Ge-Ko R&D Network
Workshop on Perovskite Spintronics

Date

21.08.- 22.08.2023

Venue

Johannes Gutenberg
University Mainz, Germany

Program Day 1

Time	Talks
12:30 ~ 13:30	Lunch
13:30 ~ 13:45	Welcome
13:45 ~14:15	***Doping Challenges in Metal-Halide Perovskites*** Keehoon Kang (Seoul National Univ.)
14:30 ~15:00	***Noncollinear antiferromagnets with antiperovskite structure*** Helen Gomonay (JGU Mainz)
15:15 ~15:45	***In-Situ Characterization of Perovskites*** Frank Schreiber (Univ. of Tübingen)
16:00 ~16:30	Coffee Break
16:30 ~17:00	***Spin Dynamics in Hybrid Metal-Halide Perovskites*** Felix Deschler (Univ. of Heidelberg)
17:15 ~17:45	***Toward Perovskite Orbitronics: Orbital Currents in Solids*** Dongwook Go (FSZ Juelich)
19:00	Dinner at Baron

Program Day 2

Time	Talks
09:00 ~ 09:30	***Structure-Property Relationships in Thienoacenes for Improved Transport Properties*** Guillaume Schweicher (Université Libre de Bruxelles)
09:45 ~10:15	***Hybrid Molecule-Metal Interfaces*** Angela Wittmann (JGU Mainz)
10:30 ~11:00	Coffee Break
11:00 ~11:30	***Density Functional Theory Studies of Two-Dimensional Halide Perovskites*** Young-Kwang Jung (Univ. of Cambridge)
11:45 ~12:15	***Non-van der Waals (n-vdW) 2D Materials for spintronics*** Aravind Puthirath Balan (JGU Mainz)
12:30 ~12:45	Closing Remarks
12:45	Lunch

Workshop on Perovskite Spintronics

This event aims to bring together leading and emerging scientists from the fields of metal-halide perovskites, two-dimensional systems, and spintronics to encourage scientific discussions on potential directions for exploring the emerging field of perovskite spintronics in cross-disciplinary research.

Date:

21. – 22.08.2023

Location:

Gernot-Gräff room (05-431, 5th floor)

Institute of Physics, JGU Mainz

Staudingerweg 7,55128 Mainz

Scientific organizers:

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Doping Challenges in Metal-Halide Perovskites

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Doping has been one of the most essential methods to control charge carrier concentration in semiconductors. In metal halide perovskite, which have revolutionized the field of solar cells and light-emitting diodes due to their favorable optoelectrical properties, extensive doping via atomic substitution still remains challenging due to their structural stability limited by tolerance factor and compensation of intentionally introduced defects by mobile halide ions. As an alternative non-invasive approach for, concepts utilizing molecular dopants for surface charge transfer doping have been previously reported for tuning the conductivity of metal-halide perovskite. However, most of the reports have been focused on charge transfer effects at the interface or grain boundaries which have limited the range of doping attainable. In this work, we use strong molecular p-dopant, tris(4-bromophenyl)ammoniumyl hexachloroantimonate (magic blue), for significantly improving the electrical conductivity of low-dimensional perovskite films. We identify that dopant incorporation into the bulk of the film as the structural origin of the improved conductivity and propose the solvent selection criteria for achieving effective molecular doping, which can potentially open up a controllable route towards tuning electronic structure for optimizing perovskite-based devices.

Noncollinear antiferromagnets with antiperovskite structure: phase transitions governed by the magnetic field

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In this talk I will give an introduction to the magnetic properties of antiferromagnets with the triangular magnetic structure Mn3XN (X=Zn, Ni). By applying an external magnetic field we can induce and electrically probe transitions between phases with different spin textures [1] or different orientations of the spin ordering planes with respect to the crystallographic axes [2]. I will also discuss the physical mechanisms behind these transitions and give an outlook on the possible applications of these materials.

[1] S. Deng, O. Gomonay, J. Chen, et al, arxiv:2306.15332.
[2] A. Rajan, T. Saunderson, F. Lux, et al, arxiv:2304.10747.

In-Situ Characterization of Perovskites

E. Kneschaurek[1], L. Merten[1], N. Scheffczyk[1], P. Zimmermann[1], A. Hinderhofer[1], **F. Schreiber**[1*]

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In many cases, a proper understanding of the material growth and performance requires in-situ characterization. Here we discuss different strategies of in-situ characterization, their experimental implementation, as well as the analysis of the corresponding kinetic data. We present both structural as well as optical data taken in real time. Specific attention is paid to the behavior of systems with a non-trivial stoichiometry and ion-exchange reactions.

We also present a new compact sample environment for the in-situ study of crystallization kinetics of thin films on synchrotron beamlines, featuring atmospheric control, automated deposition, spin-coating, and annealing stages. The setup is suitable for studying thin film growth by spin-coating in real time using grazing-incidence X-ray diffraction techniques as well as differential reflectance spectroscopy. Lastly, we discuss the application of machine learning strategies for efficient data analysis of surface scattering data.

Contributions by numerous collaborators, including the Cambridge group, the EPFL group, and the Dresden group, are gratefully acknowledged.

[1] E. Kneschaurek, A. Hinderhofer, B. Hofferberth, N. Scheffczyk, L. Pithan, P. Zimmermann, L. Merten, F. Bertram, and F. Schreiber. Compact sample environment for in situ X-ray scattering during spin-coating, Rev. Sci. Instrum. 94 (2023) 063901

[2] K. O. Brinkmann, T. Becker, F. Zimmermann, C. Kreusel, T. Gahlmann, M. Theisen, T. Haeger, S. Olthof, C. Tückmantel, M. Günster, T. Maschwitz, F. Göbelsmann, C. Koch, D. Hertel, P. Caprioglio, F. Peña-Camargo, L. Perdigón-Toro, A. Al-Ashouri, L. Merten, A. Hinderhofer, L Gomell, S. Zhang, F. Schreiber, S. Albrecht, K. Meerholz, D. Neher, M. Stolterfoht, and T. Riedl. Perovskite-organic tandem solar cells with indium oxide interconnect Nature 604 (2022) 280

[3] V. Starostin, V. Munteanu, A. Greco, E. Kneschaurek, A. Pleli, F. Bertram, A. Gerlach, A. Hinderhofer, and F.Schreiber. Tracking perovskite crystallization via deep learning-based feature detection on 2D X-ray scattering data
npj Comput Mater 8 (2022) 101

[4] N. Arora, A. Greco, S. Meloni, A. Hinderhofer, A. Mattoni, U. Rothlisberger, J. Hagenlocher, C. Caddeo, S. M. Zakeeruddin, F. Schreiber, M. Graetzel, R. H. Friend, and M. I. Dar. Kinetics and energetics of metal halide perovskite conversion reactions at the nanoscale, Commun. Mater. 3 (2022) 22

[5] A. Greco, A. Hinderhofer, M. Dar, A. Ibrahim, N. Arora, J. Hagenlocher, A. Chumakov, M. Grätzel, and F. Schreiber. Kinetics of ion-exchange reactions in hybrid organic-inorganic perovskite thin films studied by in situ real-time X-ray scattering, J. Phys. Chem. Lett. 9 (2018) 6750

Spin Dynamics in Hybrid Metal-Halide Perovskites

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Hybrid metal-halide perovskites have emerged as next-generation semiconductors for solution-processable opto-electronic applications. They further show strong spin-orbit coupling and Rashba effects in their electronic states, which has generated interest in using these materials for spintronic and magneto-optic applications.
In my talk, I will present our work on ultrafast spectroscopy of exciton and spin dynamics in layered hybrid perovskites [1,2], as well as control of exciton-spin interactions in dilute magnetic hybrid perovskites [3]. I will discuss the fundamental processes controlling spin-lifetimes, as well as approaches towards ultrafast optical alignment of magnetic moments.

[1] Bourelle, S. A.; Camargo, F. V. A.; Ghosh, S.; Neumann, T.; van de Goor, T. W. J.; Shivanna, R.; Winkler, T.; Cerullo, G.; Deschler, F., Nat. Commun., (2022), 13, 3320.
[2] Bourelle, S. A.; Shivanna, R.; Camargo, F. V. A.; Ghosh, S.; Gillett, A. J.; Senanayak, S. P.; Feldmann, S.; Eyre, L.; Ashoka, A.; van de Goor, T. W. J.; Abolins, H.; Winkler, T.; Cerullo, G.; Friend, R. H.; Deschler, F., Nano Lett. (2020), 20, 5678-5685
[3] Neumann, T.; Feldmann, S.; Moser, P.; Delhomme, A.; Zerhoch, J.; van de Goor, T.; Wang, S.; Dyksik, M.; Winkler, T.; Finley, J. J.; Plochocka, P.; Brandt, M. S.; Faugeras, C.; Stier, A. V.; Deschler, F., Nat. Commun. (2021), 12, 3489.

Toward Perovskite Orbitronics: Orbital Currents in Solids

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The orbital degree of freedom is a fundamental information that is encoded in the electronic wave function in a solid but is also known as a quenched or frozen degree of freedom which cannot be manipulated. In contrast to what is commonly believed, we have theoretically predicted that the orbital quenching in the ground state does not necessarily suppress the orbital angular momentum in non-equilibrium and showed that the orbital angular momentum can be induced and transported under external perturbations [2]. Orbital currents, which have bene long sought after since the theoretical prediction, have been finally confirmed by recent experiments [3-5]. Plethora of possibilities of investigating fundamental aspects of orbital currents as well as potential applications have led to the emergence of a new research field, *orbitronics*, which utilizes the orbital degree of freedom as an information carrier in solid-state devices [6]. In this talk, I will explain how to generate, detect, and manipulate the orbital degree of freedom of electrons and discuss implications and potential impact on other fields of research such as spintronics, multiferroics and perovskite oxides.

[1] Go *et al*. Phys. Rev. Lett. **121**, 086602 (2018)
[2] Choi *et al*. Nature **619**, 52 (2023)
[3] Ding *et al*. Phys. Rev. Lett. **125**, 177201 (2020); Ding *et al*. Phys. Rev. Lett. **128**, 067201 (2022)
[4] Lee *et al*. Nat. Commun. **12**, 6710 (2021); Lee *et al*. Commun. Phys. **4**, 234 (2021)
[5] Sala and Gambardella, Phys. Rev. Research **4**, 033037 (2022)
[6] Go *et al*. Europhys. Lett. **135**, 37001 (2021)

Structure-Property Relationships in Thienoacenes for Improved Transport Properties

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In spite of tremendous progress in molecular design, engineering and processing, only few small molecule organic semiconductors (OSCs) have reached charge carrier mobilities (μ) higher than 10 cm^2/Vs, typically with single-crystal devices. However, μ is a material property and not a molecular one. It is thus of paramount importance to take supramolecular order into consideration at all length scales. As recently evidenced, the best OSCs tend to self-organize into large plate-like single-crystals exhibiting a layer-by-layer herringbone packing motif.[1] Moreover, thermal lattice fluctuations cause temporal variations of transfer integrals (J) and impose a transient localization of charges leading to reduced macroscopic μ in these weakly bonded van der Waals solids.[2] We will present recent progress achieved in our group in terms of molecular design and understanding of the impact of thermal energetic disorder: design by theory, crystal engineering, quantum-chemical calculations and evaluation of transport properties in electronic devices.

[1] Schweicher, *Adv. Mater.* **2020**, 32, 10, 1905909; Fratini, *Nature Materials* **2020**, 19, 491
[2] Fratini, *Adv. Funct. Mater.* **2016**, 26, 2292; Fratini, *Nature Materials* **2017**, 16, 998; Schweicher, *Adv. Mater.* **2019**, 31, 43, 1902407; Banks, D'Avino, Schweicher, *Adv. Funct. Mater.* **2023**, 2303701

Hybrid Molecule-Metal Interfaces

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Controlled manipulation of a system allows for systematic investigation of the underlying interactions and phenomena. Simultaneously, tunability also enables the development of novel materials systems and devices customized for specific applications. Here, we will focus on materials systems that conventionally have not been used as active components in spintronic devices and will delve into hybrid molecule-magnetic interfaces. Molecules offer a unique way of controlling and varying the structure at the interface making it possible to precisely tune the spin injection and diffusion by molecular design[1]. In particular, chirality has gained recent interest in the context of the chiral-induced spin selectivity effect[2]. Here, we will explore signatures of spin filtering at a non-magnetic chiral molecule-metal interface[3] paving the path toward novel hybrid spintronics.

[1] Wittmann, A. *et al.*, *Phys. Rev. Lett.* **124**, 027204 (2020).
[2] Naaman, R., Paltiel, Y. & Waldeck, D. H., *Nat. Rev. Chem.* **3**, 250–260 (2019).
[3] Ozeri, M. *et al.*, *J. Phys. Chem. Lett* **14**, 48 (2023).

Density Functional Theory Studies of Two-Dimensional Halide Perovskites

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Density Functional Theory (DFT) is a computational modeling method, grounded in quantum mechanics, used to investigate the electronic structure of matter. In the field of halide perovskite research particularly, DFT studies have played a crucial role in understanding the properties of halide perovskites, such as the behavior of point defects [1], surfaces [2], and interfaces [3]. Furthermore, the combination of theoretical calculations and experimental measurements is becoming increasingly important for drawing scientifically impactful and rigorous conclusions in this research field. In this talk, we will introduce examples from our theoretical investigations into two-dimensional (2D) halide perovskites, where our collaboration with experimental researchers continues. After providing an overview of the basic concepts of DFT calculations and computational modeling, we will present how theoretical results can be used to explain or support experimental observations. We will also discuss potential causes for any disagreement between theory and experiment.

[1] W.-J. Yin, T. Shi and Y. Yan, Appl. Phys. Lett., 104 (2014) 063903.
[2] J. Haruyama, K. Sodeyama, L. Han and Y. Tateyama, Acc. Chem. Res, 49 (2016) 554–561.
[3] Y.-K. Jung, K. T. Butler and A. Walsh, J. Phys. Chem. C, 121 (2017) 27351–27356.

Non-van der Waals (n-vdW) 2D Materials for spintronics

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The unique properties of 2D materials, such as their ability for ballistic carrier transport, independence from substrate effects, and mechanical resilience within the plane, have attracted significant attention. However, the current range of 2D materials is limited, with most commercially available materials falling under the non-van der Waals category. The exploration of the impact of one-dimensional confinement on non-van der Waals materials has been largely uncharted territory due to the difficulties involved in fabricating large-area ultra-thin structures. Recent advancements in liquid phase exfoliation techniques have revitalized research efforts by enabling the production of ultra-thin layers from bulk non-van der Waals materials. This approach takes advantage of cleaving/parting planes present in specific material orientations, where bonding strength is weaker compared to other crystallographic directions. Consequently, smooth exfoliation can be achieved by applying shear forces. These developments open up new avenues for studying and utilizing non-van der Waals materials in various applications. Here the authors discuss recent developments in the field of non-van der Waals materials with emphasis on potential materials for spintronics applications.

[1] Balan, Aravind Puthirath, et al., *Materials Today*, **58** (2022), 164-200.
[2] Puthirath Balan, A., Radhakrishnan, S., Woellner, C.F. et al., *Nature Nanotechnology* **13** (2018), 602–609
[3] Puthirath Balan, Aravind, et al., *Chemistry of Materials*, **30**.17 (2018), 5923-5931.
[4] Puthirath, A. B., …. Balan, A. P., et al., *Small*, **16** (2020), 2004208.
[5] Puthirath, Anand B., Balan, A. P., et al. *The Journal of Physical Chemistry C* **125**.34 (2021): 18927-18935.
[6] Aravind Puthirath Balan, et al., *Oxford Open Materials Science*, **3**.1(2023), itac020.