., a one dimensional position sensitive detector, consisting of 32 blocks of 20 cells (Fig. 1). Each block was composed of a cathode with anode wires of 40 $\mu$m in diameter, at working voltages of $-2700$ V and $+2900$ V, respectively.
Figure 3. General view of the new detector. In white we see the polyethylene serving as shielding for the detector tubes. The ensemble is mounted on air pads allowing the movement of the whole detector array around the monochromator position.

The filling gas was $^{10}$BF$_3$ at a pressure of 1 bar, giving efficiencies of 30%, 17% and 12% for wavelengths of 1.1 Å, 0.72 Å and 0.57 Å, respectively. The spacing between two cells was 5.2 mm, which combined with a sample-detector distance of 1.5 m gave an angular step of 0.2° and an angular range of 128°. The main drawback of this detector was the low efficiency, as compared to the efficiency of $^3$He gas detectors, which motivated a project for replacing this $^{10}$BF$_3$ detector.

At present, 256 $^3$He gas tubes replace the $^{10}$BF$_3$ detector. These tubes are 0.5 inches diameter, 30 bars $^3$He filled, position sensitive detectors (PSD) from Reuter-Stokes (GE Energy company), working at high voltage (1700 V). They are also located in a banana like configuration, at 1.5 m from the sample position, as it is shown in Figures 3 and 4(top). The distance between tubes is 13.7 mm, giving an angular step of 0.52° and covering an angular range of 133°. The high pressure in the tubes, 30 bar, gives an efficiency of 80% for neutrons of 0.72 Å. This efficiency must be compared to the previous efficiency at the same wavelength, i.e., only 17%.

The tubes have a length of 500 mm and are equipped with PSD electronics from Mesytec company. This charge division electronics makes the detectors also sensitive to the vertical position, then we divide tubes in 64 vertical pixels. In this way, the detector becomes a 2D-detector. Figure 4 (bottom) shows a typical diffractogram for the Ni powder sample, which is used to calibrate the wavelength and zero-angle correction. We observe the intersection of the Debye-Scherrer cones with the detector surface, which are clear at low angles but become less apparent at higher angles.

With the new detector the angular definition passed from 0.2° to 0.52°, but this has no important consequences to the average resolution of the instrument in Q-scale. The low-to medium-resolution in Q-scale is the consequence of using short-wavelength neutrons, and depends on the scattering angle 2θ. The best value is found at around 20°, where it is $\Delta Q/Q = 0.02$, corresponding to $\Delta 2\theta \approx 0.4^\circ$, and it is worst elsewhere. Then the angular definition of 0.52° does not affect the resolution of the structure factor. This low resolution
could be a problem for polycrystalline samples, but not for disordered systems.

The new detector array represents a factor 22 in gain when compared with the previous detector: a factor 5.5 thanks to the bigger solid angle and a factor 4 because the better efficiency. Now the new 7C2 has a global efficiency comparable to the reference instrument in the field. Nowadays, the main advantage of D4 is the fact of being located in a reactor 5 times more intense than Orphée reactor.

Figure 4. Top: the 16 moduli of detectors, each one composed of 16 detectors, placed at 1.5 m from the sample in a circular section centred at the sample position. Bottom: A 2D diffractogram corresponding to a polycrystalline sample of Ni powder. The coordinates are given in pixels (256 × 64), but the abscissa represents the scattering angle and the ordinate is the vertical position along the tubes. Several peaks are clearly distinguished at low angles, but then the other peaks are less apparent due to the low resolution of the instrument.
4. Data reduction
The raw data, as those shown in Fig. 4(bottom) must be corrected for the relative efficiency of the detectors and radially integrated in order to obtain a 1D-diffractogram. The resulting diffractograms are corrected for inelasticity [9], multiple scattering [10] and attenuation [11] using standard programs like CORRECT [12] or others, which finally leads to the static structure factor (see Ref. [1]). Then, this structure factor is Fourier transformed to determine the final pair distribution functions in real space.

5. Discussion
The new 7C2 instrument with its factor of gain about 22 with respect to the previous version, is almost as performant as its main competitor D4 [13], also a reactor based instrument at the Institut Laue Langevin. The flux on the sample is still 5 times lower than that at D4, but this is only due to the different operation power of both reactors. In fact, 7C2 has two advantages when compared with D4. The first one is the banana-like multidetector covering 132° and the possibility of registering a whole diffractogram in one shot, which allows in situ experiments as thermodiffractometry. The second advantage is the 5-positions sample changer, which is an extremely useful tool for room-temperature experiments.

Figure 5. The neutron static structure factor for a series of samples of (HgI$_2$)$_x$-(As$_2$Se$_3$)$_{1-x}$ where $x = 0.1, 0.2, 0.3, 0.4, 0.5$, as determined from 7C2 data after about 8 h of counting. For the sake of clarity, the curves are shifted by $10x - 1$.

Comparing the instrument with those in pulsed sources, the main disadvantages are the limited momentum transfer range (which could be as high as 50 Å$^{-1}$ in pulsed sources [5, 6, 7])
and the low resolution in reciprocal space. But the latter requirement is less critical for high temperature measurements, for which the oscillations do not extend over a large \( Q \)-range. The widely used vanadium furnace, allowing experiments up to 1400 K \([8]\), lead to an accurate determination of structural features in important silicate liquids, such as the window glass/melt \([14]\).

6. Preliminary results

As an example of data recently collected at 7C2, we chose the structure factor determination of a series of chalcogenide glasses.

Chalcohalide glasses have optical applications that need a wide transparency window especially in the far-IR region. Increasing the atomic number of a glass former causes a significant red shift in the low-frequency spectral domain from 11 \( \mu \text{m} \) in sulphide, to 15 \( \mu \text{m} \) in selenide and finally to 19-22 \( \mu \text{m} \) in telluride glassy binaries. Moreover, the average atomic number in the glass can be further increased by heavy-metal and heavy halogen doping \([15]\). Promising chalcogenide and chalcohalide glass systems include thus heavy-metal iodides: \( \text{SbI}_3 \), \( \text{PbI}_2 \) and \( \text{HgI}_2 \). While structural features of antimony and lead iodide and chalcogenide glasses have been studied in the past using diffraction and spectroscopic techniques, the atomic structure of mercury containing chalcogenide glasses is hardly known. The high absorption cross section of \( \text{Hg} \) makes the neutron diffraction experiments difficult, but the use of the hot-neutron spectrum at Orphée reactor reduces that absorption to 1/3 of the absorption for thermal neutrons.

The Figure 5 shows preliminary results on the static structure factor for the series \( (\text{HgI}_2)_x (\text{As}_2\text{Se}_3)_{1-x} \) where \( x = 0.1, 0.2, 0.3, 0.4, 0.5 \). For the sake of clarity, the data were shifted in the vertical axis by 0, 1, 2, 3 and 4, respectively. Each diffractogram corresponds to about 8 hours of measurement on a sample of 3 g. The working wavelength of 0.576 Å allows a \( Q \)-range extending to almost 20 Å\(^{-1}\).

7. Conclusions

The two-axis instrument 7C2 is a new diffractometer dedicated to the structure of liquid, amorphous and disordered materials. It has been recently commissioned (March 2012) at the reactor Orphée in Saclay, France, substituting the previous version \([8]\). This is a state-of-the-art instrument comparable with their main competitors in the field \([5, 6, 7, 13]\). Its banana-like multidetector allows in situ experiments, such as thermodiffractometry.

Thanks to the hot neutron source, the momentum transfer range is long enough to perform proper Fourier transforms of the static structure factor, leading to the PDF with good resolution in real space. The instrument allows also experiments on nano-particles, for which the PDF analysis has demonstrated to be specially useful \([16]\).

In addition, the short-wavelength neutrons reduce the absorption cross section, increasing the feasibility of neutron diffraction experiments on highly-absorbent samples like those containing mercury or rare earths (\( \text{Sm}, \text{Eu}, \text{etc.} \))

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