FM 10: Crystal Defects and Real Structure Physics in Diamond and Functional Materials II

chair: Theo Scherer (Karlsruhe Institute of Technoloy, DE)

Time: Tuesday 14:00–15:30 Location: BEY/0E40

FM 10.1 Tue 14:00 BEY/0E40

Identification of defects in iron molybdate catalysts via first principles calculations — •Young-Joon Song and Roser Valentí — Institut für Theoretische Physik, Goethe-Universität, 60438, Frankfurt am Main, Germany

Iron molybdate ($Fe_2(MoO_4)_3$) is well known as a commercial catalyst for oxidative dehydrogenation. Recently, L. Schumacher et al. reported an experimental reduction in Raman intensity at 782 cm^{-1} during catalytic processes. The authors attribute this decrease to oxygen migration from the bulk to the surface during the reaction, in contrast to the conventional understanding that oxygen atoms are supplied only near the surface. To identify the types of defects responsible for the observed reduction in Raman intensity, we performed DFT electronic and phononic structure calculations for $Fe_2(MoO_4)_3$. Our findings reveal that optical phonon modes involving oxygen dominate the spectrum at around 790 cm^{-1}, with a small contribution from Mo, corresponding to asymmetric MoO_4 stretching modes. In the Raman calculations, a major peak appears at 789.68 cm^{-1} with a small shoulder-like feature and a minor peak at 972.05 cm^{-1}, consistent with the experimental observations. By selectively freezing specific phonon modes, we introduced an effective method to incorporate defect effects into Raman calculations without explicitly creating oxygen vacancies. Using this approach, we found that oxygen vacancies play a dominant role in the reduction of Raman intensity. Finally, we discuss the relaxed structure containing explicit oxygen vacancies. This research was supported by the German Research Foundation for funding through CRC 1487.

FM 10.2 Tue 14:15 BEY/0E40

Exsolution of metal nanoparticles by control of point defects — •Andreas Rosnes[1], Bo Jiang[2], Holger von Wenckstern[1], Øystein Prytz[1], and Jonathan Polfus[2] — [1]Department of Physics, Centre for Materials Science and Nanotechnology, University of Oslo, PO Box 1048 Blindern, NO NO-0316 Oslo, Norway — [2]Department of Chemistry, Centre for Materials Science and Nanotechnology, University of Oslo, PO Box 1033 Blindern, NO-0315 Oslo, Norway

Exsolution involves redox precipitation of metal nanoparticles from metal oxides, resulting in materials that exhibit excellent electrocatalytic properties and hold great promise for novel types of nanoscale heterostructures. However, a coherent understanding of the phenomenon is lacking. Here, exsolution is described by three point defect equations involving the reduction of the host oxide, reduction and exsolution of the transition metal, and annihilation of host unit cells. Guided by their predictions, significantly enhanced exsolution in terms of molar amount, rate, and nucleation density is shown by acceptor substitution to the system $La_{0.2}Ca_{0.7}Ti_{0.95}Cu_{0.05}O_{3-\delta}$ through atomic scale imaging and in situ X-ray diffraction and spectroscopy. It is demonstrated that the oxygen stoichiometry of the parent oxide increases upon exsolution despite oxygen loss in the reducing environment. Furthermore, strain in both the host oxide and the exsolved metal can constitute an additional thermodynamic barrier for exsolution beyond the availability of the required point defects.

FM 10.3 Tue 14:30 BEY/0E40

Machine-Learning Potentials Reveal Defect Segregation at Grain Boundaries in Lithium Solid Electrolytes — •Waldemar Kaiser[1], Hyunwon Chu[2], Jennifer L.M. Rupp[1,2], and David A. Egger[1] — [1]TUM School of Natural Sciences, Technical University of Munich — [2]Department of Materials Science and Engineering, Massachusetts Institute of Technology

Grain boundaries (GB) play a central role in ionic and electronic transport in polycrystalline solid electrolytes [1, 2], yet their local defect chemistry remains difficult to resolve. Their structural complexity and chemical heterogeneity introduce a wide distribution of possible defect configurations that are computationally demanding to characterize with first-principles methods. As a result, the origins of variations of ionic and electronic transport often remain unclear.

Here, machine-learning potentials (MLPs) are applied to representative $\Sigma5$ and $\Sigma3$ GB structures to investigate ionic defects in lithium lanthanum zirconate (LLZO). The MLPs enable the systematic and efficient mapping of lithium- and oxygen-vacancy formation energies, revealing reductions of up to 1 eV within GB cores relative to bulk sites. Structural analysis further identifies locally Zr-deficient coordination environments as preferred incorporation sites for lithium vacancies, and experiments show that Ta-doping fills these bottlenecks and enhances the material's stability.

[1] B. Gao et al., Adv. Energy Mater. 12, 2102151, 2021 [2] Y. Zhu et al., Nat. Rev. Mater. 6, 313-331, 2021

coffee break

FM 10.4 Tue 15:00 BEY/0E40

2 - Dimensional hybrid perovskite as a promising semiconductor for large area electronics — •Tomasz Marszalek, Shuanglong Wang, Zhitian Ling, Denis Andrienko, Hai Wang, Paul W.M. Blom, and Wojciech Pisula — Max Planck Institute for Polymer Research, Mainz, Germany

Two-dimensional (2D) perovskites with bulky spacer cations are promising candidates for field-effect transistors due to the suppressed ion movement caused by large size insulating ligands. However, the relationship between the chemical nature of organic cations and film morphology, crystallinity, molecular organisation and charge carrier transport in 2D layered perovskites is not yet fully understood, which significantly limits the development of 2D perovskite FETs.

This report presents a distinct odd-even effect in 2D Sn-based perovskite semiconductors for the first time, incorporating monovalent phenylalkylammonium-based organic cations with alkyl side chains of different lengths containing either an odd or an even number of carbon atoms. An odd-even oscillation of charge carrier transport was revealed using optically pumped terahertz spectroscopy and transistor devices. By combining density functional theory calculations with simulated grazing-incidence wide-angle X-ray scattering, we demonstrate that organic ligands featuring odd carbon atoms exhibit a disordered crystal lattice and tilted inorganic octahedra. This results in a larger effective mass and inferior charge mobilities compared to perovskites with an even number of carbon atoms in the organic cations. (J. Am. Chem. Soc. 2024, 146, 19128, Mater. Horiz., 2024,11, 1177)

FM 10.5 Tue 15:15 BEY/0E40

On the origin of the strange metal Hall effect in BaFe2(As1-xPx)2 — •Augusto Ghiotto[1], Darian Hall[1], Yuanqi Lyu[1], Kohtaro Yamakawa[1], John Singleton[2], and James Analytis[1] — [1]University of California, Berkeley, USA — [2]National High Magnetic Field Laboratory's Pulsed Field Facility at Los Alamos, USA

BaFe2(As1-xPx)2 is an unconventional superconductor in which the antiferromagnetic, nematic and structural order is suppressed by isovalent P substitution, leading to a quantum critical point at $x = 0.31$. It has been shown that the Hall effect of the overdoped series contains an anomalous contribution arising from the correlations within the strange metal, whose behavior emanates from a quantum critical point and, in the zero-temperature limit, decays together with the superconducting critical temperature. Here, we present new data on the underdoped series taken at pulsed high magnetic fields. To achieve a large signal to noise ratio and an accurate measurement of the Hall coefficient, we microstructured the crystals into well-defined Hall bars. In this talk, we will draw parallels between the Hall effect in the ordered state and in the strange metal.