Atomic structure of nanosystems from first-principles simulations and microscopy experiments

Physics Boat 2024

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Helsinki, Finland – Stockholm, Sweden

Organizers

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CECAM (Centre Européen de Calcul Atomique et Moléculaire)

Programme

	Tuesday		Wednesday		Thursday
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11:40	**Liljeroth**	14:20	**Lazzeri**	9:00	**Zhou**
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		15:20	Nam	10:00	Wu
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		16:00	Jestilä		
	chair: Schuler			10:40	*Coffee*
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12:20 – 13:00 **Han**
Unraveling Strain and Deformation in Two-Dimensional Materials via Multi-dimensional Electron Microscopy

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Visualizing complex electronic states in van der Waals materials

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Conventional materials hosting exotic quantum phases typically have complex atomic structures, inhomogeneities from defects, impurities, and dopants making it difficult to rationally engineer their electronic properties. This can be overcome using van der Waals (vdW) materials and their heterostructures that allow an almost arbitrary selection of the heterostructure building blocks. In a vdW heterostructure, proximity effects cause properties to "leak" between the adjacent layers and allow creating exotic quantum mechanical phases that arise from the interactions between the layers. These key features have recently made it possible to realize exotic quantum phases by design and engineer responses that do not readily occur in natural materials.I will highlight these concepts through our recent results on monolayer multiferroic materials and vdW heterostructures realizing artificial heavy fermion states [1–4]. In general, these examples highlight the versatility of vdW heterostructures in realizing quantum states that are difficult to find and control in naturally occurring materials.

[1] M. Amini, A.O. Fumega, H. González-Herrero, V. Vaňo, S. Kezilebieke, J.L. Lado, P. Liljeroth, *Adv. Mater.* **36**, 2311342 (2024).
[2] S.C. Ganguli, M. Aapro, S. Kezilebieke, M. Amini, J.L. Lado, P. Liljeroth, *Nano Lett.* **23**, 3412 (2023).
[3] V. Vaňo, M. Amini, S. C. Ganguli, G. Chen, J.L. Lado, S. Kezilebieke, P. Liljeroth, *Nature* **599**, 582 (2021).
[4] X. Huang, J. Sainio, J.L. Lado, P. Liljeroth, S.C. Ganguli, *arXiv* 2401.08296 (2024).

Unraveling Strain and Deformation in Two-Dimensional Materials via Multi-dimensional Electron Microscopy

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Two-dimensional (2D) materials and their heterostructures have emerged as key components for innovative applications and exhibit unique properties distinct from bulk materials. Understanding the behavior of strain and deformation in 2D materials is crucial for their potential device applications and offers valuable insights into precisely engineering nano-scale strain in these layered materials. Utilizing nanobeam four-dimensional scanning transmission electron microscopy (4D-STEM), here, we introduce novel approaches to investigate both in-plane and out-of-plane strain and deformation in 2D materials. Our findings reveal a new mechanism of strain relaxation in 2D materials through the formation of out-of-plane ripples. Additionally, we uncover how 2D materials employ long-range lattice rotation and confined nanoscale uniaxial strain to compensate for lattice mismatch, and we elucidate different stacking orders in van der Waals heterostructures mediated by interlayer strain effects.

[1] C. Shi, *Nature Communications* **14**, 7168 (2023).
[2] Y. Han, *Nature Materials* **17**, 129-133 (2018).
[3] Y. Han, *Nano Letters* **18**, 3746-3751 (2018).
[4] S. Xie, *Science* **359**, 1131-1136 (2018).

2D materials as host for single-atom impurities, metal nanostructures and van der Waals materials

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[1]University of Vienna

Graphene—the one-atom-thick sheet of carbon—is the most famous of 2D materials due to its unique electronic properties and mechanical strength. However, its chemical inertness makes graphene also an excellent nearly electron-transparent support for other materials and nanostructures. In this presentation, I will give an overview of our recent work enabled by a unique interconnected vacuum system [1] containing an aberration-corrected scanning transmission electron microscope Nion UltraSTEM 100 with a unique objective area that allows sample cleaning via laser, in situ chemical experiments, and direct vacuum transfer to an atomic force microscope, to-and-from an argon glove box, target chamber with a plasma ion source and evaporators, and long term vacuum sample storage.In brief, I will demonstrate that defect-engineering of graphene [2] (and hBN) enables its substitutional heteroatom doping [3] and growth of nanoclusters, as well as the direct correlation of its atomic structure and mechanical properties. I will also show that the chemical environment inside a microscope plays an important role in observed structural changes [4]. I will further show that graphene can be used as a support for the growth metal islands [5,6]. Finally, I will provide examples of otherwise unstable structures being stabilized in the van der Waals gap between two graphene sheets, including small 2D noble gas clusters [7].

[1] Mangler et al., *Microsc. Microanal.* **28S1**, 2940 (2022).
[2] Trentino et al., *Nano Lett.* **21**, 5179 (2021).
[3] Trentino et al., *2D Mater.* **9**, 025011 (2022).
[4] Leuthner et al., *2D Mater.* **8**, 035023 (2021).
[5] Zagler et al., *2D Mater.* **7**, 045017 (2020).
[6] Zagler et al., *2D Mater.* **10**, 045025 (2023).
[7] Längle et al., *Nat. Mater.* 10.1038/s41563-023-01780-1 (2024).

Confining correlated states in single-layer MoS_2

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Electrons are prone to strong correlations when confined into one-dimensional (1D) or 0D cavities. Many exotic ground states can emerge, depending on the type of interactions. Examples are Peierls transitions, Tomonaga-Luttinger liquids, Jahn-Teller distortions, or Anderson impurities.An ideal experimental testbed for the observation of correlated electronic behaviour is found in 0D vacancies and 1D mirror twin boundaries (MTBs) of the two-dimensional material MoS_2. Both types of defects function as structurally perfect cavities, are only weakly coupled to the environment and accessible to spatially resolved spectroscopic investigations using scanning tunnelling microscopy.In my talk I will show that the confined quasiparticles within vacancies undergo a Jahn-Teller transition when charged by a single electron [1]. In addition, I will describe the correlated properties of confined states within 1D MTBs, in which we observed a Kondo resonance when the highest occupied state is filled by a single electron [2]. The unique construction of our Kondo system enables us to test the predictive power of the Anderson impurity model, which is the basis of our microscopic understanding of Kondo physics.

[1] Jansen et al., *submitted* arXiv:2401.09931v1 (2024).
[2] van Efferen et al., *Nat. Phys.* **20**, 82-87 (2024).

Direct Quantifying Charge Transfer by 4D-STEM: A Study on Perfect and Defective Hexagonal Boron Nitride

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The charge density distribution, which fully defines the ground-state properties of a material system, can be accurately measured in single crystals using X-ray diffraction. However, there is still a lack of experimental techniques capable of measuring charge density redistribution in defective or heterogeneous crystals at the relevant atomic scale with the required precision. While this information can be effectively evaluated by modern numerical methods such as DFT, these theoretical predictions still require experimental validations. In recent years, four-dimensional scanning transmission electron microscopy (4D-STEM) has emerged as an attractive approach to achieve this goal. In principle, the technique can simultaneously provide precise structural determinations and capture details of local electric fields and charge densities. However, accurate extraction of quantitative data at the atomic scale is challenging, mainly due to probe propagation and size-related effects, which may even lead to misinterpretations of qualitative effects. Here we discuss the ultimate capabilities of 4D-STEM through a comprehensive study of pristine and defective h-BN flakes. Through a combination of experiments and first-principle simulations, we demonstrate that while precise charge quantification at individual atomic sites is hindered by probe effects, 4D-STEM can directly measure charge transfer phenomena with sensitivity down to a few tenths of an electron and a spatial resolution on the order of a few angstroms. In the last section, we will show examples of 4D-STEM in oxide films, whose thicknesses prevent any direct comparison with DFT volumetric data, but where oxygen vacancies [2] or interface reconstruction [3] can still be retrieved.

[1] L. Susana, A. Gloter, M. Tencé, A. Zobelli, *ACS Nano* **18** , 7424 (2024).
[2] Aravind Raji et al.„ *Small* **19**, 230487 (2023).
[3] Jia et al., , *Advanced Materials Interfaces* **10**, 2202165 (2023).

Swift Chemical Etching of 2D Materials under Electron Beam in Transmission Electron Microscope

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The interaction of energetic electrons with the specimen during imaging in a transmission electron microscope (TEM) can give rise to the formation of defects or even complete destruction of the sample. This is particularly relevant to atomically thin two-dimensional (2D) materials. Depending on electron energy and material type, different mechanisms such as knock-on (ballistic) damage, inelastic interactions including ionization and excitations, as well as beam-mediated chemical etching can govern defect production. Using first-principles calculations combined with the McKinley-Feshbach formalism, we investigate damage creation in two representative 2D materials, MoS2 and hexagonal boron nitride (hBN) with adsorbed single adatoms (H, C, N, O, etc.), which can originate from molecules always present in the TEM column. We assess the ballistic displacement threshold energies T for the host atoms in 2D materials when adatoms are present and demonstrate that T can be reduced, as chemical bonds are locally weakened due to the formation of new bonds with the adatom. We further calculate the partial and total cross sections for atom displacement from MoS2 and hBN, compare our results to the available experimental data, and conclude that adatoms should play a role in damage creation in MoS2 and hBN sheets at electron energies below the knock-on threshold of the pristine system, thus mediating the formation of electron beam-induced damage. As chemical interactions of the host material with adatoms are involved, and because defects form under the beam on a sub-picosecond time scale, we call this channel for defect production swift chemical etching.

Identifying and Probing Atomic Defects in 2D Semiconductors by Scanning Probe Microscopy

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Two-dimensional (2D) semiconductors provide an exciting platform to engineer atomic quantum systems in a robust, yet tunable solid-state system. In this talk, I will present our efforts to un-ravel the interesting physics behind single vacancies and dopant atoms in transition metal dichal-cogenide (TMD) mono- and multilayers by means of high-resolution scanning probe microscopy [1-6]. I will highlight how to generate atomic defects by different means, and how to identify them based on their characteristic scanning tunneling spectroscopy (STS) fingerprint and density functional theory modelling. Our recent studies on transition metal doped TMDs such as (n-type) Re-doped MoS_2 and (p-type) V-doped WSe_2 reveals the significance of the charge state in the spectroscopic signa-ture of these defects. By substrate chemical gating, we can stabilize three charge states of Re_{Mo}, where two of the charge states exhibit symmetry broken electronic orbitals and a distorted atomic configuration that we assign to a pseudo Jahn-Teller effect [7]. Negatively charged V dopants and dopant pairs in WSe_2 exhibit a series of occupied p-type defect states above the va-lence band edge, accompanied by an intriguing electronic fine-structure that we attribute to many-body electron interactions [8].Lastly, I will provide an outlook on our ongoing developments of ultrafast lightwave-driven scanning tunneling microscopy using single-cycle THz pulses to measure the sub-picosecond time dynamics at atomic spatial resolution [9].

[1] B. Schuler et al., *Phys. Rev. Lett.* **123**, 076801 (2019).
[2] B. Schuler et al., *ACS Nano* **12**, 10520 (2019).
[3] S. Barja et al., *Nat. Commun.* **10**, 3382 (2019).
[4] B. Schuler et al., *Sci. Adv.* **6**, eabb5988 (2020).
[5] K. Cochrane et al., *Nat. Commun.* **12**, 7287 (2021).
[6] E. Mitterreiter et al., *Nat. Commun.* **12**, 3822 (2021).
[7] F. Xiang*, L. Huberich* et al., *Nat. Commun.* , (2024).
[8] S. Stolz et al., *ACS Nano* **17**, 23422 (2024).
[9] J. Allerbeck et al., *ACS Photonics* **10**, 3888 (2023).

Imaging Dynamic Motion of Atomic Species at Solid Liquid Interfaces

S. J. Haigh[1] N. Clark[1] S. Sullivan-Allsop[1] M. Lindley[1] R. Zhang[1] Y. Zou[1] R. Gorbachev[1]

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Atomic structure of surfaces and interfaces is key to the performance of 2D materials and their heterostructures including for exploring new optoelectronic phenomena and quantum behavior. The mobility of atomic species on 2D materials determines their functionality for applications such as electrodes, membranes and catalysts. We report the use of scanning transmission electron microscopy (STEM) techniques for analysing the local atomic structure of 2D materials. We have investigated transition metal dichalcogenide (TMD) heterostructures when combined at small twist angle, to reveal unusual lattice reconstruction and strong piezoelectric textures [1], which can be engineered by the application of applied field in the electron microscope [2]. Complementing imaging with scanning local diffraction analysis (4D STEM) and elemental mapping by energy dispersive x-ray spectroscopy (EDS) allows further investigation of larger scale atomic structure variations in 2D materials, including local variability in intercalated TMD structures and how this evolves during deintercalation as a function of time and annealing temperature [3]. Additionally, I will discuss the use of 2D heterostructure liquid cells [4] for uncovering the dynamics of atomic species on the surfaces of 2D materials [5] where advanced image processing is being applied to allow quantitative understanding of atomic behaviour with statistically significant data sets of >100000 individual STEM measurements.

[1] A. Weston et al, *Nature Nanotechnology* **15**, 592 (2020).
[2] A. Weston et al, *Nature Nanotechnology* **17**, 390 (2022).
[3] S. Shao et al, *Advanced Functional Materials* **33**, 2214390 (2023).
[4] D. Kelly et al, *Advanced Materials* **33**, 2100668 (2021).
[5] N. Clark et al, *Nature* **609**, 942 (2022).

Wednesday 29.05.2024

13:50 – 14:20 *Coffee*

chair: Susi

14:20 – 15:00 **Lazzeri**
Ab initio vibrational properties of defected and disordered systems

15:00 – 15:20 Silveira
Strain-induced topological edge states in SnTe: STM/STS signatures and a theoretical model

15:20 – 15:40 Nam
Exploring in-plane interactions beside an adsorbed molecule with lateral force microscopy

15:40 – 16:00 Ghorbani-Asl

16:00 – 16:20 Jestilä
Advances in machine learning for SPM analysis and structure search

16:20 – 17:40 Coffee at posters

chair: Seitsonen

17:40 – 18:20 **Besley**
Understanding the dynamics of chemical bond dissociation under the electron beam: computational perspective

18:20 – 18:40 Susi
Near-Ideal Direct-Electron Focused-Probe 4D-STEM Data for Open-Source Phase Reconstructions

18:40 – 19:00 Kieczka
Understanding the electronic properties and mechanisms of formation of 1D defects observed in 2D MoS_2

19:00 – 19:20 Groll
Investigations of the atomic electric field and charge density distribution in 2D WSe2 by high resolution STEM Differential Phase Contrast imaging and DFT

19:30 – 21:00 *Dinner*

Ab initio vibrational properties of defected and disordered systems

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The recent advances in scanning tunneling electron microscopy (STEM) instrumentation, bringing the energy resolution of electron energy loss spectroscopy down to the sub-10 meV regime while maintaining atomic resolution, has opened a new field of research focused on the local investigation of atomic vibrations in systems, ranging from interfaces [1] to point [2] or extended defects [3]. Given the intrinsically long-range nature of vibrational modes, the proper modelisation of these newly available experimental results involves structures with a very large number of atoms, making the direct use of the available first-principles approaches rather impractical. Indeed, ab-initio description of phonon scattering from defects, even of the most elementary kind (point defects such as vacancies or substitutional defects) is sporadic, if not entirely lacking. This situation can be overcome starting from the observation that the change of the interatomic force constants (IFCs) induced by a structural or chemical defect is, in most of the cases, very well localised. This idea is at the core of the approach that we implemented in [2]: first, the IFCs of a relatively small system (hundreds of atoms) are calculated fully ab-initio (density functional theory); then, these IFCs are assembled with those of the "undefected" crystal to build the dynamical matrix of a more realistic system (several thousands of atoms). This strategy preserves the accuracy of ab initio techniques providing a direct access to the delocalised nature of the vibrational modes. In [2], this approach allowed us to determine the quasi-localised nature of the vibrations of a Si substitutional defect in graphene and explain STEM observations.The same approach can be used to study even more complex systems, such as the interface between an hexagonal SiC substrate and a few-layer-thick epitaxially-grown graphene (a system considered nowadays of technological interest [4]). In particular, I will present a detailed study of the vibrations occurring in the first graphitic layer (buffer layer) which is directly interacting with the silicon-terminated surface of the substrate, showing that, with about a quarter of carbon atoms covalently bound to the substrate, the buffer layer can be considered as a prototypical model for local chemical and structural disorder in graphene. Calculations will be used to interprete very recent atomic-resolution EELS obtained at the SuperSTEM Daresbury (group of Q.Ramasse). The evocation of disorder will then be an opportunity to discuss the results we have recently obtained on acoustic phonon branches of ice VII [5]. This high-pressure phase of ice indeed displays a

complete proton disorder while retaining a quasi-bcc oxygen sublattice. Due to its specific atomic structure, ice VII provides a very pedagogical example where the X-ray (or, equivalently, the energy loss) scattering cross-section naturally unfolds the phonon dispersion of this disordered system.

[1] R. Qi et al., *Nature* **599**, 599 (2021).
[2] F. S. Hage et al., *Science* **367**, 1124 (2020).
[3] X. Yan et al., *Nature* **589**, 65 (2021).
[4] J. Zhao et al., *Nature* **625**, 60 (2024).
[5] G. Radtke et al., *Phys. Rev. Lett.* **132**, 056102 (2024).

Strain-induced topological edge states in SnTe: STM/STS signatures and a theoretical model

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2D topological crystalline insulators (2D-TCI) represent an exotic quantum state of matter characterized by metallic edges states (MES) residing within a bulk band gap [1]. Unlike 2D topological insulators where the MES are protected by time-reversal symmetry, the edge states of a 2D-TCI are protected by crystal symmetries and are characterized by the Chern mirror topological invariant. The 3D SnTe is already a known 3D-TCI [1], hosting topological protected surface states instead of edge states, but it behaves as a trivial insulator when reduced to the few layers limit (less than 10 layers) [2]. In this work we show through DFT calculations that slowly compressing the few layers of SnTe leads to a gap-closing transition, and SnTe already starts behaving as a 2D-TCI on moderate compression of 2-3%, where a clear band inversion is observed. The intrinsic ferroelectric properties of the SnTe are also investigated within this regime, where the possibility of topological and ferroelectric phases coexisting is considered. We show that such compression can be achieved when bilayers of SnTe are grown on a NbSe2 substrate due to the incommensurability between their square and hexagonal cells. The topologically protected MES are clearly observed in STS scans taken over the step edges of a bilayer to monolayers SnTe, where very clear and symmetric islands are obtained. This work opens the possibility for the engineering of such topological states by controlling the number of layers of SnTe, and by using different kinds of substrate, where its lattice parameter can then be tuned.

[1] Hsieh, T., Lin, H., Liu, J. et al., *Nat Commun* **3**, 982 (2012).
[2] Araújo, A.L., Ferreira, G.J. & Schmidt, T.M, *Sci Rep* **8**, 9452 (2018).

Exploring in-plane interactions beside an adsorbed molecule with lateral force microscopy

S. Nam[1] E. Riegel[1] L. Hörmann[2] O. T. Hoffmann[2] O. Gretz[1] A. J. Weymouth[1] F. J. Giessibl[1]

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Hydrogen, the smallest and most abundant element in nature, plays a vital role in many molecular interactions. Their positions can determine the interactions with neighboring molecules in the form of hydrogen bonds. While atomic force microscopy can image the internal structure of flat-lying molecules, H-atoms are difficult to directly image due to their size. We directly image these H-atoms using lateral force microscopy (LFM). Furthermore, we determine a metric of when the assumption of purely radial atomic interactions breaks down and an additional angular component is required to account for the additional electrostatic interaction from the metal tip apex. The application of LFM to the sides of molecules demonstrates how in-plane molecular interactions can be directly investigated.

[1] Shinjae Nam, Elisabeth Riegel, Lukas Hörmann, Oliver T. Hofmann, Oliver Gretz, Alfred J. Weymouth, and Franz J. Giessibl , *PNAS* **121(2)**, e2311059120 (2024).

Advances in machine learning for SPM analysis and structure search

J. S. Jestilä[1] N. Oinonen[1] N. Wu[1] L. Kurki[1] F. Priante[1] S. Cai[1] P. Liljeroth[1] A. S. Foster[1,2]

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Recent years have displayed an exponential growth in the development of machine learning tools in image and data analysis, automation and optimization of experiments, as well as computational modeling. In our group, we are actively researching new methods and combinations thereof relating to each of the aforementioned categories.We have recently demonstrated the potential of neural network-based geometry prediction tools on AFM and STM images.[1][2] Also, we have shown how suitable training data can be generated with the probe particle model [3] on plausible structures obtained using machine learning interatomic potentials.Furthermore, we are taking advantage of the rapid energy evaluations provided by these potentials in exploring accelerated structure search methods, such as Bayesian optimization and minima hopping.[4] While selective chemical reactions induced by the SPM tip has been achieved in the past, there are currently no reports on their automation, much due to the highly complex parameter space. We are employing reinforcement learning to acquire the molecule manipulation parameters to selectively break C-Br bonds, providing the first example of its kind.

[1] Fabio Priante, Niko Oinonen, Ye Tian, Dong Guan, Chen Xu, Shuning Cai, Peter Liljeroth, Ying Jiang, and Adam S. Foster, *ACS Nano* **18, 7**, 5546–5555 (2024).
[2] Lauri Kurki, Niko Oinonen and Adam S. Foster, *ACS Nano* accepted (2024).
[3] Ondrej Krejčí, Prokop Hapala, Martin Ondráček, and Pavel Jelínek, *Phys. Rev. B* **95**, 045407 (2017).
[4] Joakim S. Jestilä, Nian Wu, Fabio Priante, and Adam S. Foster, *J. Chem. Theory Comput.* **20, 5**, 2297–2312 (2024).

Understanding the dynamics of chemical bond dissociation under the electron beam: computational perspective

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Chemical bond dissociation is a central concept in Chemistry. Transmission electron microscopy (TEM) has emerged as a tool for triggering bond dissociation in single molecules and materials by harnessing the kinetic energy of fast electrons of the electron beam. The use of the electron beam as a stimulus of chemical reactions and as a sub-angstrom resolution imaging probe allows investigations of the molecular dynamics and reactivity in real time and at the atomic scale. The dynamics of chemical bond dissociation can be also probed indirectly by vibrational electron energy loss spectroscopy in situ during scanning TEM experiments. In this talk, we will explain how the electron beam can trigger homolytic dissociation of the H–F or H–O bonds inside fullerene cage, leading to entrapment of F and O atoms, and discuss knock-on mechanisms of bond dissociation and atom permeation through C60. [1] A separate example of knock-on damage will be introduced in the context of understanding the electron stability of two-dimensional conjugated metal organic frameworks (thin films) which exhibit complex damage mechanisms with non-trivial fragmentation pathways. [2]

[1] J. Biskupek et al., *ACS Nano* **14**, 11178 (2020).
[2] Mücke, D. et al., *Nano Letters* **24**, 3014 (2024).

Near-Ideal Direct-Electron Focused-Probe 4D-STEM Data for Open-Source Phase Reconstructions

T. Susi[1] N. Dellby[2] R. Hayner[2] C. Hofer[3] J. Kotakoski[1] T. C. Lovejoy[2] C. Mangler[1] A. Mittelberger[2] T. J. Pennycook[3] B. Plotkin-Swing[2]

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The availability of direct-electron cameras with high dynamic ranges and very fast detection speeds is revolutionizing the ability of scanning transmission electron microscopy (STEM) to make use of every electron for virtual imaging and advanced computational phase reconstructions. State of the art detectors can now acquire four-dimensional (4D) data at STEM pixel dwell times of over 100,000 diffraction patterns per second while counting each electron. At the same time, the proliferation of open software packages to make use of this data has made such analyses widely accessible, and due to a convergence to the Python programming language, easy to compare in terms of computational efficiency and reconstruction quality.The first commercially available Dectris ARINA detector [1] has been installed in the Nion UltraSTEM100 instrument in Vienna, where an ultra-stable sample stage and flexible electron optics are ideally suited to 4D-STEM. For our initial comparisons, we use an atomically focused probe (34 mrad convergence semi-angle) and choose a camera length optimized for maximum signal in the bright-field and the first-order Bragg disks. In this contribution, we present some of the first data acquired on this new detector, namely convergent-beam electron diffraction maps of pristine monolayer graphene, which is a near-ideal dose-robust uniform atomic phase object. The ability to reliably count electrons at such speeds (the detective quantum efficiency is 0.85 at 60 keV [1]) also enables the variation in beam current to be easily measured and, if desired, corrected for, which we find has an appreciable impact on the bright-field signal and reconstructions that make use of it (most notably parallax imaging [2]).A pixel exposure time of 100 μs provided a high signal for phase reconstructions without needing to resort to multi-frame averaging. The ARINA is able to bin the native 192×192 detector array in hardware for faster acquisition, and we find that further software binning up to four times does not harm reconstructions, whereas a dense real-space sampling below 0.08 Å per pixel (512×512 px scan over the 2×2 nm^2 field of view) was noticeably helpful. The graphic shows the concurrently acquired high-angle annular dark-field (HAADF, 80–300 mrad) and virtual ADF images (∼40–80 mrad), as well as a range of open-source phase reconstructions from the binned 4D dataset:

single-sideband (SSB) and Wigner distribution deconvolution (WDD) [3], as well as iterative differential phase contrast (DPC), parallax-corrected bright-field imaging, and batched iterative gradient descent single-slice ptychography [2]. Apart from modest scan distortions, visual inspection of the phase images reveals deviations from the expected uniform atom contrast, and notable differences in phase magnitudes. Computational times also vary greatly depending on the algorithm and the binning.The quality of the phase images is assessed by evaluating the variation of atomic phase shifts using a robust parameter-based quantification method [4] and compared to data simulated with the *ab*TEM code [5] and reconstructed with the same algorithms. These quantitative comparisons will be presented at the meeting, where the data and code will also be provided. Further results on defocused-probe datasets and the prospects for live reconstructions will be discussed.

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Understanding the electronic properties and mechanisms of formation of 1D defects observed in 2D MoS_2

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Defects in 2D semiconductors play an important role in their electronic properties [1]. In 2D materials, defects are often present at high concentrations of 10^{13} cm^{-2} and therefore are an important area of research for understanding the properties of 2D materials. An effective way to observe defects in 2D TMDs such as MoS_2, is by using a 4 dimensional scanning transmission electron microscope (4D STEM), which allows access to atomic resolution. In this work, we combine ptychography-reconstructed 4D-STEM [2,3] datasets, of defects in 2D MoS_2, and use density functional theory (DFT) to understand the origin and dynamics of these defects. The datasets show that point defects aggregate into 1D defect lines. We employ density functional theory (DFT) with a non-local PBE0-TC-LRC functional in CP2K to calculate the electronic properties of 1D defects, including sulphur vacancy lines, kinks, and rhenium (which substitutes molybdenum) lines. We find that vacancy aggregation results in areas of increased electron density localized at the line defect sites, and observe an increase in the number of defect states present when the 'kink' limit is reached. The rhenium dopant lines have potential for high spin states (quartet) which could induce ferromagnetism in the material. We observe a relatively small energy gain from the clustering of sulphur vacancies into lines (of around 0.1 eV). Using nudged elastic band (NEB) calculations with the PBE functional, we calculate the most likely pathways for vacancy diffusion including effects of different charge states on the dynamics of the vacancies. We find that charged di-vacancies have a very low barrier for diffusion which can allow for rapid diffusion as observed with 4D STEM. This work gives insights into the dynamics of defects in 2D MoS_2 and their potential for use in doping.

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Investigations of the atomic electric field and charge density distribution in 2D WSe2 by high resolution STEM Differential Phase Contrast imaging and DFT

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2D materials are currently subject of intensive research in various fields due to their interesting optoelectronic properties, which are strongly influenced by the internal electric field and the charge density distribution. Due to the inherently low dimensionality of 2D materials, defects such as vacancies or impurities can significantly change the field distribution and thus the optoelectronic properties. This makes a precise fabrication of defects in 2D materials particularly interesting for tailored optoelectronic applications. Due to their tunable band gap in the visible range, transition metal dichalcogenides (TMD) are, for example, of great interest for single photon emission induced by defects in the material [1,2]. TMDs consist of molecular layers with the stochiometric form MX2 (M: transition metal, X: chalcogenide) which are bound to each other only by weak van-der-Waals interaction. Spectroscopic methods provide a detailed insight into the electronic properties of these materials. However, they are limited by their spatial resolution, which makes it difficult to investigate the influence of individual defects on the electric field distribution. Only few techniques allow for studying the internal electric field with such a high spatial resolution. Among these techniques is high-resolution differential phase contrast (DPC) imaging in the scanning transmission electron microscope. In DPC, electric fields can be measured with subatomic resolution by detecting the shift of the centre of mass (CoM) of the intensity distribution of the electron beam with a position sensitive detector. The shift of the CoM is caused by the interaction of the beam electrons with the electric potential in the material [3].We investigate the electric field and charge density distribution of mechanically exfoliated 2D WSe2 using DPC. The DPC measurements are performed in an aberration-corrected STEM using a low acceleration voltage of 80 kV and an eight-fold segmented bright-field detector. Images are compared with multislice image simulations performed for the present experimental conditions. The atomic electric field and charge density distributions in pristine mono- and multilayers of WSe2 are presented. Investigations of a vacancy-type defect at Se columns in the 2D material indicate a characteristic change in the electric field distribution, which is revealed by comparing the DPC images of pristine

and defective WSe2 samples. A relaxation of the neighboring W atomic columns towards the defect site is observed and confirmed by DFT simulations.

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Thursday 30.05.2024

chair: Friedrich

9:00 – 9:40 **Zhou**
Single-atom microscopy and spectroscopy on 2D materials

9:40 – 10:00 Lyu

10:00 – 10:20 Wu
Autonomous chemical reactions in scanning tunneling microscopy

10:20 – 10:40 Martsinovich
Structure-property relationship of oxygen-containing graphene: spectroscopic and theoretical characterisation

10:40 – 11:20 *Coffee*

chair: Ghorbani-Asl

11:20 – 12:00 **Lin**
Exploring the structure and dynamics of alkali metal and metal chlorides intercalated in bilayer graphene

12:00 – 12:20 Seitsonen
Reactions of carbon dioxide on an electro-chemical interface from computer simulations: Comparison with Au(111)

12:20 – 12:40 Friedrich
Structure, Electronic, and Magnetic Properties of Non-van der Waals Two-Dimensional Materials from Data-driven Design

12:40 – 13:00 *Closing*

13:00 – 14:00 *Lunch*

Single-atom microscopy and spectroscopy on 2D materials

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The possibility of performing real-space imaging and spectroscopy analysis at the atomic scale via low-voltage aberration-corrected scanning transmission electron microscopy (STEM) has provided exciting new opportunities for the study of two-dimensional materials, especially for defects and interfaces. Pushing the sensitivity of STEM spectroscopy techniques down to the single atom level is expected to open a new avenue for probing the local functionalities of materials, but remains challenging. In this presentation, I will discuss our recent results on pushing the sensitivity of single-atom spectroscopy techniques using dopants in monolayer graphene as a model system. With this relatively stable single-atom model system, we can explore the ultimate sensitivity of EELS at 60 kV where the dose level is no longer the limiting factor. We show that the sensitivity of single-atom vibrational spectroscopy analysis can be pushed to the chemical-bonding level and this technique could be applied to explore local vibrational signatures at defects and interfaces in 2D materials [1]. I should also discuss briefly our recent progress of atom-by-atom isotope mapping using vibrational spectroscopy technique. As for core-loss excitations, we show that electronic states contributed by specific unoccupied pz orbital around a four-fold coordinated Si point defect in graphene can be mapped out using atomic-resolution energy-loss near-edge fine structure (ELNES) spectroscopy [2]. In addition, local coordination measurement can be achieved with single-atom sensitivity via extended energy loss fine structure (EXELFS) analysis.

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Autonomous chemical reactions in scanning tunneling microscopy

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Several breakthrough studies have harnessed scanning probe microscopy (SPM) manipulations to control chemical reactions in on-surface molecular synthesis [1, 2, 3]. In general, for scanning tunnelling microscope (STM) manipulations, they are predominantly controlled via parameters of the tip position, pulse voltages and tunneling conductance. However, the selection of proper parameters requires extensive domain knowledge, which is time consuming and not necessarily transferable to new systems. Recent research has allowed the automation of a wide range of challenges in SPM, including image quality assessment, lateral and vertical manipulation [4, 5, 6]. However, the automation for breaking or forming covalent bonds, which is an indispensable step during chemical synthesis is, as yet, unexplored. To address this problem, we developed our deep reinforcement learning (DRL) approach to automate bromine removal from 5,15-bis(4-bromo-2,6-methyl-phenyl)porphyrin (Br2Me4DPP) through learning manipulation parameters in STM. Meanwhile, DFT calculations were implemented to explore the reaction mechanism in combination of STM results and DRL results.

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Structure-property relationship of oxygen-containing graphene: spectroscopic and theoretical characterisation

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Graphene is an outstanding material both thanks to its properties, such as excellent electrical conductivity and optical transparency, and because of its ability to give rise to a variety of new materials through structural modification, e.g. forming graphene oxide, reduced graphene oxide and graphene aerogels. These chemical modifications change the optoelectronic properties of graphene. Therefore, it is important to understand the relationship between the structures and electronic and optical properties of functionalised graphene-based materials. In this collaborative study, oxygen-containing graphene aerogels were produced by detonation of acetylene with oxygen and characterised using transmission electron microscopy, X-ray photoemission spectroscopy and UV-Vis absorption spectroscopy, and using first-principles theoretical modelling. The materials produced were found to contain up to 9% oxygen; the increase in the oxygen content was accompanied by morphological changes and broadening of the optical absorption spectra.Density-functional theory calculations were used to rationalise the structure-property relationship of oxygenated graphene and graphene aerogels, by modelling flat and curved graphene sheets containing epoxide and hydroxyl groups and substitutional oxygen at different concentrations (1-12% oxygen). Curvature was found to have little effect on the electronic properties of graphene: curved graphenes remained semimetallic, and their optical absorption spectra were similar to graphene. However, oxygenation had significant effects on the properties. Graphenes containing substitutional oxygen had new states at the Fermi level, while graphenes containing hydroxyl and epoxide functional groups showed band gap opening at oxygen content above 6%. Moreover, additional peaks appeared in the simulated optical absorption spectra of oxygen-containing graphenes. These results show that morphologically disordered graphene aerogels have electronic properties similar to graphene, while oxygenation significantly changes these materials' optical and electronic properties, leading to new applications in electronics and sensors.

Exploring the structure and dynamics of alkali metal and metal chlorides intercalated in bilayer graphene

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Exploring the structure and dynamics of alkali metal and metal chlorides intercalated in bilayer graphene has garnered considerable interest for its potential in tailoring the electronic, magnetic, and optical properties of graphene-based materials. Understanding the precise characterization of the intercalation process and resulting atomic arrangements is pivotal for comprehending fundamental interactions and their impact on material properties. In this investigation, scanning transmission electron microscopy (STEM) is employed to scrutinize the atomic structure of metal chlorides (AlCl3, CuCl2, MoCl5, FeCl3)[1,2] and alkali metals (K, Rb, Cs)[3] intercalated in bilayer graphene (BLG). High-resolution visualization and analysis of the atomic structure within the intercalated BLG samples are achieved through STEM imaging. Our findings unveil distinct patterns and arrangements of metal chloride and alkali metal atoms within the graphene lattice, exhibiting variations in interlayer spacing, local bonding configurations, and atomic ordering based on the specific metal chloride and alkali metal employed. Furthermore, we delve into the influence of intercalation on the electronic structure of bilayer graphene using spectroscopic techniques.

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Reactions of carbon dioxide on an electro-chemical interface from computer simulations: Comparison with Au(111)

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The chemical transformation of CO_2 into more valuable chemicals is a lucrative way to harness and store the energy from renewable sources for later use. The electro-chemical route, using molten carbonates as the electrolyte, has been explored as one efficient alternative to achieve this transformation. Recently the reduction of CO_2 into CO was investigated in eutectic molten carbonate Li_2CO_3-K_2CO_3-Na_2CO_3 on a working electrode of gold plate [1]. Subsequently the dynamics of the relevant molecular and atomic species in a prototype carbonate were studied using the atomistic molecular dynamics simulations based on the density functional theory to describe the interactions between the atoms [2]. Key results were the repeated association and dissociation reactions of CO_2 with a carbonate ion CO_3^{2-} into the pyrocarbonate species $C_2O_5^{2-}$, $CO_2 + CO_3^{2-} \leftrightarrow C_2O_5^{2-}$, and the solvation dynamics of the oxalate $C_2O_4^{2-}$, which was found to enhance the transformation CO_2 into CO in the experiments [1].Here we extend the previous simulations by including a model electrode, Au(111) surface, explicitly in the simulation. We estimate the reaction barriers both in the pure electrolyte and in the vicinity of the surface. Interestingly the CO_2 is bound to the substrate in the presense of the electrolyte at the elevated temperature used in the experiments, thus enabling the electronic activation and reactivity of the CO_2, whereas it is weakly bound at the clean substrate in the vacuum environment. We also explore the reactions involving the oxalate specie and the binding of the CO molecule onto the substrate. We compare the results to the ones obtained on the static Au(111) surface without the electrolyte, and present simulated scanning tunnelling microscope images of the adsorbed species.

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Structure, Electronic, and Magnetic Properties of Non-van der Waals Two-Dimensional Materials from Data-driven Design

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While two-dimensional (2D) materials are traditionally derived from bulk layered compounds bonded by weak van der Waals (vdW) forces, the recent surprising experimental realization of non-vdW 2D compounds obtained from non-layered crystals [1,2] foreshadows a new direction in 2D systems research. To elucidate their structure and properties, electron microscopy and first-principles calculations are indispensable tools. Contributing to the predictive design of these novel nanoscale compounds, here, we present several dozens of candidates derived from applying data-driven research methodologies in conjunction with autonomous first-principles calculations [3,4]. We find that the oxidation state of the surface cations of the 2D sheets as well as accounting for strong surface relaxations upon exfoliation are crucial factors determining their stabilization.The candidates exhibit a wide range of appealing electronic, optical and in particular magnetic properties owing to the (magnetic) cations at the surface of the sheets. Despite of several ferromagnetic candidates, even for the antiferromagnetic representatives, the surface spin polarizations are diverse ranging from moderate to large values modulated in addition by ferromagnetic and antiferromagnetic in-plane coupling [3]. These features can be accessed by experimental techniques such as (spin-polarized) scanning tunnelling microscopy (STM). At the same time, chemical tuning by surface passivation provides a valuable handle to further control the magnetic properties of these novel 2D compounds [5] thus rendering them an attractive platform for fundamental and applied nanoscience.

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Posters

Jafar Azizi
: Computational investigation of carbon based anode materials for Li- and post-Li ion batteries

Ethan Berger
: Raman spectra of 2D materials from mode projection and machine learning force field

Jana Dzibelova
: Atomic-resolution investigation of 2D hematene

Ahmad Echresh
: Single germanium nanowire-based near-infrared photodetectors

Somesh Chandra Ganguli
: Realization of heavy fermion phase diagram in van der Waals heterostructures

Sadegh Ghaderzadeh
: Revealing the Shape of Metal Nanoclusters on Defective Surfaces

Mahdi Ghorbani Asl
: Modulation of electronic properties in two-dimensional platinum chalcogenides

Alexandre Gloter
: Emergent electronic landscapes in a novel valence ordered thin-film nickelate prepared by topochemical reduction

Jie Huang
: Enhancing AFM Image Analysis Through Machine Learning with Style Translation and Data Augmentation

Patrick James
: Iron-based catalysts for oxygen reduction reaction in PEM fuel cell

Daniel Jansen
: Tip-induced creation and Jahn-Teller distortions of sulfur vacancies in single-layer MoS_2

Umair Javed
: Influence of low-pressure atmosphere on the pores formed in hexagonal boron nitride under electron irradiation

Lauri Kurki
: Automated Structure Discovery for Scanning Tunneling Microscopy

Touko Lehenkari
: From first principles to the macroscopic realm; metal (Ag, Au, Cu, Li) diffusion in vertical MoS2 memristors

Zhongpeng Lyu(lv)
: Structural characterization of MXene and its heterostructures with TEM, X-ray scattering, and simulation

Rabia Nawaz
: Effect of Strain on Electro-Optical Properties of 2D Materials

Prosun Santra
: Strain-modulated defect engineering of two-dimensional materials

Miguel C. Sequeira
: Exploring the radiation resistance of GaN by bridging theory and experiment

Computational investigation of carbon based anode materials for Li- and post-Li ion batteries

J. Azizi[1]

[1] Holger Euchner and Professor Axel Gross

While carbon derivatives are still the anodes of choice for Li- and post- Li ion batteries, the quest for improving their properties is ongoing. In particular, when considering soft and hard carbon materials the impact of heteroatoms on Alkali metal adsorption and storage is hardly investigated on the atomistic scale. To gain more insight into the underlying mechanisms, a density functional theory-based study of Li, Na, and K adsorption on pristine and defective graphite surfaces, considering different heteroatom impurities (such as N, S, Si, and O), has been performed. Our results show that on the surface of pure graphite, the adsorption of Li and K ions is energetically more favorable as com- pared to Na ions. However, in the presence of defects and impurities, Na adsorption also becomes feasible. In general, AM adsorption in the vicinity of defects and impurities is largely favored, putting constrain on the number of AM atoms that participate in charge/discharge processes.

Raman spectra of 2D materials from mode projection and machine learning force field

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Raman spectroscopy can yield rich information about the surface composition of 2D materials. Interpretation of experimental observations greatly benefits from simulated spectra, which are usually restricted to small systems due to the poor scaling of ab initio methods. We present here a new method (RGDOS) to efficiently obtain Raman spectra of large systems containing heterogeneous surfaces or defects. Raman tensors or polarizabilities of large supercells are built from projections of the vibrational modes onto those of the unit cell. It can be applied both in the harmonic approximation or using molecular dynamics trajectories and Raman spectra are then obtained by combining it with machine learning force fields. Two scientifically relevant systems are taken as examples for applications, namely the effect of point defects on the Raman spectra of MoS2 monolayers [1] and the study of heterogeneous surface of 2D titanium carbide MXenes [2].

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Atomic-resolution investigation of 2D hematene

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2D materials have attracted scientific research for decades, since they posses distinct physico-chemical properties compared to their 3D counterparts due to quantum confinement. These atomically thin structures such as graphene, hBN, etc. are typically based on so-called van der Waals systems. These 3D counterparts are defined by strong bonds oriented in-plane and solely weak bonding interaction between the layers. However, 2D materials can also be created from a parent material with strong bonding interactions in all three directions. For these, it is significantly more complicated to cleave them into individual layers. After cleavage into atomically thin layer, the non-van der Waals 2D materials could offer a playground to explore the changes in properties induced by dimensionality restriction. Recently, a new member of these non-van der Waals 2D materials has been introduced: hematene, the 2D form of α-Fe_2O_3 [1]. The dimensional confinement of hematene structure is expected to introduce intrinsic strain to the lattice. This distortion of interatomic positions affects electronic configuration and therefore the magnetic, electronic and optical behavior of the system [2]. Here, we employ transmission electron microscopy and selected area electron diffraction to investigate the atomic structure and distortions of the lattice in thin hematene sheets with the aim to quantify the intrinsic strain to facilitate the physical description of the material.

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Single germanium nanowire-based near-infrared photodetectors

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Germanium (Ge) is a good candidate for designing near-infrared photodetectors because of its bandgap (0.66 eV), which exhibits a large absorption coefficient at near-infrared wavelengths. Also, Ge has excellent compatibility with parallel processing common in silicon technology [1,2]. Photodetectors based on Ge material have been fabricated with different structures such as metal-semiconductor-metal (MSM) and p-n junctions. On the other hand, the observation of high responsivity in semiconductor nanowires with a high surface-to-volume ratio has attracted growing interest in using nanowires in photodetectors. So far, significant efforts have been made to fabricate single nanowire-based photodetectors with different materials such as Si, Ge, and GaN to achieve miniaturized devices with high responsivity and short response time [3-5]. Hence, Ge nanowires are excellent candidates to fabricate single nanowire-based near-infrared photodetectors. In this work, we report on the fabrication and characterization of an axial p-n junction along Ge nanowires. First, through a resist mask created by electron beam lithography (EBL), the p-type top Ge layer of germanium-on-insulator (GeOI) substrates was locally doped with phosphorus ions using ion beam implantation followed by rear-side flash lamp annealing. Then, single Ge nanowire-based photodetectors containing an axial p-n junction were fabricated using EBL and inductively coupled plasma reactive ion etching. The fabricated single Ge nanowire devices demonstrate the rectifying current-voltage characteristic of a p-n diode in dark conditions. Moreover, the photoresponse of the axial p-n junction-based photodetectors was investigated under light illumination with three different wavelengths: 637 nm, 785 nm, and 1550 nm. The experiments indicated that the fabricated photodetectors operate at zero bias and room temperature under ambient conditions. A high responsivity of 3.7×10^2 A/W was determined at zero bias under illumination of a 785 nm laser diode. The fabricated photodetectors exhibit a high-frequency response up to 1 MHz under pulsed excitation of the 1550 nm laser at zero bias, which makes them promising candidates for lightwave communication and optical switches [6].

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Realization of heavy fermion phase diagram in van der Waals heterostructures

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The heavy fermion (HF) compounds host a rich playground for correlated quantum states. In these compounds, the itinerant electrons in s, p or d shells interact with the lattice of localized magnetic moments in f shell via Kondo effect giving rise to Kondo lattice, resulting in a large effective mass as well as a gap in the conduction electron spectra, known as heavy fermion hybridization gap, which upon chemical doping can host unconventional superconductivity and quantum criticality. Recently, we have been able to demonstrate that heavy fermionic behavior can be created artificially using vdW epitaxy, using heterostructure of 2 different phases of the same material TaS_2. Stacking 1H-TaS_2 hosting 2-D conduction electrons, and 1T-TaS2 hosting localized magnetic moments gives rise to Kondo lattice and heavy-fermion hybridization gap [1]. In vdW heterostructure of similar material $NbSe_2$, we observe an absence of the Kondo peak. In addition, the chemical potential becomes site dependent, driving the 1T-$NbSe_2$/1H-$NbSe_2$ system into the doped Mott insulator regime with exotic charge order [2]. These observations establish artificial vdW heterostructures as a versatile platform to navigate the heavy fermion phase diagram.

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Revealing the Shape of Metal Nanoclusters on Defective Surfaces

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Metal nanoparticles play a central role in various research areas, particularly in catalysis as active sites for chemical reactions. The shapes and sizes of these nanoparticles, critical in defining their properties, can be significantly influenced by the local environment of their substrate surface and the thermodynamic conditions. In this study, we employed magnetron sputtering, a physical vapour deposition process used to produce high quality thin coatings at an industrial scale, to deposit metal atoms onto a graphitic surface, and changed environmental conditions (e.g, temperature) to stimulate the formed metal nanoparticles. Using a combination of multi-scale theoretical techniques (i.e., ab-initio/force-field molecular dynamics and density functional theory) and aberration-corrected high-resolution transmission electron microscopy imaging, we then explored the dynamics and shapes of the metal nanoparticles under various environmental conditions. Our investigations reveal that the interplay between the dynamics of metal nanoparticle and surface defects can lead to unexpected states and structural transformations of the nanoparticles.

Modulation of electronic properties in two-dimensional platinum chalcogenides

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Among layered materials, platinum chalcogenides have received great attention due to their peculiar physical properties. The strong layer-dependent electronic properties cause a band gap opening in monolayer $PtTe_2$, while the system otherwise is (semi)metallic.[1] Here we show that starting with $PtTe_2$ films, other compositions such as Pt_3Te_4 and Pt_2Te_2 can be obtained by a postgrowth desorption of tellurium or vapor-deposited Pt atoms.[2] The experiments combined with DFT calculations provide insights into these transformation mechanisms and the stabilization of the new phases. The partially converted monolayer flakes exhibit $PtTe_2$-Pt_2Te_2 heterojunctions, which enable the formation of the in-plane semiconductor-metal interface.[3] We further studied the electronic structure of edges and point defects in $PtSe_2$ monolayer where metallic 1D states with spin-polarized bands were found.[4] In addition to stoichiometry, combining different Pt-chalcogenides in vertical heterostructures provides an additional degree of engineering of materials properties.[5] Our results showed the variation of the interlayer interaction within the moiré structure locally modulates the electronic structure of $PtSe_2$/$PtTe_2$ heterostructures.

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Emergent electronic landscapes in a novel valence ordered thin-film nickelate prepared by topochemical reduction

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From topochemical reduction of a perovskite SmNiO3 thin-film, we obtain a novel valence-ordered and tri-component coordinated nickelate phase [1]. This new phase, with the chemical formula of Sm9Ni9O22 (SmNiO2.44) is formed by intricate planes of 303 apical oxygen vacancies (Vo) from the parent perovskite as revealed by four-dimensional scanning transmission electron microscopy (4D-STEM). Transport measurements indicated this phase to be highly insulating, over the measured temperature range (30K - 400K). A coherent analysis between ab-initio simulations and Synchrotron based X-ray spectroscopy techniques that evidenced a strong orbital polarization elucidated that this nickelate hosts multi-valent Ni sites that are in NiO5 pyramidal, NiO4 square-planar, and NiO6 octahedral coordinations. The resonant inelastic x-ray scattering (RIXS) measurements at the O-K edge also revealed this system to be having a strong carrier localization, marked by the disappearance of a ligand-hole configuration at low temperature. The periodicity of these polyhedral ordering, that can also be interpreted as valence ordering, follows the periodicity of the apical Vo ordering. The NiO4 square-planar sites forms at the intersection of the families of 303 apical Vo planes, indicating a route to the infinite-layer phase. This new nickelate phase addresses the ongoing debate on charge-order in infinite-layer nickelates, where presence of an apical oxygen ordered defective phase indicatively contributed to the reported charge-order signal in them [2,3]. It provides another example of previously inaccessible materials enabled by topotactic transformations and presents a unique platform where mixed Ni valence can give rise to exotic phenomena. References:

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Enhancing AFM Image Analysis Through Machine Learning with Style Translation and Data Augmentation

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Atomic Force Microscopy (AFM) is critical for atomic-scale nanostructure characterization. Simulations, especially using Particle Probe AFM (PPAFM) [1], provide a cost-effective means for rapid image generation. Leveraging state-of-the-art machine learning models and substantial PPAFM-generated datasets, properties like molecular structures [2], electrostatic force potential [3], and molecular graphs can be accurately predicted using AFM images from simulations or experiments. However, transferring model performance from PPAFM to real AFM images poses challenges due to the subtle variations in real experimental data compared to the seemingly flawless nature of simulations. Our study explores Cycle GANs [4] for style translation to augment data and improve the predictive accuracy of machine learning models in surface property analysis. Focused on mitigating the gap between simulated PPAFM and authentic AFM images, we optimize hyperparameters, showcasing the method's effectiveness through paired data comparisons. This research promises valuable insights, providing a novel approach to enhance machine learning model efficiency in the absence of abundant experimental data.

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Iron-based catalysts for oxygen reduction reaction in PEM fuel cell

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This work explores the use of platinum catalysts in proton-exchange membrane (PEM) fuel cells and compares them to more affordable and readily available iron-based catalysts. Platinum is the state of the art and most widely used catalytic material for PEMs, but it is currently limiting the mass adoption of hydrogen as a green source of electricity. To further green chemistry, alternatives should be found which don't suffer from the same scarcity and negative environmental impact as platinum production does. We investigate the mechanism of action and synthesis methods of both platinum and iron-based catalysts for the oxygen reduction reaction (ORR) in PEM fuel cells. The syntheses undertaken used different iron salts, a constant source of carbon, and mild hydrothermal conditions. Just by changing the iron precursor used in the synthesis, the structure of the carbon formed and integration of iron into that structure could be altered significantly. Carbon 'scaffolds' synthesized in the work include carbon nanotubes, carbon black and amorphous carbon. The different forms of carbon could have applications due to their different properties, such as surface area, conductivity, and interaction with neighboring atoms at the catalytic site. In this poster we present preliminary HER (hydrogen evolution reaction) and conductivity measurements. The purity and morphology of the carbon scaffold were characterized using Raman spectra and transmission electron microscopy (TEM). The catalytic ORR ability was extrapolated and discussed from the crystallinity and orderedness of the samples, by comparing to literature.The findings of this study suggest the potential for iron-based catalysts to replace platinum catalysts in PEM fuel cells, based on their performance in the ORR and much lower environmental and economic impact. In addition, when comparing other commonly used metrics such as half-wave potential and exchange current density, iron-based catalysts scored highly in activity and stability compared to platinum catalysts.

Tip-induced creation and Jahn-Teller distortions of sulfur vacancies in single-layer MoS_2

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Sulfur vacancies in MoS_2 host a multitude of physical phenomena that have led to many investigations in recent years. Among them are the discovery of single photon emission [1] and the emergence of the Kondo effect in charged sulfur vacancies [2].Here we report on a new technique for atomically precise creation of sulfur vacancies in monolayer MoS_2 grown on a Gr/Ir(111) substrate using the scanning tunneling microscope (STM) [3]. The creation technique allows us to produce single isolated sulfur vacancies that are well protected from the environment and thus maintain their intrinsic (electronic) properties. By local tip-gating, we are able to charge the sulfur vacancies and observe a Jahn-Teller effect by mapping their symmetry-broken orbitals using scanning tunneling spectroscopy (STS). Density functional theory (DFT) calculations rationalize our experimental findings. We show that two distinct Jahn-Teller distortions exist, corresponding to two symmetry-broken vacancy orbitals. Additionally, we report on observed transitions between the two Jahn-Teller distorted states that are induced by lattice strain. Lastly, we outline the potential of the newly developed sulfur vacancy creation method for the realization of extended vacancy structures and tailored electronic band structures.

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Influence of low-pressure atmosphere on the pores formed in hexagonal boron nitride under electron irradiation

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During (scanning) transmission electron microscopy ((S)TEM), the energetic electrons used for imaging can lead to damage in the sample. Electron knock-on damage caused by elastically scattered electrons in the best known of such damaging mechanisms, and has been studied extensively also for 2D materials [1]. In contrast, less is known about the damage mechanisms in insulating materials, such as hexagonal boron nitride (hBN) [2]. In early studies, it was shown that extended irradiation leads predominantly to the formation of triangular nanopores [3,4]. These pores and their triangular shape were suggested to arise from direct interaction between the electrons and the material, and it was shown that the dominated zig-zag edges were nitrogen terminated [4].The Nion UltraSTEM 100 microscope integrated into our experimental setup at the University of Vienna [5] allows experiments at low pressure atmosphere between ultra-high-vacuum (UHV) 1x10-10 mbar and 4x10-6 mbar by carefully leaking the desired gas into the column. Measurments at varying pressures have already shown that the partial pressure of different gases can have an influence in the damage observed in graphene [6]. Specifically, it was shown that different graphene edges dominate under an oxygen atmosphere and in UHV [7].Here hBN was imaged at UHV and up to an oxygen pressure of around 2x10-8 mbar. The most prominent finding was that the shape of pores that appeared under electron irradiation depends on the oxygen partial pressure. As an example, medium angle annular dark field (MAADF) images are shown in Figure 1. In UHV the pore shape is round with no preference of either boron or nitrogen termination, whereas triangular pores emerge with rising oxygen partial pressure, with edges dominated by nitrogen atoms. This suggests that the shape of the pores observed in the earlier studies was determined by the composition of the microscope vacuum.

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Automated Structure Discovery for Scanning Tunneling Microscopy

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Scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) functionalized with a CO molecule on the probe apex capture sub-molecular level detail of the electronic and physical structures of a sample from different prespectives [1]. However, the produced images are often difficult to interpret. To accelerate the analysis, we propose automated machine learning image interpretation tools to extract sample properties directly from bond-resolved STM images.In recent years, there has been rapid development in image analysis methods using machine learning with particular impact in medical imaging. These concepts have been proven effective also in SPM in general and in particular for extracting sample properties from AFM images [2,3,4]. We build upon these models and show that we can extract atomic positions directly from STM images. Finally, we establish the limits of the approach in an experimental context by predicting atomic structures from STM images of various small organic molecules [5].

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From first principles to the macroscopic realm; metal (Ag, Au, Cu, Li) diffusion in vertical MoS2 memristors

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Vertically grown MoS2 has been used to make memristors [1,2]. The switching mechanism has been identified as the formation of metals within MoS2. In this work, we study the formation and migration of metallic adatoms using density functional theory calculations and generalize the results into device operation conditions using kinetic monte carlo simulations. Our results give direct information on atom/ion speed and diffusion under any temperature and electric field which is advantageus in in device design. Vertically grown MoS2 is a great ionic conductor for all the metals studied. Both Ag and Cu are found to be viable active electrode materials for MoS2 memristors and the choice between the two could lead to different memristive capabilities.

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Structural characterization of MXene and its heterostructures with TEM, X-ray scattering, and simulation

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Two-dimensional (2D) transition metal carbides and nitrides (MXenes) with metallic conductivity, rich surface chemistry, and layered structure, suggest uncommonly broad combination of important functionalities amongst two-dimensional materials. For a comprehensive understanding of the structure-property relationship of MXenes, the quantitive structural characterization methods from atomic scale to mesoscopic scale are becoming extremely important. Transmission electron microscopy (TEM) is a powerful tool for acquiring detailed structural information about MXenes, such as crystal structure, mapping chemical composition, morphologies, etc. However, it is difficult to use TEM as a statistical analysis tool, which means the measurement bias coming from the objectively selected area can hardly be removed. On the other hand, the X-ray scattering methods, including small- and wide-angle X-ray scattering (SAXS/WAXS), are widely used tools for statistical structural analysis from sub-nanometers to hundreds of nanometers. The combination of TEM and SAXS/WAXS has been proven to be an efficient method for comprehensive structure investigation in the study of many low-dimensional nanomaterials. However, for MXene, the relevant research is still sparse. In our work, we have combined electron microscopy and X-ray scattering to study the structures of $Ti_3C_2T_x$ MXene stacking and its heterostructure with layered double hydroxides (LDH) at different length scales. From the cross-sectional TEM, we found a mesoscopic porous structure in the MXene stackings, which is caused by the 2D flake stacking deficiency. Then we employed SAXS/WAXS for statistical analysis of the porous size distribution and morphologies, as well as the anisotropic alignment degree of the 2D flakes. The results from electron microscopy and X-ray scattering show good coherency, proving the efficiency and wide applicability of our combining methods. For the study of MXene-LDH heterostructures, the combination of electron microscopy, X-ray scattering (diffraction), and various simulation methods also provides useful structural information. Specifically, we found a decreased crystalline domain size of LDH growth on MXenes. By comparing the TEM and X-ray diffraction results, we also found the changing texture of LDH, where the preferred growth direction was altered in the heterostructure. The simulation based on our experimental results indicates the various surface chemistry of MXenes may affect the growth of LDH. With this combination

method, we have proposed new a guided growth mechanism of LDH on MXene surface. We further demonstrate the high performance of the MXene stacking and MXene-LDH heterostructure with desirable structures in electromagnetic shielding and electrocatalysis respectively, where a better understanding of the structure-property relationship can facilitate further material design.

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Effect of Strain on Electro-Optical Properties of 2D Materials

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Two-dimensional materials like transition metal dichalcogenides (TMDCs) and graphene (Gr), have gotten a lot of interest from researchers in the field of semiconductor devices and electronics in recent decades [1]. However, many of these newly developed 2D materials are not capable of absorbing mechanical tension. The strain causes causes changes to their electronic band structures, which significantly affects their electronic and optical properties [1,2]. In this work, we study the growth of 2D layered transition metal di-chalcogenides (TMDCs) such as WS2, MoS2 and graphene by chemical-vapor deposition (CVD) reveal their optical and electronic properties by introducing strain. Strain engineering is an encouraging strategy for probing the optical, mechanical, and electronic, properties of 2D-materials [3]. To apply the strain successfully and avoid major slippage between the 2D materials and the substrate, we utilize a straightforward strain designing technique by compressing the monolayer 2D material in an adaptable PDMS substrate through a peeling approach. The strong connection force between PDMS and the 2D material guaranteed that the mechanical strain was successfully applied with insignificant slippage or decoupling. Different electrical, electronic, and optical techniques were employed to investigate the characteristics of the synthesized 2D materials and strain achieved in 2D-layered materials[3]. Raman spectroscopy was used to provide the structural fingerprint of the material when strain was applied and to probe the vibrational modes and confirm the number of layers grown. The surface morphology of the 2D layers was studied by atomic force microscopy (AFM). Current-Voltage (IV) measurements were used to investigate the effect of strain on the conductivity. The band structure of grown 2D layers was studied by photoluminescence (PL) spectroscopy at room temperature.

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Strain-modulated defect engineering of two-dimensional materials

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We have studied the response to external strain of h-BN, graphene, MoSe2, and phosphorene, four archetypal 2D materials, which contain substitutional impurities, using first-principles calculations. We find that the formation energy of the defect structures can either increase or decrease with bi-axial tensile strain, depending on the atomic radius of the impurity atom which can be larger or smaller than that of the host atom. Analysis of the strain maps indicates that this behavior is associated with the compressive or tensile local strains produced by the impurities that interfere with the external strain. The discovered trends are consistent across all studied 2D materials and are likely to be general. Our findings open up opportunities for combined strain- and defect-engineering to tailor the opto-electronic properties of 2D materials, and specifically, the location and properties of single-photon emitters.

Exploring the radiation resistance of GaN by bridging theory and experiment

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This study explores the resistance of thin films of Gallium Nitride (GaN) to strongly ionising radiation, using Two-Temperature Model - Molecular Dynamics (TTM-MD) simulations along with Transmission Electron Microscopy (TEM), Electron Energy Loss Spectroscopy (EELS) and Rutherford Backscattering Spectrometry in Channelling mode (RBS/C). Our results reveal a strong propensity of GaN to recrystallise along the ion paths, significantly reducing the formation of permanent radiation-induced defects, even at high fluences [1]. This recovery mechanism contributes to the high radiation resistance observed in GaN, a promising property for the next generation of radiation-hard devices. Moreover, we found distinct regimes of defect formation depending on the radiation energy, ranging from point and extended defects at moderate energies to N_2 bubbles and complex structures like voids at high energies [2].This work showcases the possible synergy between simulations and experiments, including TEM-HAADF image analyses and EELS interpretations derived from TTM-MD results. Additionally, we used a Binary Collision Algorithm to simulate RBS/C experiments on the TTM-MD cells, which resulted in excellent agreement with experimental observations, even in the presence of complex structures such as extended defects and voids. This integration of theoretical and experimental approaches, spamming from single ion impacts, observable at nanometer scales through TEM, to the cumulative effects of overlapping impacts assessed by RBS/C, led to an improved understanding of defect dynamics in irradiated GaN across several orders of magnitude.

[1] Miguel C. Sequeira, Jean-Gabriel Mattei, Henrique Vazquez, Flyura Djurabekova, Kai Nordlund, Isabelle Monnet, Pablo Mota-Santiago, Patrick Kluth, Clara Grygiel, Shuo Zhang, Eduardo Alves, Katharina Lorenz, *Communications Physics* **4**, 51 (2021).
[2] Miguel C. Sequeira, Flyura Djurabekova, Kai Nordlund, Jean-Gabriel Mattei, Isabelle Monnet, Clara Grygiel, Eduardo Alves, Katharina Lorenz, *Small* **18**, 2102235 (2022).

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