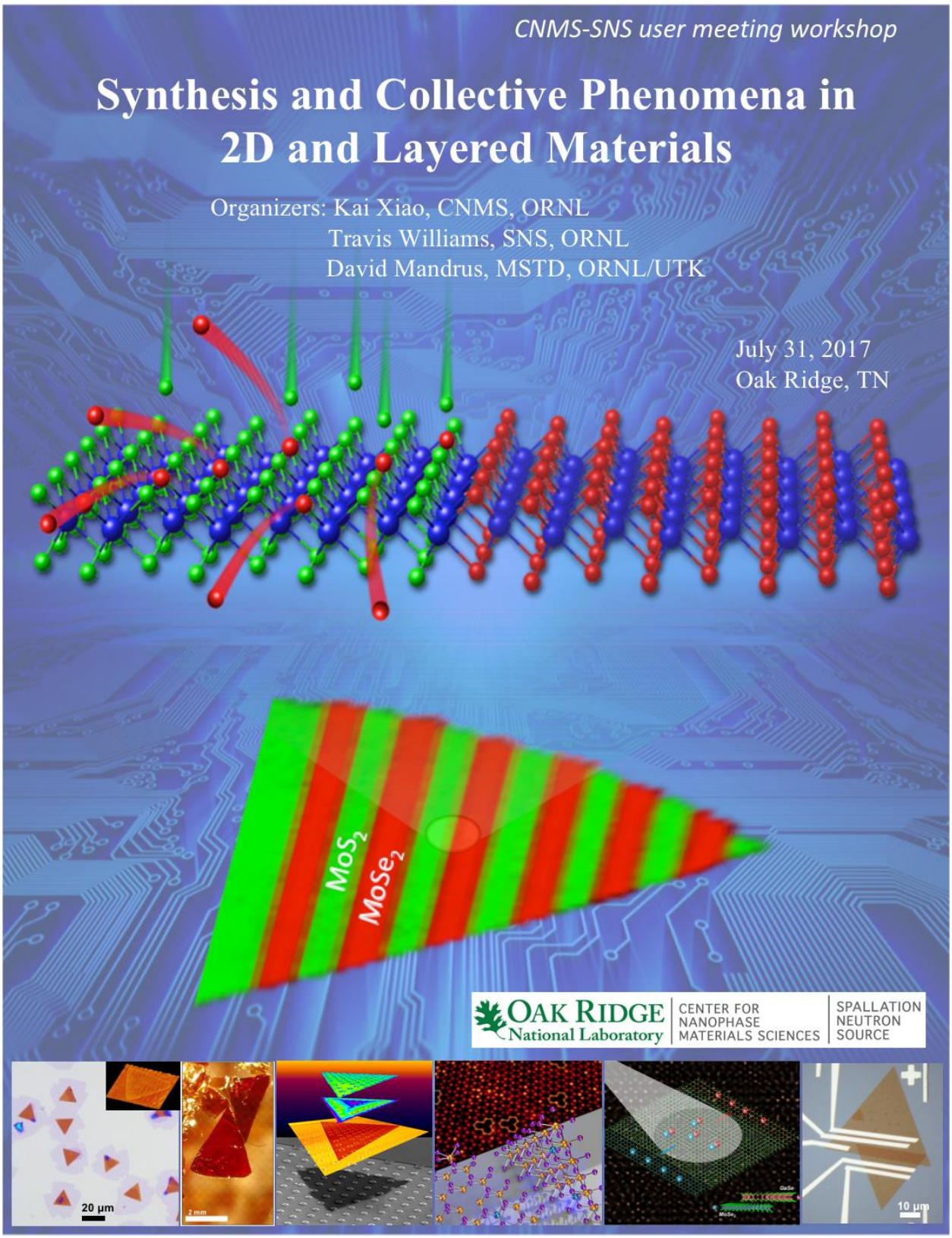
CNMS-SNS user meeting workshop
Synthesis and Collective Phenomena in 2D and Layered Materials
Organizers: Kai Xiao, CNMS, ORNL
Travis Williams, SNS, ORNL
David Mandrus, MSTD, ORNL/UTK
July 31, 2017
Oak Ridge, TN
MoS_2
$MoSe_2$
OAK RIDGE National Laboratory
CENTER FOR NANOPHASE MATERIALS SCIENCES
SPALLATION NEUTRON SOURCE
20 μm
2 mm
10 μm

Synthesis and Collective Phenomena in 2D and Layered Materials

Monday, July 31, 2017

Organizers:
Kai Xiao, Center for Nanophase Materials Sciences, ORNL
Travis Williams, Spallation Neutron Source, ORNL
David Mandrus, Materials Science and Technology Division, ORNL/UTK

This workshop aims to facilitate and strengthen the synergistic strategy to pursue the latest developments in the controlled synthesis, advanced characterization, and various applications of 2D and layered materials. The CNMS and SNS at ORNL have expertise and state-of-the-art facilities in the controlled synthesis, advanced characterization, theoretical modeling, and functional applications of 2D and layered materials. This has led a strong research program focused around the fundamental studies on physical properties in many aspects including optoelectronic, mechanical, spin and magnetic behaviors. This workshop will include topics covering intriguing collective phenomena of 2D and layered materials and heterostructures, their growth, characterization and device applications with corresponding computational modeling. In addition to fundamental significance, the workshop seeks to broaden the interest of community in the rapidly developing capabilities of CNMS and SNS for the study of 2D and layered materials, including integration with elastic and inelastic neutron scattering techniques. Tours of relevant facilities will be arranged for both SNS and CNMS.

The topics of the workshop include but are not limited to:

- Controlled synthesis and advanced characterization of 2D materials.
- Heterogeneity in 2D materials including defects, dopants, interfacial interactions and substrate effects.
- Predictive modeling and theoretical simulation of 2D materials.
- Application of neutron scattering to 2D materials.

Agenda

Monday, July 31, 2017

Bldg 8610, Iran Thomas Auditorium

8:30 -9:00
Kai Xiao (ORNL)
2D Materials Research at ORNL

9:00 – 9:30
Deji Akinwande (The University of Texas at Austin)
Emerging 2D Materials, Devices and Nanosystems

9:30 – 10:00
Michael McGuire (ORNL)
Magnetism in van der Waals Layered d^3 Transition Metal Compounds

10:00 – 10:30
Eric Henriksen (Washington University in St. Louis.)
Spectroscopy of Microscopic Graphene and $RuCl_3$ Flakes

10:30 – 10:45 *Coffee break*

10:45 – 11:15
Juan Carlos Idrobo (ORNL)
Novel Spectroscopy in Low Dimensional Materials

11:15 – 11:45
Sefaattin Tongay (Arizona State University)
Fundamentals and Applications of Anisotropic Atomically Thin Materials

11:45 – 12:05
Satish Kumar (Georgia Institute of Technology)
Phonon Transport Properties of Monolayer $MoSe_2$ from First-Principles

12:05 – 1:35 *Lunch*

1:35 – 2:05
Peide Ye (Purdue University)
1D van der Waals Materials in 2D Form

2:05 – 2:35
David B Geohegan (ORNL)
Exploring 2D Materials Synthesis with Nonequilibrium Growth Techniques and Laser Spectroscopy

2:35 – 3:05
Travis Williams
Capabilities at the Spallation Neutron Source for Studying 2D and Layered Materials

3:05 – 3:35
Arnab Banerjee (ORNL)
Field Dependence of Magnetic Order and Excitations in the Kitaev Candidate alpha-$RuCl_3$

3:35 -3:50 *Coffee break*

3:50 – 4:20

Volodymyr Turkowski (University of Central Florida)

Excitations and Ultrafast Dynamics of Charge Carriers in 2D Transition Metal Dichalcogenides

4:20 – 4:50

Linyou Cao (North Carolina State University)

Room-Temperature Exciton Condensation in Monolayer MoS_2

4:50 – 5:20

Liangbo Liang (ORNL)

Theoretical Modeling of Raman Scattering for Characterization of Low-Dimensional Materials

5:20 Dismiss

List of abstracts

Emerging 2D Materials, Devices and Nanosystems

Deji Akinwande
Department of Electrical and Computer Engineering, The University of Texas at Austin

This talk will present new directions and emerging device concepts based on layered nanomaterials, and transition from laboratory ideas to commercialization. In particular, 2D semimetals (e.g. graphene), 2D semiconductors (e.g. MoS_2 and phosphorene), and 2D topological insulators (e.g. silicene and Xenes) will be highlighted and the enabling material/device concepts ranging from advanced classical and topological transistors (charge transport) to non-volatile switching and memory (ionic phenomena) to wearable sensors for mobile health and machine control will be featured.

Magnetism in van der Waals Layered d^3 Transition Metal Compounds

Michael A. McGuire
Materials Science and Technology Division, Oak Ridge National Laboratory

Among the handful of families of cleavable magnetic materials, binary halides [1], and chromium trihalides in particular [2], have received considerable attention. Recent work with CrI_3 has resulted in the first demonstration of a ferromagnetic monolayer cleaved from a bulk crystal [3], as well as integration of magnetism into van der Waals heterostructures [4]. Here I will give an overview of recent progress on this material and closely related $CrCl_3$ [5], which is isostructural and isoelectronic to CrI_3, with a Cr-$3d^3$ electronic configuration. I will also present results from our study of the $4d^3$ analogue $MoCl_3$, which has a structural instability that masks inherently strong magnetism, and the van der Waals layered semiconductor $CrTe_3$, which exhibits low dimensional magnetic behavior with long range antiferromagnetic order at low temperature [6].

[1] M.A. McGuire, "Crystal and Magnetic Structures in Layered, Transition Metal Dihalides and Trihalides" *Crystals* 7, 121 (2017).
[2] M.A. McGuire et al., "Coupling of crystal structure and magnetism in the layered, ferromagnetic insulator CrI_3" *Chemistry of Materials* 27, 612 (2015).
[3] B. Huang et al., "Layer-dependent Ferromagnetism in a van der Waals Crystal down to the Monolayer Limit" *Nature* 546, 270 (2017).
[4] D. Zhong et al., "Van der Waals engineering of ferromagnetic semiconductor heterostructures for spin and valleytronics" *Science Advances* 3, e1603113 (2017).
[5] M.A. McGuire et al., "Magnetic behavior and spin-lattice coupling in cleavable van der Waals layered $CrCl_3$ crystals" *Physical Review Materials* 1, 014001 (2017).
[6] M.A. McGuire et al., "Antiferromagnetism in the van der Waals layered spin-lozenge semiconductor $CrTe_3$" *Physical Review B* 95, 144421 (2017).

Spectroscopy of microscopic graphene and $RuCl_3$ flakes

Erik Henriksen
Physics Department, Washington University in St. Louis.

We present results on the low temperature infrared magneto-spectroscopy of high mobility graphene. Several interband transitions are observed in a 250 μm^2 device. These transitions contain unmistakable signatures of many-particle effects, discussed theoretically for nearly a decade but not observed until now. Additionally, we will show initial Raman results on exfoliated $RuCl_3$ flakes, where we see an interesting evolution of the phonon peaks with thickness and temperature.

Novel Spectroscopy in low dimensional materials

Juan Carlos Idrobo
Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, USA

The development of aberration correctors and monochromators have completely changed the landscape of how we studied materials using electron microscopes. Here, I will show that now we can peer into the bonding and metastable energy states of individual impurities in monolayer graphene, reveal the temperature and thermal expansion coefficient in BN, and even determine the isotopic configuration of materials with sub 10-nm spatial resolution. I will discuss the common challenges faced in these kind of experiments.

This research was supported by the Center for Nanophase Materials Sciences (CNMS), which is sponsored at ORNL by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy (JCI).

Fundamentals and Applications of Anisotropic Atomically Thin Materials

Sefaattin Tongay
School for Engineering of Matter, Transport and Energy
Arizona State University

Anisotropic 2D materials (pseudo-1D crystals) are a new class of materials in which atoms are confined in 2D but are arranged in a way that they form 1D chain-like features running across one specific lattice direction. They exhibit direction and polarization dependent properties that allow for a new degree of freedom, which are particularly attractive for a number of advanced photonic, optics, and optoelectronic applications. In a sense, they offer unique properties that fall between traditional 1D and 2D material systems. This talk summarizes recent advances made in pseudo-1D material synthesis, characterization, fundamental understanding, and applications by the team led by Prof. Tongay at Arizona State University. Special emphasis will be given to recent projects by Tongay's team using one-of-a-kind spectroscopy, microscopy, scanning transmission electron microscopy (STEM), high-resolution TEM (HRTEM), and spectroscopy facilities at Arizona State University.

Phonon transport properties of monolayer $MoSe_2$ from first-principles

Satish Kumar, Associate Professor, satish.kumar@me.gatech.edu
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$MoSe_2$ as one of the promising 2-D transition metal dichalcogenides shows many interesting electronic and optical properties, such as large intrinsic band gap and strong photoluminescence. The large band gap and hexagonal planar lattice make it promising for many nano-electronic and opto-electronic applications. A fundamental understanding of phonon transport properties of $MoSe_2$ is of high importance for improving reliability and energy efficiency for the $MoSe_2$ based devices. We use the density functional theory (DFT) and the phonon Boltzmann transport equation (BTE) to study the phonon transport properties of monolayer $MoSe_2$. We developed a model using iterative solution of the BTE to predict the thermal conductivity of 2-D layers using the inputs form DFT. The developed model consider the effect of sample size, boundary and anharmonic phonon scattering, vacancies on the thermal conductivity of $MoSe_2$. The study provides insights into how doping $MoSe_2$ monolayers using tungsten (W) affect its thermal properties for different defect % when these monolayers are suspended.

1D van der Waals materials in 2D form

Peide D. Ye

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E-mail: yep@purude.edu

Tellurium (Te) or Selenium (Se) is a one-dimensional material consisting of spiral atomic chains bonded together by van der Waals forces. Due to its 1D nature, Te or Se has a strong tendency to grow into nanowire forms, which has largely hindered the exploration of its potential device applications. By using liquid-based hydrothermal synthesis method or physical vapor deposition method, for the first time, large-size high-quality air-stable 2D films of Te and Se are realized. For example with Te films, field-effect mobility is as high as 700 cm^2/Vs at room temperature and the maximum drain current of fabricated scaled transistors exceeds 1.1 A/mm with dielectric engineering. The devices are stable stored in air for 4-5 months without any degradation.

The research is in collaboration with Prof. Wenzhuo Wu's group at Purdue University and supported by NSF, AFOSR, ARO and SRC.

Exploring 2D Materials Synthesis with Nonequilibrium Growth Techniques and Laser Spectroscopy

David B. Geohegan[1*], Masoud Mahjouri-Samani[1], Xufan Li[1], Kai Wang[1], Wesley Tennyson[1], Aziz Boulesbaa[1], Liangbo Liang[1], Mengkun Tian[3], Alex A. Puretzky[1], Bobby Sumpter[1], Gerd Duscher[3], Mina Yoon[1] , Gyula Eres[2], Chris M. Rouleau[1], Ray Unocic[1], Miaofang Chi[1], Leonardo Basile, [1,3] Juan C. Idrobo[1], and Kai Xiao[1]

1) *Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA*
2) *Materials Science and Technology Div., Oak Ridge National Laboratory, Oak Ridge, TN, USA*
3) *Dept. of Materials Science and Engineering, University of Tennessee, Knoxville, TN, USA*
4) *Departamento de Física, Escuela Politécnica Nacional, Quito 170525, Ecuador*

**D. B. Geohegan, geohegandb@ornl.gov, 865-742-8995*

Realizing the bottom-up growth of two-dimensional materials with reliable properties that are comparable to those of exfoliated bulk crystals is currently hampered by a lack of understanding of key synthesis questions that are common among low-dimensional nanomaterials, such as carbon nanotubes, graphene, and now transition metal dichalcogenides. In each case, it is essential (but typically very difficult) to understand the key aspects of nucleation and growth kinetics, the key "building blocks" for growth, and the factors that control the types of defects, or heterogeneity, of the crystals. In this workshop, I will describe some of the approaches that we are undertaking to understand and control the synthesis of 2D materials with controllable levels of defects through the development and application of nonequilibrium growth methods, including pulsed and laser-based techniques, designed to exert control over the synthesis process. Laser characterization methods, such as low-frequency Raman spectroscopy, low-temperature photoluminescence, and ultrafast pump-probe spectroscopy each reveal different aspects relating synthesis and function such as atomistic stacking configurations between layers, band gap shifts due to doping, the nature of defects, and quasiparticle dynamics. Recent results in engineering the dopants and vacancies in 2D $MoSe_2$ using different growth approaches reveal the importance of defect engineering in controlling optoelectronic properties, and conversely the opportunity for an *in situ* diagnostic approach employing optical spectroscopy. Using examples from our recent results in 2D materials synthesis and their optoelectronic characterization I will describe the facilities available for collaboration at the Center for Nanophase Materials Sciences (CNMS). The facilities include atomic-resolution Z-contrast STEM imaging, atomic resolution scanning tunnelling microscopy, and associated computational simulations that permit atomistic understanding of the important role of heterogeneity in 2D materials properties.

Research sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science).

Capabilities at the Spallation Neutron Source for Studying 2D and Layered Materials

Travis J. Williams
Quantum Condensed Matter Division, Oak Ridge National Laboratory

The SNS instrument suite is composed of 19 neutron scattering instruments, each with unique capabilities for addressing forefront problems in condensed matter physics, chemistry, biology, soft matter and engineering. This talk will introduce the capabilities present at the SNS for studying 2D and layered materials using neutron scattering. In particular, it will focus on four types of instruments: diffractometers, spectrometers, reflectometers, and small-angle scattering, and give an overview of the scientific strengths of these instruments. Finally, this talk will discuss the prospects of future neutron scattering capabilities through upgrades to the existing instruments, and the construction of the second target station.

Field dependence of magnetic order and excitations in the Kitaev candidate alpha-$RuCl_3$

Arnab Banerjee
Quantum Condensed Matter Division, Oak Ridge National Laboratory

The search for new quantum states of matter has been one of the forefront endeavors of condensed matter physics. The 2-dimensional Kitaev quantum spin liquid (QSL) is of special interest as an exactly solvable spin-liquid model exhibiting exotic fractionalized excitations. Recently, alpha-RuCl3 has been identified as a candidate system for exhibiting some aspects of Kitaev QSL physics. The spins in this material exhibit zig-zag order at low temperatures, and show both low energy spin wave excitation arising from the ordered state as well as a remarkable continuum excitation extending to higher energies that has been taken as evidence for QSL relate Majorana fermions. In this talk, we show that the application of an in-plane magnetic field suppresses the zig-zag order possibly resulting in a state devoid of long-range order. Field-dependent inelastic neutron scattering on single-crystal shows a remarkable effect on the excitation spectrum above the critical field to a pure quatum paramagnetic state. Possibly, this is the state to search for the solid-state non-abelian anyons. I will end with discussing experiments and material synthesis efforts needed in this direction.

Excitations and ultrafast dynamics of charge carriers in 2D transition metal dichalcogenides

Volodymyr Turkowski
Department of Physics, University of Central Florida, Orlando, FL 32816-2385, USA

Single- and few-layer transition metal dichalcogenides (TMDCs) appear to be promising materials for applications in optoelectronics, catalysis and other areas due to their several striking properties, including intrinsic visible-spectrum direct band-gap, extremely strong absorption and emission and strongly-bound exciton, trion and biexciton states. In this talk, after a review of the novel optical properties of 2D TMDC materials, we present basic features of the Density-Matrix Time-Dependent Density-Functional Theory (DM-TDDFT) – a theoretical tool we have been developing to study the properties of novel semiconductor and strongly-correlated materials. We proceed with our DM-TDDFT results on the excitation spectrum in single- and bi-layer TMDCs demonstrating that the reduced electron screening and specific spatial characteristics of the excited charges lead to large binding energies of excitons, trions and biexcitons,[1] in a good agreement with experimental data. In addition, we predict strongly-bound states for several other 2D systems. Next, we present our theoretical results on details of the experimentally-observed [2] ultrafast charge dynamics in MoS_2-WS_2 and several other bi-layers. In particular, we show that the ultrafast inter-layer hole migration in these systems is facilitated by unusually far-extended hole wave functions. We also analyze details of the formation, recombination and/or dissociation of the inter- and intra-layer excitons and the possibility of the Bose-Einstein condensation in a laser-pulse excited exciton cloud in these materials. We show that such a transition can take place at temperatures ~50-100K and discuss how this state is revealed in our results on the optical and transport response of the systems.

[1] A. Ramirez-Torres, V. Turkowski, and T. S. Rahman, Phys. Rev. B 90 (2014) 085419.
[2] X. Hong, et al., Nature Nanotechnology 9 (2014) 682.

*Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354.

Room-Temperature Exciton Condensation in Monolayer MoS_2

Linyou Cao
Department of Materials Science and Engineering and Department of Physics,
North Carolina State University

Condensation in real and/or momentum spaces represents the ultimate control of quasi-particles like excitons. It may give rise to collective quantum states with exotic functionalities that may not exist in nature. However, the condensation often requires cryogenic temperature, which has limited the prospect in practical application. By leveraging on the strong exciton binding energy in monolayer MoS_2, we demonstrate the condensation of gas-like non-interacting free excitons into a strongly correlated liquid-like state, i.e. electron-hole liquid at room temperature. The experimental observation matches theoretical prediction from thermodynamic perspective very well. This result makes the liquid-like condensate of excitons a viable platform for device development such as lasers and LEDs.

Theoretical modeling of Raman scattering for characterization of low-dimensional materials

Liangbo Liang[1,2], Alexander A. Puretzky[1], Xi Ling[3], Shengxi Huang[3], William M. Parkin[4], Masoud Mahjouri-Samani[1], Kai Xiao[1], David B. Geohegan[1], Marija Drndic[4], Mildred S. Dresselhaus[3], Vincent Meunier[2], Bobby G. Sumpter[1]

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[4]Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Raman spectroscopy is among the most useful characterization techniques to understand 2D materials, owing to its capability to identify minute structural and electronic effect. We show that the integrated experimental/theoretical Raman approach can help to determine many crucial properties of 2D materials, such as the number of layers, the layer-layer relative stacking, and the defect concentration. For many 2D materials, low-frequency (LF) interlayer Raman modes, including the shear and breathing modes, are much more sensitive to the interlayer coupling, and can be more effective at determining layer thickness and stacking, compared to the typically studied high-frequency (HF) intralayer Raman modes. We show that the thickness dependence of the LF modes' frequencies can be explained by a simple linear chain model. We also proposed a generalized interlayer bond polarizability model to explain the stacking dependence of the LF modes' intensities. Furthermore, the LF shear and breathing modes are also found in 1D graphene nanoribbons, and they can also be the fingerprints of the nanoribbon widths. Of course, HF Raman modes are of no less importance, as our recent Raman measurements on defective MoS_2 and $MoSe_2$ found that HF modes exhibit unique dependence on S or Se vacancy concentration, corroborated by first-principles phonon calculations.