Statement of Research Interests and Plans

Exploring New Physics in Low-dimensional Materials via Advanced Electron Microscopy/Spectroscopy, Pair Distribution Function and First-Principles Calculations

Nanomaterials and nanostructured materials have generated a great deal of interest, as their optical and electronic properties can be significantly altered from their bulk counterparts due to the electronic wavefunction being confined in one or more dimensions. A unique opportunity to experimentally study low-dimensional advanced materials at nanometer or atomic scale is offered by advanced analytical electron microscopy, particularly combination of scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). Equally important is an insightful theoretical interpretation for the experimental observations. Thanks to the advent of modern density functional theory (DFT) packages such as WIEN2K, VASP, ABINIT, etc., accurate and fast modeling of electronic structure of nanomaterials has become feasible. To better understand nanomaterials and their nanostructures, quantitatively solving 3D structure of nanomaterials is also essential. Electron pair distribution function (ePDF) analysis combined with nano-beam diffraction (NBD) technique provides a unique approach to determine 3D structure in a university laboratory environment. At Texas Tech University, I would extend my current research to explore new physics in various materials using advanced electron microscopy and DFT calculations. To achieve this goal, I would focus on the following three main areas:

1. Atomic-scale STEM-EELS and DFT study of 2D layered materials
   (a) Iron-based superconductors
   (b) Transition-metal dichalcogenides
2. Solving 3D structure of nanomaterials using electron pair distribution function
   (a) Further development of electron pair distribution function
   (b) Solving 3D structure of biomolecular materials
3. Phase change materials for data storage application

I. RESEARCH INTERESTS

1. Atomic-scale STEM EELS and DFT study of 2D layered materials

2D layered nanomaterials, has also attracted a lot of attention since the discovery of graphene due to their emergent properties when a bulk crystal is thinned down to a few atomic layers. Probing both structural and electronic properties at nanometer or atomic scale is crucial to better understand layered materials. One of the Ph. D. projects I completed at the University of Illinois at Urbana-Champaign (UIUC) was to investigate the role of interstitial oxygen in inducing superconductivity in layered $Fe_{1+y}Te$ films. As-grown $Fe_{1+y}Te$ films are non-superconducting, but superconductivity is observed in the $Fe_{1+y}TeO_x$ thin films with T_c close to 12 K after oxygen incorporation [1]. We collaborated with Prof. Eckstein's molecular beam epitaxy (MBE) group at Urbana to utilize the MBE's capability of growing atomically flat films. A typical atomic-resolution STEM image of $Fe_{1+y}Te$ grown on $LaAlO_3$ substrate is shown in Fig. 1(a). Our atomic-resolution line-scan EELS results clearly showed that oxygen preferentially occupies the interstitial site, bonded to the Fe layer (Fig. 1(b)). To further pin down the location of interstitial oxygen, I performed DFT calculations to model the structure by considering different possible oxygen configurations and found oxygen is bounded in the Fe layer in a pyramid-like configuration resulting in the lowest energy (Fig. 1(c)). Also, bicollinear antiferromagnetic (AFM) configuration was found to be the ground state with interstitial oxygen disrupting long-range AFM order, which is favorable to superconductivity [2].

At Texas Tech University, I would establish my collaboration with thin-film/synthesis groups and theoretical groups, as well as continue my collaboration with UIUC, Brookhaven National Lab (BNL), and Intel Corporation. I would focus on the following two main systems:

1(a) Iron-based superconductors, particularly FeSe thin films. While superconductivity emerges at 9K in bulk FeSe, single-layer films of FeSe grown on $SrTiO_3$ (001) substrates demonstrate superconducting transition temperature, T_c, above 100 K[3]. I will extend my prior research to address the following key scientific questions: (1) Interfacial strain by using atomic-resolution STEM imaging and nano-beam electron diffraction. (2) Interaction between FeSe films and $SrTiO_3$. Changes in electronic structure around the interface will be probed by fine structure of Fe-$L_{2,3}$ of FeSe and Ti-$L_{2,3}$ of $SrTiO_3$ to capture charge transfer or any other phenomena. (3) Possible change in atomic and/or electronic structure below T_c. In-situ characterization will be performed using a cold stage with liquid nitrogen or liquid helium. This would enable us to better understand the physics behind emergency of superconductivity in FeSe films and design new superconducting materials.

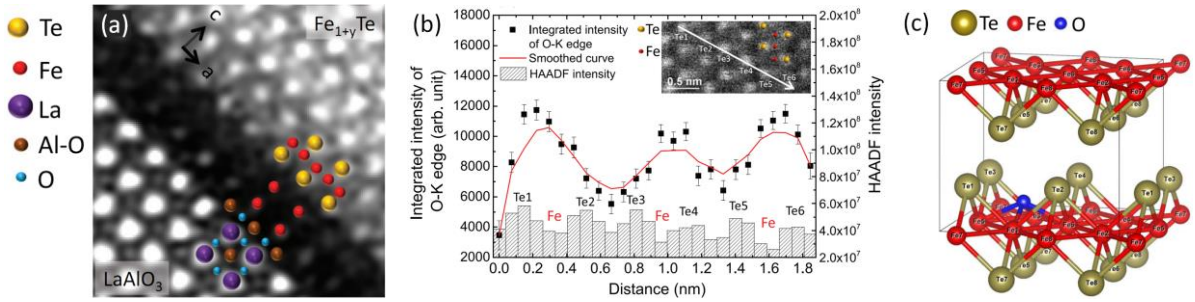

Figure 1. (a) Atomic-resolution STEM image of a FeTe film on $LaAlO_3$ substrate. (b) The integrated intensity of O-K, plotted by solid square as a function of the scan path shown by the STEM image in the inset. (c) A 2×2×1 supercell used for structrual modeling.

1(b) Transition-metal dichalcogenides (TMD). Transition-metal dichalcogenide materials can be metallic, semimetallic or semiconducting materials of the type MX_2, with M a transition metal atom and X a chalcogen atom. The properties of MX_2 vary dramatically with the number of layers. For esample, some TMD materials have an indirect band gap in the bulk form, while a direct band gap is formed in monolayers[4], which exhibits different electronic, optical and mechanical properties. STEM-EELS would be an ideal tool to study electronic structures of these materials. Fine structures of characteristic core-loss edges directly reflect (unoccupied) density of states of the material, and low-loss EELS is closely related to dielectric function of the material. Hence, I propose to address the following key scientific issues: (1) Response of low loss EELS, particularly surface plasmon, to thickness change. Subtle changes or energy splitting in low-loss will be examined. (2) DFT simulation to interpret experimental low loss spectra. (3) Probing core-loss fine structure to investigate bonding environment with change of sample thickness.

2. Solving 3D structure of nanomaterials using electron pair distribution function

Quantitatively determining the atomic arrangement of nanomaterials is essential in nanoscience. While the traditional method of X-ray crystallography fails because of limited size of coherent structural domains within nanomaterials, a specialized approach, known as the atomic pair distribution function (PDF) method, has emerged as a powerful tool to obtain quantitative 3D structural information of nanomaterials[5]. However, currently, most PDF experiments are carried out at X-ray synchrotron or neutron sources from a large user facility, where access is limited. I have developed the protocol to collect ePDF data in a standard transmission electron microscope to make the PDF technique more convenient

for other research groups to access[6]. SnO_2 nanoparticles of ~2nm were used to develop the ePDF protocol. A typical electron diffraction pattern of SnO_2 nanoparticles is shown in Fig. 2(a). Reduced electron structure function, $F(Q)$, is shown in Fig. 2(b), and the resulting PDF, $G(r)$, is shown as blue symbols in Fig. 2(c). The best-fit PDF from a structural model is plotted in red with a difference curve offset below. The result of ePDF is very consistent with X-ray PDF, and furthermore, real-space images can be easily recorded in TEM.

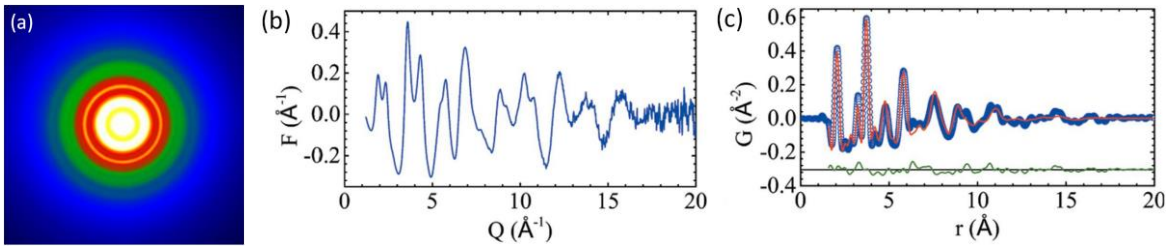

Figure 2. (a) Diffraction pattern of SnO_2 nanoparticles. (b) reduced electron structure function calculated from (a). (c) The resulting PDF shown as blue symboles, and the best-fit PEF from a structural model is plotted in red with a difference curve offset below.

At Texas Tech University, I would continue my research on ePDF with strong collaborations with internal and external groups. Two aspects will be focused:

2(a) Further development of electron pair distribution function. Different from X-ray and neutron diffraction, electrons interact with matters through the Coulomb forces, making multiple scattering play an important role in electron diffraction. This multiple scattering influences the intensities of the reflections, which potentially causes quantitative ePDF modeling inaccurate in certain conditions. Meanwhile, X-ray, neutron and electron diffraction have different sensitivity to light (low-Z) elements. Neutrons are very sensitive to low-Z elements, while X-ray is not. The sensitivity of electrons to low-Z elements is between that of neutrons and X-ray. Hence, I will extend my prior ePDF development with the following key scientific questions to be addressed: (1) how size or composition of nanomaterials influences the accuracy of ePDF modeling. (2) how sensitive is ePDF modeling to low-Z, medium Z and high-Z materials.

2(b) Solving 3D structure of biomolecular materials. There will be many applications of solving 3D structure of nanomaterials by using ePDF. Particularly, ePDF will be useful for biomaterials and pharmaceuticals that are difficult to produce, as only a small amount of samples is sufficient due to strong interaction between electrons and matters [7]. In additional to ePDF analysis in TEM, images and EELS or energy dispersive X-ray (EDX) can be easily recorded, which would enable us to correlate structural properties to sample morphology and chemical information.

3. Phase change materials for data storage application

Since the invention of computers, data storage technology has been continuously developed to achieve faster speed and larger capacity. Phase change materials (PCM), with $Ge_2Sb_2Te_5$ (GST-225) being the most promising candidate, utilize the large difference of resistivity between crystalline and amorphous phases to store information. PCM has attracted a lot of attention recently, especially after Intel and Micron announced 3D Xpoint in 2015 [8]. Because of its properties of fast speed and non-volatility, PCM can be used for both storage- and memory-level products. Although the first commercial PCM product became available in 2017, many fundamental questions still remain. For example, the mechanisms of performance degradation are still not very clear. Therefore, I will extend my current research to particularly address the following two scientific questions:

3(a) Elemental segregation/contaminations. Chemical instability is considered as one of the failure mechanisms for confined PCM cells [9]. Raoux *et al*. showed that there is Ge depletion and Sb enriching in the switched area after 1000 switching cycles [9]. Foreign contamination migrating from outside the cells could also affect the cell performance. STEM-EDX analysis will be an ideal method to quantify such chemical information. I will address the following key questions: (1) how elemental segregation changes over cycling and how much of elemental segregation contributes to PCM performance degradation. (2) how much of foreign contaminations migrates into PCM cell from surrounding dielectrics over cycling.

3(b) Structural evolution. GST-225 has two stable states – low resistance crystalline phase (state '1') and high resistance amorphous phases (state '0'), which can be rapidly switched by using electrical pulses. However, there has been no systematic study on how the structure of PCM degrades with cycling. Nano-beam diffraction (NBD) with a probe size of as small as 4nm will be perfect to probe structural evolution of nanometer-scale PCM devices. Hence, I will apply my prior NBD experience to investigate: (1) how d-spacing changes of crystalline phase with cycling. (2) how short-range ordering of amorphous state changes with cycling by ePDF analysis combined with NBD.

II. Summary

This proposed research should fit extremely well within the Department of Physics and Astronomy at Texas Tech University, and would strongly benefit from the extraordinary expertise in both Experimental and Theoretical Condensed Matter Physics at Texas Tech University. Overall, these projects aim to investigate unconventional structural and electronic properties of low-dimensional nanomaterials or phenomena, as well as to develop novel techniques to quantitatively solve 3D structure of nanomaterials. These research subjects are of fundamental scientific interest and promising industrial application, and, at the same time, provide great research opportunities for the undergraduate and graduate students at Texas Tech University in a quest to unravel the secrets of NATURE.

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