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

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Chapter 5

Structural Investigation of the Phase Separation in Titanates

In chapter two we reviewed earlier work which indicates that the metal insulator transition in the Y\textsubscript{1-x}Ca\textsubscript{x}TiO\textsubscript{3} system is thought to be accompanied by a succession of two phase transitions. The high temperature orthorhombic phase, labeled HTO, has an insulating signature in the sense that the resistivity rises on cooling. This increase in resistivity seems to be connected to a gradual lowering of the symmetry of the HTO structure into a low temperature monoclinic structure, labeled LTM. At even lower temperatures around the MIT transition, a transformation into a low temperature orthorhombic (LTO) phase is observed, with signs of phase coexistence with the LTM phase.

In chapter four, we have described that at temperatures around the metal insulator transition, the coherent diffraction patterns of the closely related system Er\textsubscript{0.6}Ca\textsubscript{0.4}TiO\textsubscript{3} are very complex, indicating the presence of a complicated spatial distribution of phases and thus supporting the claim for the existence of phase separation during the MIT. We found that the coherent diffraction patterns and hence the structure change on changing the sample temperature, but are static at thermal equilibrium at timescales of and longer than our minimum sampling time of 1 s. After a change in temperature, the ’settling times’ - over which the system relaxes to match the new temperature - were also shown to be faster than this 1 second timescale.

In this chapter, we investigate the thermal evolution of the mixed phase structure of Er\textsubscript{0.6}Ca\textsubscript{0.4}TiO\textsubscript{3} and experimentally examine its typical length scales. To this end we combine diffraction data that were obtained in the course of the speckle experiments on the (011) reflection from beam line P10 at Petra-III with the (022) reflection data from LCLS. In addition, we performed a scanning X-ray microdiffraction experiment at P10 that was specifically aimed to map out the mixed phase structure.
We will first discuss the observation of the splitting of the diffraction peak in the mixed phase temperature region for both the (011) and (022) reflections. We then report on the spatial arrangement of the phase separated system seen in the X-ray microdiffraction data, which unveils an intriguing stripe order, indicative of a self-organization of the mixed phases. At the end of this chapter, we will discuss a complete picture of the MIT in Er$_{0.6}$Ca$_{0.4}$TiO$_3$ by combining the the results of this and the previous chapter.

5.1 Evolution of the (011) and (022) reflections as a function of temperature

In order to directly capture the phase separation in the Er$_{0.6}$Ca$_{0.4}$TiO$_3$ system, we followed the thermal evolution of the (011) Bragg peak. For this we used the incoherent, high flux beam (10$^{13}$ ph/s focused to 150x75 $\mu$m) in combination with the Pilatus detector at P10, Petra III. The sample mounting and other conditions were as described earlier in chapter 4. Before starting the temperature-dependent run, the diffractometer was optimized on the intensity of the (011) diffraction signal at 300 K, which was found at an incident angle of $\theta_{in}=9.870^\circ$.

Fig. 5.1 (a) shows as a red, solid line the temperature dependence of the detector intensity (integrated over 540 detector exposures) taken during a cool-down from 300 K to 132 K. This curve displays a broad peak reaching a maximum at 200 K, followed by a relatively rapid decrease below 180 K. The shape of the curve in itself is an indication of a phase transition. It can be linked to the shape of the resistivity curves shown in Fig. 2.8, although a precise match cannot be made, because the resistivity data are representative of the percolative network of the metallic phase through the bulk of the sample while our X-ray data represent the properties of the small volume probed by the beam. Furthermore, the resistivity data of Fig. 2.8 (b) show that the sample properties are extremely sensitive to the doping level, which can vary locally even within a single crystal.

Earlier work by Kato [21], and Komarek [16] established a link between the maximum in the resistivity and the presence of the low temperature monoclinic charge ordered phase in Y$_{1-x}$Ca$_x$TiO$_3$. Below we demonstrate that this scenario also holds for Er$_{0.6}$Ca$_{0.4}$TiO$_3$.

As a first step, we show some exemplary detector images at different temperatures in Fig. 5.1 (b), where the color scale has been peak-normalized to better enable comparison. The images show that during the cooling scan, the original peak visible at 240 K - which we label with $q_S$ (S standing for small momentum transfer, thus big lattice parameter) - starts to broaden in the horizontal direction, as the detector image at 175 K shows. Looking at panel
(a), this is the temperature at which the intensity starts to decrease quickly, and at lower T, the (011) reflection has split into two well-defined peaks. The detector image for T=160 K clearly shows two diffraction peaks - that on the right (smaller \( \theta_{out} \), smaller momentum transfer) is \( q_S \), and that on the left, at bigger \( \theta_{out} \) or larger momentum transfer is labeled \( q_L \). By T=133 K the new, larger momentum transfer peak \( q_L \) can be seen to be dominant, but the smaller momentum transfer peak \( q_S \) still remains visible, although its total intensity is more than 10 times lower than it was at room temperature, before the cooling scan was started.

In order to analyze the temperature evolution of the horizontal peak-splitting along (011), we integrated each of the 540 detector images over the out of plane direction \( \chi \), so as to obtain the horizontal peak profile vs.T. These are collected and displayed in a 3D plot in Fig. 5.2 (a), in which the horizontal pixel positions on the detector have been projected on the \( q_{011} \) direction using the formula given by Eq. A.1 in Appendix A. This figure gives a good impression of the evolution of the total intensity and the peak splitting as the temperature is reduce, whereby after an initial increase in intensity of the (011) reflection, the strength of this reflection then falls off for temperatures below 200 K. At around 170 K, (weak) intensity becomes visible at \( q_L \), and at lower temperatures this \( q_L \) intensity dominates the diffraction profile.

A similar cool-down data set (for T 190 K to 155 K), obtained at LCLS for the (022) reflection is shown in Fig. 5.2 (b). Here the behavior is similar, with the high temperature peak, \( q_S \), giving way to a low temperature peak at higher \( q \). However, in these data, the \( q_S \) peak has much less intensity below 170 K, and instead of becoming a small, but well-defined second peak, it is only seen in the form of a small shoulder next to \( q_L \). This despite the fact that \( \theta_{in} \) was optimized for the \( q_S \) peak.

The evolution of the peak positions is clearer still in the gray-scale temperature vs. \( q \) maps shown in Fig. 5.3. Overlaid on the gray-scale images of panels (a) and (b) are the results of a fit single or double Lorentzian profiles. Panel (d) shows the quality of the fits to be very good. In Fig. 5.3(c), the fitted peak positions have been converted into the (011) interplanar spacing \( d_{(011)} \), with the d-spacing from the LCLS data on the (022) simply being divided by two, so as to land on the same plot as the \( d_{(011)} \)-data from Petra III. In both cases, the diffractometer angles \( \theta_{in} \) and \( \theta_{out} \) were calibrated on 300 K powder diffraction results [105]. The comparison shown in panel (c) is quite satisfactory, given the fact that the datasets were obtained on two different instruments designed for coherent experiments rather than high precision lattice studies. The data attest to the power of these instruments for high resolution studies: thanks to the long exit arm and the high pixel resolution of the cameras, very detailed data sets can be obtained.
Fig. 5.1 (a) The intensity of the (011) reflection of Er$_{0.6}$Ca$_{0.4}$TiO$_3$ during cooling from 300 K to 132 K. (b) 100 by 100 pixel detector images taken at temperatures indicated by the black dots in (a). The vertical direction corresponds to the out of plane angle $\chi$ and the horizontal direction to $\theta_{out}$. With the crystal orientation used here, and using the orthorhombic notation, these correspond to the crystallographic directions as indicated (see Appendix A). The false color indicates the peak-normalized intensity. The red lines indicate the positions of $q_L$ and $q_S$, where $q_L$ is the feature at larger momentum transfer due to the low-T orthorhombic phase, and $q_S$ denotes the smaller momentum transfer peak related to the monoclinic phase.
5.1 Evolution of the (011) and (022) reflections as a function of temperature

Fig. 5.2 Comparison of the temperature evolutions of the intensity profiles of (a) the (011) reflection obtained at Petra III and (b) the (022) reflection, measured at LCLS.
Fig. 5.3 (a) and (b) The temperature evolution of the (011) and (022) reflections against $q_{(011)}$ and $q_{(022)}$. At each temperature the horizontal peak profile $I(q)$ has been normalized to 1. The gray-scale ranges from 0 (black) to 1 (white). The red and blue overlays show the evolution of the maximum of the small $q$ (red) and large $q$ (blue) components obtained by fitting a subset of the profiles with two Lorentzian components, with an exemplary fit being shown in (d) whose middle panel shows the original data points (red), and the overlaid fitting result (blue). The two Lorentzian components are shown at the bottom and the fitting residue is given on top of graph in red. Panel (c) shows the $d_{(011)}$ interplanar spacing derived from the peak positions in the Petra III and LCLS data. The (022) d-spacing is rescaled to fall in the (011) plot via a simple multiplication by two.
The \( d_{(011)} \) data show very clearly that starting from room temperature the (011) interplanar separation drops for temperatures down to \( \sim 180-200 \) K. Below these temperatures, the diffraction peak starts to broaden and the d-spacing levels out and starts to rise again. At lower temperatures the \( q_L \) feature can be fitted (for temperatures below 168K for the (011) data), and the d-spacing connected to new branch drops on further cooling, and the associated Bragg peak taking over most of the diffraction intensity. In the same T-range, the d-spacing belonging to the remnants of the original \( q_S \) peak shows a clear increasing trend.

The (022) data, shown in panel (b) and with solid symbols in (c) follow the same trend, although the curves differ in details. In this (022) dataset, we can fit the peak profile with two peaks over the whole T-range measured, although below 160 K the low momentum transfer \( q_S \) feature has become very weak. Extrapolating both \( q_L \) datasets (blue data points; open and close squares) to higher temperatures would seem to indicate that already between 200 - 220 K, a nascent splitting into a \( q_S \) and a \( q_L \) feature could be expected.

This behavior is very similar to that observed in \( Y_{1-x}Ca_xTiO_3 \) powder diffraction studies [16, 21], in which the high temperature lattice peaks \( q_{(0nn)} \) were observed to split into large and small \( q \) components, indicative of phase separation, and even the difference in lattice plane spacing between the \( q_L \) and \( q_S \) phases is comparable. On the basis of these similarities, we therefore identify the \( q_S \)-peaks with reflections from the monoclinic LTO phase, and the low-T side branch \( q_L \)-peaks we link to the smaller unit cell, low temperature, orthorhombic LTO phase of \( Er_{0.6}Ca_{0.4}TiO_3 \).

### 5.2 Intensity ratios

In the measurements just presented and discussed in the previous section we are probing a single, fixed plane in reciprocal space, while the reciprocal space structure itself is changing strongly with temperature, as sketched in Fig. 5.4. Although this complicates the interpretation of peak widths and intensities, some important inferences can be made from the two datasets.

Firstly, in the low temperature (022) results, most intensity shifts to the LTO branch and the LTM peak is only visible as a weak shoulder, even though the detector position was optimized at room temperature to maximize the signal from the latter. Assuming that the form factors of the (022) reflection in the monoclinic and orthorhombic structures do not differ too much, this indicates that at the lowest temperature measured in this LCLS cool-down run - 132 K - the system is almost completely in the LTO phase.

Secondly, it is surprising that we observe the LTO component so clearly in the (011) data, as this reflection is symmetry-forbidden in the orthorhombic structure. Furthermore, in the
Fig. 5.4 Reciprocal space representation of the detector motion during a rocking scan in a phase separated system. The two coexisting phases are represented as two clouds of diffuse scattering surrounding their reciprocal lattice positions along the orthorhombic (011) direction, with the subscripts m and o standing for monoclinic and orthorhombic. Not that the lattice vectors and the size of the clouds are not to scale. See also Appendix A.

(011)-data, $\theta$ was optimized on the LTM signal. We ascribe the visibility of the LTO (011) intensity to local symmetry breaking effects due to lattice deformations caused by disorder in the Er and Ca site occupancy and due to local strain effects, to which we will come back later in this chapter. Apparently these effects are quite significant in the low-T data, since this “impurity” reflection carries more diffraction intensity than the peak linked to the residual, symmetry-allowed (011) LTM reflection. Considering the higher temperature data, similar arguments can be used to explain the presence of the (011) LTM diffraction intensity at temperatures as high as 270 K, when the sample should be wholly in the HTO phase.

5.3 2D detector rocking scans of the mixed phase system

As became clear during the analysis of the data, a much better - albeit slower - manner of probing the temperature dependence of the reciprocal space structure is provided by rocking scans, in which the sample is rotated over a small $\theta$ interval while the detector is kept in place. When using a large area pixelated detector, rocking the sample causes the detector to sweep like a fish net through reciprocal space, as is illustrated schematically in Fig. 5.4. In this figure we have represented the reciprocal space structure of the mixed phase system by two points on the (011) reciprocal lattice axis, surrounded by color clouds of diffuse scattering intensity as a crude representation of the form factors of the LTO (black) and LTM (red) structures in the diffraction volume.
We performed rocking scans of the (011) reflection by filming the diffraction spot while stepping the sample angle $\theta$ from 9.7 to 10.7°. The information obtained from such a scan can be used in two ways. In the most simple manner, one records the total integrated intensity of each image to construct an overall rocking curve. Fig. 5.5 shows the resulting curves obtained at different temperatures between 132 and 300 K. The curves obtained at 132 and 300 K (top panel) were acquired with the 17x4 $\mu$m$^2$ unfocused beam, while the data for the 5 intermediate temperatures (bottom panel) were taken with the 3x4 $\mu$m$^2$ focused beam.

One point to bear in mind when considering the rocking-curve data is that the beam could possibly move over the surface while the sample angle is rocked, due to imperfect (horizontal) alignment between the incoming beam and the $\theta$ rotation axis. In homogeneous samples this is not a problem, but here, since the mixed phase sample is intrinsically inhomogeneous, if the beam were to wander, positional and angular information would become entangled. These kind of effects could and probably do lie behind some of the fine structure of the curves shown in Fig. 5.5, and we do not possess enough independent experimental information to disentangle the spatial and angular factors involved.

Nevertheless, the overall behavior seen in Fig. 5.5 is compatible with the structural models for $Y_{1-x}Ca_xTiO_3$ put forward in the papers of Komarek et al. and Kato et al. [21, 16]. In particular, the top panel of Fig. 5.5 shows that at 300 K the diffraction peak is at low angles, implying a short wave vector ($q_S$), which naturally ties in with the high temperature, orthorhombic phase. Similarly, at the lowest temperature, $T=132$ K, only the LTO feature is seen. The curves taken in the temperature region around the MIT are shown in the bottom panel of Fig. 5.5. In this regime, two peaks are clearly observed, and the intensity ratio gradually shifting in favor of the higher angle peak as the temperature is reduced. This behavior can be understood from Fig. 5.4 because, when we rock the sample, the detector plane first sweeps through the low temperature monoclinic peak before reaching the low temperature orthorhombic peak, as the former has the smaller wave vector.

It should be noted that the intensity under the rocking curves gives a fairly good measure of the diffraction strength at each temperature. The fact that for the 300 K and 132 K results (top panel) these intensities are nearly the same agrees with the Komarek/Kato structural models developed for $Y_{1-x}Ca_xTiO_3$, according to which these reflections are produced by the HT and LT orthorhombic phases respectively, and for both of these phases the (011) reflection is symmetry forbidden.

Unfortunately, we are not able to directly compare the scattering intensity of the data recorded with the focused and unfocused beams, as their relative intensity is not known.

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1 If the horizontal misalignment is $h$, the rate of change of the beam position $x$ with rocking angle $\theta$ is $dx/d\theta = -h \cos \theta / (\sin \theta)^2$ which evaluates to -32.7 $h$ for $\theta = 10^\circ$. 
Fig. 5.5 Integrated detector intensity during (011) rocking scans taken at the different temperatures indicated. Top panel: measured using the unfocused 150x75 µm$^2$ beam. Bottom panel: recorded using focused 3x4 µm$^2$ beam. The symbols next to the temperature labels indicate the direction of T profile within which each of the constant sample temperatures shown has been realized: up-arrow is warming; down-arrow is cooling and a dash is no T profile.
Nor can the amount of LTM and LTO phases at each temperature be inferred since the LTO reflection is coming only from those parts of the crystal in the LTO structure which additionally have reduced (local) crystal symmetry, so that the (011) reflection - which is subject to extinction in the regular LTO structure - can even exist.

In a more elaborate approach, instead of integrating the total detector intensity at each angle in the rocking curve, the detector images can be integrated over the out-of-plane angle \( \chi \), in order to obtain the horizontal profile \( I(\theta_{\text{out}}) \) at each angle \( \theta_{\text{in}} \). These individual profiles can then be assembled into a \( \theta_{\text{in}}-\theta_{\text{out}} \) intensity map. We first consider Fig. 5.6, which shows the intensity map of the rocking scan taken at 132 K using the unfocused beam. This figure shows the complete scattered intensity of the LTO (011) peak, collapsed onto the diffraction plane. The top, false-color, image shows data on an absolute intensity scale and in the the lower (monochrome) image each vertical slice (at constant \( \theta_{\text{in}} \)) is first normalized and then added to the map.

These maps carry a wealth of information and in fact contain all the information of both the traditional slit detector rocking scans as well as those of \( \theta - 2\theta \) scans. Firstly, integration over \( \theta_{\text{out}} \) yields the rocking curves like those shown in Fig. 5.5. As a reference we show the \( q \)-space trajectory of a traditional slit detector during a \( \theta - 2\theta \) scan using the slanted red line. In this particular instance this trajectory was aligned to hit the most intense pixel of the map. It is clear that to capture the information contained in this map with a slit detector, many scans would have been necessary.

Returning to the top-most image of Fig. 5.6, we note that the detailed shape of the diffracted intensity is quite complicated, consisting of a sharp ridge at \( \theta_{\text{out}} = 9.8^\circ \) with a base that spreads out in a triangular shape towards higher \( \theta_{\text{in}} \). In the corresponding 132 K curve shown in the top panel of Fig. 5.5 this ‘base’ is visible as a shoulder between \( \theta = 10^\circ \) and 10.1°. Although a detailed interpretation is hindered by the mix of spatial and angular information (due to small misalignments), the map indicates the presence of extensive disorder or, in more conventional terms, mosaicity in the sample.

The representation chosen for the bottom panel of Fig. 5.6 more clearly reveals the existence of a small \( q_S \) (LTM) component at \( \theta_{\text{out}} = 9.7^\circ \) on the left hand side of the map. We identify this as being the specular reflection of the sample. This intensity is hidden in the left shoulder of the rocking scan curve shown in the top panel of Fig. 5.5. The vertical blue line represents the the cut through reciprocal space a detector would make for \( \theta = 9.870^\circ \), showing again that the ability to pick up intensity from the two phases depends critically on access to the correct \( \theta \) values, at the level of tenths of a degree.

Fig. 5.7 show the rocking-scan maps analogous to that shown in Fig. 5.5, but now at different sample temperatures. The red \( \theta_{\text{in}}-\theta_{\text{out}} \) scan-line is reproduced in all maps, and as a
Fig. 5.6 θ_{in}-θ_{out} rocking-scan maps from Er_{0.6}Ca_{0.4}TiO_{3} taken at 132 K. The top panel shows the data on an absolute intensity scale. In the bottom panel each scattering curve was peak-normalized individually before constructing the map. The slanted line (red) represents the trace of a conventional θ − 2θ scan taken with a slit or point detector. The vertical blue line in the lower panel represents the detector plane cutting at θ = 9.870°.
reference three yellow lines are overlaid at three particular $\theta_m$ values that will be used in the forthcoming discussion. Combining the information in these images, data presented in the previous section and information in the literature on the $Y_xCa_{1-x}TiO_3$ system, a scenario for the phase transition in $Er_{0.6}Ca_{0.4}TiO_3$ can be set up as follows.

Starting at the highest temperature of 300K the map shows a relatively sharp HTO-peak surrounded by a diffuse scattering halo. On lowering the temperature to 172 K the peak moves towards what we believe to be the LTM position at smaller $\theta_m$ values. In the 168 and 166 K cases, clear satellites are visible, some of which can be linked to fine-structure in the corresponding integrated rocking-curves shown in Fig. 5.5. These satellites indicate a substantial degree of phase separation within the scattering volume. At temperatures below 164 K the diffracted intensity moves back to $\theta_m$ values matching the orthorhombic structure (in this case LTO), but the peak width is roughly thrice that of the HTO case. This is a clear indication that the structural correlation lengths in the LTO phase are of order three times shorter than those in the LTM and HTO phases in the topmost four data panels of Fig. 5.7. The LTM phase seems to linger on in the form of a faint blue horizontal stripe at $\theta_{out} = 9.7^\circ$, even in the data recorded at 132 K. In the next section we will seek to confirm these assignments using results from microdiffraction data.
Fig. 5.7 Right-hand panel: $\theta_{\text{in}}-\theta_{\text{out}}$ rocking scan maps of the diffracted intensity at the seven different sample temperatures shown. Slanted lines (red) represent the traces of conventional $\theta-2\theta$ scans that could be taken using a slit or point detector. The vertical (yellow) lines indicate the $\theta_{\text{in}}$ values of 9.870°, 9.8450°, and 9.770°. Left-hand panel: a stack of zooms of the same detector images around the main regions of interest for each temperature.
5.4 Mapping the phase separation in $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ with $\mu$XRD

Having established the overall evolution of the phase separation as a function of temperature through the MIT, we now turn to experiments aimed at establishing the real space distribution of the phases using scanning X-ray microdiffraction ($\mu$XRD). This novel technique only became possible recently by advances in synchrotron brightness in combination with rapid advances in X-ray optics [124, 125]. These developments have made it possible to focus down hard X-ray beams to micron sizes and in extreme cases even as far as 50 nm. This not only allows the real-space imaging of materials by stepping them through the beam, but also brings the possibility to combine real space resolution with $q$-space resolution of diffraction. The experimental principle of $\mu$XRD is illustrated in Fig. 5.8 and is very simple: the single crystal is aligned to a given lattice reflection and the diffracted intensity of a highly focused X-ray beam is recorded as a function of the in-plane sample position.

This technique has been proven to be extremely useful in studies of the spatial structure of doped transition metal compounds, see e.g. [126, 127, 39]. Compared to the analogous TEM based mapping techniques [40, 41], $\mu$XRD has a 10 to 100 times lower transverse resolution, but a much larger penetration depth, and does not require the preparation of ultra thin sample slices. Scanning probe techniques such as STM [128] have a better resolution but give only information on the electronic structure of the surface and lack sensitivity to bulk crystal structure.

5.4.1 Experimental details of $\mu$XRD

In our microdiffraction experiments we used the focused beam of P10, Petra III, which has a cross section of $3 \times 4 \ \mu m^2$, to probe the spatial dependence of the intensity of the (011) reflection. As before, the sample was mounted with the [0-11] direction lying in the diffraction plane, and the [100] direction pointing downwards, parallel to the sample $\theta$ rotation axis.

From Fig. 5.8, it can be seen that the spatial resolution is determined by the footprint of the beam on the sample surface. At the diffraction angle for the (011) reflection, $\theta_m=9.8^\circ$, this results in an elliptical $17 \times 4 \ \mu m^2$ X-ray footprint on the sample. At the energy used, the X-ray penetration depth is $1 \ \mu m$, as calculated using the CXRO database [117]. At the relevant incidence angle this translates into a probing depth of roughly $0.5 \ \mu m$, so that effectively we are probing a volume of $\sim 17 \times 4 \times 0.5 \ \mu m^3$ (x,y,z) at each sample position.
Fig. 5.8 A schematic representation of scanning X-ray microdiffraction. The scattered light of the tightly focused incident beam tuned to a Bragg reflection forms a coherent diffraction image on the detector. With a fixed position of the X-ray beam, the sample is scanned in both the $x$ and $y$ directions parallel to the surface using piezo-motor drives. Figure courtesy of A. Ricci.

The sample could be translated along the horizontal [0-11] and vertical [100] directions using two piezoelectric-driven linear stages having a 10 nm resolution. The maps were recorded by stepping the sample over a rectangular grid parallel to the sample surface with a coherent diffraction pattern of the (011) reflection being recorded at each grid position using the Pilatus-300k detector (exposure time of 1 s). The total integrated intensity of each detector image was used to form one pixel value on the final, real-space map. The total acquisition time of a map (e.g. with an area of hundreds x hundreds of $\mu m^2$) was typically two hours. All in all, nine microdiffraction maps were recorded at different temperatures and rocking angles $\theta_{in}$.

5.4.2 $\mu$XRD results and discussion

The first two maps from a sample of $Er_{0.6}Ca_{0.4}TiO_3$ were taken at 132 and 172 K, using a 40x40 pixel grid with horizontal and vertical step sizes of 20 and 4 $\mu m$, resulting in a map covering a total surface area of 800x160 $\mu m$. The step size in these maps is chosen to match the beam footprint on the sample. The diffraction angle was set to $\theta_{in} = 9.870^\circ$, corresponding to the maximum intensity of the 132 K rocking curve shown in the top panel of Figure 5.5 and was therefore optimized for detection of the (011) reflection from the LTO phase.
5.4 Mapping the phase separation in $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ with $\mu$XRD

Fig. 5.9 Microdiffraction maps of single crystal $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ taken at 132 K (top) and after then heating up to 172 K (bottom). Both maps are recorded with a scattering angle $\theta_{in} = 9.870^\circ$, which corresponds to the right-most yellow guideline in the main panel of Fig. 5.7, and favors diffraction from the (011) reflection of the LTO structure. Each of the 40x40 pixels represents the total scattered intensity, and they are separated by horizontal[vertical] steps 20[4] $\mu$m, which is comparable to the $\sim 17 \times \mu$m$^2$ X-ray footprint for the given incidence angle. The color scale represents the normalized scattering intensity as described in the text. The black boxes superimposed on the map indicate regions of interest at which some of the later maps were taken. The two red lines mark arrays of pixels on hill[valley] that were used to calculate the line profiles shown in Fig. 5.19.

The color scale of the map was obtained by the following procedure: for each area detector image, taken at grid position $(x,y)$, we first established the average intensity of the weak diffuse intensity at a detector region far from the diffraction peak. This intensity was taken as the $I_0$ signal representative of the incoming beam intensity. Similarly, we took the intensity $\bar{I}$ in a region of interest covering the most intense part of the diffraction pattern. Together, these yield the self-normalized diffracted intensity value $s(x,y) = \bar{I}/I_0$ for each grid position, $(x,y)$. Finally, the whole map is again normalized to the average map intensity $\bar{s}$, such that the color coding of each pixel corresponds to $s(x,y)/\bar{s}$.

The 132 K map, shown in the top panel of Fig. 5.9, is taken at $\theta_{in} = 9.87^\circ$. This corresponds to the right-most yellow guideline in the main panel of Fig. 5.7, and this means the map mainly measures the spatial distribution of the LTO phase. Regions of elevated intensity are therefore representative of those parts of the crystal in the LTO structure with additionally reduced crystal symmetry, which allow the (011) reflection, despite the global
Structural Investigation of the Phase Separation in Titanates

LTO crystal structure. Under the assumption that the symmetry-lowered LTO regions are homogeneously distributed within the LTO phase itself - i.e. are to be found throughout the sample - the fact that the T=132 K map shows relatively homogeneous intensity would signal a fairly homogeneous distribution of the LTO phase. The upper microdiffraction image suggests that there may be variation in the LTO concentration over long length-scales (more than 100 $\mu m$), visible as a higher diffraction intensity on the left-side of the map, a lower center-region and a partial recovery on the right-side. Locally, the intensity varies by at most 10-15%.

In contrast, the 172 K map, shown in the lower panel of Fig. 5.9, shows a clear pattern of diagonal stripes, with each stripe having a width in the $x$-direction of approximately one pixel. This map was again taken at $\theta_{in} = 9.870^\circ$, which emphasizes the LTO signal. Looking at panel (a) of Fig. 5.3 and/or the lower panel of Fig. 5.5, it appears that at a temperature of 172 K, the LTO fraction in the probed volume of the sample is very small, and the LTM peak dominates. However, the (022) data shown in panels (b) and (c) of Fig. 5.3 indeed show signs of the LTO phase even at 172 K. Thus, the microdiffraction map is able to uncover a small but periodically-arranged spatial pattern in the distribution of the LTO phase in a matrix of LTM, which would have gone unnoticed without the micron-scale mapping capability. In a later section we will consider the nature of this very interesting stripe contrast in more detail, but first a more detailed description of the properties of the pattern itself is given.

With the benefit of hindsight (i.e. ‘conditioned’ by the lower panel of Fig. 5.9), weaker stripe-like correlations can also be seen in the T = 132 K map in the upper panel of Fig. 5.9. The stripes make an angle of $\sim 18.3^\circ$ with respect to the (horizontal) [0-11] lattice vector. Overall, the right hand side of the lower panel of Fig. 5.9 has higher intensity, but the relative amplitude of the stripes is fairly constant across the map. This can be seen more clearly in Fig. 5.10 in which the intensity modulation profile along the direction perpendicular to the stripe has been extracted from the maps taken at both temperatures (132 K and 172 K).

This profile was obtained by averaging the intensity of the pixels along the stripe direction (see the exemplary red guide-lines in the figure for the on-stripe pixels to be averaged) and dividing out the overall background intensity variation, obtained by fitting a high-order polynomial curve to the resulting trace.

For T = 172 K, confirming the impression from the naked eye, the intensity profile shown in red shows a clear, periodic modulation with a fairly constant amplitude of $\sim 25\%$ and a period of 24 $\mu m$. Applying the same method to the 132 K map data yields the black profile, and this curve turns out to display a similar modulation over part of the field of view, but here the amplitude variations are generally on the 10 % level. Comparison of the two profiles

\footnote{The signal from which could be boosted by the particular choice of the angle of incidence}
Fig. 5.10 The average stripe intensity modulation from the 132 and 172 K maps obtained by averaging the pixel intensity along the stripe direction, and plotting this vs. the distance perpendicular to the stripe rows with respect to the origin of the maps in Fig. 5.9. The x-scale and field of view of this figure is arrived at after rotation of the experimental pattern to get vertical stripe orientation, followed by averaging of the on-stripe (hill) and between-stripe (valley) lines. The largest horizontal and vertical full field of view was then selected. The valley[hill] guidelines indicated in red in Fig. 5.9 are positioned at 115[130] µm on the x-scale of this figure, as highlighted with red arrows. The shaded background indicates the part of the map within the black box frames in Fig. 5.9.
shown in Fig. 5.10 indicates that the stripe period at 132 K is around 10% larger than at 172 K (e.g. the red curve shows 17 maxima, while the black one 14 or 15). This implies that the spatial distribution of the LTO phase in the LTM matrix must be re-organizing on length-scales of order or larger than 500 µm on warming up from 132 K to 172 K, with the stripe period decreasing with increasing temperature, which goes coupled with an increase of the stripe contrast.

Fig. 5.11 shows a pair of microdiffraction maps, the first taken after cooling from 172 K to 162 K, and the second on subsequent heating to 164 K. These maps were taken on a 50x50 pixel grid, but with two times smaller horizontal[vertical] step sizes of 10[2] µm compared to the maps of Fig. 5.9. The pixel-pixel separation in Fig. 5.11 is about half of the 17x4 µm² X-ray footprint. With this reduced step size, we reach the theoretically optimal sampling limit [102, 103]. Nominally, the center-points of the four maps shown in Figs. 5.9 and 5.11 are identical. Apart from the smaller step-size, the maps in Fig. 5.11 were recorded with the scattering angle set to \( \theta_{in} = 9.770^{\circ} \), which gives somewhat more sensitivity to the signal from the monoclinic LTM phase. This can be seen from the bottom panel of Fig. 5.5, and the 164 K dataset in the rocking scan map shown in Fig. 5.7. However, given that this change involved a rotation of the sample, an unknown displacement of the beam position on the sample cannot be ruled out.

These two new maps are remarkably similar to each other, and in each case a diagonal stripe pattern running in the same direction of that seen at 174 K is clearly visible. The two maps shown in Fig. 5.11 indicate the stability/reproducibility of the mesoscopic-scale structure with respect to the 2K warming step from 162 to 164 K. The corresponding intensity profiles, depicted in Fig. 5.12, show an amplitude of roughly \( \sim 20\% \), although the T=164 K amplitude does look to be a little reduced compared to that at 162 K. As was the case previously at T = 172 K, the stripe period is 24 µm.

It is interesting to try and re-locate the same details in the hill-valley pattern between the 172 K and the 162 & 164 K data. Such an analysis shows that although the stripe patterns are similar, the exact spatial locations of the peaks and troughs of the stripe patterns differ. Also different between the 172 K data and those of Fig. 5.11 are the long range intensity variations under the stripe pattern. Thus, taken at face value, the changes seen on cooling from 172 to 162 K can be seen as probing the differences after a ‘slip’ of the stripe pattern, launched by the considerable temperature change. The 162 & 164 K data then show the ‘re-stuck’ stripy pattern of the mesoscopic distribution of the distorted LTO phase. In it only fair to point out that the difference in diffraction angle \( \theta_{in} \), or a change in the contrast mechanism as reciprocal space is being sampled in a slightly different plane could also be playing a role in
5.4 Mapping the phase separation in $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ with $\mu\text{XRD}$

![Microdiffraction maps](image)

Fig. 5.11 Microdiffraction maps taken at 162 K and 164 K of single crystal $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$, after initial cooling from 172 K to 162 K. The scattering angle was set to $\theta=9.770^\circ$, and each map is built up of the integrated intensity from 50x50 scattering images. The horizontal/vertical step size with which the sample surface was scanned under the beam was 10[2] $\mu\text{m}$.

yielding the altered stripe pattern seen at 172K and the pair of practically identical patterns recorded at 162 and 164 K.

The last set of microdiffraction maps we present are shown in Fig. 5.13. These probe a temperature regime in which the presence of both the LTM and LTO peaks was clear in the rocking scans shown in the lower panel of Fig. 5.5. As regards the incidence angle, this set of spatial maps were recorded with $\theta_{\text{inc}}=9.845^\circ$, close to the value used for the 132 and 172 K maps of Fig. 5.9, so that again the sample/detector set-up is most sensitive to the (distorted) LTO phase in the $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ single crystal. The temperature trajectory for these map datasets is the following: the 168 K map was taken directly after the 164 K map just discussed in the context of Figs. 5.11 and 5.12. Subsequently, the sample temperature was brought to 159 K, as a starting point for the series from 159 to 165 K taken at constant temperatures but on a warming cycle.

In the following, we first discuss one feature of the higher-T maps as this can be used to say something about the relative fields of view of the map datasets discussed in this section of the thesis, and the consequences thereof. We then return to the T-dependent series of Fig. 5.13, and the further analysis of the images, with the aim of connecting the observed
Fig. 5.12 The average intensity modulation profiles at 162 K and 164 K for single crystal $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$, after initial cooling from 172 K to 162 K. The scattering angle was set to $\theta=9.770^\circ$. The x-scale and field of view of this figure is arrived at in an analogous manner to that in Fig. 5.10.

For temperatures of 163 K or higher, a strong valley stripe (i.e. line of suppressed (011) diffraction intensity) can be seen in the lower right area of the map. Given the fact that all microdiffraction maps are centered on nominally the same location on the sample, we can use this characteristic feature, as well as other structures in the map image, to locate the probable field of view (FOV) of the smaller maps with finer spatial step-sizes [Fig. 5.13] in the larger FOV of Fig. 5.9. The resultant probable FOV for the smaller maps of Fig. 5.11 is shown on Fig. 5.9 as a black rectangle, indicating a +30 µm horizontal offset for the smaller maps, most likely due to a change in beam position caused by the 0.025° change in angle of incidence. Using this calibration of the possible beam shift vs. incidence angle, an estimation can be made that the field of view covered by the 162 and 164 K data shown in Fig. 5.11, and the conclusion is that these images probably involve a 120 µm horizontal offset. Given this new information on the probable FOV of the data shown in Fig. 5.11 we can once again compare the 172K and 162 & 164 K map data, and once again see similar stripy patterns, but no spatial co-location thereof in the data, supporting the hypothesis put forward above of a 'slip and re-stick' behavior of the mesoscopic LTO phase organization taking place as a response to the 10K cooling step from 172 to 162 K.
5.4 Mapping the phase separation in Er$_{0.6}$Ca$_{0.4}$TiO$_3$ with $\mu$XRD

Fig. 5.13 Maps of Er$_{0.6}$Ca$_{0.4}$TiO$_3$ sample taken in time order 168 K, 159 - 165 K. The scattering angle was $\theta=9.845^\circ$. All other conditions were as for the T=162 and 164 K maps.
Fig. 5.14 The normalized intensity modulation profiles from the 159 to 168 maps taken at $\theta_{\|}=9.845^\circ$ and of the 172 K map taken at $\theta_{\|}=9.870^\circ$. The curves have been shifted vertically by multiples of 0.5 for clarity. The numbers at the top give the sequence number of the stripes in the 172 K profile. The 172 K profile is aligned with respect to the rest of the profiles by applying a 30 $\mu$m horizontal shift that aligns the large valley between stripe number 8 and 9 at $\sim 200 \mu$m. The x-scale and field of view of this figure is arrived at in an analogous manner to that in Fig. 5.10.

Returning now to the spatial mapping series shown in Fig. 5.13, as was the case in the first map-pair shown in Fig. 5.9, the visibility of the stripes clearly increases with temperature. There are differences in stripe contrast between the left and right-hand side of the images for the different temperatures in Fig. 5.13, and this same quantity is also different in the 172K data of Fig. 5.9. As mentioned previously, this points to other, longer, length-scales on which the organization of the distorted LTO phase giving the (011) diffraction intensity changes versus temperature.

In Fig. 5.14, the normalized modulation profiles for the data of Fig. 5.13 are shown, together with those from the 172 K for comparison. In this series, unlike the case for the 162 and 164 K data, there are portions of the stripe patterns that are evolving with temperature. For the left-hand side of the traces shown in Fig. 5.14 the evolution barely goes beyond changes in contrast. In the right-hand side, however, more qualitative changes are visible, for example in the region around the pronounced minimum seen between 190 and 200 $\mu$m on
the x-scale of Fig. 5.14. This attests to thermally-induced rearrangements of the peak and valley positions in the stripe pattern of the LTO phase which are taking place in a temperature regime not far from where strong hysteretic effects are seen in the resistance of 60% Er-doped CaTiO$_3$ (see Fig. 2.8 of this thesis). Our microdiffraction data do not provide a causal link with the hysteretic resistivity and susceptibility, but they can be seen as a smoking gun, pointing to the phase separation and its spatial (re)organization as an important underlying factor in in determining the complex response in both transport and magnetization. In general, we note that these phenomena are reminiscent of the settling dynamics of domains observed during minor hysteresis loops [129] ferromagnetic systems, and this analogy would point to the importance of spatially separated domains of distorted LTO as forerunners of the global LTO phase that hosts the metallic ground state at low temperatures in these Er-doped Ca titanates.

### 5.4.3 Intensity probability density function

In a number of papers, the intensity probability distribution of microdiffraction maps has been used to infer details of the structure [10, 127, 39], and in particular as an argument for scale invariant or spatially fractal behavior of dopants in complex oxides. This is an interesting idea, and thus in this section we follow this approach, and in Fig. 5.15 we present the normalized probability intensity distributions of the seven high resolution spatial maps we have been discussing in the previous section, recorded at temperatures between 159 and 164 K. The probability intensity distributions were obtained by constructing the histogram of all map pixel intensities $s(x,y)/\bar{s}$ and then normalizing the area under the histogram to unity.

Before discussing Fig. 5.15 in any detail, we remark that if the Er-doped CaTiO$_3$ crystal were to be comprised of a perfectly ordered stripe structure operational only on a single and periodically repeating length-scale, only two intensity values would be expected. Consideration of the data of Fig. 5.15, shows that the data points rather follow a smooth curve. In fact, the intensity probability distribution resembles a Gamma probability density function, as is shown by means of a fit to the 161 K data, which is shown as an orange solid line. Such a Gamma probability density function indicates a random distribution of intensities, and so, although the microdiffraction maps are able to pick out subtle yet clear indications of stripy texture in the spatial distribution of the distorted LTO phase patches in the insulating LTM matrix, underlying longer range intensity variations and the mixed phase domain structure washes the stripe information out of the intensity probability distribution to yield a Gamma density function behavior.

Following the analysis method presented in [10, 127, 39], we now go on to examine whether the high intensity tail of the distributions can be fitted using a power-law distribution $P(x) = x^{-\alpha}$ [130]. In Fig. 5.15, we highlight the two datasets that yielded the highest and
Fig. 5.15 Normalized distributions of the pixel intensities $s(x,y)/\bar{s}$ in the seven maps of 60% Er-doped CaTiO$_3$ taken at temperatures between 159 and 168 K. A Gamma probability density function (PDF) has been fitted to the 161 K data and is shown as an orange line. The inset shows the high normalized intensity tail of the 159 and 162 K data, plotted on a log-log scale together with two exemplary power law fits.
lowest power exponents, $\alpha(159K) = 9.4$ and $\alpha(162K) = 5.7$, and we show the fits in the inset to Fig. 5.15. Such a power law behavior has been linked to scale invariance in the domain size distribution in a mixed phase structure [127, 131]. Taken at face value, the significant and changing level of stripe disorder or background seen at length-scales beyond the FOV of the microdiffraction maps presented in section 5.4.2 could be seen as supporting the idea of organization of the LTO patches at multiple length scales. However, in Fig. 5.15 we find a power-law scaling that could indicate scale invariance only over a very small range of normalized intensities: from 1.5 to 4, i.e. not even over a single order of magnitude, compared to the almost two orders of magnitude reported in [127, 131]. Therefore, although the observed intensity distribution points to there being numerous length scales involved in the problem, we cannot extract meaningful support for scale invariance from these data. Thus, either such fractal behavior is simply not there in the Er-doped CaTiO$_3$, or such effects are too weak to survive in the data due to the randomness on top of the stripe pattern and the existence of long range intensity variations. At the very least it can be stated that if present, a susceptibility towards fractal self-organization of the distorted LTO phase in this system is a sub-dominant phenomenon.

Drawing this discussion of the microdiffraction maps to a close, we can conclude that the structure has many aspects of a mixed phase with a wide range of domain structures onto which a stripe pattern is superposed, a stripe pattern which involves a modulation of the ratio of the two phases. In the next section, we will elaborate further on this model.

### 5.4.4 Ensemble-averaged coherent diffraction patterns

Each pixel of the microdiffraction maps has a color corresponding to the total intensity of a coherent diffraction image that encodes information on the structure of the illuminated volume. So far the information in these images themselves has been ignored, and in this section we will investigate what this information can tell us.

Firstly, averaging the coherent diffraction images behind all of the pixels of a microdiffraction map gives a very good ensemble-averaged diffraction pattern of the area covered by the map, and, in other words, corresponds to the incoherent diffraction pattern of the sample as it it were recorded using a beam as large as the whole map area. From these average diffraction patterns we can obtain the scattering profiles $I(\theta_{out})$ by integrating the map-averaged diffraction patterns over the out of plane angle $\chi$.

The left-hand stack of three panels in Fig. 5.16 shows these scattering profiles extracted from the different microdiffraction map datasets. Each panel of the figure groups data recorded with the same $\theta_{in}$ value. The $\theta_{out}$ dimension of the original data has been converted into the longitudinal momentum transfer component, $q_{(011)}$, which forms the $x$-scale of the
plots. The fourth panel of Fig. 5.16 reproduces part of the data covering the temperature dependence of the (110) reflection, the original data being shown as panel (a) of Fig. 5.2. The temperatures at which the microdiffraction maps have been recorded are indicated as color-coded, horizontal lines.

The 132 K scattering profile, shown in Fig. 5.16 (a), consists of a single peak at \( q = 1.3920 \) Å\(^{-1}\), the same position as was found during the temperature scan reproduced in panel (d). The 172 K profile shows a clear double-peak structure, with components at \( q = 1.3895 \) Å\(^{-1}\) and \( q = 1.3905 \) Å\(^{-1}\). This splitting can also be found back in the data in panel (d) and seems to indicate the start of the phase separation.

As mentioned before, the series of 5 maps taken at \( \theta = 9.870^\circ \) straddling the phase coexistence temperature region was taken at \( \theta_m = 9.845^\circ \), slightly more optimized for detection of the low \( q \) orthorhombic reflection. Panel (b) shows the curves to decrease in amplitude and broaden with temperature, compatible with the gradual disappearance of the LTO phase.

Fig. 5.16 (b) shows the results for the 162 and 164 K maps, that were taken at \( \theta_m = 9.770^\circ \) where we have a greater sensitivity to the monoclinic peak. Indeed, these profiles are much sharper, and both show a clear double peak structure. The high \( q \), LTO-related peak is roughly three times stronger than the low \( q \), LTM feature. The fact that these curves are much narrower can apparently be attributed to a better alignment of the detector plane with the top of the triangular shape of the rocking maps (see yellow vertical lines in Fig. 5.7).

In kinematic diffraction theory [83], the single crystal is assumed to have imperfections such as mosaicity that limit the correlation length of the lattice structure. In such cases, the width of scattering profiles should be inversely proportional to the correlation length of the crystal, which hereafter is interpreted as being representative of the domain size of the scattering phase.

An estimation of the in-plane correlation lengths of the mixed phase system can therefore be obtained by fitting the curves in Fig. 5.16 with two Lorentzian functions. Similarly, the out of plane scattering profiles obtained by integrating the map-averaged diffraction images over \( \theta_{out} \), were fitted with a single Lorentzian in order to obtain an estimation of the out of plane correlation lengths. The results for the 159 to 168 K series of Fig. 5.16c are shown in Fig. 5.17. We find that the correlation length of the LTM component along the (0-11) direction (red symbols) seems to decrease with temperature from \( \sim 1400 \) to 900 Å over the interval between 159 K and 168 K, while that of the LTO component (blue symbols) is roughly 40% smaller, decreasing from 800 to 550 Å. The overall out of plane correlation length (black symbols) decreases from 180 to 150 Å. Due to the fact that the detector is - to
Fig. 5.16 The left three panels show the map-averaged scattering profiles $I(\theta_{out})$, in which $I(\theta_{out})$ has been converted to a $q_{011}$ scale. The three panels correspond to the three sets of maps taken at different $\theta_{in}$. Panel (d) is a top view of the (011) peak in Fig. 5.2a, in which the temperatures of the maps are shown as colored horizontal lines, with the colors corresponding to those of the left hand panels. Note that the data in Fig. 5.2a were taken at $\theta_{in}=9.870^\circ$ and therefore can only be compared directly with panel (a) of this figure.
Structural Investigation of the Phase Separation in Titanates

Fig. 5.17 Trends in the correlation lengths obtained from the map-averaged diffraction peak. Red and blue: the in-plane correlation lengths of the LTO and LTM phases obtained by fitting two Lorentzian to the profiles in Fig. 5.16. Black: the out of plane correlation length for the average of both phases. Note that the numbers given here represent lower boundaries only.

some degree - cutting through the edge of the diffuse scattering blobs, it should be borne in mind that the correlation lengths given above represent lower bound values. However, the apparent triangular shape of the intensity in the rocking angle maps of Fig. 5.7 shows that kinematical models with exponentially decaying structure correlations are too simple, and a more refined model is required before a more precise interpretation can be made in terms of correlation length. Despite this, it is fair to say that the characteristic length scale of the charge order along the in plane [0-11] direction is much larger than that along the out of plane [100] direction, and that both length scales decrease on warming towards the temperature at which the two-phase situation disappears.

5.4.5 Modeling of the contrast in the microdiffraction maps

The microdiffraction map data were clear in their implication of a striped superstructure in which the ratio of orthorhombic to monoclinic material varies in a sinusoidal manner. However, strictly speaking the two phases are detected with a relative efficiency that depends on $\theta_m$, so that a priori it is not simple to link the observed diffraction intensity to the relative concentration of the two phases. In order to get some insight into this issue, we introduce a simple model here for diffraction from the striped, mixed phase.
Let $O(T)$ be the average percentage of orthorhombic phase at a given temperature $T$. Perpendicular to the stripe direction this percentage is taken to vary as a cosine function with amplitude $A(T)$. The low temperature monoclinic LTM and orthorhombic LTO phases are detected with efficiencies $\alpha(T, \theta_{in})$ and $\beta(T, \theta_{in})$ respectively, which are dependent on both temperature and angle of incidence. The intensities of the orthorhombic and monoclinic fractions are then given by

$$I_O = \alpha(O + A \cos 2\pi x/\tau),$$

$$I_M = \beta(1 - O - A \cos 2\pi x/\tau),$$

where $\tau$ is the period of the stripe, which the data of Fig. 5.14 tell us is approximately independent of temperature. Note that the amplitude $A$ cannot be larger than either of the fractions, so that $A < O$ and $A < 1 - O$, and its maximum value is $A = 0.5$.

In such a model, the amplitude variation between the peaks and valleys of the intensity profiles relative to the average intensity $\bar{I}$ is given by

$$\frac{I_{\text{max}} - I_{\text{min}}}{\bar{I}} = \frac{2A(R - 1)}{1 + O(R - 1)}.$$ (5.3)

Here $R(T, \theta_{in}) = \alpha/\beta$ is the ratio of the detection efficiencies, which is dependent on the way the detector is positioned in reciprocal space. The correct positioning of the detector is, in turn, dependent on the temperature of the sample. The highest contrast is obtained when $A = O = 0.5$. The contrast vanishes when both phases are detected with equal efficiency ($R = 1$) and flips sign depending on whether $R$ is larger or smaller than one. Judging from the rocking curves, we estimate $R$ to be between one and two for the 162 K and 164 K maps taken at the lowest $\theta_{in}=9.770^\circ$, and around 8-10 for the maps taken at higher $\theta_{in}$.

It should be noted that even if $R$ were known, we cannot use this model to obtain the true values of $A$ and $O$, since the signal from the low-T orthorhombic phase detected using the forbidden (011) reflection does not represent the total volume fraction of this real phase, as only a portion of it has the locally lowered symmetry required to generate diffraction intensity in the (011) Bragg peak.

Nevertheless, the model can be used to discuss some of the trends in the data. As an example, in the 159 - 168 K series, the fraction $O$ of low temperature orthorhombic phase is decreasing rapidly, and since the modulation amplitude $A$ is negative, by definition, also the LTO and LTM modulation amplitude must be decreasing. Under these conditions, the model indicates that the increase in contrast observed in Fig. 5.14 is probably mainly caused by an increase of the ratio of detection efficiency $R$, caused by motions of the reciprocal space.
structure away from the detector, as is also visible in the rocking scan maps shown in Fig. 5.7.

**5.4.6 Nature of the stripes**

In order to test this model, we investigated the nature of the contrast in the stripes more closely. In Fig. 5.18(a) we give a portion of the 168 K map, for which the rocking curve shows a large monoclinic peak at $\theta_{h0} = 9.77^\circ$ with a small orthorhombic shoulder at $\theta_{h0} = \sim 9.89^\circ$. We represent the map here in square pixels, and in the zooms indicated in panels (b) and (c), we also show a 3x3 collection of coherent diffraction images, one for a high and one for a low intensity area. In this map dataset, the real-space step size is half the beam width (in both directions), so adjacent pixels partly overlap. Since the coherent diffraction image is the reciprocal space snapshot of the illuminated area, adjacent images should therefore resemble each other and indeed this can be seen to be the case.

In panels (d) and (e) of the same figure we show the average of each of the sets of 3x3 images. The average diffraction image of the nine high intensity pixels shown in (d) shows a sharp and intense diffraction contrast, roughly at the position of the orthorhombic peak. On the other hand, the average diffraction image of the 3x3 low intensity pixels is much broader, has a much lower intensity per detector pixel and lies at lower $q$, suggesting that the intensity in the low intensity, stripe-valleys of the microdiffraction map is produced by the monoclinic phase. However, as the map was taken with $\theta = 9.845^\circ$ the orthorhombic signal is still strongly favored, with the monoclinic phase not formally meeting the diffraction condition.

Panel (a) of Fig. 5.19, shows the average scattering peak profiles $I(q_{011})$ of the 3x3 pixel areas shown in panels (d) and (e) of Fig. 5.18. The 2D detector image data of Fig. 5.18 is projected onto the intensity with respect to the $q_{011}$ axis. The result shows a clear difference in the position of the reflection from the high(low) intensity regions of the original stripy microdiffraction map, indicating that the high intensity stripes are richer in the orthorhombic phase.

As a further test as to whether the origin of the stripe contrast indeed lies in the LTM to LTO ratio, we repeated this procedure for lines of thirteen pixels on the ridges (high intensity) and valleys (low intensity) indicated by the red lines in the 132 and 172 K maps shown in Fig. 5.9. Panels (b) and (c) of Fig. 5.19 compares the resulting peak normalized scattering peak profiles $I(q_{011})$ (red[blue]=ridge[valley]) with the total map-averaged profiles portrayed in black.

The 172 K result in panel (b) indeed confirms the results from the 3x3 pixel areas: the average of the of thirteen valley pixels give a scattering peak position that corresponds to the
5.4 Mapping the phase separation in $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ with $\mu$XRD

Fig. 5.18 (a) A small region of the map at 168 K [the full map is shown in Fig. 5.13]. The red (blue) squares indicate two 3x3 map pixel regions with high (low) intensities. Panels (b) and (c): The most intense area (300x260 detector pixels) of the coherent diffraction patterns corresponding to the 3x3 tiling of pixels indicated in (a). Panels (d) and (e): corresponding average images of the nine speckle patterns shown in (b) and (c), respectively. These show a clear difference in q-space position of the scattered intensity, indicating a different diffraction angle for the high and low intensity regions of the microdiffraction map. The horizontal band of zero intensity in the individual diffraction patterns is an artifact of the detector chip used at the microdiffraction set-up.
Fig. 5.19 (a) The scattering profiles $I(q_{011})$ for the sum of the 3x3 pixel areas indicated in the previous figure. Red (blue): on stripe (in valley). Panels (b) and (c) show the equivalent results obtained from averaging thirteen pixels along lines on the crest (labeled 'high') and in the valleys (labeled 'low'), as indicated by the red lines on top of the large scale microdiffraction maps of Fig. 5.9. In both panels (b) and (c) a comparison is also made with the map-averaged scattering profiles taken from Fig. 5.16(a) shown as black solid lines). In (b) and (c), each profile is peak normalized, so as to accentuate changes in position and line shape in each case.
LTM phase, while the average of thirteen ridge pixels is close to the LTO position. In addition, the maxima of the two curves in panel (b) match relatively well with the two components of the map-averaged scattering curve shown in panel (a).

Panel (c) shows an analogous analysis as that carried out for panel (b), but now at a temperature of 132 K, at which the sample is almost completely in the LTM phase. In this case, the scattering profiles of the high (red) and low (blue) intensity pixel rows almost coincide with the map-averaged profile (black). Although this would suggest a lack of spatial structure, the 132 K map shown in Fig. 5.9 still shows stripy contrast, albeit low. This would seem to suggest that the residual, partially developed stripy structure in this map is due to remnants of the monoclinic phase whose reciprocal space (011) diffuse scattering cloud is mostly missed by the detector, as expected from the earlier statement that $R > 10$ at this temperature and diffraction angle.

We close this discussion of the microdiffraction data by turning to the possible microscopic origin of the stripe pattern. It is well known that stripe order can result from competition between a local ordering mechanism with long range fields that in turn are produced by the local order. A beautiful example of such self organization is found in magnetic materials with a uniaxial anisotropy, such as a wide range of magnetic thin film materials [121, 132, 133, 17]. In such systems the stripe period can be tuned from tens of nanometers to tens of microns simply by changing the composition. Following this analogy further, the short-range ordering, then, is of the LTM and LTO phases, and it exactly this coexistence of two phases with differing lattice parameters that sets up a complicated, long-range strain field which results in self organization of the system into regions with on average larger and smaller unit cell volumes. This echoes theoretical work by Ahn et al. [15, 122] who predicted that the the strain field produced by phase separation between a large unit cell charge ordered phase and a small unit cell metallic phase can induce long-range order.

The microdiffraction data show the domain period to be quite stable, although there are some indications of a shrinking of the period with temperature in the 132 and 172 K maps. Such stiffness could have several origins. Firstly, if the domain period needs to grow, all stripes have to be moved across the pinning landscape and somewhere stripes have to be annihilated or be pushed out of the sample. Even in magnetic systems in which stripe domains do not involve charge and orbital order it is known that domain wall pinning by lattice defects has a strong influence on domain wall movement and the formation of stripe patterns. In addition, domain walls can have an effective mass, making them resistant to acceleration. This aspect has also been looked at in model calculations of CO/OO transition metals oxides [15, 122], and it has been found that the structure needs to be altered over a two unit cell length scale in order to move a domain wall between a checker-board charge order
domain and a metallic domain (i.e. both black and white sub-lattices of the checkerboard need to reorganize). This involves large changes in unit cell volume in both phases, implying that such a domain movement is a very costly process.

5.5 Conclusion

In this chapter, the structural evolution of Er$_{0.6}$Ca$_{0.4}$TiO$_3$ across the MIT has been discussed on the basis of diffraction data collected during speckle intensity correlation experiments. We have presented detailed data on the peak splitting of both the “forbidden” (011) and the allowed (022) lattice reflections during temperature scans under fixed diffractometer settings. These allow us to follow the evolution of the high temperature orthorhombic structure into the low temperature monoclinic structure and the ensuing emergence of the large unit cell, low temperature orthorhombic (LTO) phase, believed to be the metallic fraction in the Ca-doped ErTiO$_3$ system. Our data clearly provide for the scenario proposed earlier for the doping-dependent behavior in the related system Y$_{1-x}$Ca$_x$TiO$_3$ [21, 23, 16], but refine it by stressing the gradual nature of the appearance of the LTO phase.

Furthermore, data is shown from rocking scans with area detectors on a long exit arm, and they go to show the efficacy of this approach in probing a large volume of reciprocal space. On the one hand, these scans confirm the gross features of the picture sketched above. On the other, they also raise questions about the details of the structure of the diffraction peaks that warrant further study.

The main body of experimental results presented in this chapter, however, are a series of hard X-ray microdiffraction maps. These maps indicate that the large unit cell volume, monoclinic (LTM) phase coexists with the smaller unit cell, low temperature orthorhombic (LTO) phase over a large temperature range around the MIT. This coexistence is arranged in more or less randomly-sized domains within the single crystal structure. Although the voxel in the experiment is 3x5x0.5 micron$^3$, the correlation lengths that can be inferred from the ensemble-averaged diffraction results point to much smaller domain sizes. At 158 K - the low temperature end of the MIT region - the correlation length along the direction normal to the (100) plane is 100 Å for both the LTO and LMO fractions, independent of temperature. Along the (0-11) direction, the correlation length has lower limits of 800 Å for the LTO and 1400 Å for the LTM fraction, and for both phases these length-scales decrease on warming up.

For temperature in the MIT region, the microdiffraction maps uncover a remarkable self organization superimposed on the domain structure in the form of a strip patterns of period 24 $\mu$m. This ordered structure is all the more remarkable as the direction of propagation
Fig. 5.20 Model of the stripy phase. Charge ordered LTM domains with a range of sizes and possibly elongated in the (011) direction (orange) self-organize into microscopic stripes in a background of the metallic LTO phase (blue).

of the stripe lattice cannot immediately be linked to a high symmetry plane of the crystals structure. There are signs of temperature hysteresis in the stripe pattern, and has been pointed out previously[41], such hysteresis can form a natural basis to explain the observed hysteresis in the resistivity, as the electric current would have to find a percolative path through such a strongly anisotropic system of organized charges and spins.

An analysis of the intensity distribution of the microdiffraction maps shows that the domain size is randomly distributed, following an overall Gamma distribution, in which the stripe pattern does not emerge. An additional analysis of the high intensity tail of the intensity distribution function shows at best only weak signs of the presence of scale invariance [127, 131, 39, 134].

Taken together, these diffraction data for temperatures around or just under the MIT in the Ca-doped ErTiO$_3$ system suggest that the structure is organized along the lines of the sketch shown in Fig. 5.20. In this picture, a collection of essentially randomly-sized LTM domains, elongated along the (011) direction, are embedded in a matrix of the LTO phase. Both phases possess a sinusoidal-like concentration profile with a period of 25 µm with a propagation vector that makes an angle of 18.3° with respect to the (100) axis. Connecting
this micro-structural model to the transport data, we note that the electrical current will only run in the metallic, LTO phase, shaded blue in Fig. 5.20. On warming the system up, the LTM domains (orange) increasingly nucleate throughout the system, slowly washing out the stripe periodicity, but also compromising the percolative pathway through the remaining LTM phase: heralding the metal to insulator transition.

Furthermore, by zooming in on the ridges and valleys of the stripe structure, it could be shown that the stripe modulation is, in fact, a concentration modulation of the LTO and LTM phases, despite the fact that the local concentration of the two phases could not be determined since the orthorhombic (011) signal is a parasitic reflection caused by local symmetry breaking effects such as dopant concentration disorder. Nevertheless, the stripe structure could be analyzed in terms of a simple model that takes into account the detection efficiency of the two phases as determined by the angle of incidence of the X-ray beam, a model in which the observed reversal of the stripe contrast can be explained in a natural manner. It is therefore also not clear by what amount the local fractional concentration of the two phases varies.

Given the probing depth of these microdiffraction experiments of order 0.5 micron, whether the stripes are living only at the near-surface region of the crystal or also in the bulk remains a moot point. Assuming for the moment that these data are relevant for the bulk, they suggest that the mixed phase consists of a multilayer of LTM and LTO rich material.

In this case, the stripe spacing observed would represent the upper limit for the layer periodicity, as the angle the multilayer makes with the sample surface is not known.

Integrating all the information above yields the following overall scenario for the evolution of $\text{Er}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$ on cooling from high temperatures across the MIT.

- At high temperatures, the system takes on an orthorhombic structure: thermal excitations overcome the correlation and charge order tendencies.

- On cooling, these gain the upper hand and the HTO structure gradually distorts into the charge ordered insulating LTM structure, and this is coupled to a large increase in the resistivity.

- On further cooling, the bulky LTM unit cell impedes the natural lattice contraction at lower temperatures, and the system reacts by nucleating domains of the small unit cell, metallic LTO phase starting at temperatures around 250 K.

- Each LTO nucleus has a smaller volume than the volume in the LTM matrix from which it originated, and thus the LTO is surrounded by a local strain field, which also contains torsional components, as the LTO phase formation is accompanied with a tilting of the unit cell c axis.
• These strain fields self organize the system of mixed phase domains into a stripe structure in which lattice (unit cell) and charge/orbital degrees of freedom are spatially modulated in a highly anisotropic manner.

• The stiffness of such a strain modulated superstructure leads to temperature hysteresis in the spatial arrangement of the mixed phase structure, which naturally explains the strong hysteresis found in the resistivity curves.

Clearly, many open questions remain: are the stripes only living on the ’surface’, ’sub-bulk’ (< 0.5μm) or are they the sign of a bulk multi-layering structure? Do the torsional strains between the LTM and LTO domains lead to speckle structure and can this be linked to the concept of mosaicity in kinematical diffraction, and do these effects perhaps explain the strange forms of the diffraction spots in the rocking scan maps? How important is the tolerance factor for stripe formation? How ubiquitous is stripe formation as a means of relieving strain in a mixed phase system? In this respect it should be remarked that in parallel studies on Y₀.62Ca₀.38TiO₃ performed in this thesis project, we observed anomalous satellites around the (011) peak, which could be indicative of the emergence of an incommensurate order.

Looking back over the whole project, we can conclude that our bold efforts to find slow equilibrium dynamics of the charge order in Er₀.6Ca₀.4TiO₃ have, despite some early data that looked promising, not brought any sign of such dynamics to light. This inability of the system to show anything other than very slow equilibrium dynamics is most likely due to the strong coupling of the electronic and lattice degrees of freedom, coupled to the sluggish nature of the phase transition and the resulting hysteresis in structure and electrical properties.

However, even in these inherently strongly disordered systems, the stability of our experimental setup has allowed rapid ‘settling’ dynamics to be identified in Ca-doped ErTiO₃. These effects can still lead to changes in the domain landscape after minor temperature excursions or thermal fluctuations.

The final question to answer is thus what X-ray speckle techniques can contribute to our knowledge of the dynamics of charge and orbital ordering phenomena. The answer still lies in the idea that speckle images taken with a pulsed source produce snapshots that can be used to detect fast changes in the lattice, electronic and spin structures. Thus, XFEL-based speckle experiments using pump probe techniques will still be extremely interesting for the study of non-equilibrium femto- to nanosecond scale dynamics. Use of a split-and-delay technique as was proposed by Grübel, Stephenson, and Gutt et al. [75, 113, 101, 108] would give access to intrinsic fluctuations in the interesting pico- to nanosecond time window. It is therefore
to be expected that with the further development of sources, detectors and experimental setups that speckle techniques will in due time mature as a relevant technique for probing the intrinsic dynamics of spins, charges and orbitals.