Center for Nanoscale Materials, Advanced Photon Source

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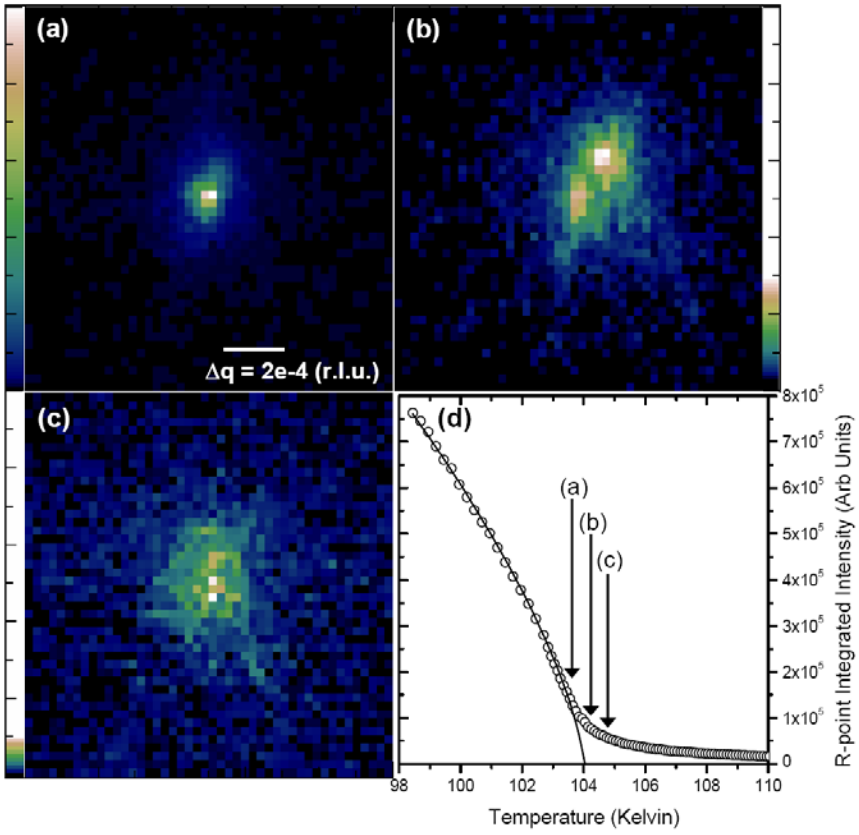
Nanoscale phenomena near phase transitions via temperature-dependent nanodiffraction

Requested Funding: $1,360,000



Executive Summary

The understanding and control of the nanoscopic properties of phase transitions in solids remains a great challenge for materials physics and an area of active research. Multiscale phenomena in materials exhibiting such behavior as superconductivity, piezoelectricity, ferromagnetism, or ferroelectricity arise from the complex interaction of these systems with their constituent nanostructure. This local, nanoscale critical phenomena can lead to interesting and unexpected behavior, in some cases dominating the macrostructural properties of the material. The development of new capabilities, such as temperature-dependent nanoscale diffraction microscopy at the CNM/APS Hard X-ray Nanoprobe (HXN), will allow the observation of nanoscale critical behavior at previously unattainable spatial resolution and sensitivity. The thrust of this proposal is to experimentally study nanoscale phenomena of phase transitions in the presence of defects, domain boundaries, local disorder and reduced dimensionality, and to collaborate with the theory community towards furthering development of modern theories of phase transitions.

Scientific Thrust

The interaction of a bulk phase transition with defects or externally engineered lattice imperfections is the topic of current theoretical and experimental work. Most modern theories of phase transitions depend on a scaling hypothesis and a group theoretical knowledge of universality – that is, the assumption that one relevant length scale taken with a known symmetry of lattice interactions can predict all the critical features of the phase transition. Lattice defects and their associated local random strain field break this hypothesis, leading to regions of the crystal operating with an entirely distinct Hamiltonian and critical behavior. This was observed recently in the structural phase transition of strontium titanate using coherent x-ray diffraction (Figure 1).[i]

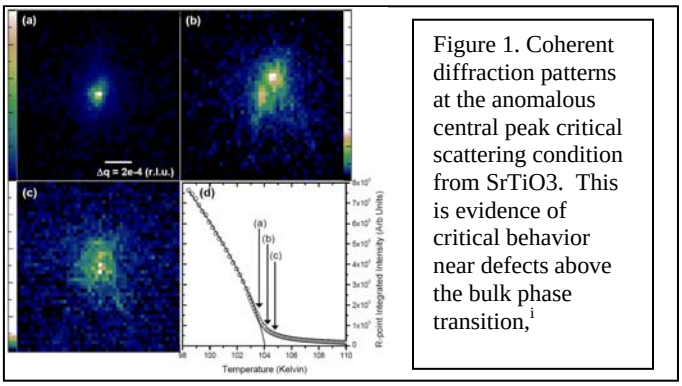


Figure 1. Coherent diffraction patterns at the anomalous central peak critical scattering condition from SrTiO3. This is evidence of critical behavior near defects above the bulk phase transition,[i]

These effects are expected to be of even greater importance in a system of reduced scale and perfection such as an engineered nano-device. Utilizing temperature-dependent nanodiffraction to unambiguously determine and map out critical behavior near defects and imperfections is therefore key to understanding these phenomena.

An example of nanoscale cooperative phenomena is the shape-memory effect. The shape-memory effect observed in many martensitic metal systems holds great potential for micro-scale and nano-scale device fabrication as it can in principle be harnessed to create reversible large-scale deformations in systems of arbitrarily reduced size and dimensionality.[ii,iii,iv] These devices have the potential to outperform traditional piezo

transducers at the micro-scale and beyond owing to their high work output per volume and ease of scaleability. The successful engineering of nano-devices via patterned shape-memory thin films will depend on an advanced experimental and theoretical understanding of two major areas: (i) the microscopic mechanism of how the complex local interactions between martensitic domains results in cooperative, reversible motion, and (ii) how the local, non-scalable physics of this process will respond to defects and external patterning.

The microscopic mechanism of the shape-memory effect is thought to be an elastic absorption of applied stress into the martensitic domain structure resulting in domain wall motion and a large – and exactly reversible – interfacial bound strain.[iii,iv] This mechanism however, has never yet been directly observed. Recent theoretical advances for thin-film martensites have made the surprising prediction that the domain interfaces of the thin film differ substantially from the bulk, and may have a unique response to patterning.[v] Temperature-dependent diffraction microscopy is uniquely suited to answering several fundamental questions on the critical behavior of active materials at the nanoscale.

We propose to pursue temperature-dependent nanodiffraction of nanoscale materials and devices based on advanced nanoscale materials, such as shape-memory alloys, ferroelectrics and multiferroics, with the goal of characterizing and understanding their phase transition behavior, and the role intrinsic and engineered defects play.

Required Instrumentation

The HXN at APS sector 26 is uniquely suited to study nanoscale cooperative phenomena through a combination of nanodiffraction, transmission nanotomography, and x-ray fluorescence at the nanoscale. Nanotomography will provide a three-dimensional representation of e.g. deformations in shape memory alloy devices following martensitic phase transition. Nanodiffraction with a spatially coherent wavefront will yield local strain state and structure, as well as allow quantification of the dynamics of such phenomena via, for example, photon correlation spectroscopy of time-evolving nanoscale disorder. Nanoscale fluorescence allows quantification of the elemental constituency of the illuminated volume at the same time. These capabilities allow us to study both intrinsic properties of nanoscale materials as well as engineered local inhomogeneities, such as patterned defects, doping, or composition spread, and their impact on materials properties or device performance by directly quantifying local changes in the mechanics and energetics of the phase transition.

Study of nanoscale phase phenomena near phase transitions requires change of specimen temperature by a large amount and under accurate maintenance of the temperature while at the same time minimizing thermal drifts. The HXN provides a specimen positioning system with position readout accuracy of a few nanometers, and feedback controls with high bandwidth. The HXN specimen modules that are compatible with this nanopositioning system currently allow room temperature characterization of nanoscale materials in nanodiffraction and nanotomography. A temperature controlled

nanodiffraction module suited for studying phase transitions while maintaining compatibility with our nanopositioning system can be procured through XRADIA Inc. We propose acquisition of such a module from XRADIA. The module operates with liquid nitrogen as a coolant, and is expected to achieve a lowest temperature of 100 K or below. It provides moderate heating capabilities, with an upper temperature of at least 80ºC. In addition, we have developed a prototype heating adaptor (Fig. 2) that allows us to extend the upper temperature to 200º C or above, and we intend integration of that adaptor into the HXN.

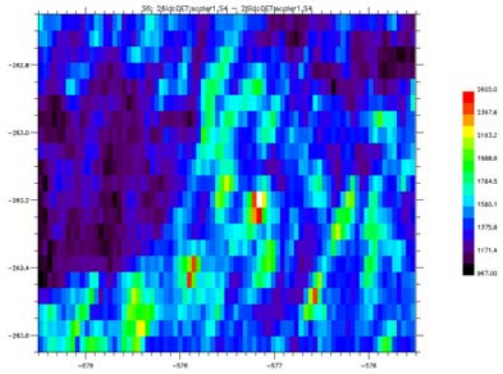


Fig. 2: Temperature dependent study of metallic precursor domains in VO2 near the Mott transition. Nanodiffraction data were taken at the HXN Beamline with a prototype heater assembly.

Curtesy O. Shpyrko, D. Basov (UCSD)

Acquisition Strategy and Cost

In developing this proposal, we have interacted closely with XRADIA Inc., the company that constructed the existing Nanoprobe Instrument based on prototype Argonne designs. The proposal cost estimate is based on a budgetary quotation from XRADIA for a cryo transfer module for nanotomography. Integration of the transfer module with the nanodiffraction capability and added heating capability was discussed extensively with XRADIA, and feasibility of this integration agreed on.

Heating/Cooling nanodiffraction module for HXN		**K$**
Equipment (includes 10% overhead)		
	Basic Heating/Cooling Module for HXN	$770.00
	High-temperature heating adaptor	$88.00
Effort		
Design of high-temperature heating adaptor	1/2 FTE engineer, 1 years	$75.00
System Integration	Instrumentation scientist, 1/2 FTE/yr, 2 years	$150.00
	Postdoc (3 years)	$278.00
Total Equipment		**$858.00**
Total Effort		**$503.00**
Total Cost		**$1,361.00**

The budget includes Argonne overheads of 10% for capital procurements; fabrication costs and staff effort estimates are fully loaded.

Procurement and installation of the basic cooling/heating module is estimated to take one year. R&D towards development of a high-temperature heating adaptor is expected to take 1 year. Commissioning is expected to take 2 months.

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[i] Holt, M., et al., "Dynamic Fluctuations and Static Speckle in Critical X-ray Scattering from SrTiO3," *Phys. Rev. Lett.* **98**, 065501 (2007).

[ii] Bhattacharya, K., and R.D. James, "The Material is the Machine", *Science* **307**, *53* (2005).

[iii] Dong J.W., et al., "Shape Memory and Ferromagnetic Shape Memory Effects in Single-Crystal Ni^2MnGa films". *Journ. Appl. Phys.* **95**, 2593 (2004).

[iv] Krenke, T., et al., *Phys. Rev. B* **72**, "Martensitic transitions and the nature of ferromagnetism in the austenitic and martensitic states of Ni-Mn-Sn alloys", 014412 (2005).

[v] Bhattacharya, K., and R.D. James, "A theory of thin films of martensitic materials with applications to microactuators", *J. Mech. Phys. Solids* 47, **531** (1999).