ESRF	**Experiment title:** X-ray photon correlation spectroscopy on premartensitic heterophase fluctuations in shape memory alloys	**Experiment number**: MA-257
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Report:

This experiment aimed at the observation of heterophase fluctuation in the immediate vicinity of a (very weakly) first order martensitic transformation (MT) in bulk single crystals. From the shape memory alloys suggested in the proposal (Ni-Al, Au-Cd and In-Tl), a Ni-Al and an Au-Cd single crystal sample could be investigated.

Resemblance to phenomena associated usually with second-order phase transitions has been previously observed in these material systems, however it is not clear yet how deep the analogy is. If the similarity points to an essential feature of the MT, a strong temperature dependence of the embryonic fluctuations is expected and the well-known effect of critical slowing down should be observable. In that case the relevant time scales range from nanoseconds (phonon assisted nucleation) via very slow dynamics to the static, transformed sample. In a preceding experiment at the ESRF a first hint on very slow dynamics was found in grazing incidence geometry (see report on experiment MA-21). Furthermore, in an experiment at BESSY in Bragg geometry a hint of non-trivial dynamics was found close to the transformation temperature T_C. For clarification, this follow-up experiment providing high temporal and spatial resolution was performed at the ESRF.

For an experimental realisation of the proposed investigation a standard Bragg geometry was chosen to observe the suspected fluctuations in the bulk of a $Au_{50.5}Cd_{49.5}$ and a $Ni_{63}Al_{37}$ single crystal (denoted as Au-Cd and Ni-Al, respectively) both with polished (001) surfaces. During the experiment the transformation temperatures were determined as T_C = 305.25 K for the Au-Cd and approximately T_C = 273 K for the Ni-Al sample. The necessary temperature stability of ±3 mK in the relevant temperature range from 260 K to 370 K was provided by a dedicated sample chamber brought to the experiment. Coherent illumination of a sample area was provided by a 10 µm pinhole placed in front of the sample. The scattered intensity was detected by a CCD camera with a pixel size of 22.5 µm placed 135 cm behind the sample. To avoid an elevated fluorescence background the x-ray energy was set to 8 keV.

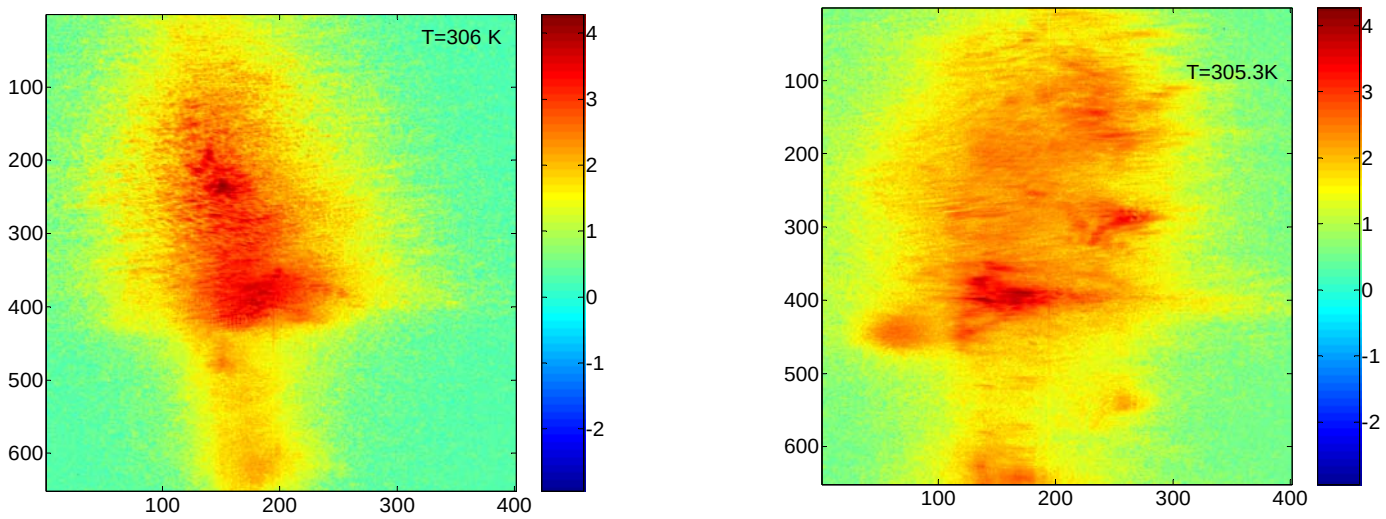

Fig. 1: CCD images (summed over 30 exposures) for two different temperatures close to the transformation. On approaching the phase transition the diffraction image changes and begins to show first precursors of the low temperature phase. This change appears to be continuous until the phase transition, where an abrupt change occurs.

In this report we restrict ourselves to the measurements on Au-Cd. The time characteristics of the (001) reflection which is sensitive to the structural transformation was recorded for temperatures in the vicinity of the transformation. The temperature was lowered from approximately 5 K above the transformation in steps of 1 K and in steps of 0.1 K for temperatures below 306 K until the transformation occurred. Thus a range of about 1.5 orders of magnitude was covered in reduced temperature $(T\text{-}T_C)/T_C$. However, reference measurements at 360 K, 330 K and 270 K were included as well. Data were taken with a time resolution of 1.4 s (0.2 s exposure time followed by 1.2 s readout time). For each temperature a set of data typically contains 1100 exposures.

I. Temperature dependence of the Bragg reflection

The above described setup allowed the simultaneous observation of an angular range of about 0.57° (vertically) x 0.38° (horizontally) centered at the (001) reflection, which is sufficient to observe structural changes as a function of temperature.

On approaching the phase transition a gradual change in the recorded image can be observed (Fig. 1). This effect starts to be observable even at temperatures as high as T_C + 30 K, indicating structural rearrangements in the sample already well above the transition. Although this continuous precursor is reminiscent of second order behaviour, isolated regions that transform individually at higher temperatures owing to some inhomogeneities could give rise to similar behaviour. However, this does not appear to be likely due to the

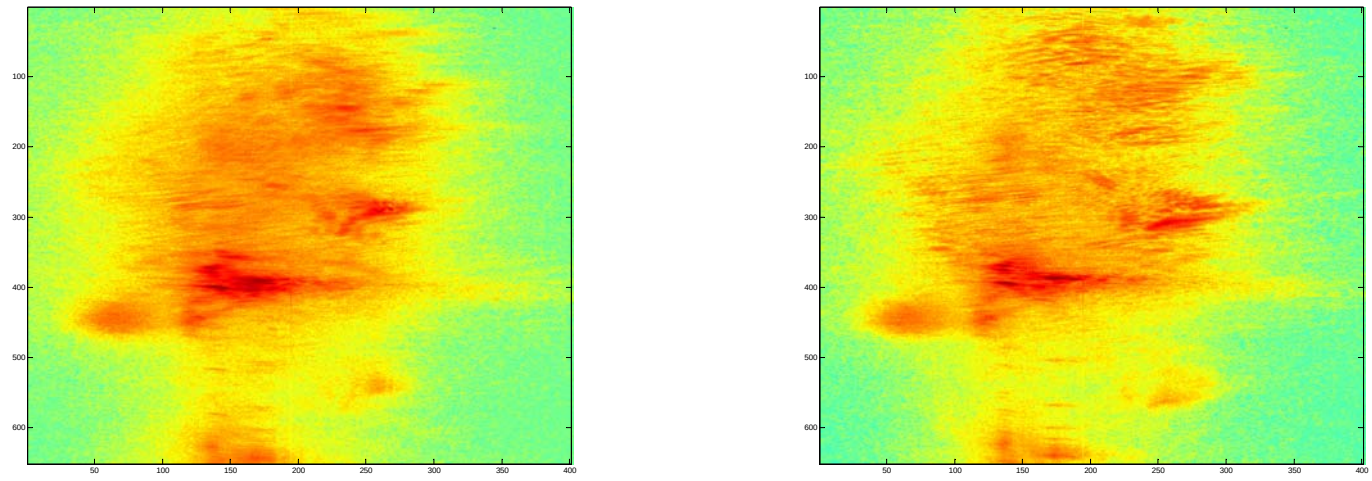

Fig. 2: Diffraction image summed over 30 exposures at a fixed temperature of 305.3 K at the beginning of a measurement (left) and at the end of a measurement (right). The time difference between the two images is about 30 min. A change is clearly observable.

very small illuminated sample region. At the phase transition the diffraction image changes abruptly within a temperature interval of less than 0.05 K, pointing at a distinct first order behaviour of the sample.

II. Time dependence of the Bragg reflection

From all sets of data taken the correlation function was calculated in various regions of interest. These regions were selected in the measured part of reciprocal space at the most prominent Bragg peak and in the diffuse around the peak. As the Bragg peak can be seen as a measure of the order parameter, and the thermal diffuse scattering from phonon dynamics is large near the peak position, this choice appears reasonable. At some temperatures dynamics can be seen even by eye as a movement of the features of the speckle pattern (Fig. 2). In an evaluation using a program with an implemented multitau algorithm available at the beamline, rather a decrease of a characteristic time than the expected slowing down was observed (Fig. 3). Interestingly, a standard correlation algorithm fails to reproduce these functions, which might hint at non-equilibrium behaviour of the sample. Hence a conclusive picture could not yet be archived.

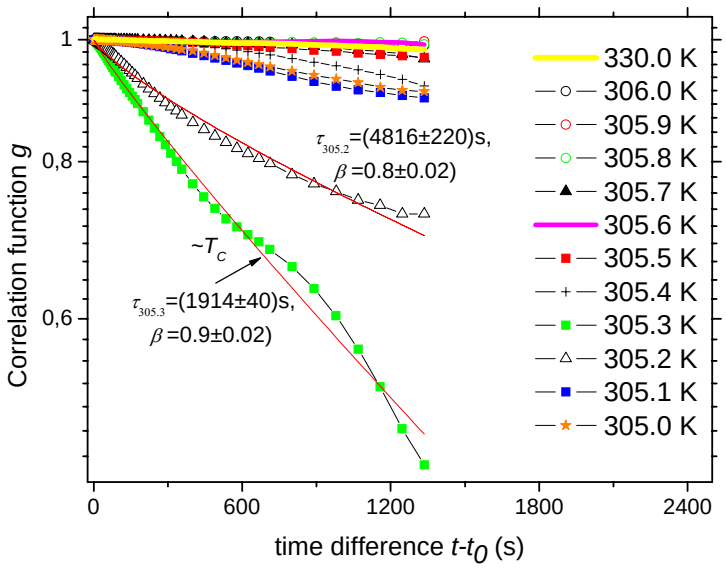

Fig. 3: Evaluation of the data using a multitau algorithm with symmetric normalisation. The region of interest is centered at the Bragg reflection. Interestingly this systematic behaviour with a minimization of the characteristic time at the phase transition is not mirrored when a standard correlation procedure is used. This may be attributed to non-equilibrium dynamics.

III. Conclusion and outlook

The potentially fluctuating diffraction patters of the (001) reflection of a Au-Cd single crystal have been observed on long time scales by coherent x-rays. The detailed temperature resolution of 0.1 K in a carefully selected interval including the phase transformation allowed the observation of temperature and time dependence of the diffraction image. So far the following conclusions can be drawn:

- On approaching the phase transition the diffraction image changes considerably already well above T_C. This behavior is consistent with findings from previous experiments. Still a discontinuous phase transition occurs at a specific temperature, at which all features change abruptly.
- Dynamics can be seen in some sets of data in form of features moving with respect to the rest of the diffraction image. However so far a conclusive quantitative analysis was not possible using one-time correlation functions. This may hint at non-equilibrium dynamics despite our very slow temperature changes.
- Our findings do not support a critical slowing down scenario. Therefore an interpretation of the various precursor phenomena as signatures for a 2nd order like phase transition seems not to be justified from this point of view.

Since the data analysis hitherto points to non-equilibrium dynamics in the sample, a two-time correlation algorithm will be used for further data analysis.