Coherent X-ray scattering of charge order dynamics and phase separation in titanates
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Chapter 1

Introduction

Novel materials in which multiple low energy excitations simultaneously determine the physical properties of the electron system are a much-studied and important class of quantum matter. These systems exhibit complex phase diagrams as a function of composition, temperature, pressure or external electromagnetic fields, characterized by nearly degenerate phases with strongly differing physical properties, emerging in their transport, magnetization, susceptibility, etc.

One of the famous classes is that of strongly correlated transition metal oxides (TMO), which reveal unconventional high temperature superconductivity [1–4], and colossal magnetoresistance (CMR) [5, 6]. Moreover, heterointerfaces between insulating, titanate-based TMO systems have been found to be conducting [7], magnetic [8] and even superconducting [9].

The rich physics of TMO’s involves phenomena such as charge and orbital ordering, phase separation, formation of real-space striped and other self-organized structures on the nm and larger length scales. Solving the fundamental, intricate puzzle posed by these systems might also open the door towards engineering technologies harnessing the special properties of these materials in future quantum devices [10–14].

Impressive advances have been made in the theoretical description of various aspects of these systems, in part supported by computer simulations [14, 15]. However, the complexity of these systems on different levels, linked to their balanced energy scales for numerous microscopic parameters means the development of an overall picture remains a great, open challenge for the field. The impact of this complexity makes itself felt most strongly in the phase transitions these systems exhibit, in which multiple phases can coexist [10–13, 16]. Furthermore, phase transitions will be accompanied by fluctuations, and for charge ordered systems in particular the question whether this ordering can fluctuate and if so, on what length and time scales, is still a matter of debate. Clearly, experimental probes are required
that can distinguish the different phases - for example the insulating and metallic phases in a 
Mott metal-insulator transition - and these probes should also provide information on the 
structure of the system, spanning from atomic to mesoscopic length scales and over a large 
range of time scales.

In a PhD thesis in the same group in which this research was carried out [17, 18], it 
was shown that coherent X-ray scattering is a promising approach in the investigation of 
the slow dynamics of spin fluctuations in holmium antiferromagnetic thin films. Based on 
this lead, the work in the thesis presented here is devoted to the investigation of possible 
fluctuations of charge order that can occur in doped transition metal oxides such as the 
titanates, manganites and cuprates. Concentrating our experimental effort on doped titanates, 
we show that the speckle patterns produced by coherent X-ray scattering indeed allow the 
determination of the fingerprint of the mixed phase structure emerging at and close to the 
metal-insulator transition. The experiments reveal many interesting new results as regards 
the spatial (re)organization in the charge and orbital sectors during the Mott metal-insulator 
transition. These help us to better understand the physics of the titanates, in particular, 
but also have their role to play in the evolution of what could be called the big picture for 
TMOs in general. Lastly, the experiments presented here provide a guiding framework 
towards future studies of charge/orbital dynamics in TMOs that could be carried out using 
'split-and-delay' speckle studies at x-ray laser sources.

Within the course of this thesis project, coherent X-ray scattering has been used to 
investigate the CMR manganite systems Pr\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3} (PCMO) and La\textsubscript{2-x}Sr\textsubscript{x+2}Mn\textsubscript{2}O\textsubscript{7} (LSMO), and two titanates from the R\textsubscript{1-x}A\textsubscript{x}TiO\textsubscript{3} (R=Y, Er) family. The latter show an 
equally remarkable metal insulator transition (MIT), coupled to alterations in the crystal 
structure and charge/orbital ordering. The advantage of the titanates for our studies is that the 
MIT is not connected to a change in magnetic state, thus enabling undiluted attention to be 
given to the charge and orbital sector. In addition, the titanates provided the best experimental 
data of the systems studied, and thus they form the mainstay of this thesis. In the doped 
rare-earth titanium oxides with the generic structure formula R\textsubscript{1-x}A\textsubscript{x}TiO\textsubscript{3}, the R and A ions 
have a valence of 3+ and 2+ respectively. By choosing the appropriate stoichiometric ratio 
of R to A atoms, the average valence of the Ti ions can be tuned continuously between 3+ 
and 4+, implying that locally the Ti ions have either an empty d orbital or a single electron 
in the t\textsubscript{2g} orbital manifold, in which case Mott-Hubbard correlation effects are important 
[19, 20]. Furthermore, the ionic radii of the R and A ions strongly influence the Ti-O-Ti 
bond angles, thus changing the electronic hopping parameter. Together, these effects lead to 
a great richness in behavior and complexity of the phase diagrams [19–21].
Chapter 2 presents a brief introduction of the field. We start with a description of the colossal magnetoresistance (CMR) manganites, which have been widely studied [22, 13]. We then generalize the discussion to metal insulator transitions (MIT) controlled by doping and temperature, where we also highlight the role of charge and orbital ordering and its connection to electronic phase separation [20, 13]. At the end of this chapter, the main system studied in this thesis, the calcium doped rare-earth titanate oxides (R$_{1-x}$Ca$_x$TiO$_3$), and their characteristic MIT are described. For intermediate doping levels ($x = \sim 0.4$), a number of R$_{1-x}$A$_x$TiO$_3$ compounds show a strong first-order-like MIT displaying resistivity hysteresis [16]. In the past few years neutron and X-ray diffraction experiments have shown that charge and orbital ordering of the t$_{2g}$ electrons on the Ti sites play an important role in these transitions [23, 16]. Also there have been indications that phase coexistence and phase separation can be present [13–15].

However, very little is known about the dynamics of the coexisting phases in these kind of complex oxide MITs. This led us to investigate dynamical aspects of the phase transition using the novel technique of coherent soft X-ray scattering, which had been successfully applied earlier in our laboratory to the study of the dynamics of soft matter [24] and domain dynamics magnetic thin films [17, 18]. In chapter 3, we explain the basics of the time-resolved coherent scattering technique and then describe the instrumentation that was set-up and further developed during this PhD project to achieve greater experimental stability, so as to allow meaningful analysis of the time-dependent signals in terms of the physics of the sample. We also introduce the first operational hard x-ray free electron laser light source, LCLS [25], which was used in an experiment whose data are discussed in chapter 4.

In chapter 4, we present the study on dynamics of the charge order in Er$_{0.6}$Ca$_{0.4}$TiO$_3$ using coherent scattering. The coherent scattering patterns, or speckle patterns, produced by the (011) charge order reflection are discussed in detail. In the course of the thesis project, a number of experimental runs were performed at beamlines at the BESSY II synchrotron source in Berlin and at beamline P10 at DESY in Hamburg. We also carried out our first hard X-ray free electron based correlation spectroscopy (XCS) study on the XCS station at the Linac Coherent Light Source (LCLS) at SLAC, and these results are also presented in chapter 4. Since we were only the second research collaboration to work with this newly opened XCS beamline, the experiment at LCLS is discussed in some detail.

Chapter 5 is focused on the structural results obtained during the dynamical experiments. We compare the temperature dependence of the (011) charge order and the (022) structural reflections in order to shed light on the phase separation occurring around the metal insulator transition in Er$_{0.6}$Ca$_{0.4}$TiO$_3$. In the first part of this chapter, we discuss the phase separation by means of a temperature-dependent rocking scan dataset, in which we also broaden the
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scope of a normal rocking scan experiment into a 2D reciprocal mapping technique. A detailed explanation of this is given. The second part of this chapter is dedicated to the real space mapping of the coexisting phases around the metal insulator transition. Using scanning X-ray microdiffraction technique ($\mu$XRD), we were able to record the spatial intensity distribution from two coexisting electronic phases for temperatures close to the MIT. Here, an unexpected real-space stripe order was observed on the micron scale for the first time in this system. This last chapter concludes with both a synthesis of all the information we have gathered on the physics of the metal insulator transition in the titanates as a model complex oxide system, and an outlook to the further development of x-ray speckle techniques for use in the study of condensed matter systems.

These main thesis chapters are supplemented by three appendices. Appendix A deals with the diffraction geometry used in the experiments. Appendix B describes the operation principle of the advanced Timepix detector that was used during the LCLS experiment. Furthermore, the coherence properties of the LCLS beam during our experiment is discussed in Appendix C.