Emergent orders in the two dimensional limit

I. Introduction and Overview

I am interested in exotic orders emerging from the complex interplay between lattice, charge, spin and orbital degrees of freedom (DoF) in low dimensions, especially at interfaces of van der Waals (vdW) and molecular-beam-epitaxy (MBE) heterostructures, by both developing laboratory-based ultrahigh-vacuum (UHV) linear/nonlinear optical spectroscopy techniques and exploiting synchrotron-based photoemission spectroscopy/microscopy.

Low dimensional materials provide a fertile platform for exploring emergent orders. First of all, the reduction of dimensionality can introduce broken symmetries. A notable example is the broken inversion symmetry in single layer transition metal dichalcogenides (TMDCs) that lifts the Kramer's degeneracy of spins and gives rise to the coupled spin and valley DoF [1]. Second, the physical properties of low dimensional structures can be conveniently tuned by their local geometry and environment such as interlayer twist between a bilayer structure, strain engineering and substrate interactions. A very recent exciting progress is the discovery of unconventional superconductivity in the magic-angle bilayer graphene [2]. Third, the strong quantum confinement and the consequent reduced dielectric screening can strongly modify electronic structures and Coulomb interaction, which is evidenced by the indirect-to-direct bandgap transition and the enhanced photoluminescence in TMDCs [3]. More importantly, for vdW materials with strongly correlated electrons, reducing dimensionality could also efficiently affect a rich spectrum of cooperative phenomena including charge density waves (CDW) [4], superconductivity [5], etc.

Technically, the advances in synthesis techniques have opened up new opportunities for achieving the “materials-by-design” goal. On the one hand, vdW heterostructures [6] in which two-dimensional (2D) atomic planes are vertically stacked without lattice parameter constraints dramatically enhances the flexibility of creating interfaces with desired properties. An extensively studied system is TMDCs heterostructures which host robust interlayer excitons [7]. On the other hand, MBE technique allows painting various 2D films on selected substrates and engineering the delicate interplay among different DoF [8]. A notable example is to tailor the strain strength at the interface of perovskites heterostructures through bond-length changes and octahedral rotations. Moreover, the integration of synthesis techniques with *in situ* probes such as angle-resolved photoemission spectroscopy (APRES) and scanning tunneling microscopy/spectroscopy (STM/STS) has led to fruitful discoveries of novel quantum phases. However, up to now, such a integration of synthesis techniques with ultrafast optical spectroscopy techniques, which can provide access to excited states with state-of-the-art temporal resolution, remains nearly unexplored and therefore calls for devoted efforts.

Driven by both scientific opportunities and technical development, I will leverage my unique expertise in femtosecond laser based optical techniques and synchrotron-based photoemission spectroscopy/microscopy to study the emergent orders in low dimensional materials with the particular emphasis of the following three topics:

- Explore vdW heterostructures involving 2D magnetic materials;
- Study magnetoelectric coupling of vdW multiferroic heterostructures;
- Reveal electronic and magnetic orders in 1T phase VSe_2 on vdW substrates.

The proposed projects and experimental technique developments are discussed in depth as follows.

II. Proposed Experimental Projects

1. Explore vdW heterostructures involving 2D magnetic materials

The realization of 2D magnetic materials [9, 10] adds an important class of building blocks to the vdW heterostructure toolbox and unlocks new approaches to engineering electronic and magnetic orders at the interfaces of heterostructures. In our recent Raman studies of 2D CrI_3, we have found unique properties of this newly discovered 2D magnet, which hosts two branches of exceptionally high frequency (THz) surface spin waves (Fig. 1) [11]. Implementing these novel features of 2D magnets in a vdW heterostructure holds the promise for discovering novel phases or realizing new device applications.

Manipulating spin or pseudospin is the key part for spin- and valley-tronic applications, which can be realized by exploiting the proximity effect within a heterostructure involving a magnet. The magnetic exchange field induced by 2D magnets break the time reversal symmetry (TRS) of the adlayers and thus provides this new route to controlling spin or pseudospin via vdW interface engineering [12]. For example, in the WSe_2/CrI_3 heterostructure, CrI_3 lifts the valley degeneracy in WSe_2 and enables the switchable valley polarization [13]. Built upon and going beyond these existing results, I propose to study magnetic insulator/topological insulator (MI/TI) heterostructure, in which broken TRS is introduced in the TI and leads to a gap opening in its Dirac surface states (SS). This is believed to give rise to novel quantum phases such as quantum anomalous Hall effect, which is realized via chemical doping in TIs [14]. The magnetic proximity effect proposed here has numerous advantages over the chemical doping method, for example, preserving intrinsic crystalline structure of TIs and eliminating dopant-induced scattering and inhomogeneity, etc. An extensively studied example is EuS/Bi_2Se_3, in which, strong interplay between the magnetization of EuS and SS of Bi_2Se_3 is observed [15]. Here, CrI_3 is a promising candidate to construct vdW heterostructures with TIs for introducing broken TRS. In Bi_2Se_3/CrI_3 heterostructure, I plan to explore the chiral edge states along the ferromagnetic domain boundaries [16]. Optical techniques are suitable to study this system because the magnetic domains and domain boundaries can be imaged by second harmonic generation (SHG) microscopy and the TRS breaking SS of Bi_2Se_3 is expected to be detected by magneto-optical Kerr rotation technique. In addition, I will combine pump probe spectroscopy with SHG and Kerr rotation probe to study the relaxation dynamics of lattice, charge and spin DoF and resolve how they are coupled at the interface of Bi_2Se_3/CrI_3 heterostructure.

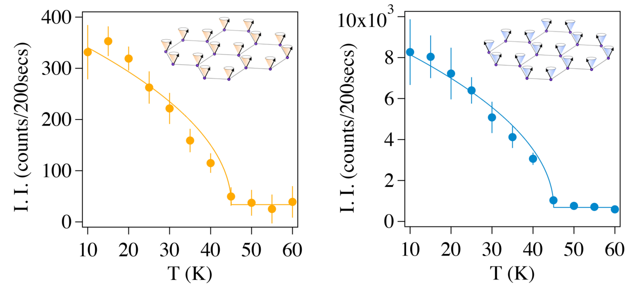

FIG. 1: Temperature dependence of the integrated intensity (I.I.) of the two zero-momentum magnon modes. Insets depict the in-phase and out-of-phase precession of the spins on two Cr^{3+} sublattices.

2. Study magnetoelectric coupling of vdW multiferroic heterostructures

Multiferroics with strong magnetoelectric coupling are rare in nature. From the prospective of symmetry consideration, among all the 233 Shubnikov magnetic point groups, only 13 point groups allows spontaneous polarization and magnetization. At the same time, in perovskite transition metal oxides, ferroelectricity favors empty *d* orbitals while the ferromagnetism desires partially-occupied *d* orbitals, making these two ordered states mutually exclusive within one material. Therefore, despite decades of efforts in single-phase multiferroic materials, the magnetoelectric performance such as controlled switching of polarization (magnetization) by magnetic (electric) field remains unsatisfactory. Multiferroic heterostructures [17], however, relief these restrictions and provide an alternative route to realizing strong magnetoelectric effect.

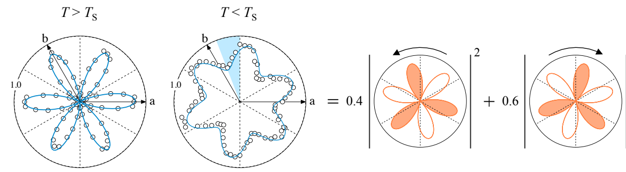

FIG. 2: RA-SHG patterns above and below ferro-rotational order onset (T_s) in $RbFe(MoO_4)_2$ showing the appearance of two types of domains with clockwise and counterclockwise rotations.

To build multiferroic heterostructures, 2D magnets and 2D ferroelectrics are required. 2D magnets can be selected out of the chromium trihalides pool while 2D ferroelectric order is predicted to emerge in 2D layered monochalcogenides GX (G = Ga, Ge; X = S, Se, Te). For example, recent research has demonstrated giant Rashba effect and ferroelectric polarization in GeTe thin films [18]. I plan to fabricate GX/CrI_3 heterostructures and explore potential interfacial multiferroic ordering in these 2D artificial structures. Probing domain structures is the crucial part for identifying multiferroic order and realizing magnetoelectric coupling applications [19]. SHG microscopy is a laboratory-accessible technique that can couple to vector or tensor order parameters. It has been employed to map the ferro-toroidal domain structures in which spatial inversion and TRS are simultaneously broken [20]. Recently, we have enhanced the sensitivity of rotational anisotropic (RA)-SHG [21] and used it to demonstrate the ferro-rotational order across an inversion-symmetry-preserved phase transition in $RbFe(MoO_4)_2$. Two types of ferro-rotational domains (Fig. 2) are resolved through the high-rank multipole coupling to the ferro-rotational order parameter. Based on RA-SHG, I plan to study the magnetoelectric coupling at the GX/CrI_3 interface. I will conduct spatial-resolved RA-SHG measurement and wide field SHG imaging to probe the domain structures across the Curie temperature of CrI_3. I will apply electric field to tune the ferroelectric domain patterns and measure potential response in CrI_3 magnetic domains. If multiferroic domains are demonstrated, synchrotron-based x-ray photoemission microscopy (XPEEM) with nanometer resolution will also be employed to detect the 1D domain walls.

3. Reveal electronic and magnetic order in 1T phase VSe_2 on vdW substrates

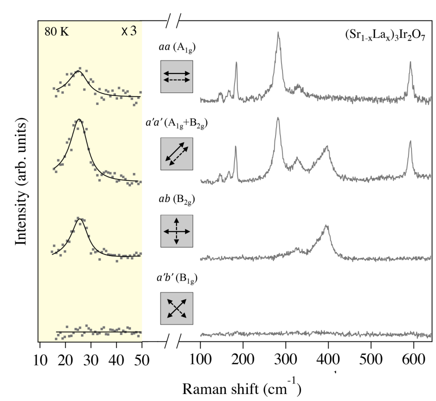

FIG. 3: Symmetry of the charge order (highlighted by yellow shade) and phonon modes of La-doped $Sr_3Ir_2O_7$ resolved by polarized Raman spectroscopy selection rules.

How the CDW states evolve when reducing the thickness of several TMDCs such as 2H-$NbSe_2$ and what role the adjacent substrates play on CDW ordering remain outstanding questions. On the one hand, the reduced dimensionality strengthens Fermi surface nesting and electron-phonon coupling, and is therefore expected to enhance CDW. On the other hand, the stronger fluctuations at lower dimension hinder the formation of long-range orders. Up to now, a consistent picture remains missing [4, 22]. Very recently, a series of works report enhanced CDW in MBE-grown monolayer 1T VSe_2 on various vdW substrates including MoS_2, highly oriented pyrolytic graphite (HOPG) and bilayer graphene (BLG) on SiC. Particularly, in VSe_2 grown on BLG/SiC, APRES measurements also reveal Fermi arc features above CDW temperature [23], while in VSe_2 grown on MoS_2 and HOPG, strong ferromagnetism is observed with an anomaly of magnetization at CDW temperature, which implies coupling between magnetism and CDW [24]. However, the magnetic order is absent in VSe_2 grown on BLG/SiC and the underlying reason remains elusive. Therefore, 1T VSe_2 opens up new opportunities of studying interplay between lattice, charge and spin in the 2D limit as well as the impact from the substrates.

In my Ph.D. research, I used to study the CDW of 2H-$NbSe_2$ using APRES [25]. In our recent research, using rotational-anisotropic (RA) polarized Raman spectroscopy, we carried out symmetry-resolved, temperature- and doping-dependent measurements in a spin-orbit coupled metallic $(Sr_{1-x}La_x)_3Ir_2O_7$ [26]. We distinguished the symmetry of the charge order from the underlying lattice distortion (Fig. 3) and found its disorder-interrupted behavior. Based on these experiences, I propose to study the emergent charge and magnetic orders in MBE-grown 1T VSe_2 on various substrates, and explore explicitly the role of the substrates in forming long-range orders.

Polarized optical spectroscopy technique can access distinct order parameters by selectively tuning the excitation energy and polarization. In particular, RA-SHG is proved to be a powerful technique for resolving structural, electronic and magnetic order parameters with concurrent onset temperature [27]. I will carry out careful temperature dependent RA-SHG measurements across the CDW onset temperature to track its full symmetry evolution. To study the MBE-grown thin films that are typically highly sensitive to the ambient exposure, I plan to make the RA-SHG setup compatible to an UHV chamber that is equipped with low-energy electron diffraction (LEED) [28]. The VSe_2 thin film with capping layers will be mounted in the UHV chamber, and prior to RA-SHG measurement, the capping layers will be removed by thermal annealing under LEED monitoring.

III. Collaboration

Like my previous work, my research group will continue working in close collaboration with synchrotron facilities and materials synthesis groups. I have past and current collaborations with the following synchrotron facilities and MBE growers:

- Dr. Jerzey Sadowski of Brookhaven National Laboratory and Center for Functional Nanomaterials: Electron Spectro-Microscopy beamline in NSLS-II.
- Prof. Hong Ding of Institute of Physics, Chinese Academy of Sciences: Dreamline ARPES in Shanghai Synchrotron Radiation Facility.
- Dr. Alexey Barinov of Elettra Sincrotrone Trieste: sub-micron-probe ARPES in Spectromicroscopy beamline.
- Prof. Huili Grace Xing of Materials Science and Engineering, Cornell University.

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