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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:** Studying anisotropies in vapor-deposited metallic glasses	**Experiment number**: HC-4683
Beamline:	**Date of experiment**: from: 26 Jan 2022 to: 29 Jan 2022	**Date of report**:
Shifts:	**Local contact(s)**: MELNIKOV Alexey	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Summary

During this beamtime, we performed WAXS measurements on various metallic glass samples with the nano-diffraction setup at ID13. The results confirmed our previous observations of anisotropy in the vapor-deposited PdCuSi metallic glass sample. We are in the process of further analysis, and we expect to summarize the results into a manuscript in a few months. In the ZrCu sample, we did not observe anistropy as in the PdCuSi sample; however, some samples were found to exhibit unexpected structural inhomogeneities on the micrometer scale, and we hope to further investigate this phenomenon in follow-up experiments.

Methods

The experiment was done with the nano-diffraction setup at ID13. The beamsize was determined to be around 70nm × 70nm using a Siemens star.

The samples are metallic glasses produced *via* vapor deposition at controlled substrate temperatures. The compositions include $Pd_{77.5}Cu_6Si_{16.5}$ (at.%) and $Zr_{50}Cu_{50}$ (at.%). All samples are a few micrometers thick and free-standing, allowing for measurements with a simple transmission geometry.

The scans are mainly done over a 2D regular grid on the sample, with various step sizes on the order of 100 nm to 1 μm.

Results

Anisotropy in PdCuSi – One of the main goals of the experiment was to confirm the existence of local anisotropies in the PdCuSi sample. This goal has been achieved. In Figure 1, the first row shows five diffraction patterns during a 2D scan on the as-deposited PdCuSi sample. The diffraction patterns are divided by the average pattern of the scan, so that geometric effects common to all images (such as the polarization factor) would be cancelled out. These images show clear anisotropies around the ring of the first diffraction peak indicated by the dotted black lines. The anisotropies primarily show up as a maximum (red) on one side of the ring and a

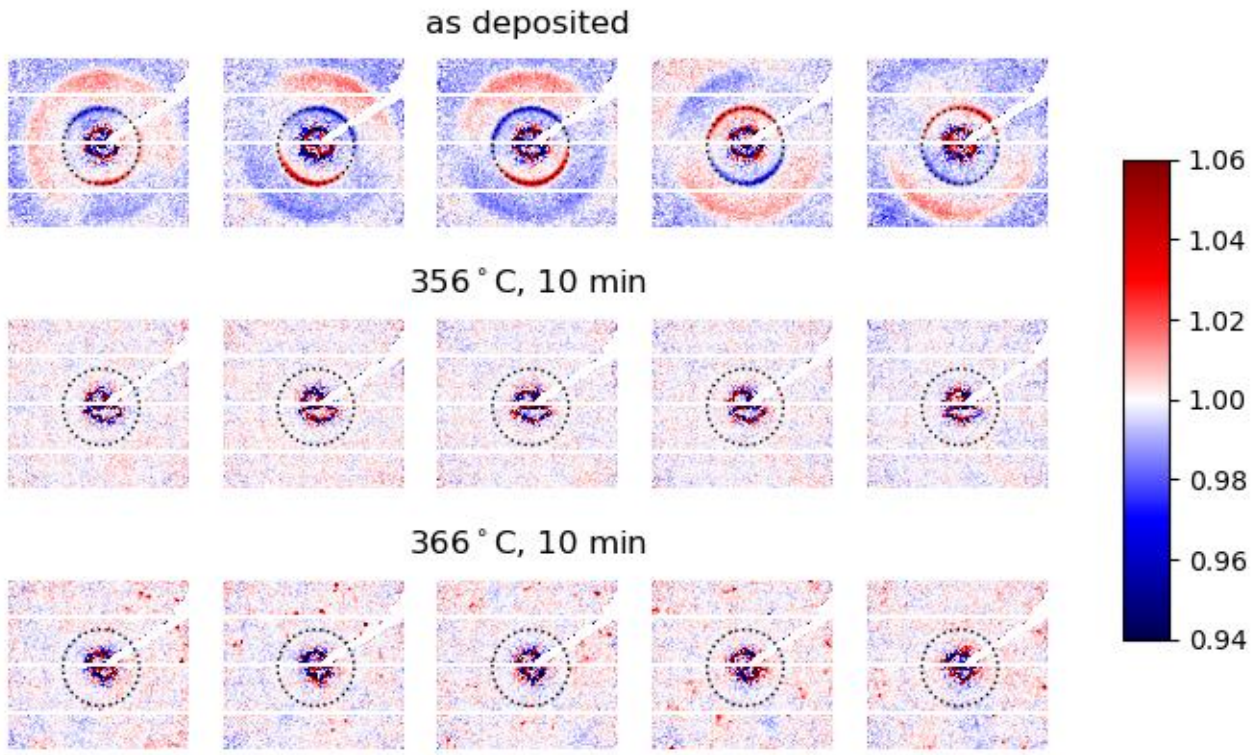

Figure 1: Anisotropy in PdCuSi. The rows show the as-deposited sample, and the sample annealed at 356 °C and 366 °C for 10 minutes. Each diffraction pattern is divided by the average of the those from approximately 100 positions on the sample. Dotted black lines indicate the position of the first diffraction maxima.

minimum (blue) on the opposite side. Even though these are consecutive images during a scan with 400 nm step size (i.e., they correspond to sample positions that are 400 nm apart), the position of the maxima and minima appear random.

The anisotropies around the ring appears to reach ±6%, which is surprising for the following reasons. Since no sharp peaks can be seen in the diffraction images, the ordered regions in the sample should not exceed ~2 nm in size. Thus, in the probed sample volume of ~70nm × 70nm × 5µm, there should be no less than 3×10^6 of ordered regions. Random fluctuations in the orientation of such a large number of regions cannot reach a level of ±6%. Therefore, some kind of long-range ordering must be present in the sample, which is surprising given that the sample appears completely amorphous.

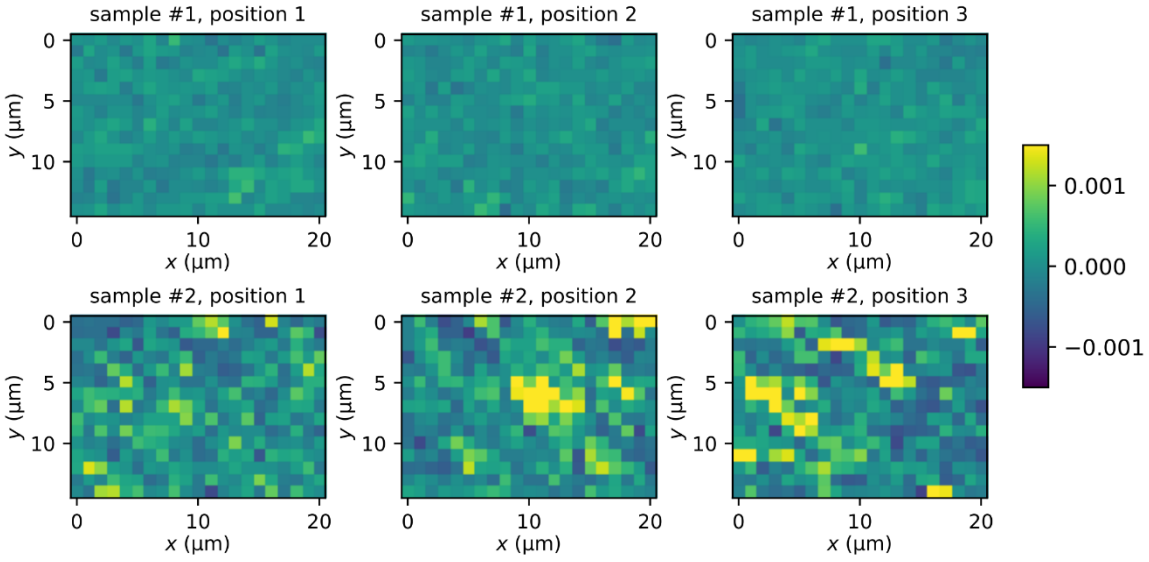

Figure 2: Structural inhomogeneities in ZrCu. The first row shows a ZrCu sample deposited at room temperature (sample #1), and the second row another sample deposited with the substrate at 242 °C (sample #2). Each image corresponds to a 2D scan (21×15 grid, 1 µm step size) at a different position on the sample. The color scale shows the deviation of the Q position of the diffraction maximum from the median value, i.e., $(Q_m - Q_m^{\text{median}})/Q_m^{\text{median}}$.

We have further investigated the sample by annealing at 356 ℃ and 366 ℃ for 10 minutes. The results of the same analysis as for the as-deposited sample are presented on the second and third row of Figure 1, respectively. It is clear that after annealing at 356 ℃, the anisotropy is no longer observable, while annealing at 366 ℃ led to the formation of small crystallites indicated by the presence of sharp peaks in the diffraction pattern. We are in the process of further analysis to understand these results.

Structural inhomogeneities in ZrCu – During the experiment, we also investigated two vapor-deposited ZrCu samples: one deposited at room temperature (smaple #1), and another deposited with the substrate at 242 °C (sample #2), while other parameters for deposition were kept the same. These ZrCu samples did not exhibit the kind of anisotropy observed in the PdCuSi sample. Instead, we found significant structural inhomogeneities in sample #2 but not sample #1. These inhomogeneities showed up as fluctuations in the Q position of the diffraction maximum from its median value during the scan, i.e., $(Q_m - Q_m^{\mathrm{median}})/Q_m^{\mathrm{median}}$; see Figure 2.

The level of these fluctuation appears to reach 0.15%, which corresponds to a volume change of ~0.45%. This is unusual given that the X-rays probe what is essentially a bulk region (~70nm × 70nm × 5μm), so intrinsic density fluctuations are expected to be small. Furthermore, density variations are expected to be mitigated during the vapor deposition process, since each layer should have sufficient time to relax with a deposition rate of ~0.3 nm/sec. We note that the 0.15% change in Q_m cannot be solely a geometric effect (e.g., surface roughness): it would correspond to a ~120 μm change in sample position, which is impossible because the sample is only ~4 μm thick and the scanned area is only ~20 μm in size.

This is an intriguing and somewhat surprising finding because the samples deposited at elevated temperatures were found to show enhanced mechanical homogeneity [1,2], presumably due to higher levels of relaxation (akin to annealing effects). In addition, the length scale of the fluctuations appears to be on the ~μm level, as shown in Figure 2. This length scale is larger than usually discussed [3], although it is compatible with the fractal-like density fluctuations described in Ref. [4]. Thus, in order to better understand these results, we propose to continue our study with a systematic measurement of samples deposited at different temperatures and over large areas on the sample. We will also collect scattering intensities up to high Q, which will provide details on the local structures and their variations.

References

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[2] T. Dziuba, Y. Luo, and K. Samwer, *J. Phys.: Condens. Matter* **32**, 345101 (2020), doi: 10.1088/1361-648x/ab8aa2
[3] J. C. Qiao et al., *Prog. Mater. Sci.* **104**, 250–329 (2019), doi: 10.1016/j.pmatsci.2019.04.005
[4] B. Huang et al., *Acta Materialia* **115**, 69 (2018), doi: 10.1016/j.actamat.2018.05.064