ESRF	**Experiment title:** **Correlation spectroscopy of embryonic fluctuations in shape memory alloys**	**Experiment number**: MA 21
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Report:

The aim of this experiment was to observe heterophase fluctuations above (weakly first order) martensitic transformations. In particular, the experiment aimed at distinguishing between conjectured “dynamic” and “static” fluctuations. In the dynamic case, a close analogy to second-order phase transitions is expected, implying a strong temperature dependence of the number of embryonic regions. In addition, an analogy to critical slowing down should be observable as well, covering the time scales between phonon-assisted nucleation (nanoseconds) and the static surface relief.

For an experimental realization, a grazing incidence geometry was chosen to observe the manifestation of such fluctuations at the surface in the form of premonitory roughness build-up. Experimental data were taken at temperatures from approximately 10 K above the transition in decreasing steps until the transition occurred. Thus a range of ca. one order of magnitude was covered in reduced temperature. Since we are not aware of any similar experiment performed before, a more extended temperature range did not seem warranted for a first test of the above-mentioned notions. However, a temperature well above the transition ($\Delta T = 70$ K for Ni-Al and $\Delta T = 50$ K for Au-Cd) was included for reference.

The temperature-dependent behaviour of two single crystals from shape memory alloys were in the focus of this experiment: a $Ni_{63}Al_{37}$ sample (denoted in the following as Ni-Al) and a $Au_{50.5}Cd_{49.5}$ sample (denoted as Au-Cd). For each temperature, the samples were studied by means of conventional (incoherent) and coherent non-specular reflectivity, and by x-ray photon correlation spectroscopy (XPCS) at two different q - values. A dedicated sample chamber brought to the ESRF provided a temperature stability better than ± 3mK. A standard setup of the beamline was used, implying a x-ray beam energy of 8 keV and a sample – detector distance of 1235 mm. The slits defining the incident beam were $10 \times 10\,\mu m^2$ and held constant during the entire experiment.

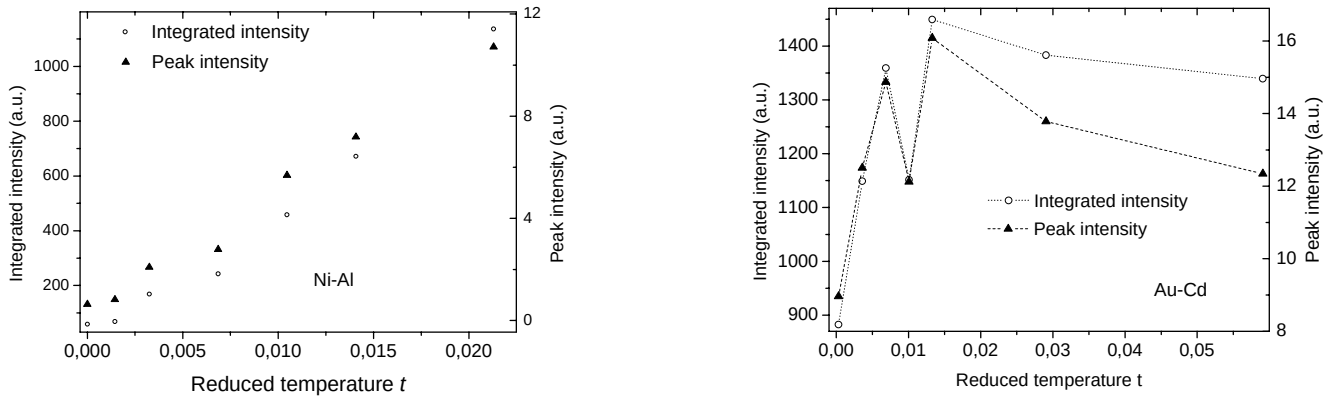
I. Non-specular Reflectivity

At all temperatures detector scans at an incidence angle of 0.3° were carried out in the incoherent and the coherent modes. Switching between the different setups was simply done by changing the detector slit widths ($1\times1\,\mathrm{mm}^2$ and $20\times20\,\mu\mathrm{m}^2$, respectively).

For Ni-Al both the Yoneda peak intensity as well as the integrated intensity decrease monotonically on approaching the phase transformation. This behaviour is observed for coherent as well as for incoherent diffuse reflectivity scans and attributed to an increasing surface roughness which becomes macroscopic at the transition temperature T_C. While these results are qualitatively in agreement with previous data, the linear variation with reduced temperature (Fig. 1a) is at variance from a previously measured power law with an exponent of 0.5. We have currently no explanation for this difference.

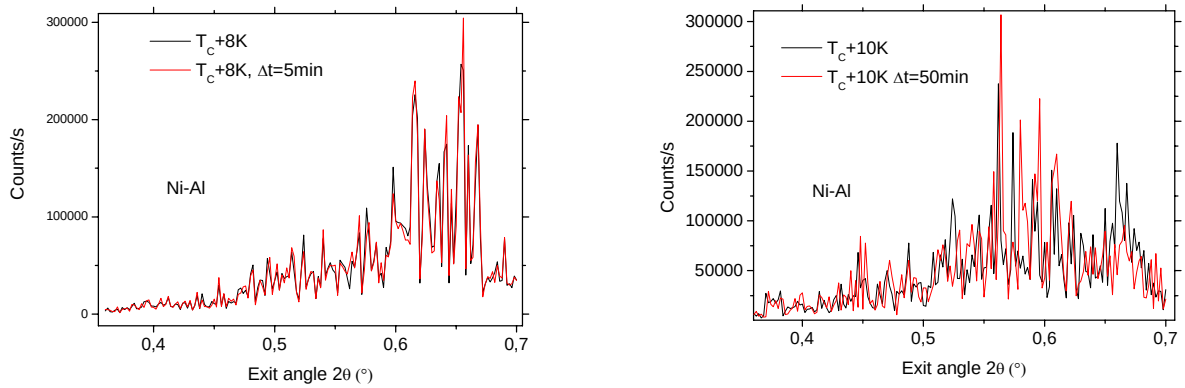
The Au-Cd sample exhibits also temperature-dependent precursor effects in the diffuse reflectivity (Fig. 1b), however, the observed pattern turned out to be more complex and requires further experiments for interpretation.

In addition, coherent diffuse reflectivity scans were also repeated at fixed temperature after Δt ~5 min and 50 min to check potential time-dependent behaviour of the surface reflectivity on scales not meaningfully accessible by XPCS in this experiment (see next section). The results indicate indeed changes on long time scales (Fig. 2b), the follow-up on which however was not the focus of the scheduled beamtime.



a **b**

Fig. 1: Both figures show results from incoherent scans with data normalized with respect to the integrated monitor signal. **a) Ni-Al:** The integrated intensity and the peak intensity vary essentially linearly with the reduced temperature $t = (T - T_C)/T_C$, which is attributed to an increase in surface roughness towards the phase transition. **b) Au-Cd:** Premonitory changes in surface reflectivity are observed as well, however a more complex pattern appears. Similarly to Ni-Al, the diffuse reflectivity finally decreases on approaching T_C .



a **b**

Fig. 2: Two successive detector scans from the Ni-Al sample taken fairly above the phase transition with different repetition intervals: **a**) 5 minutes, **b**) 50 minutes. The results indicate surface changes on long time scales.

II. XPCS

Correlation functions were taken for all temperatures at an incidence angle of 0.3° and 2θ angles of 0.6° (q_x = 0 Å^{-1}; q_z = 0.0425 Å^{-1}) and 0.468° (q_x = -3.8 · 10^{-5} Å^{-1}; q_z = 0.0331 Å^{-1}).

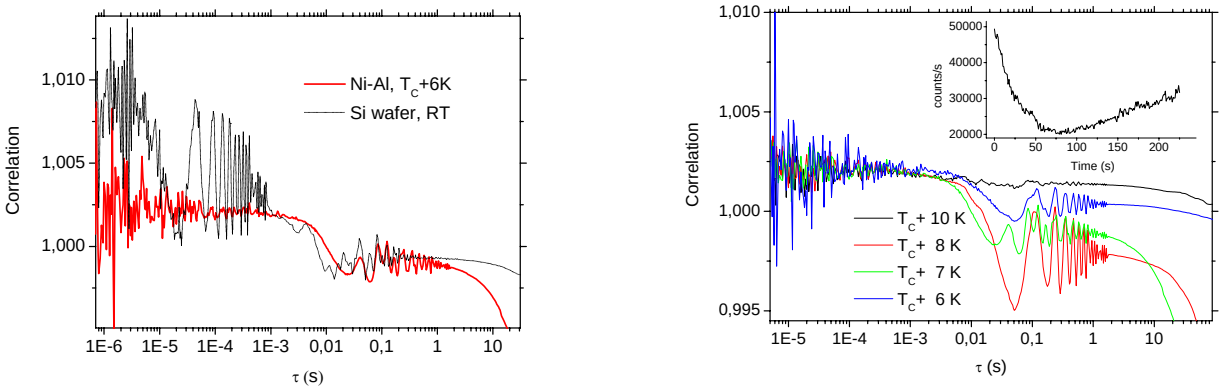


Fig. 3: a) Correlation function of a silicon wafer in comparison with a correlation function of the Ni-Al sample, both taken at a detector angle of 0.468°. For the measurement of the Si wafer the water circulator and the vacuum pump were switched off to exclude the possibility of vibration pick-up from these sources. No significant contrast is discernible. The fine structure between 10 ms and 1 sec is presumably due to feedback loops in the beamline optics, and dominate the plot solely for the lack of a significant contrast signal. **b)** Temperature-dependence of normalized correlation functions from Ni-Al, taken at a detector angle of 0.468°. The correlation functions are essentially identical, except for the 10 ms-1s range mentioned in the previous section, and strong falloffs at time scales >> 1 s. However, these depended on the exact starting time of the XPCS measurement, caused by occasional strong intensity drifts of the primary beam. The inset shows an example of such an uncontrolled drift of the primary beam intensity (with the sample chamber removed from the beam to clarify the situation). The reason for the drifts was not known at the time of the experiment.

Normalized correlation functions are shown for the Ni-Al sample in Fig. 3. A normalization of the correlation functions was necessary because the recorded correlation functions frequently acquired some arbitrary vertical offset. The value of this offset was determined by the falloff typically starting at a time scale of about 1s, induced by intensity drifts of the direct beam (inset in Fig. 3b). After normalising the correlation functions in the region from 0.1-1 ms by adding a constant, the correlation functions are comparable at short time scales (up to about 5 ms). The oscillatory structure at timescales between 10 ms and 1 s is attributed to the beamline optics. It also occurs in a reference measurement of a simple silicon wafer without any sample environment (Fig. 3a). Moreover, a true signal from the sample would be expected to give a contrast in the order of 10% whereas the correlation functions taken here never exceeded a contrast of 0.6%.

III. Conclusion

From the three shape memory alloys suggested in the proposal (Ni-Al, Au-Cd, In-Tl), the beam time allocation allowed to investigate Ni-Al and Au-Cd samples. The following conclusions can be drawn:

- The sample surface is not invariant on approaching the phase transformation, but exhibits premonitory effects already well above T_C. These are manifest as changes of the surface roughness, as evidenced by diffuse reflectivity scans.
- Whereas this effect is present both for Ni-Al and Au-Cd, a remarkable linear relationship is observed for Ni-Al, whereas Au-Cd shows a more complex behaviour.
- If the nanoscale roughness build-up is interpreted as a surface manifestation of heterophase fluctuations, then only static precursors could be observed in the accessible correlation time range from µs – s for all temperatures. This hints at a static origin of the “tweed” pattern observed in electron microscopy of premartensitic materials. However, an independent confirmation from XPCS measurements using Bragg reflections from the bulk of the samples would be important.
- An unexpected time dependence on the scale of 10^3s may point to an hitherto unknown very slow dynamics in these materials. This effect requires further investigations.