ESRF	**Experiment title:** Two level states in ultra-stable and conventional glasses	**Experiment number**: HC 5322
Beamline: ID18	**Date of experiment**: from: 08 Mar 2023 to: 13 Mar 2023	**Date of report**: 18 Sept 2023
Shifts: 15	**Local contact(s)**: Dimitrios Bessas (bessas@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Irene Festi*
Department of Physics, University of Trento (IT)

Dr. Cristian Rodriguez-Tinoco*
Departament de Física. Facultat de Ciències, Universitat Autònoma de Barcelona (ES)
Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB (ES)

Erica Alfinelli*
Department of Physics, University of Trento (IT)

Prof. Javier Rodriguez-Viejo
Departament de Física. Facultat de Ciències, Universitat Autònoma de Barcelona (ES)
Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB (ES)

Mr Federico Caporaletti
Laboratory of Polymer and Soft Matter Dynamics, Experimental Soft Matter and Thermal Physics (EST), Université libre de Bruxelles (BE)

Dr. Giacomo Baldi
Department of Physics, University of Trento (IT)

Report:

The purpose of the experiment is to measure the vibrational density of states (DOS) at low frequencies of an ultra-stable glass, at temperature 150 K. By comparing it with the DOS measured at room temperature on an equivalent sample (see exp. report HC-4933), these data allow us to understand the behaviour and the temperature dependence of the an-harmonic contribution at low energies (below 1 meV). The goal of the experiment has been slightly modified with respect to the text of the proposal. Additional data analysis on the previous experiment allowed us to realise that the low temperature data would have been more useful than the measurement of the extended spectrum on the conventional TPD glass.
In the previous experiment, we needed approximately one day of integration to obtain enough statistics for the high-resolution spectra. The low temperature measurements, at 150 K, needed at least four days of integration to obtain a comparable signal to noise. For this reason, we asked and obtained an extension of the beamtime from 6 to 15 shifts.

The DOS measurement was performed at the beamline ID18 of the ESRF on a film of TPD ultra-stable glass, 50 μm thick. The sample was placed inside a Helium exchange-gas cryostat and set at 150 K. The experiment was conducted in inverse geometry, where the output energy was fixed at E_0 = 14.413 keV, which is the nuclear transition energy of ^{57}Fe. Through a spectrometer for inelastic X-ray scattering with nuclear resonance analysis (NRAIXS), it was possible to reach an energy resolution of 130 μeV. The X-ray beam hit the sample in transmission geometry and the inelastic scattered X-ray radiation was collected by a detector located 1 mm far apart from the sample, reaching nearly π of solid angle. The transmitted beam was collected by a similar detector in a forward position to measure the instrumental response. Each detector consisted of large area avalanche photodiode (APD) covered by a 10 μm thick ^{57}Fe foil, to exploit the Mössbauer effect, which allows to measure the scattered photons at fixed energy E_0 with an energy resolution in detection (0.5 μeV), which is negligible with respect to the input energy uncertainty.
The high-resolution energy spectra were measured as a function of the exchanged energy. The energy range was [-6,10] meV, with an energy step of 0.02 meV; for each point, the integration time was set to 2 seconds. The total amount of collected scans is 168.
Since at frequencies higher than 10 meV the energy spectra are not expected to depend on the temperature, spectral measurements in an extended energy range at 150 K were not required. To evaluate properly the DOS at 150 K, we used the extended spectra measured at room temperature during the experiment HC-4933.
During the experiment, the structure factor of the glasses was measured several times by exploiting the theta-2theta geometry, to check the sample's conditions. The static structure factor appeared unaffected by the beam, suggesting stability of our sample under this level of X-ray radiation.

The raw data of the energy spectrum of the ultra-stable glass at temperature 150 K are shown in figure (1). To obtain them, the scans are summed all together and the elastic peak is removed (figure (2)). The DOS we evaluate from these data exhibits some difference below 0.6 meV from that measured at room temperature, suggesting that an anharmonic contribution is present in the DOS in the low energy region at finite temperature. This allows us to evaluate correctly the specific heat starting from the DOS, since anharmonic contributions at high temperature are more and more suppressed as the temperature decreases in the specific heat. In addition, the specific heat obtained starting from the DOS at 150 K agrees with that measured via calorimetry experiments at the University of Barcelona.
These results and those from the previous experiment are very promising. We plan to submit the results in a high impact factor journal in the next few months.

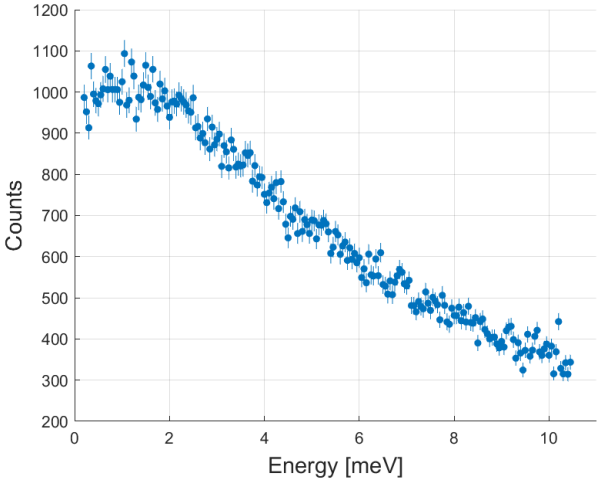

Figure (1): energy spectra of the ultra-stable glass at 150 K, raw data. The intensity is obtained by subtracting the elastic peak, by exploiting the instrumental response measured by the forward detector.

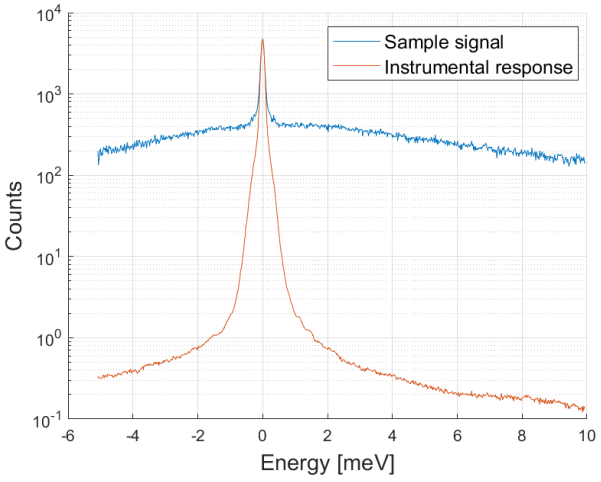

Figure (2): the inelastic spectrum and the instrumental response, which allows to subtract the elastic peak from the inelastic signal and to deconvolve them.