EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: Probing the impact of liquid wetting on phonon dispersion of solid surfaces**	**Experiment number**: MA-5574
Beamline: ID28	**Date of experiment**: from: 29/11/22 to: 05/12/22	**Date of report**:
Shifts: 9	**Local contact(s)**: Luigi Paolasini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Introduction : The possibility that a liquid modifies the solid (phonon) dynamic without (flow, heat) transport is generally academically not addressed. Recent pioneering experiments have however shown that at several millimeters from an interface, the liquid temperature is non-uniform implying that the solid wall induces long range vibrational correlations. The mechanism at the origin of interfacial temperatures has to be related to a change of the vibrational states; i.e. a modification of the density state of phonons of the solid surface and in the bulk.

Context and methodology : High energy inelastic Synchrotron radiation was used to focus on the phonon dynamics of the solid. As a sample α-Al_2O_3 monocrystals were chosen, known for being extensively studied in the bulk and surface.Wetted α-Al_2O_3 c-axis (0001) surfaces are known to form a Gibbsite-like intermediary layer in contact with liquid water, and surface consequences on macroscopic quantities –such as surface energy- are common in the litterature. However, no work has been done on the impact of wetting on acoustic phonons in the bulk of the solid. IXS experiment with 3 meV resolution were performed at the ID28 beamline at ESRF with 17.794 keV energy. A small energy window was chosen - from -40 meV to 40 meV- to be able to mainly observe acoustic phonons.

The methodology is as follows :

- The experiments were carried out at room temperature and atmospheric pressure.
- The incident beam probed the sample oriented with the c-axis normal to the disk plane probed in reflectometry geometry.
- α-Al2O3 monocrystals were heated to 450°C then kept at 125°C to ensure no environment surface contamination. Monocrystal treated in such a way are considered dry.
- Placed in a nitrogen filled containment, the dry crystal was then scanned using reflectometry in two Brillouin zones at different depths, (0 0 12) and (-1 0 14), at ~300µm and ~150µm respectively,
- The crystal was then sprayed with liquid, replaced in the nitrogen atmosphere, and each Brillouin zone was scanned alternatively for ~ 12h, to see if a kinematic effect due to wetting takes place.

The influence of multiple liquid wettings were tested on: H_2O, D_2O, Ethanol-H and Ethanol-D.
Furthermore, a small 4h experiment was performed once with H_2O wetting which followed the same procedure, but only scanning between 20 and 30 meV, to follow the displacement of a given transverse phonon with better time resolution (each scan counts ~12min).

Each scan was then fitted using fit28 and addIXS. All experiments were carried out smoothly and efficiently, and we thank all the ID28 staff for their precious help and expertise.

Experimental results : For brevity, only the results due to H_2O wetting are discussed. Similar trends have been observed in D_2O, as well as ethanol-H and ethanol-D, but these results have not yet been fully analysed.

Key results have been obtained :

1. Dramatic changes of the phonon spectrum when wetting, fully justifying the present experiment and definitively establishing a deep impact of the surface wetting on the solid bulk dynamics.
2. Wetting induced hardening has been observed for both transverse and longitudinal phonons over a large time acquisition (Fig.1a).
3. Long term kinematics of hardening takes place in ~6h (Fig.1a and 1b).
4. Identification of an elastic peak (at E=0) that disappears when wetting (Fig.1c)
5. The elastic peak vanishes at a timescale of ~3h (Fig.1c), thus exhibiting different kinematics than hardening kinematics.
6. Wetting induced hardening is depth dependent. 150µm depth scan reveal hardening, increasing both longitudinal and translationnal velocities (Fig.2a). However, at 300µm penetration depth, no clear hardening and difference in longitudinal sound velocities were observed (Fig.2b).

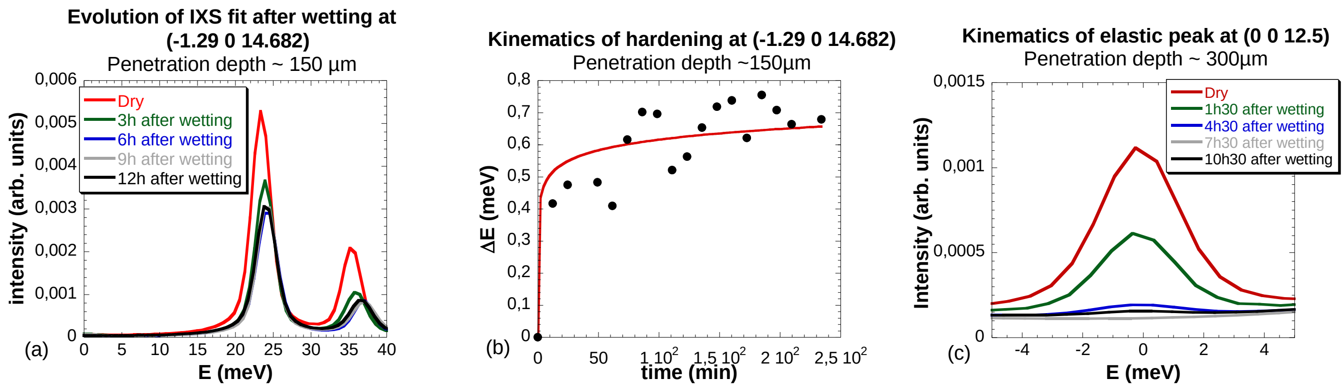

Fig 1 : (a) IXS spectra at (-1.29 0 14.682) at penetration depth ~150µm. A clear change of phonon spectra is observed with wetting, with phonon peaks shifting to higher energies, corresponding to hardening. (b) Kinematics of hardening at (-1.29 0 14.682). A slow relaxation is observed that lasts more than 4h. (c) Kinematics of elastic peak (0 0 12.5) at ~300µm penetration depth. The E=0 peak vanishes after 3hrs, exhibiting a different kinematic than hardening.

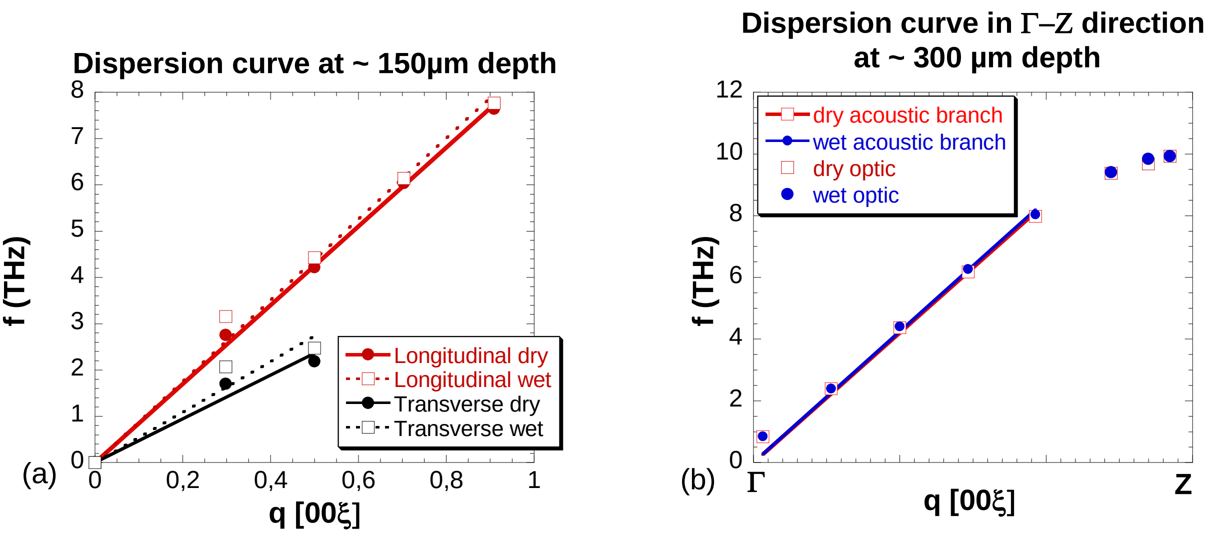

Fig 2 : (a). Dispersion curves obtained with 4 analysers in a given direction at ~150 µm penetration depth. The relative effects of wetting after 12hrs on sound velocities are 3% for the longitudinal and 5% for the transverse branches. (b) Dispersion curves in Γ-Z direction from (0012) Bragg peak, at large depth (300µm): the impact of wetting after 12hrs on longitudinal acoustic phonons is not visible.