ESRF	**Experiment title:** Impulsive nanoparticle melting –The pulse length effect	**Experiment number**: SI 1331
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Report:

The aim of the present experimnt was to address irreversible structure changes on gold nanoparticles induced by an impulsive laser excitation. We have observed earlier [1], that water suspended gold particles can be heated considerably by laser pulses and melted. At the same time this reaction was found not to be fully reversible, although recrystallisation could be observed for moderate laser fluence. The irreversible aspect was found to be caused by a seemingly exotic nonthermal laser ablation process. This ablation process is a consequence of the strong near fields present through resonant excitation of the conduction electrons and the size effect [2]. At the same time, when exciting free metal particles supported on a surface, it was observed, that by far lower fluences were needed to cause a gradual degradation of the samples, which may also be related to the ablation effect. On the other hand particle loss (laser cleaning) could also be caused by elastic responses, such as the observed phonon modes.

We attempted to clarify this question by once applying the SAXS scheme to the pump-probe experiment in order to measure the size changes of the particles through laser excitation and secondly use wide angle scattering to precisely determine the threshold upon which particle loss is observed. Both of these schemes are modified by the pulse length tailoring of the laser and polarization change (the latter being either parallel or perpendicular to the surface in a wide angle reflection setup). The SAXS setup was performed with particles in transmission (the substrate was a cover slide surface).

As can be seen from fig. 1, the SAXS pattern shows an anistropic scattering pattern, when deriving the difference with and without laser excitation, which shows the ablation process on the quasi free particles along the laser polarization axis.

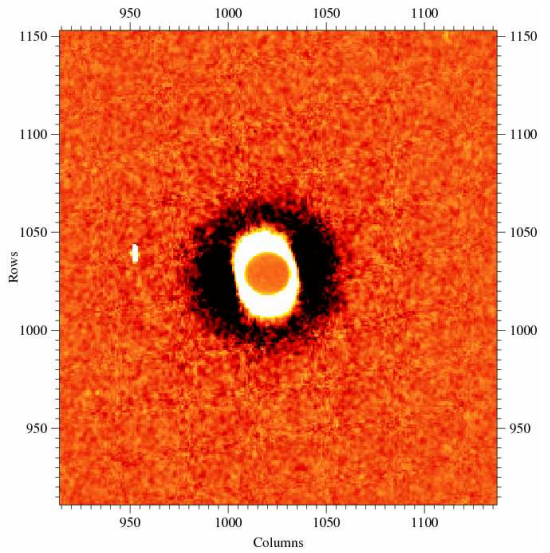

Fig. 1: Difference scattering pattern on the CCD after subtraction the dark state pattern from the excited state pattern of gold nanoparticles (45 nm) adsorbed on a cover slide surface in transmission (single shot exposures at 100ps delay). The laser was aligned with almost vertical polarization. The central circular part is hidden by the beam stop.

At the same time the powder scattering patterns show a loss in intensity at the gold (111) reflection already at a laser power of 35 mW with a rather low lattice expansion (0.6 %, which would relate to a temperature of about 320 °C). This loss is considerably reduced when using stretched laser pulses (pulse length about 1 ps) as seen in fig. 2. This underlines the above statement, that particles are damaged by the peak field of the laser, which is shown to be a nonlinear effect [3].

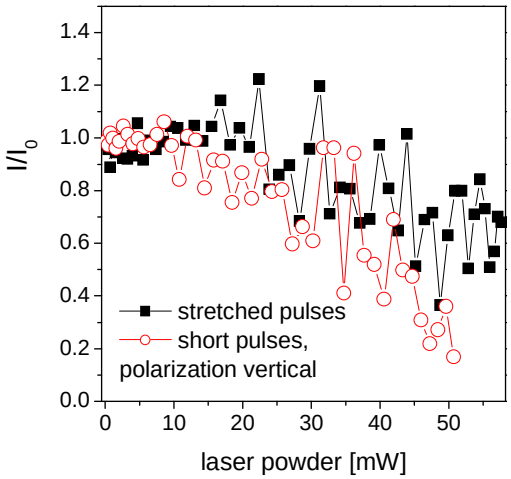

Fig. 2: Scattering intensity of the (111) powder ring of gold particles (150 nm)excited by repetitive laser pulses as function of laser power (at 1 kHz). The open circles denote short laser pulses of about 100-150 fs, whereas the symbols refer to an experiment with temporally stretched pulses to 1 ps. The öaser to x-ray delay was held at 100ps.

The laser cleaning effect, i.e. the particle desorption from the surface is also present. This can be seen, when comparing data of free particles with measurements on embedded particles, where the loss in scattering intensity occurs only at much higher laser power (80 mW, not shown). Interestingly, some change in scattering intensity is observed at extremely low laser power of 11 mW (fig. 2), which compares to a lattice temperature of only 125 °C and is far below the observed threshold for irreversible particle modifications as observed in the water phase [3]. On the other hand at this temperature we have recently observed surface melting to occur on steady state heated gold particles [4].

[1] A. Plech, et al.: *Laser-Induced heating and melting of gold nanoparticles studied by time-resolved x-ray scattering*, Phys. Rev. B 70 (2004) 195423.
[3] A. Plech, et al.: *Time resolved multiscale X-ray scattering of near field ablation from gold nanoparticles*, Nature Phys. 2 (2006) 44.
[4] A. Plech, et al.: *A surface phase transition of supported gold nanoparticles*, Nano Lett. (2007) in press, scheduled in issue 7(4).