UNIVERSITY OF AMSTERDAM

Charge Order Dynamics and Phase Separation in Titanates.

B. Shi

Summary

Oxides of transition metals display a plethora of fundamentally interesting and potentially technologically relevant properties, including metallic, semiconducting, insulating, magnetic and superconducting behavior. The foundations for this flexibility lie in the close balance between the factors controlling the charge, orbital and spin degrees of freedom in such oxides. One characteristic of many complex oxides are phase transitions between different quantum states of matter, for example between a conducting and insulating state or between a paramagnetic and magnetically ordered state. In this thesis, we describe the experiments on the metal-insulator transition (MIT) in a family of doped titanium oxides, $Er_{0.6}Ca_{0.4}TiO_3$. Rather than simply switching between metallic and insulating states, these systems display co-existence of these antagonistic phases, and the investigation of their interplay and dynamics lies at the heart of this thesis project. Advanced X-ray techniques, using both hard and soft X-rays - from storage ring and free electron laser sources - have been adopted and adapted to probe the phase separation occurring near the MIT in the $Er_{0.6}Ca_{0.4}TiO_3$ system.

After introducing the contents and scope of the thesis in Chapter 1, the relevant theory is reviewed in Chapter 2. Chapter 3 treats the experimental state-of-the-art. For the Ca doping level studied, there is a first-order like MIT at temperatures around 160 K, which is accompanied by charge and orbital ordering. Much challenging and interesting physics is hidden in both the dynamics of the ordering phenomena during the MIT and in the manner by which the separated phases spontaneously spatially arrange across the transition, and these themes form the basis of Chapters 4 and 5.

Chapter 4 reports a thorough and careful search for the effects of dynamics of this phase separation using the scattering of coherent X-rays. Great effort was expended to improve the stability of advanced coherent X-ray scattering set-ups at synchrotrons and to use the unique capabilities of the X-ray free electron laser course, LCLS. We were successful in pushing the temporal limits for coherent X-ray scattering to capture *equilibrium* charge order dynamics in a solid to only a single second. Nevertheless, the charge order in the Ca-doped titanate is found to be static at thermal equilibrium, although we do show it to display stick-slip dynamics when subjected to a temperature change.

In the final results chapter (Chapter 5), advanced X-ray microdiffraction and related structural probes unexpectedly uncovered beautiful, self-organized, meso-scale patterns of stripes in the co-existing, spatially separated metallic and insulator phases occurring at and close-to the metal-insulator transition. Their significance in this case and also as a general phenomenon in other complex oxide MITs is discussed.