ESRF	Local phase transition in wet spider dragline silk	**Experiment number:** SC 1743
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Report:

We have carried out an x-ray micro-diffraction study of single spider silk fibers under mechanical load. It is already known from various experiments on spider silk fiber bundles that the structural elements of spider silk are subject to change depending on mechanical load, humidity and temperature [1][2][3]. Parameters of the crystalline beta-sheet component like crystallite size, lattice parameters and the nematic order parameter of the crystallites were reported to change. However these changes were not far from the detection limit of the respective experiments, and it is unclear how well defined the mechanical load, in particular the strain is for a bundle of fibers, where the load can distribute quite unevenly. We have recently carried out the first single fiber diffraction measurements over the entire stress-strain curve until fracture, and have monitored the structural changes of the crystalline components. Samples were obtained by forced silking of three types of spiders: *Nephila clavipes*, *Nephila senegalensis* and *Nephila madagascariensis* .

The experiment was carried out using the KB focussed beam at ID13 with a beam size of $7\mu m$ and a photon intensity of approx. $2.62 \cdot 10^{11}$cps at 13.7 keV. The single fiber stretching apparatus (LEX 810, Diastron, England) was placed onto the sample goniometer, and the diffraction images were recorded at a distance of 139 mm behind the sample using a CCD cameras (MAR Research, detector type MARCCD 165). The detector was operated in a mode of binning 2x2 pixels, leading to an effective pixel array of 1024x1024 with a pixel size of 157.88 μm. The detector was calibrated by Al_2O_3 calibration standard (NIST).The fibers were translated in between exposures of 0.2-1 sec to minimize radiation damage. The stress-strain curves were recorded in situ.

The preliminary analysis of our data clearly shows shows structural changes, as a function of strain, e.g. see Fig.1 (data shown for *Nephila madagascariensis*). However the variation is small and not very dramatic. On the level of the raw data the normalized intensity distribution obtained by cutting the image along a line perpendicular to the fiber axis, shows that the strongest (120) peak and the shoulder attributed to the (200) peak broaden at 7% strain with respect to small or zero strain. The angular cut which is a measure of the angular distribution of the crystallite director (nematic order parameter) also shows a slight broadening. Fig.2 shows the peak position of the (120), the crystallite size L calculated from the (120)-peak, and the nematic order parameter (op), as a function of strain. The variation of the peak position (a) or correspondingly the lattice parameters is very small and close to the threshold of statistical significance. While a detailed statistical analysis is in progress, the peak position seems to

first slightly increase and then to decrease. The decrease in L is much clearer and in line with previous observations obtained on fiber bundles [1]. Finally, the data also clearly indicates a broadening of the orientational distribution, corresponding to a decrease of the *op*. With values between $op = 0.971$ and $op = 0.977$, the beta sheet crystallites can be considered as very well aligned, and again the variations are very small. However, the tendency to decrease is opposed to the previous result on fiber bundles of [1], were an increase in the order parameter was reported. We suspect that the bundle experiments are influenced by an ensemble average and the tilt distribution of individual fibers, which must becomes smaller under strain. In the present single fiber experiments we conclude that the peak width both in angular and radial direction slightly broadens under strain. We suspect that this reflects the intrinsic silk properties. The analysis of these findings is still in progress. It will shed some light on whether the beta sheets play a rather passive role (filler material), or whether the small variations are significant enough to account for an active role of the crystalline components in the storage and dissipation of energy. We note that variations in the amorphous scattering contribution are still to be analyzed. This will not be easy since the scattering of this contribution is small. Both the SAXS pattern and the variation with rel. humidity needs to be investigated the next beamtime.

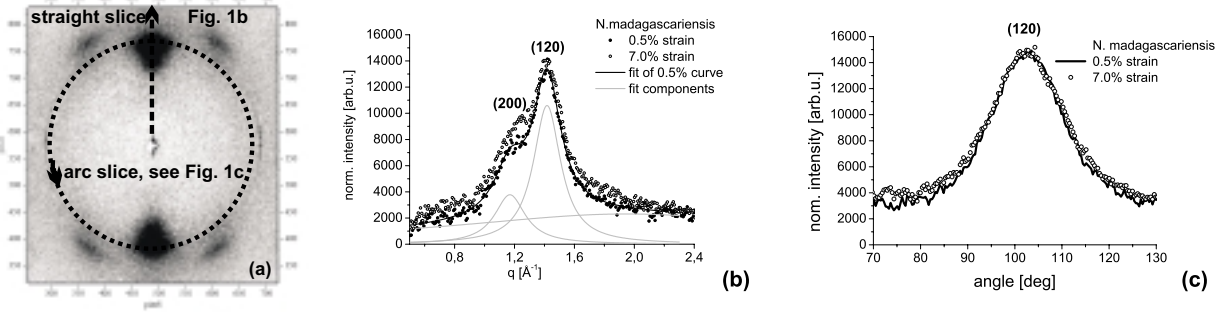

Fig. 1 (a) 2D-diffraction pattern of a *Nephila madagascariensis* single fiber with the geometry of the two 1D slices shown in (b) and (c). (b) Comparison between two *Nephila madagascariensis* diffraction patterns (straight slices) at different strain. The diffraction pattern broadens with increasing strain what indicates a shrinking of the crystallites.
(c) Comparision between two arc slices at different strain. A region of interest around one (120) peak is shown. The peak-width slightly increases with increasing strain.

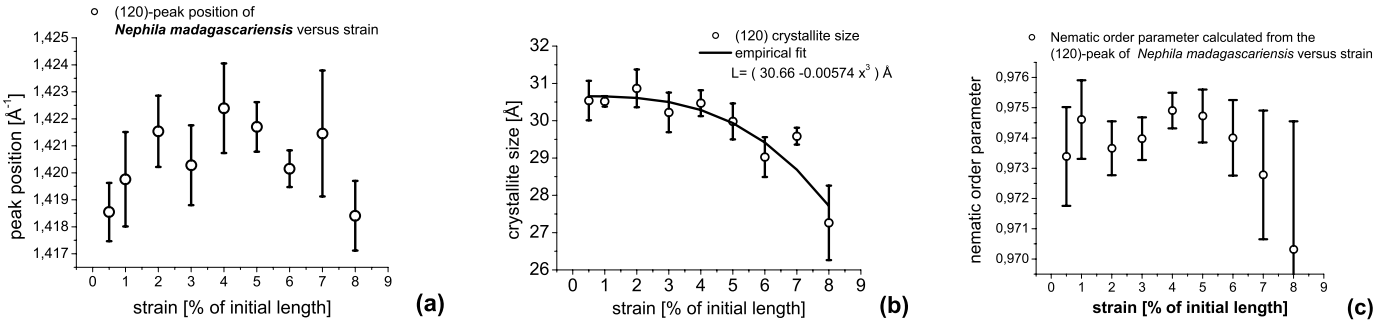

Fig. 2 (a) (120)-peak position of *Nephila madagascariensis* versus strain.
(b) Crystallite size calculated from the (120)-peak of *Nephila madagascariensis* versus strain. The crystallite size decreases with increasing strain.
(c) Nematic order parameter (op) calculated from (120)-peak.

[1] D.T. Grubb and L.W. Jelinski, *Macromolecules* 30 2860-2867 (1997)
[2] J.M. Gosline, *Journal of Experimental Biology* 202 3295-3303(1999)
[3] A. Glišović, Röntgenstrukturanalyse von Spinnenseide, Diplomarbeit, Univ. des Saarlandes (2004)