TT 16: 2D Materials I: Electronic Structure (joint session O/TT)

Time: Monday 15:00–17:30 Location: MA 005

TT 16.1 Mon 15:00 MA 005

Electronic and magnetic properties of single chalcogen vacancies in MoS_2/Au(111) — Sergey Trishin[1], •Christian Lotze[1], Nils Krane[2], and Katharina J. Franke[1] — [1]Fachbereich Physik, Freie Universität Berlin, Germany — [2]nanotech@surfaces Laboratory, Empa - Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

Two-dimensional (2D) transition-metal dichalcogenides (TMDCs) are considered highly promising platforms for next-generation optoelectronic devices. Because of their 2D structure, the performance of potential devices is strongly impacted by defects. Nowadays a lot of research aims to optimize growth methods towards defect-free TMDCs. However, defect engineering has also gained a lot of attention, as it may allow for control and design of new properties of 2D materials.

Here, we create single S vacancies in a monolayer of MoS_2 that was grown on Au(111). Using combined scanning tunneling and atomic force microscopy, we show that these defects are negatively charged and give rise to a Kondo resonance. The latter reveals the presence of an unpaired electron spin that is exchange-coupled to the underlying metal substrate. The strength of the exchange coupling depends on the density of states at the Fermi level, which is modulated by the moiré structure of the MoS_2 lattice and the Au(111) substrate. We also show that in the absence of direct hybridization of MoS_2 with the metal substrate, the S vacancy remains charge-neutral. Our results suggest that defect engineering may be used to induce and tune magnetic properties of otherwise nonmagnetic materials.

TT 16.2 Mon 15:15 MA 005

Non-ambient Raman spectroscopy combined with ion bombardment — •André Maas, Joel Verlande, Leon Daniel, Lucia Skopinski, Lars Breuer, and Marika Schleberger — Universität Duisburg-Essen, Fakultät für Physik and CENIDE, Germany

Characterizing materials in non-ambient conditions poses a persistent challenge, particularly in understanding irradiation-induced defects and their effects on crystal structure and electronic/optoelectronic properties. While ambient conditions often saturate defects with adsorbates, investigating the influence of unsaturated defects remains crucial for a comprehensive understanding.

In the first part of this study, we focused on analyzing defect formation in CVD-grown WS_2 by irradiating it with low-energy Ar^+ ions ($E_{\mathrm{kin}} \leq 500$ eV) to create sulfur vacancies. Subsequent analysis via Raman and photoluminescence spectroscopy revealed insights into the nature of these defects. A custom-built cell was used enabling us to characterize the electrical and optical properties at a pressure of $p = 10^{-6}$ mbar, to study the effects of temperature (77 K to 600 K) and the presence of sulfur hexafluoride on the irradiated samples.

In a novel experiment, defects were induced in graphene using highly charged ions (Xe^{17+} - Xe^{40+} at around $E_{kin} = 200$ keV). In-situ optical measurements at ultra-high vacuum ($p = 10^{-9}$ mbar) allowed us to detect the influence of saturated defects on the properties of this important 2D material.

TT 16.3 Mon 15:30 MA 005

Local creation and manipulation of sulfur vacancies in two-dimensional MoS_2 — •Daniel Jansen[1], Tfyeche Tounsi[1], Jeison Fischer[1], Arkady Krasheninnikov[2], Thomas Michely[1], Hannu-Pekka Komsa[3], and Wouter Jolie[1] — [1]II. Physikalisches Institut, Universität zu Köln, Köln, Germany — [2]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany — [3]Faculty of Information Technology and Electrical Engineering, University of Oulu, Oulu, Finland

Point defects in two-dimensional semiconductors can exhibit spatially confined and electronically isolated quantum states in the band gap of their host material. A prerequisite for the use of such point defects in quantum applications is to gain control over defect creation and manipulation.

Here, we report on a new technique for the local creation of individual sulfur vacancies in two-dimensional MoS_2 involving the tip of a scanning tunneling microscope and single Fe adatoms that we utilize as chemical markers. We exemplify how this technique can be employed to tailor the in-gap states by the creation of a vacancy dimer, giving rise to hybrid orbitals. Additionally we show that the tip can also be used to manipulate the sulfur vacancy charge state through local gating. When negatively charged, two distinct Jahn-Teller distortions are observed and characterized using scanning tunneling spectroscopy and density functional theory.

TT 16.4 Mon 15:45 MA 005

Charge State-Dependent Symmetry Breaking of Atomic Defects in Transition Metal Dichalogenides — •Lysander Huberich[1], Feifei Xiang[1], Jonas Allerbeck[1], Preston A. Vargas[2], Riccardo Torsi[3], Anne Marie Tan[2], Pascal Ruffieux[1], Roman Fasel[1], Oliver Gröning[1], Yu-Chuan Lin[3], Richard Henning[2], Joshua Robinson[3], and Bruno Schuler[1] — [1]Empa - nanotech@surfaces Laboratory, 8600 Dübendorf, Switzerland — [2]University of Florida, Gainesville, FL, 32611, USA — [3]The Pennsylvania State University, University Park, PA, 16802, USA

The electronic properties of atomically thin 2D materials are strongly influenced by occuring atomic defects and their interaction with the host lattice. Here we report on the direct imaging of charge state-dependent symmetry breaking of single rhenium dopants (Re_{Mo}) and negatively charged sulfur vacancies ($Vac_S{}^-$) in mono- and bilayer MoS_2 by atomically-resolved STM and nc-AFM. While $Vac_S{}^-$ occur in both the symmetric and the symmetry-broken state, Re_{Mo} exhibit charge-dependent symmetry breaking stabilized by the difference in substrate workfunction. The local lattice distortions and symmetry-broken defect orbitals of $Vac_S{}^-$ as well as $Re_{Mo}{}^0$ and $Re_{Mo}{}^{-1}$ are attributed to the (pseudo-)Jahn-Teller effect. By mapping of electronic orbitals and geometric structures, we can disentangle effects of spatial averaging, charge multistability, configurational dynamics, and external perturbations that often mask the presence of local symmetry breaking. [Xiang, Huberich, et al., arXiv:2308.02201]

TT 16.5 Mon 16:00 MA 005

Tuning Intrinsic Transition Probabilities in CVD-Grown WS_2 through Introduction of Sulfur Vacancies — •Leon Daniel, Charleen Lintz, Osamah Kharsah, Andre Maas, Stephan Sleziona, and Marika Schleberger — Universität Duisburg-Essen

Monolayer transition metal dichalcogenides (TMDCs) like tungsten disulfide (WS_2) are highly interesting materials for optoelectronic and valleytronic applications. Although WS_2 has a significantly higher quantum efficiency compared to its MoS_2 counterparts, its intrinsic properties are much less studied. This study investigates the controlled creation of sulfur vacancies in chemical vapor deposition (CVD)-grown WS_2 by high-temperature annealing in vacuum conditions up to 627 K. Employing in-situ photoluminescence (PL) spectroscopy, we observe a selective reduction in the intensity of the A exciton, while the B exciton remains unaffected upon introduction of vacancies. This distinctive behavior provides valuable insights into intrinsic transition probabilities associated with deliberately induced defect levels in WS_2. Additionally, an increased trion emission was detected, indicating increased doping by selectively removing sulfur. Intriguingly, despite the vacancy introduction, no observable localized states are detected. Similar results are achieved through 100 eV argon ion irradiation, if the sample is annealed with high laser powers before PL measurements are conducted; we therefore attribute this to the desorption of adsorbates. Our findings suggest that low energy ion bombardment is a suitable option for selectively tailoring the material's optical properties.

TT 16.6 Mon 16:15 MA 005

Formation of complex CDW patterns in single-layer TiSe2 — •Wen Wan, Paul Dreher, Maria Gastiasoro, Fernando de Juan, and Miguel Ugeda — Donostia International Physics Center, San Sebastián, Spain

While the CDW in TiSe2 emerges naturally with a commensurate 2x2x2 symmetry below ~200 K, superconductivity only develops induced by pressure, doping, and intercalation. Interestingly, these external stimuli triggering superconductivity also induce a CDW phase transition from a commensurate (CCDW) to an incommensurate state (ICCDW). Therefore, it has been speculated that superconductivity in TiSe2 is triggered by the CCDW to ICCDW transition in an unprecedented, exotic mutual interplay.

In this work, we explore the CDW state of TiSe2 in the single-layer limit by means of low-temperature STM/STS measurements. nm-scale

STM imaging reveals the presence of a CDW with a local 2x2 atomic periodicity as in bulk TiSe2 which, in contrast, is markedly inhomogeneous in space. On a larger scale, we find that such inhomogeneity is due to incommensuration of the CDW, which leads to the formation of complex 4-fold 2D matrix of CDW domains. Our high-resolution large-scale STM images allow us to spatially map the full complex CDW order parameter (amplitude and phase) with sub-nm precision. This analysis reveals that the CDW develops π-phase shifts at the domain walls. Lastly, while the matrix of CDW domains is unaffected by point defects in the Se layer, artificially introduced defects in the Ti plane pin the domain walls.

TT 16.7 Mon 16:30 MA 005

Unconventional charge-density-wave gap in monolayer NbS_2 — Timo Knispel[1], Jan Berges[2], Arne Schobert[3], Erik van Loon[4], Wouter Jolie[1], Tim Wehling[3], Thomas Michely[1], and •Jeison Fischer[1] — [1]II. Physikalisches Institut, Universität zu Köln, Köln — [2]Universität Bremen, Bremen — [3]I. Institut für Theoretische Physik, Universität Hamburg, Hamburg — [4]Lund University, Lund, Sweden

Here, we report scanning tunneling microscopy and spectroscopy measurements for a monolayer of H-NbS_2 grown by molecular beam epitaxy on graphene/Ir(111). We find that monolayer NbS_2 displays a 3×3 modulation superstructure due to a charge density wave (CDW), which is not present in bulk NbS_2. Evidence for the CDW is given by bias voltage contrast inversion and temperature suppression of the CDW signal. Our high-resolution differential conductance spectra display a pronounced gap of the order of 20 meV at the Fermi level. Within the gap low energy features are present. The gap structure with its low energy features is at variance with the expectation for a gap opening in the electronic band structure due to a static CDW distortion. Instead, comparison with ab initio calculations indicates that the observed gap structure is due to combined electron-phonon quasiparticles. The phonons in question are the elusive amplitude (Higgs) and phase (Goldstone) collective modes of the CDW transition [1].

[1] Knispel et al., arXiv:2307.13791.

TT 16.8 Mon 16:45 MA 005

Orbital character and ground-state electronic properties in van der Waals semiconductors VI3 and CrI3 — •Alessandro De Vita[1,2], Thao Nguyen[3], Roberto Sant[4], Gian Marco Pierantozzi[1], Danila Amoroso[5], Chiara Bigi[1,6], Vincent Polewczyk[1], Giovanni Vinai[1], Loi Nguyen[7], Tai Kong[7], Jun Fujii[1], Ivana Vobornik[1], Nicholas Brookes[4], Giorgio Rossi[1,2], Robert Cava[7], Federico Mazzola[1], Kunihiko Yamauchi[3], Silvia Picozzi[5], and Giancarlo Panaccione[1] — [1]IOM-CNR, Laboratorio TASC, Trieste, Italy — [2]Dipartimento di Fisica, Università di Milano, Italy — [3]ISIR, Osaka University, Japan — [4]ESRF, Grenoble, France — [5]CNR-SPIN c/o Università G. D'Annunzio, Chieti, Italy — [6]University of St Andrews, United Kingdom — [7]Department of Chemistry, Princeton University, NJ USA

Layered van der Waals magnetic semiconductors CrI3 and VI3 hold promise for novel electronic and spintronic 'few-layers' functionalities; however, detailed experimental information on the electronic structure, the interplay with relevant interactions (e.g. spin-orbit coupling), and the crossover of 3D vs 2D properties, is lacking. By combining X-ray electron spectroscopies and density functional theory calculations, we report a complete characterization of CrI3 and VI3 electronic ground states. We show that the transition metal-induced orbital filling drives the stabilization of distinct phases. X-ray absorption measurements on VI3 reveal that its electronic properties are strongly influenced by dimensionality effects. Our results have direct implications in band engineering and layer-dependent properties of two-dimensional systems.

TT 16.9 Mon 17:00 MA 005

Exchange splitting in the electronic structure of quasi-2D antiferromagnet CrSBr — •Matthew D. Watson[1], James Nunn[1,2], Swagata Acharya[3], Laxman Naga-Reddy[2], Dimitar Pashov[4], Malte Rösner[5], Mark van Schilfgaarde[3], Neil R. Wilson[2], and Cephise Cacho[1] — [1]Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK — [2]Department of Physics, University of Warwick, Coventry, CV4 7AL, UK — [3]National Renewable Energy Laboratory, Golden 80401 CO, USA — [4]Theory and Simulation of Condensed Matter, King's College London, The Strand, London WC2R2LS, UK — [5]Institute for Molecules and Materials, Radboud University, Heijendaalseweg 135, 6525AJ Nijmegen, The Netherlands

We present the evolution of the electronic structure of CrSBr from it's antiferromagnetic ground state to the paramagnetic phase above $T_N = 132$ K, in both experiment and theory. The ground state angle-resolved photoemission spectroscopy (ARPES) results, obtained using a novel method to overcome sample charging issues, are very well reproduced by our QSGW calculations including Bethe-Salpeter Equations (BSE) self-consistently. By tracing band positions as a function of temperature, we identify certain bands at the X points to be exchange-split pairs of states with mainly Br and S character, with the splitting disappearing above T_N. Our results lay firm foundations for the interpretation of the many other intriguing physical and optical properties of CrSBr.

TT 16.10 Mon 17:15 MA 005

Ultrafast momentum microscopy of hybrid exciton dynamics in homobilayer 2H-MoS_2 — •Paul Werner[1], Jan Philipp Bange[1], Wiebke Bennecke[1], David Schmitt[1], Giuseppe Meneghini[2], Anna Seiler[1], AbdulAziz AlMutairi[3], Marco Merboldt[1], Sabine Steil[1], Daniel Steil[1], Stephan Hofmann[3], G. S. Matthijs Jansen[1], Samuel Brem[2], R. Thomas Weitz[1], Ermin Malic[2], Marcel Reutzel[1], and Stefan Mathias[1] — [1]I. Physikalisches Institut, Georg-August Universität Göttingen, Germany — [2]Fachbereich Physik, Philipps-Universität Marburg, Germany — [3]Department of Engineering, University of Cambridge, United Kingdom

Transition-metal dichalcogenides (TMDs) monolayers host a rich landscape of excitonic states. If, in addition, these monolayers are stacked on top of each other, novel interlayer and hybrid excitonic states can form. Hybrid excitons, where either the excitons' hole or electron is layer-delocalized as a result of interlayer hopping, are responsible for efficient charge transfer between the layers [1, 2]. In homobilayer MoS_2, hybrid excitons are predicted to be the energetically most favorable excitonic state, making it an ideal system to study their properties. We employ time-resolved momentum microscopy to study the ultrafast exciton dynamics in H-stacked homobilayer MoS_2. By directly imaging the electron and hole contributions of the hybrid excitons, we are able to track their ultrafast dynamics.

[1] Schmitt *et al.*, Nature **608**, 499-503 (2022)
[2] Bange, Werner *et al.*, 2D Mater. *10* 035039 (2023)