ESRF	**Experiment title:** **Surface melting on gold nanoparticles - On the picosecond time scale ?**	**Experiment number**: SI1594
Beamline:	**Date of experiment**: from: 03-09-07 to: 06-09-07	**Date of report**: 5-03-08
Shifts:	**Local contact(s)**: Dr. M: Wulff	*Received at ESRF:*

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Report:

The aim of the present experiment was to resolve ultrashort time morphological changes of supported gold nanospheres on a substrate. We have seen earlier, that the elastic properties of gold particles on a inert surface show a strong modification if the temperature reaches a rather low threshold [1]. For 60 nm gold particles this threshold has been detected just above 100 °C. Above 150 to 200 °C this change is followed by massive particle sintering. That indication points towards a surface phase transition, possible some kind of surface melting or reconstruction.

While in the quasi continuous case the morphology change is accompanied by irreversible sample modifications, in a short excitation regime this is not necessarily the case. However, different studies, including ours, have yet not seen any threshold phenomenon of the particle properites at such low temperatures [2, 3].

Whithin the present experiment we tried to enhance the sensitivity on structural modifications by using high quality crystalline gold particles (BBI International) and trying to correlate the Scherrer width of the (111) reflection with the lattice expansion during the laser excitation transients. The lattice expansion can be correlated to the lattice temperature of the particles [3], while the Scherrer width shows the quality of the crystal lattice, including non-thermal motion [4]. This relation can be derived, while a fixed delay between laser and x-ray pulse is set and the fluence of the laser is raised continuously. For example at a delay of 100ps the highest temperature can be observed, whereafter the lattice cools down within a relaxation time of some nanoseconds. At 100ps, however, a strong contribution of non-thermal motion is expected, which is known as shape oscillations of the particles.

A second pathway is looking at the delay at fixed laser fluence. In this case the particles, which initially have reached a certain well defined temperature, will be examined at falling temperatures, which can be continuously followed down to room temperature. If a morphological transition in an intermediate temperature range, the Scherrer width, should show a signature of a possible disordering.

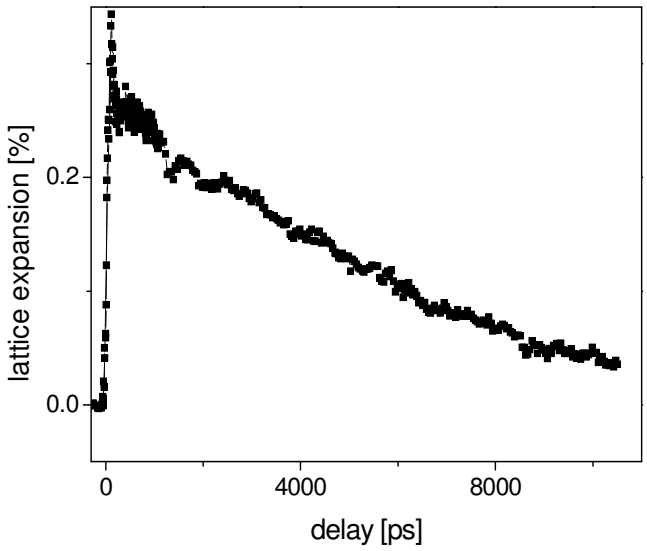

Fig. 1: Lattice expansion of 150 nm gold particles as function of delay between laser and x-ray pulses.

In the experiment, the gold (111) reflection of 100 and 150 nm particles on a silicon surface has been recorded with the CCD camera. As the particles are oriented on their <111> facets mainly the lattice movement perpendicular to the surface is recorded. Fig. 1 shows a trace of the lattice expansion as function of delay with a first steep increase within the time resolution of the x-ray pulses of 100ps and then a slow, almost exponential decay with 6ns cooling time. The fluctuations in fig. 1 are not entirely statistical, but in particular during the first nanosecond due to coherent lattice excitation. With a resolution of 7*10^-5 one can resolve temperature changes of about 4-5 K. When looking at the SCherrer width as function of lattice temperature, one can determine 2 regimes for the above data, as seen in fig. 2. At the highest temperature (the resolution limited part is excluded) the peak broadening is substantial, but decays without being accompanied by a temperature change. Then a linear relation between broadening and temperature is seen until the particles reach ambient temperature. In the first part the broadening is caused by the coherent motion, wich decays to local thermal equilibrium. The linear behaviour in local equilibrium is not intercepted by any discontinous change, which could happen for a threshold transition. For comparison the broadening is shown at 100ps for increasing fluence (large squares with lines), which shows the maximum, strain induced broadening. In conclusion, we attempted to observe the indication of fast morphology changes in gold particles, which, however, was not evident from the data within the present parameters of delay and fluence, while the ultrashort time behaviour is limited by strain from coherent motion.

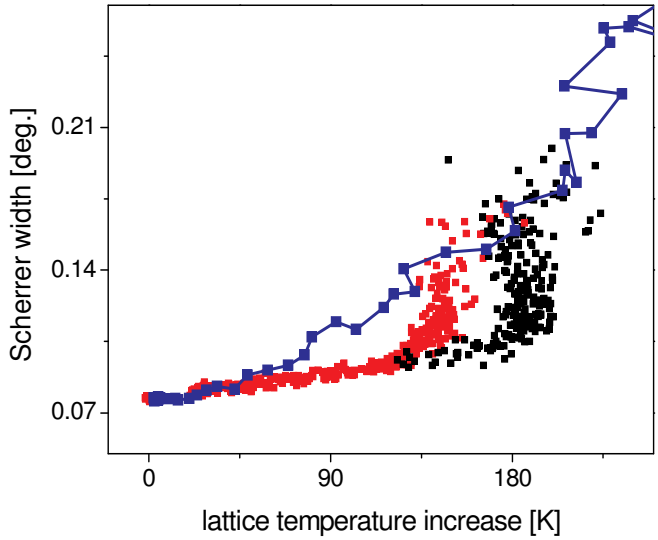

Fig. 2: Scherrer width as function of lattice expansion, which is expressed as lattice temperature. The (blue) lined symbols refer to a 100 ps delay measurement with variable fluence, while the (red and black) squares are taken from a delay scanned measurement for two different fluences. In the latter experiment the initial strong broadening up to 0.18 degrees decays independent of cooling, followed by a linear change with cooling for later times.