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Neutron scattering at high temperature and levitation techniques

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Abstract. Studies of the liquid state present an obvious fundamental interest and are also important for technological applications since the molten state is an essential stage in various industrial processes (e.g. glass making, single crystal growing, iron and steel making).

Most of the physical properties of a high-temperature liquid are related to its atomic structure. Thus it is important to develop devices to probe the local environment of the atoms in the sample. At very high temperature, it is difficult to use conventional furnaces, which present several problems. In particular, physical contact with the container can contaminate the sample and/or modify its structural properties. Such problems encouraged the development of containerless techniques, which are powerful tools to study high-temperature melts. By eliminating completely any contact between sample and container, it is possible to study the sample with a very high degree of control and to access very high temperatures. An additional advantage of levitation methods is that it is possible to supercool hot liquids down to several hundred of degrees below their equilibrium freezing point, since heterogeneous nucleation processes are suppressed.

1. Introduction

While studies of liquids at high temperatures present an obvious interest from a fundamental point of view, they also present significant technological interest since the molten state is an essential stage in various industrial processes (glass making, semiconductor technologies, aerospace companies, iron and steel industry, etc.). The high-temperature properties of oxide minerals or iron-based liquid alloys also play a crucial role in the geophysical behavior of the Earth.

Despite a considerable number of studies performed over the past 50 years, the liquid state is still not well understood. It is therefore important to develop experimental techniques as well as numerical simulation capabilities for studying the properties of high-temperature liquids.

Studies of liquid materials at high-temperature have to contend with various problems when they are carried out in a traditional furnace where the sample is held in a container:

- Chemical reactions between the sample and the container.
- Contamination of the sample from the container.
- Difficulty of reaching temperatures above 1500°C.
- Difficulty of undercooling the sample due to heterogeneous nucleation.

The use of containerless methods avoids these problems. Over the past few years an increasing number of studies devoted to high-temperature molten materials have been carried out as a result of the development of levitation techniques. Several laboratories around the world have developed various kinds of levitation apparatus, including acoustic, electromagnetic, electrostatic and aerodynamic levitation techniques. They have been applied to determine physical properties of levitated liquids. A recent review can be found in Ref. [1]. Some of them have been combined with x-ray and neutron scattering techniques to study the structure and the dynamics of molten materials.

The CEMHTI in Orléans has chosen to combine aerodynamic levitation with a CO_2 laser heating [2, 3, 4]. The advantages of the technique are the simplicity and compactness of the device that allows its integration into different kinds of experiments. This technique makes it possible to access very high liquid temperatures while maintaining the sample's purity, and to investigate metastable states in the undercooled temperature range, down to a few hundred degrees below the equilibrium melting temperature.

2. Levitation techniques

The principle of levitation is to create an opposing force to counteract the gravity of the sample and lift it away from support structures. In the past, five main levitation methods have been combined with x-ray and neutron scattering techniques at synchrotron and neutron sources: single-axis acoustic levitation (SAL), electromagnetic levitation (EML), electrostatic levitation (ESL), conical nozzle levitation (CNL) and gas film levitation (GFL).

2.1. Electromagnetic levitation

Electromagnetic levitation is mainly suitable for electrically conductive materials. It will be discussed here only briefly since a detailed description of the EML can be found elsewhere [5, 6].

With EML a radio-frequency electromagnetic field is generated by a levitation coil and Foucault currents are induced in the sample. This leads to an inductive heating of the sample, and at the same time, the interaction of the Foucault currents with the magnetic field of the coil leads to a force that counteracts gravity and makes it possible to levitate the sample. The electromagnetic force applied on the levitated sample depends on the power absorbed by the latter. It is essentially a function of the square of the magnetic field strength and the electrical conductivity of the sample material. So by varying the heating power, one can control the temperature of the sample. The levitation coil is situated in a vacuum chamber which is first evacuated and then filled with a very high purity gas, usually He or a mixture He plus a few percent of H_2.

2.2. Electrostatic levitation

With ESL [7, 8], the sample is electrically charged and levitated in a vertical electro-static field between two electrodes. Two pairs of smaller side electrodes are used to position the sample horizontally. When it levitates, the sample is melted using lasers. With this method, it is possible to study all samples that can be electrically charged. This method has various advantages. First, it works under vacuum, preventing contamination, and allows studying poor electrical conductors or materials with a low melting point. One drawback is the complexity of the setup that limits its combination with various spectroscopies. While some insulating oxides can be studied with this technique, it is used mostly with metals.

2.3. Acoustic levitation

Acoustic levitation can suspend small objects via the acoustic radiation force that results from an impedance difference between the suspension medium, normally a gas, and a solid or liquid

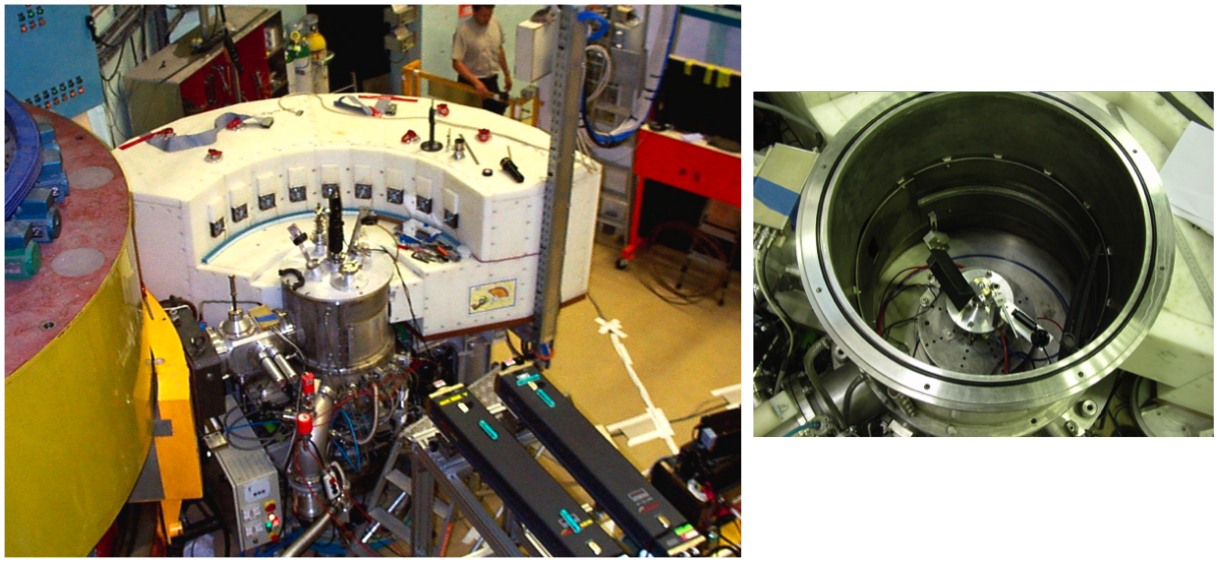

Figure 1. Aerodynamics levitator for neutron diffraction measurements of liquids and supercooled samples. Installation at D4 instrument at ILL.

sample. A single-axis acoustic levitator consists mainly of two parts: a vibrating source (or transducer) generating ultrasound (a few tens of kHz) and a reflector with a concave surface to improve the efficiency. The vibrating source-reflector axis is parallel to the direction of gravity and an acoustic wave is generated along this direction to counteract gravity.

SAL can be used to study low melting point alloys and non-conducting materials as well as room temperature liquids. In the past, Trinth developed a device enabling to work up to 700°C [9]. Resistive heating coils were used to heat the sample. But even though, the accessible temperature range is limited and this technique is not for very high temperature studies.

2.4. Gas film levitation

Developped by Granier and Potard [10], gas film levitation enables the levitation of an object against gravitational force by floating on a thin gas film formed by gas flow through a porous membrane. The gas film thickness is typically several tens of micrometers. With this technique, it is possible to levitate a large amount of material (a few grams), which can be heated using a furnace, for instance. This technique could be also employed for viscosity measurements [11]. This is the main drawback of this levitation technique for its use in neutron scattering experiments, because the beam touches the membrane and its support. Moreover, the shape of the levitated sample is almost flat, which is not well suited for diffraction experiments, although it could be useful for reflectometry. The proximity of the sample to the membrane prevents the use of high temperature with GFL.

2.5. Conical nozzle levitation

Aerodynamic levitation was first developed in the seventies [12] then later adopted at the CEMHTI [13] for RMN studies. It has proved to be a powerful and versatile technique for studying highly reactive liquids in the equilibrium melt and the supercooled liquid state several hundred Kelvin below the melting point [14]. In particular, it is now widely used with neutron and x-ray diffraction techniques to investigate the structural properties of liquids [14, 15, 16]. The working principle of aerodynamic levitation is well known and is described in detail elsewhere [17]. The basic idea is to circulate levitation gas (usually argon) through a nozzle onto the sample

from below in order to counteract gravity and lift it above the nozzle. The sample is then heated to the desired temperature by means of one or two focused CO_2 lasers. The levitation gas flow is accurately regulated and monitored by a mass flow controller enabling to maintain the sample sufficiently stable for long counting times.

In comparison to the other levitation techniques (e.g. applying electrostatic [7], electromagnetic [18] or acoustic [19] fields), it has the outstanding advantage of supporting and melting any type of material ranging from insulators through semiconductors to metals. A current drawback is that samples need to be relatively small (ø $\approx$ 3 mm) in order to assure aerodynamic stability, but progress is now being made in this area.

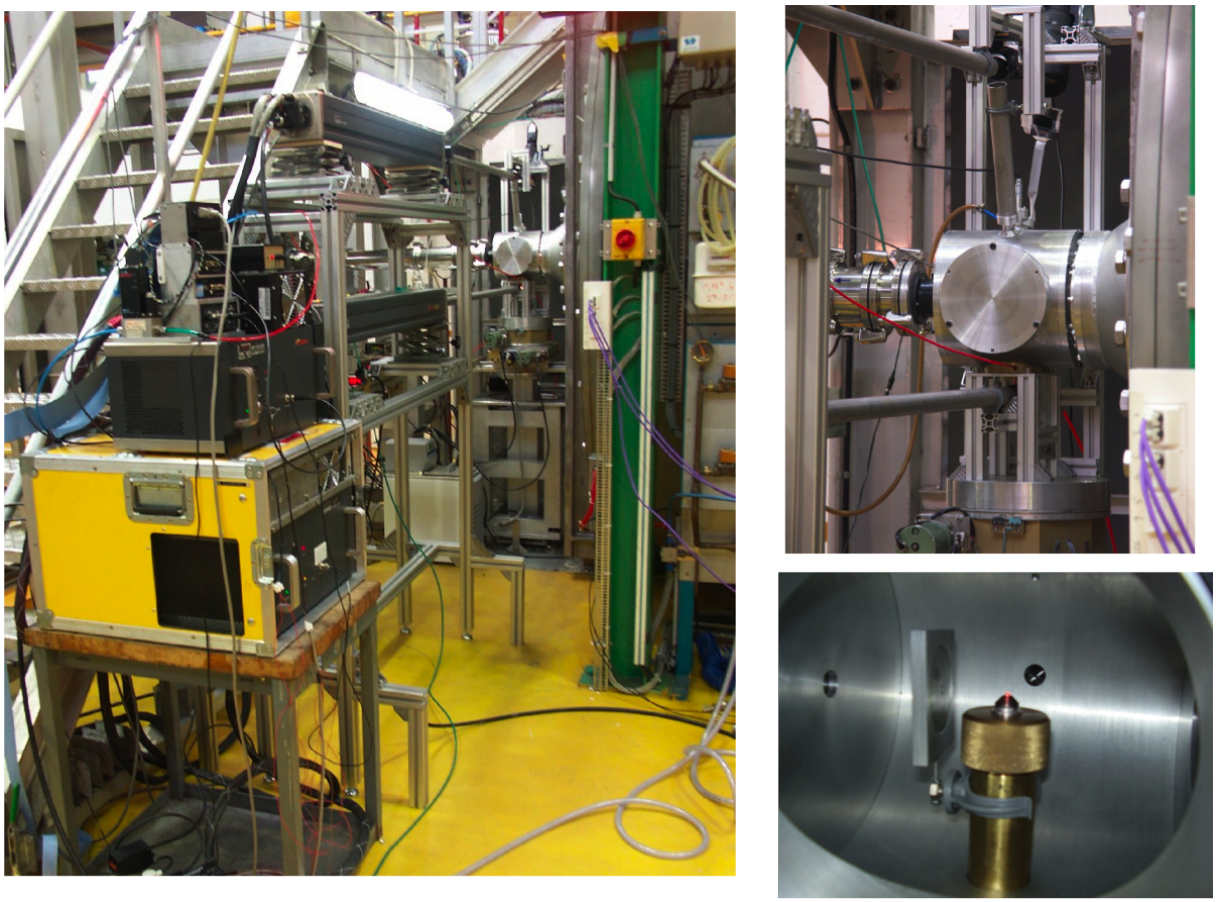

Figure 2. Aerodynamics levitator for small angle neutron scattering. A photo from measurements on D22 instrument at ILL.

3. Levitation at ILL

At the Institute Laue-Langevin (ILL) almost all previously mentioned techniques have been used on different instruments. The majority of such experiments have been performed in collaboration with external groups bringing the equipment to ILL. In the case of SAL and CNL techniques, the ILL staff is developing standard systems that in a near future should be available as standard environment for several instruments.

3.1. Aerodynamic levitator

An aerodynamic levitation setup has been specially designed for neutron diffraction experiments. Figure 1 is a schematic view of the levitation setup integrated into the D4c diffractometer at ILL. This device is described in detail by Hennet et al. [14] and we give here a short description of the working principle. The spherical sample is levitated in a convergent/divergent nozzle under an argon/oxygen (3%) gas flow and heated to the desired temperatures by two 125 W CO_2 lasers directed from above. The laser beams are focused on the sample by means of spherical mirrors at two different angles in order to obtain a homogeneous temperature distribution. Two NaCl windows are used to transmit the beam into the vacuum chamber. The pyrometer is placed inside the chamber to avoid window corrections. A third laser directed at the sample from below through the nozzle is used to compensate the cooling of the sample by the gas flow. A high-quality video image of the sample taken from above is continuously displayed in order to monitor the levitation of the sample during heating. Video images of the sample are also displayed with a horizontal camera in order to determine the sample position in the levitator and to monitor the vertical stability.

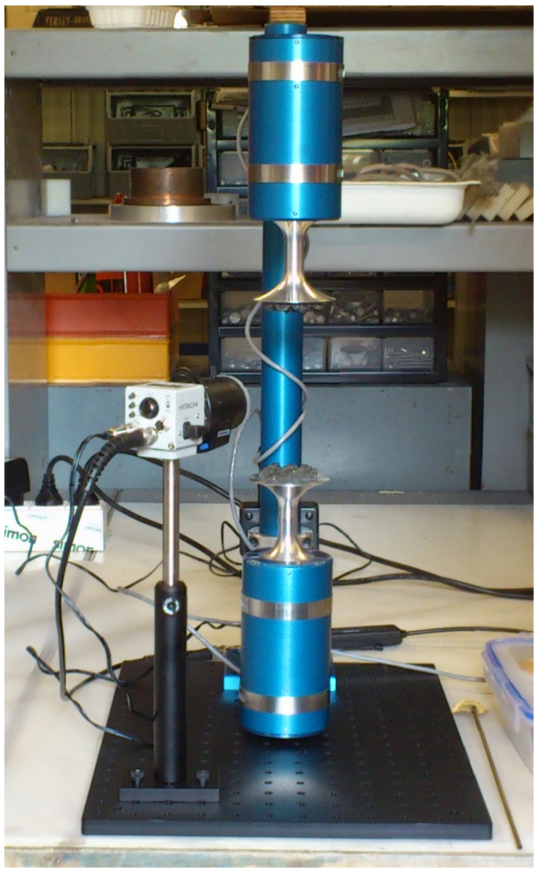

Figure 3. The single-axis acoustic levitator present at ILL.

For small angle neutron scattering measurements the laser-heated containerless aerodynamic levitation technique was adapted to D16 and D22 instruments at ILL. A picture of the set-up on D22 instrument for SANS measurements is showed on Figure 2. It uses two lasers, one from above and another from below, to heat a small sample (2.5 mm to 3 mm diameter) that is aerodynamically levitated about 1 mm above a small nozzle. For metallic samples, we use Ar gas whose oxygen content has been reduced to about 0.1 ppm by our gas purifier, whereas for

oxide samples we use Ar with 3% oxygen content. Our setup at D22 uses stainless-steel gas-flow tubing. One pump-down and then filling with pure Ar in order to run metallic samples at high temperature for several hours without oxidation problems.

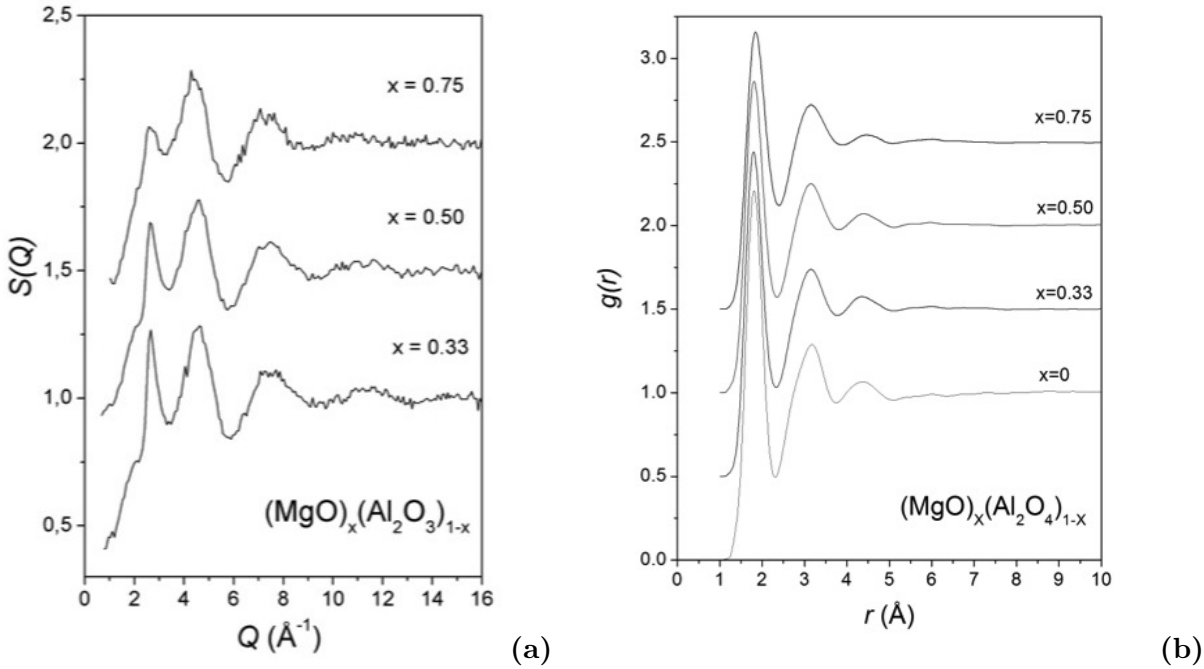

Figure 4. (a) Average structure factor $S(Q)$ for liquid $(\mathrm{MgO})x(\mathrm{Al_2O_3})_{1-x}$ at 2400 K measured on D4 at ILL. Curves have been shifted up for clarity. (b) Corresponding pair distribution functions $g(r)$. [20]

3.2. Acoustic levitator

A single-axis acoustic levitator installation has been recently used for neutron scattering measurements at ILL [19]. This apparatus consists of two vertically-opposed, high-output acoustic transducers that operate at a frequency of 22 kHz and can produce sound pressure levels to 160 dB. The produced acoustic waves are monitored from the amplifier using an oscilloscope. The levitator is composed of three main parts (Fig. 3): the levitator assembly, the ultrasonic power amplifier, and the acoustic controller. The transducers are mounted in aluminum tubes and located on a metal stand. Acoustic absorbing foam disks approximately 50 mm in diameter were glued onto the face of the transducer horns to reduce unwanted reflections that can cause instabilities in the levitated sample. Samples are introduced into the "sound field" using a small syringe or a wire gauze spoon and can be translated by adjusting the phase between the transducers or squeezed by modulating the acoustic levels with variable frequencies. To remove the sample we have simply to use the spoon for the solid samples or a flat surface for liquids. In order to avoid missing samples in the basement of the levitator a plastic film is positioned in a way to cover the entire surface. At present the levitator can only be used at room temperature. For doing experiments at low temperatures, the use of a cryostream is necessary, but this possibility is still under study. The cryostream nozzle would be arranged at approximately 50 mm to 100 mm from the sample in a way that the cooling gas is flowed over the levitated sample. The SAL is easily to install and can be integrated in several instruments present at ILL for the in-situ investigation of materials and aqueous solutions.

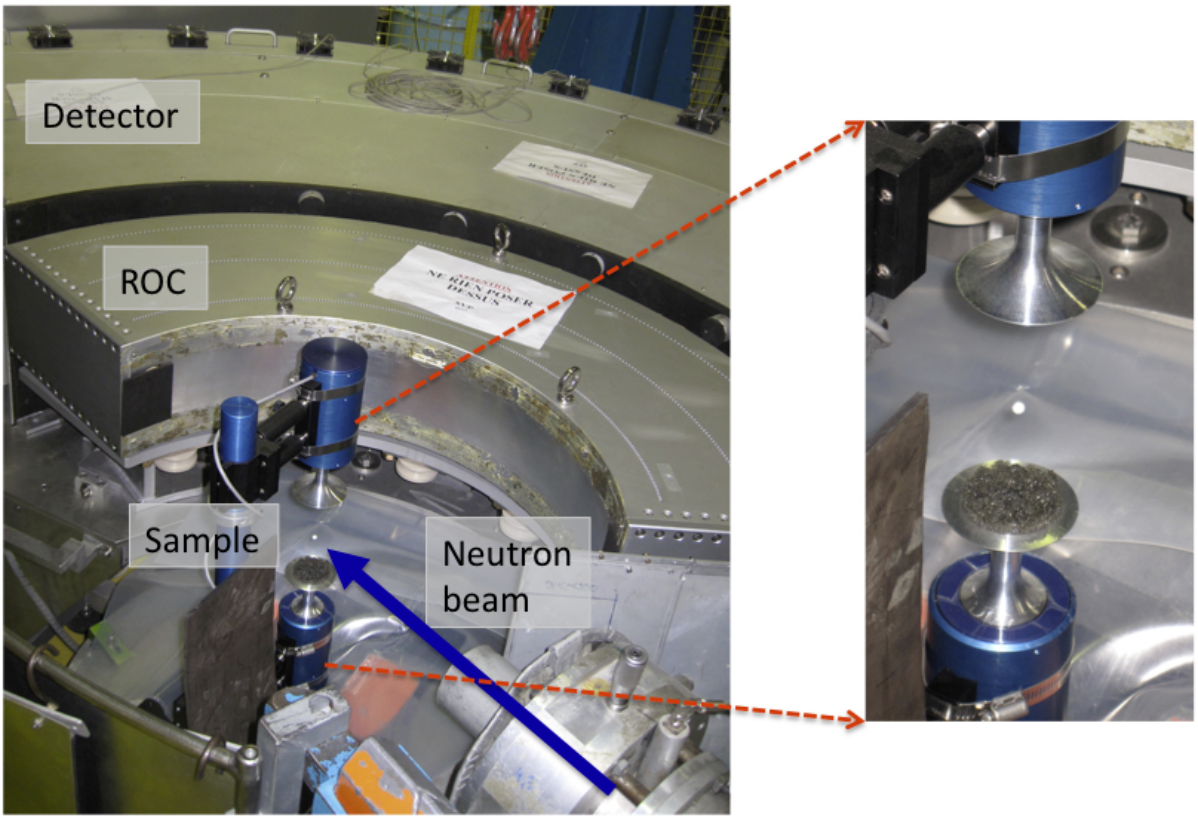

Figure 5. The left picture shows the acoustic levitator placed at the two-axis neutron diffractometer D1B. The neutron beam, sample, ROC and detector are shown. The right picture zooms on the levitated polystyrene sphere.

3.3. Examples

We present in the following a study of three $(MgO)_x(Al_2O_3)_{1-x}$ liquid magnesium aluminates oxides. MgO- and Al_2O_3-containing materials have a strong geophysical and technological importance. They constitute a large fraction of Earth's mantle and they are being considered as inert matrices for nuclear waste confinement, due to their stability under irradiation, high melting point, and high thermal conductivity. In particular, the high melting point (T_m = 2400 K) makes their structural investigation extremely difficult, for that reason the levitation device become essential to carry out the measurements.

Figure 4a shows the $S(Q)$s measured on some magnesium aluminates with x = 0.33, 0.50 and 0.75 using the levitation set-up integrated into the D4c diffractometer [14]. With the aerodynamic levitation, statistics are limited by the relatively small sample size that can be levitated. However, reasonable statistics can be obtained. In figure 4b $g(r)$s are presented. Fitting these curves is possible to determine the interatomic distances and the coordination numbers for each pair of atoms for each sample in order to characterize the structure in function of the composition.

Recently it has been tested the feasibility of accomplishing a levitation experiment at D1B using the acoustic levitator, as shown in Fig. 5. D1B is a high flux, medium resolution powder diffractometer at ILL. Although this instrument was designed mainly for determining magnetic structures and phase transition studies on powder samples, several times it has proved its capabilities for studying structural properties of liquids and gases [22, 23, 24, 25]. Due to its

geometrical characteristics and set of monochromators, it is possible to obtain in a few minutes a diffraction pattern over a Q range of 8.82 Å^{-1}.

For this test, polystyrene samples were placed in the center of D1B neutron beam while levitating (Fig. 5). As usual, a radial oscillating collimator was used to reduce the background produce by the sample's surroundings. Solid samples are stable for several hours and it is possible to place few samples in the beam along the vertical axis of the levitator, using the nodes of the standing wave. We have also levitated drops of light and heavy water and collected the corresponding diffractograms; in this case, some sample is lost due to the slow evaporation at ambient conditions. In the case of polycrystalline powder samples, the main problem is to finding a way to keep the powder in the beam. In this test we use Si powder as sample, and this powder was wrapped in Al foil. The Fig. 6 illustrates the diffraction pattern of 17 mg of Si wrapped in 12 mg of Al foil collected along 60 minutes. One can observe the diffracted peaks arising from the Si and Al, which are perfectly suitable for Rietveld refinement.

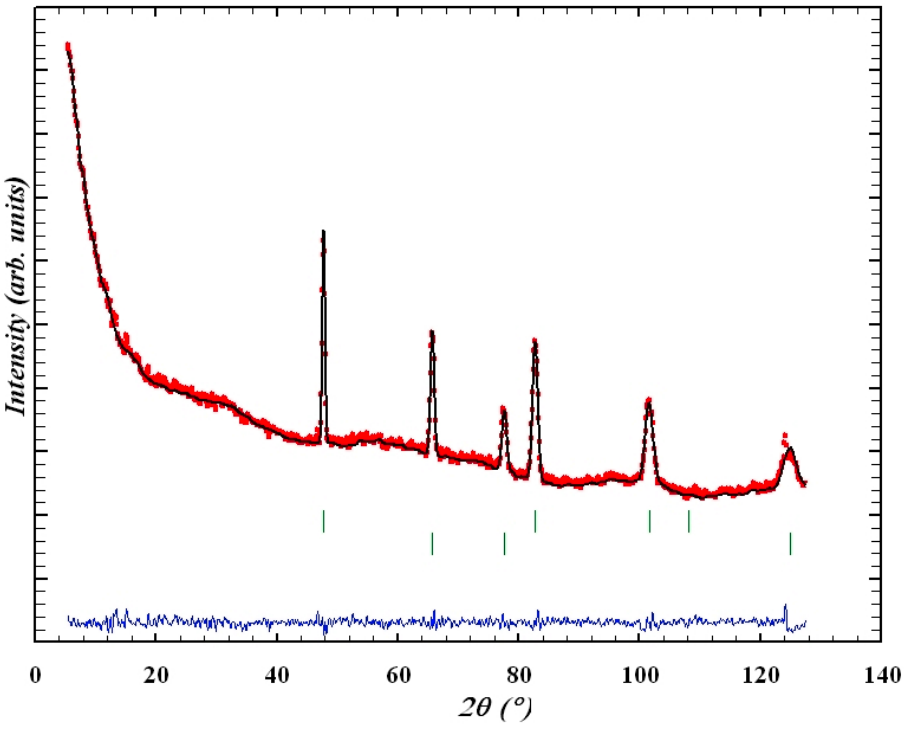

Figure 6. (colour online) Observed (dot) and calculated (solid line) diffraction pattern of 17 mg Si wrapped in a 12 mg Al foil, after a data collection of one hour at a wavelength of 2.52 Å. The vertical bars indicate the position of the Bragg diffraction reflections; first row corresponds to the Bragg reflections belonging to Si and the second to those of the Al. The difference between observed and calculated is depicted on the bottom of the figure.

4. Conclusions

The sample environment is a critical component of research programs in advanced materials, geological systems, biology, and energy-related research and development. Levitation techniques have an increasing interest in recent years as important tools for scattering experiments. The main reasons for this interest are the low background signal, the purity of the sample and the possibility of performing experiments with small amounts of samples. In particular, we have shown that diffraction experiments are possible on D4, D1B and D22 with samples of only a few tens of mg. Among the different containerless methods, aerodynamic levitation combined with laser heating has proved to be a powerful and versatile technique for studying the structure, dynamics, and macroscopic properties of high-temperature liquids including insulating compounds (glasses, ceramics, and oxides) and metallic materials. The use this techniques is mainly adapted for studies of materials above the melting point and in the supercooled state condition maintaining a high degree of control in temperature. In particular, the atomic structure of liquid materials can be determined by measurements of the structure factor $S(Q)$ and calculation of the corresponding pair correlation function $g(r)$, as reported in this paper. The acoustic levitation is originally designed for the investigation of supercooled liquids and aqueous solutions in the temperature range from about -40 C to $+40$ C. This temperature range covers the supercooled region for water and many salt and biological solutions. By eliminating contact with container walls, sources of heterogeneous nucleation are avoided and it often becomes possible to cool liquids substantially below their equilibrium melting point. Here we show that this technique can be also adopted for powder diffraction with a small amount of sample in the beam obtaining good data quality necessary to make the data refinement. In particular, we have shown that diffraction experiments are possible on D4, D1B and D22 with samples of only a few tens of mg. The high adaptability on different neutron instruments of the levitation devices presented in this article offers the possibility to combine different neutron techniques. This is a very important point for an exhaustive analysis of materials based on multi-techniques and multi-scale approach.

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