Coherent X-ray scattering of charge order dynamics and phase separation in titanates

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Chapter 4

Searching for Dynamics of the Charge Order in Titanates

Coherent x-ray scattering, tuned to diffract from an ordered phase, probes spatial inhomogeneity in the host system, expressed in the form of speckle patterns. The speckle pattern of the diffracted beam can be used as a fingerprint of the structure of the illuminated area, and the dynamics can be extracted by analyzing the temporal evolution of a series of speckle patterns, as was discussed in chapter 3. In the past, our group used this technique to investigate the dynamics of the spiral antiferromagnetic domains of holmium thin films, where it was found that at the Néel temperature the magnetic domain dynamics speed up [18, 17]. In the experiments discussed here, we aim to move one step further, namely by studying the charge dynamics in a complex oxide.

In this chapter we discuss the results from coherent x-ray scattering experiments on the (011) charge order reflection and the (022) lattice reflection of the hole-doped perovskite titanate Er$_{0.6}$Ca$_{0.4}$TiO$_3$ in the temperature region in which the metal-insulator transition takes place. As mentioned in Chapter 2, this transition involves a structural transformation from a high temperature, orthorhombic, insulating phase to a low temperature, orthorhombic phase with metallic character. However, during the transition a relatively strong and broad (011) diffraction peak is observed using x-ray scattering, which is forbidden in both of the orthorhombic structures. This peak is believed to be due to contributions from a monoclinic charge-ordered component embedded in an orthorhombic matrix.

We probe these phases using well-focused, coherent X-ray beams, thereby gaining access to the details of the phase-separated structures in the scattering volume. The questions that we want to answer here are how the phase separated structure evolves under temperature variations and whether or not the separated phases are fluctuating at thermal equilibrium. For these purposes, the (011) charge order reflection of an Er$_{0.6}$Ca$_{0.4}$TiO$_3$ single crystal is
recorded using both soft and hard coherent X-rays. In both cases, clear speckle patterns are obtained that change with temperature. Recording these speckle images repeatedly over longer time periods, we generated and analyzed a great number of speckle movies taken at thermal equilibrium so as to try within a timescale window given by the technical boundary conditions of the instrumentation to pin down the dynamics of the charge order using a correlation analysis. These synchrotron based experiments were complemented with a pioneering experiment using the world’s first hard X-ray laser at LCLS (introduced in chapter 3). This experiment was the first free electron laser based XCS experiment on a hard condensed matter system. At the end of this chapter, we give conclusions and some recommendations for performing XCS experiments in near future at XFEL sources.

4.1 Soft X-ray coherent scattering

The soft X-ray scattering experiments were carried out during multiple runs at several beamlines at BESSY II synchrotron facility in Berlin. The data described here in this section were obtained at the UE46-PGM1 beamline.

The single crystal of $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$, grown by A. C. Komarek (Cologne University) using the floating zone method, was cut and polished such that the orthorhombic (011) plane was parallel to the sample surface. The surface thus exposed is parallel to the charge ordered planes and contains the (100) and (0-11) axes. The sample was mounted on the diffractometer with the (100) and (011) axes in the diffraction plane, as described in Appendix A.

As explained in chapter 2, the (011) reflection of $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ becomes allowed in diffraction thanks to the ordering of Ti 3d electrons. From the point of view of sensitivity, the choice could quickly be made to probe this reflection resonantly at the Ti-L absorption edge at around 454 to 460 eV photo energy. At this edge, the incoming X-rays are resonant with a $2p \rightarrow 3d$ transition in the Ti atom, which would greatly enhance the sensitivity to the 3d charge order itself \cite{83, 114}. However, at this energy the wavelength is too large to meet the scattering condition for the (011) charge order in reflection experiment. Thus, the photon energy was chosen so as to maximize the X-ray photon flux (10$^{12}$ ph/s) with a Bragg angle that could be accessed using our soft X-ray diffraction chamber (see chapter 3). This energy is 1.4 keV, corresponding to a wavelength of 8.9 Å and a scattering angle of 79.4°. The energy resolution of the grating monochromator was set to be about 0.2 eV, resulting in a longitudinal coherence length of 4.4 μm (see Eq. 3.1).

The necessary transverse coherence of the X-ray beam was generated by placing a 15 μm pinhole in the center of the 64x16 μm$^2$ (FWHM) focal spot of the beamline and subsequently...
4.1 Soft X-ray coherent scattering

Fig. 4.1 Speckle patterns of the (011) reflection of Er$_{0.6}$Ca$_{0.4}$TiO$_3$ taken at 130 K, 145 K, and 150 K using a photon energy of 1.4 keV. The image sizes are all 400x400 pixels and the exposure time was set to 5 min. The contrast values, C, are indicated on each image.

reducing the divergence by adjusting the upstream slits according to Eq. 3.3. The resulting coherent, soft X-ray beam had a flux of $10^9$ ph/s.

The (011) scattered intensity was recorded using a Pixis 2048 soft X-ray CCD camera with a pixel size of 13.5x13.5 $\mu$m$^2$ located 1 m from the sample at the end of a flight tube which was coupled to the chamber by means of a vacuum bellows. During the experiments, the diffractometer vacuum was maintained at the level of $10^{-9}$ mbar using turbo pumps.

4.1.1 Soft X-ray coherent speckle patterns

Fig. 4.1 shows three examples of coherent diffraction patterns from the (011) reflection, recorded at three different temperatures all within the MIT temperature region. The patterns are highly disordered, with coherent diffraction fringes visible in multiple directions. The finest details in these patterns are the speckle modulations (resulting from the interfering coherent beams), whose average sizes can be estimated by

$$S = \frac{\lambda L}{D},$$

where $L$ is the distance from the sample to the detector screen and $D$ is the beam diameter [115]. Clearly, Fig. 4.1 shows that the patterns change markedly with temperature. For the experimental conditions as used here, the expected speckle size is $\sim 80 \mu$m or 6 pixels.
Fig. 4.2 Top: the autocorrelation images of the speckle patterns shown in Fig. 4.1. The false color scale now represents the correlation coefficient. Horizontal (red) and vertical line (blue) cuts through the center of the autocorrelation images are plotted in the middle panel. Bottom: zooms of the central panels show the details of the central peak and include an indication of the speckle size. The 145 K cuts have an additional very shape central peak (of width 1 pixel) due to shot noise in the image.
Fig. 4.3 Schematic of the scattering of an x-ray beam by a single crystal containing mixed electronic phases. The beam enters the crystal at the Bragg angle for diffraction from the (011) planes of the monoclinic charge ordered regions, which are sketched as patches with red and green stripes. The incoming and outgoing beams are attenuated by both absorption and diffraction effects.

The experimental speckle size can be calculated from the autocorrelation function of the speckle patterns [116], which are given in Fig. 4.2, together with horizontal and vertical line cuts through the autocorrelation maxima. The broader, underlying peak spanning roughly 200 pixels is the autocorrelation function of the global intensity distribution of the coherent diffraction pattern. The sharp central spikes in the horizontal profiles correspond to the autocorrelation of the finest structures, the speckles themselves, which indeed have a width (FWHM) of 6 pixels, comparable to the expected speckle size. The horizontal and vertical width are not completely equal, possibly due to differences in the collimation of the incident beam along these two directions.

**4.1.2 Formation of speckle patterns in phase separated crystals**

In order to understand the formation of the speckle patterns we will describe the scattering process as if it were composed of as number of steps (see Fig. 4.3). The incident beam is a narrow, coherent, pencil beam with cross section \( A \), with - to first order - plane wave fronts.
As was mentioned earlier, the structure of the $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ single crystal when it is held in temperatures close to the MIT is, in fact, a mixture of monoclinic (CO) and orthorhombic patches. In the orthorhombic fraction of the system, the (011) reflection is forbidden and this fraction only contributes to extinction of the X-ray beam by absorption. Thus, as the beam penetrates into the sample it is attenuated by absorption and also somewhat by the weak (011) scattering we will come to in a moment. Note that if the small difference in unit cell parameters between the two phases is ignored, the overall atom density of the material is the same throughout the system, and the absorption can be taken as uniform throughout the sample. This attenuation means that the measured speckle signal has proportionally smaller contributions from the structure in deeper sub-surface regions of the sample. The attenuation length can be estimated to be $\sim 0.5 \mu m$, using the simulation software developed by the CXRO [117], meaning that the total scattering volume under the 15 $\mu m$ wide beam can be estimated to be about $90 \mu m^3$.

As the next step we take into consideration the fact that the charge ordering in alternating planes of trivalent and quadrivalent titanium atoms in the monoclinic patches breaks the orthorhombic symmetry and makes the (011) diffraction partially allowed. These monoclinic regions all retain the crystallographic orientation of the orthorhombic host material so that when the (011) diffraction condition is met, each of them will diffract out a coherent beam towards the detector, as depicted schematically in Fig. 4.3. The phase shifts of the X-ray beams from the individual monoclinic patches cause interference, resulting in a strong deformation of the outgoing wave fronts such that a coherent diffraction pattern - or speckle - develops on the detector in the far field.

In this particular case, a second possible mechanism for speckle formation can be considered, due to the possible presence of two subsets of domains in which the charge order layering of the ‘3+’ and ‘4+’ layers are shifted with respect to each other along the (011) direction by a single cubic unit cell. The X-ray beams scattered by these two subsets therefore have a relative phase shift of $\pi$, interfering destructively in the far field.

The qualitative picture given above can, of course, be made more precise. In scattering theory, the detected intensity in the far field is the result of the superposition of all the radiation from all the scattering centers in the illuminated volume. In single crystal diffraction theory, this intensity can be expressed in terms of the form factor of the unit cell and the structure factor of the lattice. For a more realistic treatment, mosaicity and extinction can also be included (see [83]). However, to explain the speckle images of a mixed phase system, we do need to take the exact charge distribution within the illuminated volume into account. To a reasonable level of approximation, the speckle pattern can be described by a form factor-like expression for the illuminated region in which these effects are combined:
4.1 Soft X-ray coherent scattering

\[ I(q) = \int |\{ -r_0 \rho(r) e^{iqr} dr^3 \}|^2 e^{-2\mu z/sin(\theta)} dz \]  

Here \( r_0 \) is the Thomson scattering length, \( \rho(r) \) describes the variations of the electronic density in the phase separated system, \( \mu \) is the extinction coefficient and \( \theta \) is the Bragg angle.

It is clear from this formula that the coherent diffraction pattern is determined by the particular distribution of crystallites in the illuminated volume. It is equally clear that it is not possible to retrieve the exact form of \( \rho(r) \) from one series of CXD patterns using phase retrieval algorithms [64]. However, the speckle pattern obtained under the conditions relevant here still forms a unique fingerprint of \( \rho(r) \) and in the rest of this chapter we will use this property to search for dynamics of the charge order.

4.1.3 Correlation lengths probed by the speckle pattern

Fig. A.3 in Appendix A shows the position of the detector in reciprocal space for the geometry used in our experiments. It can be seen that the detector cuts the [011] direction at the Bragg angle, so that the speckle images are mainly probing the correlations in the (011) plane. We can obtain information on the correlation lengths of the domain volume in this plane by linking the scattering pattern to kinematical diffraction theory, applicable to systems with disorder and/or significant absorption. Within this framework, Lorentzian line shapes can be shown to indicate exponentially decaying structural correlations in the plane perpendicular to the scattering vector [83].

In these coherent experiments however, the Lorentzian diffracted beam profile is further modulated by diffraction fringes and speckles, making it more challenging to identify the profile to be fitted. However, on averaging many different instances of these speckle images, a smooth beam profile with a Lorentzian-like line shape re-emerges. In order to assign scattering vectors to the detector images of Fig. 4.1, we assume that the barycenter of the intensity is the center of (011) reflection. The mapping of pixel position to the relative scattering vector \( q \) is calculated using the equations given in Appendix A. Such an analysis of the images in Fig. 4.1 yields typical correlation lengths of 100 nm in both in-plane directions \( q_x \) (along the [100] direction) and \( q_z \) (along the [0-11] direction).
4.1.4 Contrast and stability of the speckle patterns

The contrast, $C$, was introduced in chapter 3 as a measure of the strength of the intensity fluctuations in a speckle pattern (Eq. 3.10). The $C$-values of the images in Fig. 4.1 range from 0.5 to 0.7, indicating a high degree of transverse coherence. While in itself this is a prerequisite for time correlation spectroscopy, the high values for the contrast also indicate that the mixed phase structure of the $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ single crystal in the MIT region is not fluctuating strongly over the 5 minute exposure time of the measurements.

In order to check this in more detail, we tracked the time evolution of the speckle images. In the first instance the aim was to extract the correlation time from a $g_2(\tau)$ analysis of the data. However, this was hampered by the low intensity, which necessitated long exposure times per frame of the time-line. From the strength of the diffracted beam, the scattering efficiency was calculated to be of order $10^{-6}$. This small number is not surprising in view of the fact that the (011) reflection is forbidden in the orthorhombic structure, only being made possible by the monoclinic deformation of the lattice and the checkerboard charge modulation. Together with the relatively low coherent flux available after spatial filtering of the soft X-ray synchrotron beam, this inherent inefficiency of the diffraction process limits the frame rate of the movies to minimally 2 - 5 minutes. As at least 50 to 100 frames are required, this leads to total acquisition times of several hours. Over this time period the beamline and end-station/diffractometer should be operating very stably, indeed.

Many speckle movies from hole-doped titanates were acquired at different sample temperatures. For all these movies, the $g_2(\tau)$ time correlation function was calculated, and several promising decay curves were obtained with decay times in the hour range. However, after significant investment of time and effort in the investigation of the stability of the setup, culminating in the implementation of the ‘ultrastable’ coherent scattering insert shown in Fig. 3.7, the conclusion was inescapable that no traces of slow dynamics in coherent soft X-ray scattering (as the timescale of several minutes) could be observed under these conditions, i.e. those of relatively low coherent flux (synchrotron + spatial filtering of the beam), combined with a small scattering cross section.

4.2 Hard X-ray coherent scattering

Faced with the inherently low coherent intensity at storage ring based soft X-ray sources, a second set of experiments was performed using hard X-rays, in this case utilizing the coherent hard x-ray scattering beamline P10 at Petra III of DESY, Hamburg. The source for this beamline is a 5 meter long undulator (U29), installed in a low beta straight section of the Petra III storage ring. The beamline operates in the medium to hard X-ray regime (5-25
4.2 Hard X-ray coherent scattering

keV), and is specially designed for coherent X-ray scattering and diffraction experiments (see chapter 3 for more details). An additional advantage of this station is that the Petra III ring operates in top up mode, in which the ring current is kept constant by means of continuous small injections to compensate for scattering losses, ensuring an almost constant incident flux. This brings with it significant additional advantages in stability as the heat load and other technical factors are also constant in time, rather than decaying followed by a large jump every eight hours during normal injection, as was the case for the experiments at BESSY II at the time point when the experiments were carried out.

A detailed description of the sample environment at the P10 station has been given in chapter 3. The same sample was used as in the soft x-ray experiments, however this time with the [100] axis aligned parallel to the \( \theta \) rotation axis. Spectral filtering for P10 was carried out using a Si(111) double crystal monochromator with an resolving power of 0.01 \%, yielding a longitudinal correlation length of \( \sim 1 \mu m \). The beamline has post-monochromator focusing options using compound refractive lenses [118, 119]. We used the beam both in incoherent mode with a beam size of \( \sim 150 \times 75 \mu m^2 \) and a flux at the sample of \( 10^{13} \text{ph/s} \) and in the focused coherent mode using the compound refractive lenses, which yielded a focal spot of \( \sim 3 \times 4 \mu m^2 \) with a flux of \( 10^{11} \text{ph/s} \). This coherent flux is thus two orders of magnitude higher than obtainable at typical soft x-ray spectroscopy beamlines, bringing acquisition times in the range of seconds within reach and thus offers new possibilities in the search for equilibrium charge fluctuations and non-equilibrium dynamics driven by temperature changes in complex oxides, such as the titanate studied here.

From an early hard X-ray test run carried out at ESRF [105], we found that the resonant enhancement at the Ti K-edge for the (011) reflection in the hole-doped titanates is negligibly small. So, as in the soft X-ray case, it was decided to use a photon energy yielding the highest flux, which in the case of P10 was 8.08 keV. At this energy the scattering angle for the (011) reflection is \( \theta = 9.6^\circ \), and the absorption limited probing depth is estimated to be 1 \( \mu m \) [117]. Because of the small angle of incidence, the lateral footprint of the beam in the coherent scattering experiment is increased by a factor of 5 in the horizontal direction. However, the total scattering volume of \( \sim 90 \mu m^3 \), is comparable to that of the soft x-ray experiments.

According to experimental needs, we switched between two detectors, located at the end of the 5 meter long evacuated flight tube. At this distances, the focused, 8.08 keV beam should result in a speckle size of \( \sim 200 \mu m \). A Pixis-1300 camera with 1340x1300 pixels and individual pixel size of \( 20 \times 20 \mu m^2 \) was used to obtain high resolution speckle images with \( \sim 10 \text{ pixels/speckle} \). As was the case for the Pixis-2048 camera used in the soft X-ray experiments, the Pixis-1300 camera has a readout time of 4 s, which limits the frame rate to multiples of 4 seconds.
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Fig. 4.4 Coherent, hard x-ray diffraction patterns from the (011) reflection of Er$_{0.6}$Ca$_{0.4}$TiO$_3$ obtained with 8.08 keV photons at 162 K, 164 K and 166 K. The coherent diffraction fringes are clearly visible. The origin of the $q$ scales was set to the barycenter of the diffraction pattern (see text). The exposure time for each image was a little under 17 minutes, recorded over a 50 min. time period averaging over 500 6s-frames. The contrast values are indicated on each image.

The second detector available to us was a Pilatus-300K, which has 487x619 pixels and a much larger pixel size of 175x175 $\mu m^2$. The detector chip of this camera consists of three modules separated by 2.92 mm wide gaps. With this pixel size, the Pilatus-300K cannot resolve the individual speckles. However, because it has a sub-millisecond readout time, with no readout noise and no dark current signal, the Pilatus is ideal for attempting to catch possible ‘fast dynamics’ taking place on the sub-second timescale.

4.2.1 Frame-averaged hard X-ray speckle images at thermal equilibrium

We will first discuss some typical hard X-ray speckle images obtained at thermal equilibrium using the Pixis-1300 camera, which enables resolution of the individual speckles. The exposure time was set to 2 s, resulting in a frame rate of 6 s in the speckle movies due to the read out delay of the detector. In Fig. 4.4 we show examples of the speckle patterns obtained by averaging 500 frames of the relevant speckle movies recorded at three different temperatures close to the phase coexisting temperature range 2.6. As in the soft X-ray case, the speckle patterns are very well developed, and change radically with these small changes in temperature. In particular, the 162 and 164 K patterns show clear coherent fringes, separated by the speckle width. The speckle contrast in the first two images is very high (namely 0.9 and 0.8), indicating a high degree of coherence and essentially an absence of fluctuations.
over the total exposure time used. The 166 K data show a much lower contrast figure. On the one hand this might be interpreted as a sign of speckle dynamics at this temperature, since changes in the structure within the exposure time would blur the speckle image. On the other hand, however, drifts of the beam during the exposure would also lead to the same effect, and a more careful analysis of the data is required to clarify the origins of the contrast reduction.

The autocorrelation functions of these speckle patterns are shown in Fig. 4.5. The horizontal line cuts (red) show clear speckle peaks with a width of 4 pixels or 80 µm, which is somewhat narrower than the expected 200 µm, which could be due to a 2.5 times larger beam size than expected. The vertical profiles are fairly featureless, which is most likely an expression of the differences between the transverse coherence lengths in the horizontal and vertical directions. In the 162 K and 164 K results, the horizontal cuts through the autocorrelation data show pronounced diffraction side bands. These fringes are thought to be caused by the finite size of the coherent incident beam. In contrast, the 166 K raw image is more blurred, showing a lower speckle contrast of 0.3, and thus a broadening of the speckle size from four to nine detector pixels is observed in the autocorrelation data of Fig. 4.5 for the higher temperature data.

### 4.2.2 Equilibrium dynamics

In order to search for possible slow, thermal equilibrium fluctuations of the mixed phase structure in the charge order of the hole-doped titanate, we recorded a great number of speckle movies (2 s exposure per frame, 6s frame rate) at 8.08 keV and at constant temperatures in the MIT region using the Pixis-1300 camera at P10, optimized for the best speckle resolution. The temperature stability during these measurements was typically 100 mK, and the fixed temperature set points were separated by 2 K intervals and the settling time was usually around 20 mins.

Fig. 4.6 (a) shows the total sum of a complete speckle movie taken at 168 K, for which data collection was only started after the system had stabilized for 3 hours. The color scale indicates the averaged intensity. The image shows the irregular scattering pattern to be very sharp. The time correlation function $g_2(\tau)$ (see chapter 3 for definition) for this series of images is given in panel (b) of Fig. 4.6. It presents a clear static correlation, but shows no sign of time-dependent decay. This testifies both to the stability of the setup (which is no mean task to achieve) and the apparent absence of equilibrium dynamics for the titanate charge order on these time scales.

The data shown in Fig. 4.6 represent the tip of the iceberg in terms of the total data recorded. Extensive efforts were made to analyze all such speckle movies in terms of the time correlation function $g_2(\tau)$. In a number of cases a decrease in correlation with time was
Fig. 4.5 Top panels: Autocorrelation images (1400x1400 pixels) of the hard x-ray coherent diffraction patterns shown in Fig. 4.4. The false color represents the correlation coefficient. Center panels: The horizontal (red) and vertical (blue) line-cuts through the center of the autocorrelation images. Bottom panels: details of the line-cuts, zoomed in to the central peak, in which the speckle size is indicated.
Fig. 4.6 (a) The average of a complete hard X-ray speckle movie (500 frames) recorded at the (011) reflection of Er$_{0.6}$Ca$_{0.4}$TiO$_{3}$ at a sample temperature of 168 K. The Pixis 1300 camera was used and the color scale represents the value of pixel intensity. The total acquisition time of the movie was 1000 s, spread within a total time period of 3000 s. (b) The correlation function $g_2(\tau)$ for the series of detector images which make up the frames of the movie.

observed, but in all these cases this could be ascribed to instabilities in the experiment, rather than equilibrium charge order dynamics in the sample.

4.2.3 Non-equilibrium dynamics

The data shown in Fig. 4.6 were recorded at 168 K. Recording data at different temperatures, we noticed that the averaged speckle patterns exhibited significant changes from one sample temperature to the next. Given the very high degree of mechanical stability and reproducibility of the sample stage vs. changes in the sample temperature, this presented the opportunity to probe the non-equilibrium dynamics of Er$_{0.6}$Ca$_{0.4}$TiO$_{3}$ following a change in the sample temperature. To test this, we followed the speckle patterns during and after controlled 2 K temperature steps.

Here we discuss data from a typical example of such a movie, taken with the Pilatus-300K camera at a frame rate of 1 s. The sample was heated from 166 K to 168 K with a PID control-and-feedback loop, at a rate of 1 K per second. Although the temperature reaches the new set point after several seconds (according to the calibrated temperature sensor), we purposely recorded the speckle movie over 25 minutes, so as to allow comparison of the thermal evolution rooted in the sample, with the effects of possible experimental drifts in the experiment.

In Fig. 4.7, six representative time slices out of the full data movie are shown, each separated from its neighbours by 19 s. Already in the second frame, changes with respect to
Fig. 4.7 Time series of the charge order speckle patterns of $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ recorded using coherent, hard X-rays. The series of images was captured during and after heating the sample from 166 to 168 K over a time period of two seconds, as explained in the text. The images shown succeed one another by 19 s.
Fig. 4.8 Two-time correlation matrices of the data series described in Fig. 4.7. (a) all 1100 frames; (b) detail of the first 100 frames. The color here represents the value of the correlation coefficient. Panels (c) and (d) give the corresponding evolution of the total scattered intensities in these movies. The intensities of the highlighted scattering patterns in Fig. 4.7 are indicated by black arrows in panel (d).

The original pattern are visible, although the overall intensity distribution is maintained. For the data at 58 s, the total scattering intensity had dropped by 20 % of the original value. The last two patterns (77 and 96 s) are virtually indistinguishable.

To provide a quantitative analysis of this data series, we used a combination of the XPCSGUI toolbox developed by M. Sprung and Z. Jiang [119], as well as self-programmed routines to calculate the two-time correlation function of this dataset. In Fig. 4.8 (a), the two-time correlation matrix of $g_2(t_1,t_2)$ is shown, which is calculated by correlating the speckle patterns of all possible 2 time pairs in the series (see Eq. 3.15). Panel (b) shows a zoom of the first 100 seconds (i.e. the top left-hand corner of panel (a)), and as can be seen from the color scale, $g_2(t_1,t_2)$ ranges from 1 (totally uncorrelated, dark blue) to 1.2 (white). These highest values are found on the diagonal of the matrix (from top-left to bottom-right) which represent the autocorrelations at each given time, or equivalently, the contrast of the
individual speckle images [120]. For comparison the evolution of the total scattered intensity is also plotted in panels (c) and (d).

The overall matrix shows that the correlations are lost very quickly (over the first 50 s), signaled by a drop in $g_2(t_1,t_2)$. However, the two-time correlation values pick up again as the new speckle pattern stabilizes. Considering the zoom shown in panel (b), it is clear that the correlation coefficient drops from 1.2 to 1.1 in the first 20 s, even though the intensity has dropped only by 10%. This link between the weakening of the two-time correlations and the diffraction intensity can be seen by comparing the zoomed 2D image (panel (b)) with the total intensity trace of panel (d), both of which share the same time-scale. It is apparent that - with a slight offset - when the total diffraction intensity is changing most rapidly, the two-time correlation is reduced, but that it recovers after the diffraction intensity has stabilized again. This kind of delayed reaction is reminiscent of the ongoing movement of domain walls in a magnetic system after the time-dependent alteration of an external magnetic field is finished. In magnetic systems, such behavior is due to either pinning of domain walls to impurities, energetic penalties that are involved with moving domain walls even in homogeneous systems or topological effects where a domain wall that needs to move is obstructed by other domain walls [121]. In the case of the CO dynamics in the titanates, it is important to note that the coherent contrast remains high during each of the 1s exposure times, indicating that the settling dynamics are at least one or two orders of magnitude faster than this acquisition time.

Thus a picture emerges of a multi-scale response of the CO and the spatial pattern between the coexisting orthorhombic and monoclinic patches to a change which occurs in the form of fast avalanches. It implies that the domain structure becomes metastable by the temperature change, but also that relaxation can not occur immediately. In analogy to magnetic domain wall motion after effects, this must imply that also in this case domain walls are difficult to move. At this point it is unclear what the impeding mechanism is, but again a possible intrinsic inertia, pinning to lattice defects and topological lock-in are candidates, which we will discuss shortly.

In doped transition metal oxides, the lattice is intrinsically disordered, giving an intrinsic and potentially strong pinning potential landscape. This will tend to suppress equilibrium fluctuations whether they be of the charge order pattern itself or of the spatial distribution of charge ordered domains.

However, it can also be envisaged that when two checkerboard domains meet, they can have an anti-phase domain wall. Thus the collision of two such domains will lead to jamming dynamics.
Finally, it has been argued by Ahn et al. from simulations of manganites [15, 122] that the charge order in these systems is stabilized in the mixed phase by the energy penalty that accompanies the growth of a CO region in the orthorhombic host, since CO formation involves a large scale re-organization of the lattice. The present results may be the first observation of dynamical effects in charge ordered systems, and as such open a way to disentangle these three causes.

Whatever the true cause, we have established that on changing the temperature, a new CO configuration may settle in by a series of rapid avalanches or ‘slips’ separated by stable ‘stick’ periods. The clear signal of post ‘slip’ dynamics within the new, ‘stick’ CO pattern seen in Fig. 4.8 make it clear that there is some medium-to-long time dynamics operative after a temperature change.

The timescale of the latter - ‘stick’ - process can be seen from Fig. 4.8 (a) and (b) to be of order 10 s. If access is to be gained to the fast ‘slip’ processes, coherent X-ray experiments need to be conducted at significantly faster timescales, and for the next step towards achieving this, we turn to the world’s first hard X-ray laser source, as described in the following section.

### 4.3 A first XFEL-based, coherent scattering experiment

A consortium from BESSY, DESY and the University of Amsterdam secured 5 shifts (1 shift = 12 hours) of beamtime at the X-ray correlation spectroscopy (XCS) experimental station of the LCLS in SLAC. This X-ray Free Electron Laser produces fully transversely coherent laser pulses with a duration of only $\sim 30$ fs at a repetition rate of 120 Hz. The average coherent photon flux of the source is around two orders of magnitude higher than to a typical third generation synchrotron source, meaning a single 30 fs LCLS pulse contains as many photons as arrive in one second at DESY. These characteristics open up new possibilities to enter the millisecond time domain in XCS using area detectors, provided X-ray cameras are available that can record scattering movies at the same pace. In our LCLS experiment, we used the Timepix detector which was produced for this purpose by Amsterdam Scientific Instruments (ASI) [123]. This camera is derived from pixel detectors developed within the Medipix collaboration, which grew out of high energy physics particle detection at CERN. A more detailed discussion of this detector is given in Appendix B.

In Fig. 4.9, the experimental concept for speckle-based experiments at LCLS is illustrated. The X-ray laser pulses arrive at the sample with the maximum repetition rate of 120 Hz, thus separated by a time interval of 8.3 ms. Each pulse generates a scattering speckle pattern on the Timepix camera, such that a scattering movie is recorded at the maximum repetition rate of LCLS.
The experimental setup has been described in the previous chapter. A photon energy of 8.8 keV was selected, which together with a measured beam size at the sample position of 12x18 $\mu m^2$ and a detector distance of 7 meters gives an estimated speckle size of $\sim 50 \mu m$. The LCLS can be operated in three different modes. In the continuous mode, pulses are recorded at the full 120 Hz rate, requiring a detector such as the Timepix camera. The bunch and the single shot modes are such that the detector is illuminated by either a pulse train or single pulse, separated in both cases by a user-defined interval. These modes allow the use of conventional CCD cameras with readout times of seconds. These last two modes were used to compare the data from the Timepix camera with those from a Pixis-1300 camera, the same instrument as we used at Petra-III. For convenience, the parameters of the two detectors are summarized in Table 4.1.

<table>
<thead>
<tr>
<th>Detector</th>
<th>Dimension (pixel)</th>
<th>Pixel size</th>
<th>Background</th>
<th>Readout time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pixis</td>
<td>1300*1340</td>
<td>20 $\mu m^2$</td>
<td>yes</td>
<td>4 s</td>
</tr>
<tr>
<td>Timepix</td>
<td>512*512</td>
<td>55 $\mu m^2$</td>
<td>no</td>
<td>8.3 ms</td>
</tr>
</tbody>
</table>

Table 4.1 Comparison of the specifications of the Timepix and Pixis-1300 detectors used at the LCLS.

For fear of heating the sample with the intense X-ray pulse train, absorbers were inserted in the beam that reduced the incoming intensity by a factor of 80 when operating in the continuous mode using the Timepix camera. In the burst mode and single shot mode, the
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Fig. 4.10 (a) A typical single-shot coherent scattering detector image from the (022) reflection of Er$_{0.6}$Ca$_{0.4}$TiO$_3$ taken with the Timepix camera. An area from the most intense part of the image indicated by the small white square has been zoomed out in the lower right hand corner. (b) The time-averaged image arrived at by summation of 451 single-shot frames.

The sample has time to cool down during the readout time of the detector, so intensity reduction is not needed. In order to compensate for the loss in primary beam intensity during continuous mode, it was decided to switch to the (022) lattice reflection which is a true symmetry-allowed lattice reflection and therefore possesses a scattering efficiency some 100 times higher than that of the (011) reflection. As will be shown below, the (022) reflection is also sensitive to the monoclinic lattice distortion that accompanies the charge order in the hole-doped titanate under investigation.

As we were only the second user group at the LCLS’s XCS station, many experimental issues needed to be resolved before and during the experiment. A number of these are addressed in the Appendices to this thesis: Appendix B deals in some detail with various aspects of the Timepix camera; while in Appendix C, the longitudinal coherence characteristics of the X-ray pulses arriving at the XCS station during our experiment are discussed.

4.3.1 (022) Coherent diffraction patterns

In Fig. 4.10(a), we show a typical example of a raw detector image of (022) diffraction (Bragg angle $\theta=19.6^\circ$), originating from a single 30 fs X-ray pulse; recorded at a sample temperature of 168 K using the Timepix detector. The Timepix was operated in the so-called Time-over-Threshold (ToT) counting mode, which is explained in Appendix B. In this
counting mode, the output is given in ToT units, for which a single 8.8 keV photon yields 34 ToT counts on average.

Evidently, even for the more intense (022) lattice reflection, the image consists of a few single, non-zero pixels on a dark background, because of which the speckle pattern itself is not recognizable. Within all the millions of frames that were recorded during the five shifts, only a few tens of multi-photon events at a single pixel location were detected. Clearly, in such sparse datasets the coherent diffraction pattern can only be recognized after binning a large number of frames. The typical probability density function for such sparse data is given in chapter 3 and Appendix B.

Fig. 4.10 (b) shows the average of 451 single shots in 4s, and now a clear coherent diffraction pattern is visible. The black cross at the center of the averaged pattern is in the real data, and is the signal-less area due to the connection between 4 Timepix chips, this only being visible in the summed images. As the speckle size is comparable to the pixel size of the Timepix detector (55 µm²), individual speckles are not resolved.

An example of one of the more intense single shot Pixis-1300 frames is given in Fig. 4.11 (a). Here the speckle pattern can be observed, mainly because of 80-fold higher incoming X-ray intensity due to the absence of absorbers. Following the routine of the earlier sections, Fig. 4.11 (b) shows the autocorrelation of this image, while (c) and (d) give the full and zoomed horizontal and vertical central profiles of the autocorrelation function. In both cases a central peak with a width of 2 pixels is found, indicating that the experimental speckle size is measured to be 40 µm, close to the expected value of 55 µm. Interestingly, in these data we see diffraction side bands in the vertical profile, while in the synchrotron data we found these mainly in horizontal profiles, indicating that this difference is not per se due to the horizontal scattering plane geometry of the experiment, but rather reflects the source coherence properties.

The data obtained with both cameras shown in Fig. 4.10 and Fig. 4.11 illustrate that - as was the case for the forbidden (011) reflection - the (022) diffraction peak is broken up into a coherent diffraction pattern, with correlation lengths comparable to those of the (011) reflection. This implies that the (022) reflection is sensitive to the same type of local patterns due to the CO phase patches as the (011). However, in the case of the (022), the speckle contrast is now the result of interference between outgoing X-rays from two patches of differing structures, both of which have an allowed lattice reflection. This means that the local order and disorder to which the speckle pattern is sensitive must now be due to the differences in lattice structure and the very small density differences between the two phases.

As is known from regular X-ray diffraction, the monoclinic phase differs from the orthorhombic one by a small difference in lattice parameters and an angular deformation
Fig. 4.11 (a) An example of the coherent diffraction patterns recorded at (022) reflection of \(\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3\) using the Pixis-1300 camera and a single pulse of X-ray radiation from the free electron laser. Panel (b) shows the corresponding 2D-autocorrelation function and (c) and (d) show horizontal/vertical (red/blue) line-cuts at two different magnifications through the autocorrelation data.
Fig. 4.12 Comparison of the $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ (022) diffraction signal taken at the LCLS using the (a) Timepix and (b) Pixis detector, covering the same range of diffraction angles. In both cases the images shown represent an integration over 100 LCLS X-ray pulses. Intensities for the color scale are given in terms of ToT (Timepix) and ADU (Pixis) units respectively. (Note the $x$ and $y$ pixel scales are different in the two images due to the different pixel size of the two cameras. The total areas in $q$-space, however, are identical.)

Thus, when the orthorhombic and monoclinic phases coexist in the same portion of the crystal (and in this context, this means in the illumination volume), a highly strained situation results, with the overall crystal structure being mosaic in nature. We will come back to the implications of the strain between the coexisting phases during the MIT in the next chapter. Here we limit ourselves to the conclusion that these crystallographic effects are sufficient to lead to a considerable diffraction contrast between the two phases, also when measuring the (022) reflection, and that this lies at the root of the speckle formation observed in these LCLS data.

4.3.2 Comparison of Pixis and Timepix detector

In Fig. 4.12, we show images of the (022) reflection of $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ recorded at $T = 168$ K, taken with the Timepix (panel (a)) and Pixis-1300 (panel (b)) cameras. The Pixis image that from the 1300x1300 pixel area, illuminated by 100 LCLS pulses in burst mode. The Timepix image is extracted from part of a larger image obtained by digitally summing 100
4.3 A first XFEL-based, coherent scattering experiment

Fig. 4.13 Integrated intensity of 451 single shot coherent scattering images from the Er$_{0.6}$Ca$_{0.4}$TiO$_3$ (022) reflection recorded at a sample temperature of 168 K using the Timepix camera. On the bottom graph, the contrast of the summed images (C$_2$) is plotted as a function of time delay, illustrating a lack of dependence on the increasing delay time.

single shot frames, with the selection such that the areas covered by the two camera images are identical. Comparison between the two images shows that the Timepix detector - run in the ToT mode is capable of giving speckle datasets similar to those of the Pixis detector. Both images show the (022) reflection to be comprised of a similar-sized intensity blob, with well-resolved, coherent diffraction fringes in both cases. Thus, these data show that the Timepix detector is able to track the same sort of physics in the sample, here via the (022) reflection, as the Pixis detector, but the Timepix does allow - given sufficient incoming coherent X-ray intensity - a much faster sampling rate of up to 120 Hz. In the following section, Timepix data from the (022) reflection will be presented and analyzed with a view to determining whether equilibrium fluctuations of the charge order can be accessed using speckle-based techniques.
4.3.3 Search for fluctuations in the (022) speckle data from the LCLS

Fig. 4.13 (a) shows the shot to shot variation of the total number of ToT counts on the Timepix detector during a continuous mode movie recorded over a total time-period of 1.5 s with the absorber in the beam. This particular data series was selected as being one of the most stable portions of a movie that has in total 50608 frames. Despite this selection to favor stability, it can still be seen that the ToT count rate varies by as much as a factor of ten from shot to shot. The statistics of these variations are discussed in detail in Appendix B and C. Here, however, we are interested in the question whether it is still possible to observe speckle fluctuations in these data that could be linked to possible equilibrium dynamics of the charge order in the Er$_{0.6}$Ca$_{0.4}$TiO$_3$ crystal.

In standard speckle time correlation experiments, it is assumed that the incident light intensity is stable as a function of time, which is clearly not the case using this SASE X-ray laser source [91]. Obviously, given these strong fluctuations in the incident intensity, a correlation analysis is impossible, and thus the data have been analyzed in terms of their contrast. In Fig. 4.13 (b), the contrast of the sums of two single-shot images taken at different time delays is plotted, and it is immediately clear that the data show no time dependence. The initial drop is merely due to statistical averaging. Although signs of dynamics are not easy to spot in these data, the initial impression from Fig. 4.13 (b) is double checked, so as to investigate whether dynamical information lies hidden in the data, by carrying out an analysis of the contrast reduction of the binned images using two slightly different approaches.

4.3.4 Contrast reduction due to statistical averaging

As a first step, the number of Timepix images that needed to be binned in order to obtain a recognizable coherent diffraction pattern with a well defined contrast value was determined. This number was of order 200. In Fig. 4.14, we show the contrast reduction occurring upon summation of successively larger numbers of such binned images. The first data-point corresponds to the contrast of a sum of 200 frames, and each subsequent point involves summation of a further 200 frames. Taken at face value, Fig. 4.14 would seem to indicate a typical time-scale of 10 s over which the contrast drops by 50%.

The observed behavior could be taken as a sign of charge order dynamics, since this would be expected to blur the images as the summation continues, thereby reducing the contrast. However, the same decay of contrast could also be a result of statistical averaging as mentioned above for the single-pulse analysis. To distinguish between these two situations, the analysis was repeated, but this time not adding successive 200 frame bins in their time order of being recorded, but adding them in a random, shuffled time-order. As can be seen
Fig. 4.14 The contrast reduction resulting from averaging successively larger numbers of 200 frame bins. The blue square symbols show successive sums calculated in the right time order (blue square) and in random order (red triangle).

from the red curve in Fig. 4.14, the result from the random order series barely deviates from the original. As a consequence, it has to be accepted that this apparent time-dependent contrast reduction is not due to equilibrium dynamics of the CO in Er0.6Ca0.4TiO3. For this reason a second route towards the analysis of the data was taken, as described in the following section.

**4.3.5 q-dependent contrast analysis**

In a more elaborate approach to analyzing the data, we re-binned 16800 images of single-shot LCLS data taken at continuous mode into 84 bins of 200 frames each, thus each bin corresponds in total to 1.6 s of data. An example of one binned dataset is given in Fig. 4.15 (a), in which also a number of constant contours of the in-plane scattering vector $|q|$ have been superimposed. These contours delineate the following $|q|$ regions: red ($|q| \leq 1 \times 10^{-3}$ Å$^{-1}$); light green ($1 \times 10^{-3} \geq |q| \leq 2 \times 10^{-3}$ Å$^{-1}$); blue ($2 \times 10^{-3} \geq |q| \leq 3 \times 10^{-3}$ Å$^{-1}$) and black ($3 \times 10^{-3} \geq |q| \leq 4 \times 10^{-3}$ Å$^{-1}$), which corresponding to real space structural length scale ranging from 0.25 and 1 µm. For reference, the average image of all 84 bins in the movie (i.e. 16800 frames) is shown on the right in panel (b). In panel (c) the contrast for the different
Fig. 4.15 (a) A single bin of 200 Timepix individual (single LCLS shot) frames from the (022) reflection of Er$_{0.6}$Ca$_{0.4}$TiO$_3$. $|q|$ contours are overlaid on the image which correspond to correlation lengths of 100, 50, 33 and 25 nm. (b) The average coherent diffraction image of 84 such 200-frame bins, thus corresponding to 16800 frames in total. The false color scale represents the intensity in ToT units for both panels (a) and (b). (c) The time dependence of the contrast of the binned images for the $|q|$ regions: red ($|q| \leq 1 \times 10^{-3}$ Å); light green ($1 \times 10^{-3} \leq |q| \leq 2 \times 10^{-3}$ Å$^{-1}$); blue ($2 \times 10^{-3} \leq |q| \leq 3 \times 10^{-3}$ Å$^{-1}$) and black ($3 \times 10^{-3} \leq |q| \leq 4 \times 10^{-3}$ Å$^{-1}$). (d) The averaged pair contrast function $C_2(\tau)$ for the same $|q|$ intervals.

$q$-ranges is plotted for each of the 84 binned datasets. In Chapter 3, the time-dependence of the speckle contrast was introduced, illustrated schematically in Fig. 3.5. For the case of a fully developed, static speckle pattern, the contrast should be unity.

As can be seen in panel (a) of Fig. 4.15, even after binning 200 detector images, the illuminated pixels (i.e. those with non-zero intensity) are sparse. This means the speckle pattern cannot be fully developed and the speckle contrast can then be greater than unity [97]. For the integration over the data sequence covering larger $q$, the illuminated pixels are further reduced in intensity, leading to a reduction of the contrast. Of more interest in the context of this research is exploring whether there is a time dependence of the contrast of each binned image, and the traces shown in panel (c) whose color coding matches the $q$ contours shown
in panel (a) show that - apart from some fluctuations in the value - no sign of dynamics can be extracted.

The final approach adopted in the analysis of these speckle movies is to examine whether dynamics can be uncovered if possible changes in contrast are searched for not within a single series of binned, consecutive ‘stills’ in the movie, moving forwards in time, but with respect to possible contrast changes between any two binned images separated by a time delay $\tau$. In Chapter 3, this method, involving what is known as the pair contrast $C_2(\tau)$ function (see Eq. 3.18), was described. The procedure involves as a first step, the evaluation of the contrast between all pairs of binned images separated in time by the minimum amount of $1.6$ s (the time between bins). This is done for all adjacent bins and the result is averaged over the number of pairs considered. The next step involves what could be called ‘next nearest neighbor’ bins (i.e. separated by a time delay of $2 \times 1.6 = 3.2$ s), now normalized be the (lower) number of these bin-pairs, and so on. The result gives the averaged pair contrast, and this is shown in panel (d) of Fig. 4.15. $C_2(0)$ for time delay $\tau$ equal to zero gives the average contrast of all binned images (i.e. the average of the traces shown in panel [c]). $C_2(\tau)$ then drops immediately to give a constant value. Clearly, this sophisticated analysis brings sharply into focus the fact that the apparent dynamics seen in Fig. 4.14 are indeed due to statistical averaging. Therefore, albeit given the somewhat reduced sensitivity of this method due to the fact that the speckle size is equal to the detector pixel size in these data, the analysis shown in Fig. 4.15 points to a lack of fluctuations in the charge order (at accessible time-scales) in the illuminated region of this doped titanate with correlation lengths between 0.25 and 1 $\mu m$.

### 4.4 Conclusion and outlook: speckle experiments

In this chapter, speckle patterns from the (011) and (022) reflections of $Er_{0.6}Ca_{0.4}TiO_3$ obtained with soft and hard X-ray synchrotron radiation and with the world’s first hard XFEL source have been presented and discussed. A model has been put forward that explains the formation of speckle patterns in the (011) reflection in terms of the existence of a mixed phase situation with diffraction-transparent orthorhombic and diffraction-generating monoclinic patches coexisting within the illuminated volume of the single crystal. For the (022) lattice reflection, the speckle contrast is assigned to differences in the crystal structure of the two phases, accompanied by strain fields resulting in mosaicity. If this is the right picture for the (022) reflection, by extension these effects should also be playing a role in the (011) speckle patterns.
In the cases of both the (011) and (022) reflections, we argue that the speckle patterns can be used as fingerprints of the complex three-dimensional structure in the illuminated volume, and therefore can be used to track possible dynamics in the coexisting phase system. In all three sets of experiments conducted - soft and hard X-rays at the storage ring and hard X-rays at the free electron laser - we therefore attempted to uncover signs of fluctuations between these two competing phases by filming the speckle patterns over (long) periods of time. After investing heavily in experimental know-how, instrumental efficiency and stability, we are forced to conclude that our experiments indicate that no equilibrium fluctuations are present within the time-window to which these experiments are sensitive.

However, we obtained first indications of non-equilibrium dynamics following temperature steps. From the high contrast of 1 s exposures we conclude that the actual dynamics must take place on a very fast time scale. However, there are indications that the domain structure in the mixed phase evolves over time scales of 10 s or more, indicative of jammed dynamics. The underlying physics is not clear but could be either pinning of domain walls to crystal defects such as cation disorder, topological lock in of domain walls or intrinsic inertia of domain walls due to possible energy penalties involving domain wall motion.

We will return to the physical meaning of this findings in the conclusion of the next chapter, where we place them in the perspective of our results on the spatial organization of the charge order in the same titanate systems.

Seeing as our experiments at the X-ray laser were the first attempts to detect dynamics in a hard condensed matter system using speckle techniques, this chapter closes with some comments on the possibilities for future XCS experiments at LCLS. As can be expected, it is clear that we were on a steep part of the learning curve. The interpretability of the data suffered from the low scattered intensity, a situation that could be improved drastically in future experiments, in which the absorbers should be removed from the beamline, also in continuous mode. Having said this, radiation damage and beam-induced heating would need to be monitored carefully, for instance by recording integrated speckle patterns with increasing intensity to confirm that the intensities the sample is exposed to are - to an acceptable statistical degree - such that there is insufficient beam damage to influence the physics conclusions being drawn.

A part of these considerations is the fact that the LCLS is a source that has intrinsically large shot-to-shot intensity fluctuations. At first sight, this poses a serious impediment for traditional time correlation analysis of X-ray speckle data. However, it should be possible - a posteriori - to sort the frames according to the intensity of the shots, thus creating data subsets taken in different intensity regimes that can be better compared. Although standard analysis codes for XCS data analysis assume that data points are separated by a fixed time
4.4 Conclusion and outlook: speckle experiments

interval this is not per se necessary as long as the time label for each data point is known, as is the case at the LCLS.

A further issue that needs resolution is the effect of possible pointing instability of the beamline. In XCS, it is vital that shots illuminate the same sample volume, since in a system with significant spatial variations in local order such as charge ordered complex oxides, each volume would give its own, different speckle pattern. In the data presented in this chapter, the average images taken over long time periods exhibit a recognizable and stable speckle pattern, indicating that the shot to shot pointing stability is sufficient with respect to the intrinsic spatial disorder in the sample. However, for future experiments, an additional aperture near the sample might be a useful addition, although it would again cost precious intensity.

As a final outlook towards future possibilities for detecting charge order fluctuations or other dynamics in crystalline systems using speckle techniques, we mention that a ‘split-and-delay’ line is currently under development at LCLS [75, 101], and that this may provide access to time scales that are much shorter than the ones we have been able to probe here. This device will make it possible to split a single LCLS pulse into two parts, giving one a time delay of up to a few fs with respect to the other. This instrument would therefore make it possible to determine possible changes in the contrast in the sum of two (non-sparse) speckle patterns recorded with a variable - up to fs - time delay between the two. Clearly, pulse to pulse intensity variations are then not a drawback in this approach.

Finally, also LCLS II is already under way. This facility will have a repetition rate in the MHz range, opening access to the time regimes between our ‘early adapter’, albeit very slow time scale speckle experiments and the ultrafast split-and-delay type experiments. As has been shown at synchrotron sources via small angle scattering from colloids, XCS can access sub-µs time-scales using point detectors. LCLS II may make this possible for the study of electronic and magnetic dynamics in hard condensed matter systems using large angle scattering experiments. In the end, continued improvement in sources and beamlines will mean that eventually access will be provided to the time-scales in which the equilibrium dynamics of the charge and orbital textures of complex oxides such as the doped titanates studies in this thesis are to be found.