Swiss Society for Crystallography
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“Materials Discovery”

Book of Abstracts

Correlated disorder in Prussian Blue analogues: from understanding to control of the local structure

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While disorder is often perceived as random and unwanted, in crystals, it is usually correlated on a local scale and can even enhance material properties. In this work, we demonstrate that such correlated disorder in solution-grown Prussian Blue analogue crystals (PBAs) can be systematically manipulated through crystallization parameters that affect growth kinetics—temperature, precursor concentration, chelating agents, and gel media. This control allows us to achieve defect correlation lengths ranging from short-range to long-range, which directly impacts optical anisotropy, gas sorption capacity, and framework stability without altering chemical composition.

We also discovered that not only is crystallization kinetics important but also the crystal growth direction. [1] Defects tend to align anisotropically along growth directions, creating macroscopic domains with lower symmetry than the symmetry one can extract from an average structure based on Bragg peaks. By growing crystals along different directions, we can modify the symmetry and thus properties like birefringence.

Disorder can also be responsive: local structure can undergo transformations triggered by post-synthetic treatments without detectably changing the average structure. We demonstrate that these modifications in PBAs can be achieved by treatments like dehydration or freezing. Dehydration induces an irreversible reshuffling of the vacancy network from a checkerboard arrangement to diagonal channels, altering transport pathways and improving pore connectivity. Similarly, when rapidly cooled, these crystals develop a reversible corrugated structure as water freezes within their pores. These ``hidden" phase transitions, invisible to conventional Bragg diffraction, significantly impact material properties, including dehydration kinetics, symmetry, and optical anisotropy.

Our findings transform correlated disorder from an uncontrolled variable into a design parameter complementing standard compositional tuning approaches. The principles developed here extend beyond PBAs towards other solution-grown crystalline systems, particularly metal-organic frameworks (MOFs) and related porous materials, opening new possibilities for engineering materials with tailored properties by controlling their local structure.

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High-Pressure Crystallography as a Tool for Materials Discovery

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Materials behavior in confined environments often differs significantly from what scientists observe when exploring chemical reactions or phase transformations at atmospheric pressure. In this talk, we delve into high-pressure and high-temperature crystallography as a powerful tool to unravel the effects of extreme conditions on solid matter *in situ*.

We have experimentally investigated various compound classes, including oxides, borides, carbides, nitrides, halides, and hydrides. These studies offer new insights into how extreme pressure-temperature conditions reshape our understanding of matter, revealing novel principles that govern material behavior. A key highlight of this research is the synthesis of compounds with homoatomic anions, representing a groundbreaking advancement in materials design.

The talk will cover both the methodological and technical aspects of high-pressure crystallography, including innovative devices and software for XRD data processing. The implications of high-pressure crystallography extend beyond a single discipline, influencing fields such as physics, chemistry, materials science, earth sciences, and planetary sciences. We will present a critical analysis of how extreme pressures and temperatures challenge conventional chemical norms, highlighting the profound impact of our approach on multidisciplinary scientific research.

Crystal Chemistry and Exotic Properties in some Low-D 6th block Transition Metal Phosphates (Cr, Mo,W).

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This presentation focuses on 6th group transition metal phosphates (W, Mo, Cr), characterized by a range of oxidation states from +II to +VI. We will explore the new series of layered monophosphate tungsten bronzes (L-MPTB) $[Ba(PO_4)_2]W_mO_{3m-3}$ ($2 \leq m \leq 5$), consisting of m-layer-thick slabs of WO_6 separated by large spacers. They all show metallic behaviour down to 1.8 K without clear evidence of instability, despite the vicinity of 1D nested topology [1]. Their genuine 2D-character is even more reinforced by the participation of mainly a central W-layers , assigned to anti-polar displacements [2]. Their oxidation under air lead to a series of W and Mo polymorphs that we have using evolutionary crystallographic algorithms (USPEX) and ab-initio DFT calculations. A special attention will be also given to chromium(II) compounds, where the rare Cr^{2+} oxidation state is stabilized by the inductive effect of phosphate groups. This, coupled with the Jahn-Teller effect, gives rise to a variety of frustrated crystal structures and spin-lattice interactions. Besides the non-collinear magnetic structures of α- and β-$Cr_3(PO_4)_2$ the incorporation of large cations (e.g. Ba) induces several low-dimensional structures with various exotic features. For instance, the 2D -$Sr_2Cr(PO_4)_2$ compounds exhibits a two-step layer-by-layer magnetic ordering with significant spin-lattice couplings, finally breaking the structural time-reversal symmetry of the room-temperature crystal structure [3].

Reference to a journal publication:

[1] H. Nimoh *et al.*, Angew. Chemie Int. Ed. 2023, 62, e202302049.
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Probing Structural Defects and Dynamic Disorder in Halide Perovskite Nanocrystals

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Lead halide perovskites (LHP) are long-known crystalline materials with ABX_3 general formula (where $A=Cs^+$, $MA=CH_3NH_3^+$ or $FA=CH(NH_2)_2^+$, $B=Pb^{2+}$ and $X=Cl^-,Br^-,I^-$), characterized by a three-dimensional $[PbX_6]^{4-}$ framework and a large A cation residing in the cuboctahedra cavities. These materials in the form of nanocrystals (NCs) are considered ideal candidates to be integrated into television displays and LEDs [1]. Due to the dynamic nature of the perovskite lattice, preventing the charge carriers from trapping, LHP NCs are highly tolerant to structural defects and surface states, which are considered benign with respect to their electronic and optical properties [2].

The flexible nature of the perovskite framework, very prone to structural defectiveness, coupled with the reduced size of crystalline domains, makes these materials unsuitable for conventional crystallographic methods. For this purpose, total scattering techniques based on the Debye Scattering Equation (DSE), have been established as effective methods for characterizing nanoscale materials and taking into account size-induced structural defects, emerging upon downsizing [3]. Through the DSE-based method developed by some of us [4], starting from real-space atomistic models, structural and microstructural information on NCs can be simultaneously derived within a unified approach, with all the well-known advantages associated with the use of reciprocal space methods.

In this talk, experimental and modeling aspects related to the DSE approach applied to provide atomic-to-nanometer scale insights on key nanoscale features of LHPs will be presented, both in steady-state conditions and involving forefront ultrafast pump-probe experiments [5].

A broad spectrum of structural and morphological features of LHPs, unveiled through a synergic combination of reciprocal space methods based on the DSE, will be analyzed, from their peculiar structural flexibility [6], defectiveness [7], to faceting and surface termination [8], to the formation of self-organized superstructures [9,10].

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60 Years in chemical crystallography (1965-2025)

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The presentation will focus on a few things that impressed me during those 60 years and a few topics where I think I contributed to the development of chemical crystallography. To put things into perspective the different topics are related to the time line of solutions of the phase problem. A glimpse will be given of the means available for single crystal structure determination during my thesis work (1965-1969) and - more importantly - of the problems that required structural information.

By the 1970s enough information was available to study the correlated deformations of a given structural fragment embedded in different environments (structure correlation). Such studies - based initially on literature searches in the library - were reported from the 1970s to the 1990s in most crystallographic meetings. With the help of structural databases and their associated software (CSD, available online in CH since 1977, and ICSD, PDB) such studies may now be done in a days or so. The best known example of such correlations is a detailed description and discussion of the approach of a nucleophile to an electrophilic carbonyl C-atom[1,2]. The only aspect left in 2025 of this study is the so-called 'Bürgi-Dunitz angle'.

Another topic is atomic displacement parameters U_{ij} (ADPs, more accurately intra-atomic ADPs, $U(n)_{ij}$).determined for every structure nowadays and representing ~2/3 of the information characterizing a crystal structure. ADP information is hardly ever interpreted to any significant degree. This is partly due to a complete lack of information on the correlations of atomic motions (inter-atomic ADPs $U(mn)_{ij}$). Due to the quantum chemical nature of atomic motion and due to anharmonicity of such motion, information on inter-atomic ADPs can be retrieved from multi-temperature data[3]. I consider this result my most original finding. It has, however, had a very modest echo in the crystallographic community.

Work on disorder, diffuse scattering and evolutionary algorithms started when Thomas Weber joined the lab as a postdoc[4]. After retirement (>2007) I continued these studies in collaboration with Tony Linden at UZH and Omar Yaghi at UC Berkeley and I would pursue them further if I had another crystallographic life. Mark Spackman and Dylan Jayatilaka (both from UWA) introduced me to quantum crystallography and let me collaborate in the development of the quantum-chemistry based Hirshfeld Atom Refinement (HAR)[5]. Another topic i am very interested in but never had an opportunity to delve into is crystal nucleation and growth.

Overall, working for 60 years in chemical crystallography with gifted students and brilliant colleagues was a great and satisfying experience.

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Memories of my relations with the Swiss Society for Crystallography

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Foundation of the Swiss Society for Crystallography (SSCr) in 1969.

How my interests changed from mathematical physics to crystallography.

Start and early development of the SGK/SSCr Newsletter.

The European Crystallographic Meeting ECM30 in Basel.

Finally, I shall show how much I owe to Howard Flack.

The new PHOTON IV Detector and benefits of hard radiation

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Single crystal structure determination from samples containing a certain number of heavy elements can severely suffer from absorption, even if relatively hard radiation Mo-Kα radiation is applied. Modern X-ray sources (IµS 3.0, IµS DIAMOND II, METALJET MC) give access to harder Ag- or In-Kα radiation. Harder radiation addresses absorption issues and additionally it provides better sample transmission, higher maximum resolution, and a very straight forward data reduction. These properties render Ag-Kα radiation, particularly, ideal for advanced applications like charge density or high-pressure pressure studies or material science investigations on heavily absorbing samples in general. However, the benefit gained from the high energy radiation can be ironed out or even turned into the contrary if not properly reflected by the detector properties. Silicon-based X-ray detectors typically miss out two out of three X-ray photons reflecting the poor absorption capabilities of Silicon for the high energy X-ray photons. With the PHOTON IV HE, a photon-counting detector is now available, which perfectly matches the properties of hard X-ray radiation, yielding an unparalleled high quantum efficiency for Ag-radiation. Along several selected examples, we will demonstrate the benefits generated combining a hard radiation source with a PHOTON IV HE.

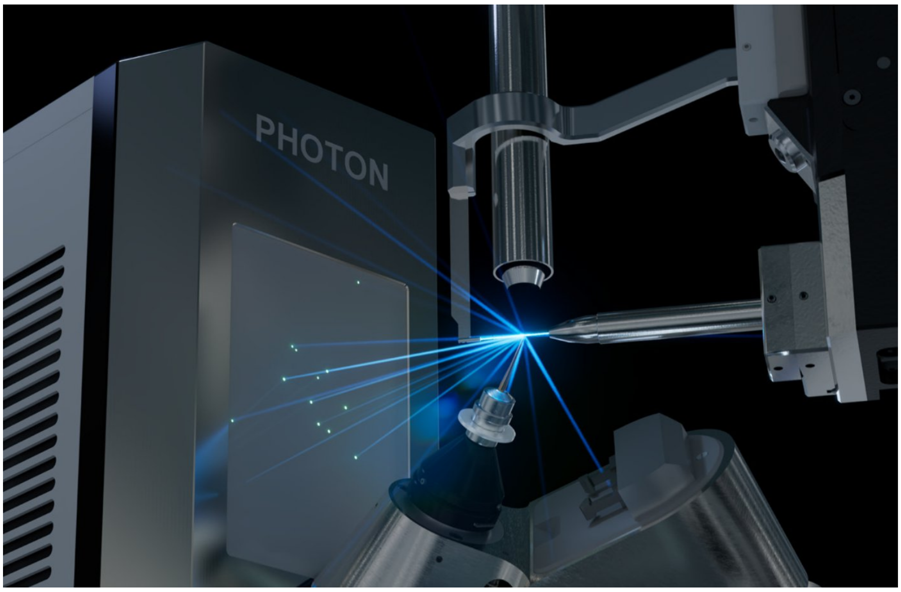

Figure 1- Artistic representations of X-ray scattering and data collection with the all new PHOTON IV X-ray detector.

Unlocking Thin Film Disorder:
High-Energy Diffuse Scattering with CdTe HPC Detectors

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Diffuse scattering, though often weak, provides crucial insights into short-range order beyond intense Bragg reflections, profoundly impacting a material's macroscopic properties (e.g. electronic, optical, and mechanical). [1]

Hybrid Photon Counting (HPC) detectors address the challenge of simultaneously measuring weak diffuse scattering and strong Bragg diffraction. They offer noise-free detection and high count rate capabilities by rapidly counting individual X-ray photons. This removes electrical noise from the data and enables the accurate measurement of weak diffuse data while maintaining precision for strong reflections. Furthermore, energy thresholds suppress interference from X-ray fluorescence or cosmic radiation. [2]

The hybrid design of these detectors allows choices for sensor materials. While silicon sensors are efficient for low to medium X-ray energies, their quantum efficiency diminishes above 15 keV. In contrast, CdTe sensors available for DECTRIS HPC detectors maintain high quantum efficiency up to 100 keV (Figure 1b). [2]

Here we show that a CdTe-based area detector can accurately measure diffuse scattering from crystalline thin films, enabling three-dimensional difference pair distribution function (3D-ΔPDF) interpretation previously limited to single crystals. For this experiment 74 keV (0.17 Å) X-ray radiation was scattered from $PbTiO_3/SrTiO_3$ multilayer on $SrTiO_3$ using an ultra-small angle for grazing incidence diffraction (GID). High energy enables full coverage of reciprocal space up to a resolution of $(2\sin(\theta)/\lambda) = 2.2$ Å^{-1} and enables a geometry that reduces reflection smearing compared to medium energy-GID (Figure 1a). The resulting high-quality 3D-ΔPDF allows quantitative analysis of the disorder patterns in the $PbTiO_3$ layers. [3]

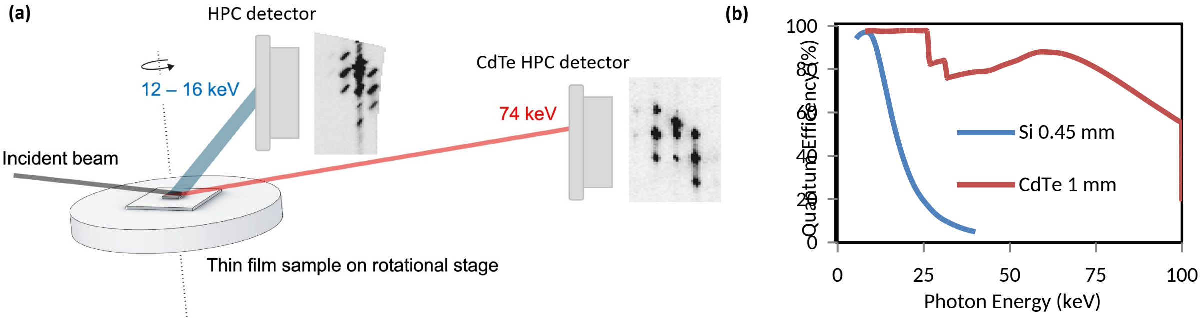

Figure 1- (a) Experimental setup for grazing incidence X-ray scattering, comparing medium-energy GID (blue) with high-energy GID (red). Detector images highlight how the high-energy setup reduces smearing around the 0 3 2 reflection. (b) Comparison of the quantum efficiency of a Si and a CdTe sensor as a function of photon energy.

By combining excellent dynamic range with modern sensor materials, HPC detectors are transforming our ability to comprehensively characterize materials. This capability is crucial for advancing our understanding of material properties and for guiding the design of next-generation functional materials where subtle structural details dictate performance.

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Control of liquid phase separation as a template for biomolecular self-assembly for industrial and biomedical applications

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As biomedical and biomaterial development accelerates and more complex systems are investigated and designed, there has been even more of a focus on battling degenerative disorders and diseases in our society.(1) Recently, Liquid-liquid phase separation (LLPS), already an interesting phenomenon that underpins many processes in the natural world and in our very bodies, has emerged as a potential platform to understand these disorders as well as template new materials and their intermediates for treatment.(2,3) Peptide mediated LLPS specifically has attracted much attention for its complex role in many disease (and treatment) pathways, as well as a platform for controlling crystallization for pharmaceutical compounds and crystals.(4) In this work we use the LLPS formation and growth pathways of oligocarbamates, peptide-like sequence defined synthetic polymers, as proof of concept for directing crystallization and stabilization of intermediate phases via ternary solution systems. Using *in-situ* coupled optical microscopy and Raman micro-spectroscopy, we monitor the evolution of sessile-drop evaporation driven LLPS and the formation of stable intermediate phases from solution. These intermediate phases are then characterized via AFM, OM and Raman micro-spectroscopy. This initial work is then used to guide the exploration of ternary-phase LLPS of two industrially and biomedically relevant peptide analogues: aspartame and kyotorphin. Formation pathways of intermediates are explored for fundamental interest and potential direct pharmaceutical and biomaterial applications.

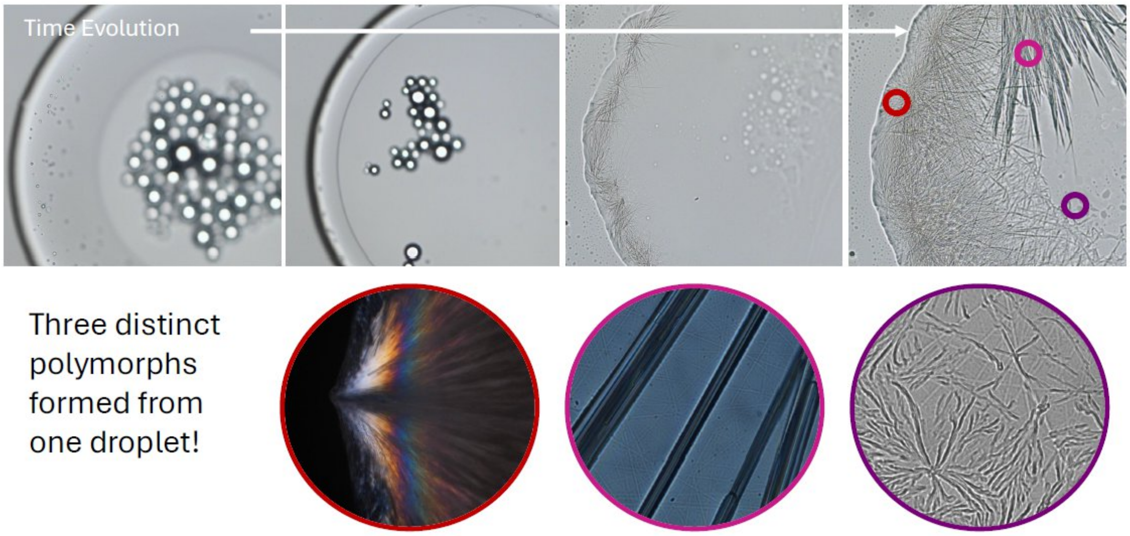

Figure 1- Time evolution of a complex, multicompartment liquid droplet formed by liquid phase separation of Aspartame solutions showing eventual assembly and crystallization of multiple different crystalline forms (measured by Raman Spectroscopy, not shown). Colored rings correspond to highlighted ex-situ optical microscopy images of three separate forms of aspartame formed from the droplet.

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Unveiling Magnetic Anisotropy in Layered Vanadyl Phosphates $Ni(VO)_2(PO_4)_2 \cdot 4\,H_2O$ and $Co(VO)_2(PO_4)_2 \cdot 4\,H_2O$ via Synergistic Magnetic, DFT+U Electronic Structure and Experimental Charge Density Studies

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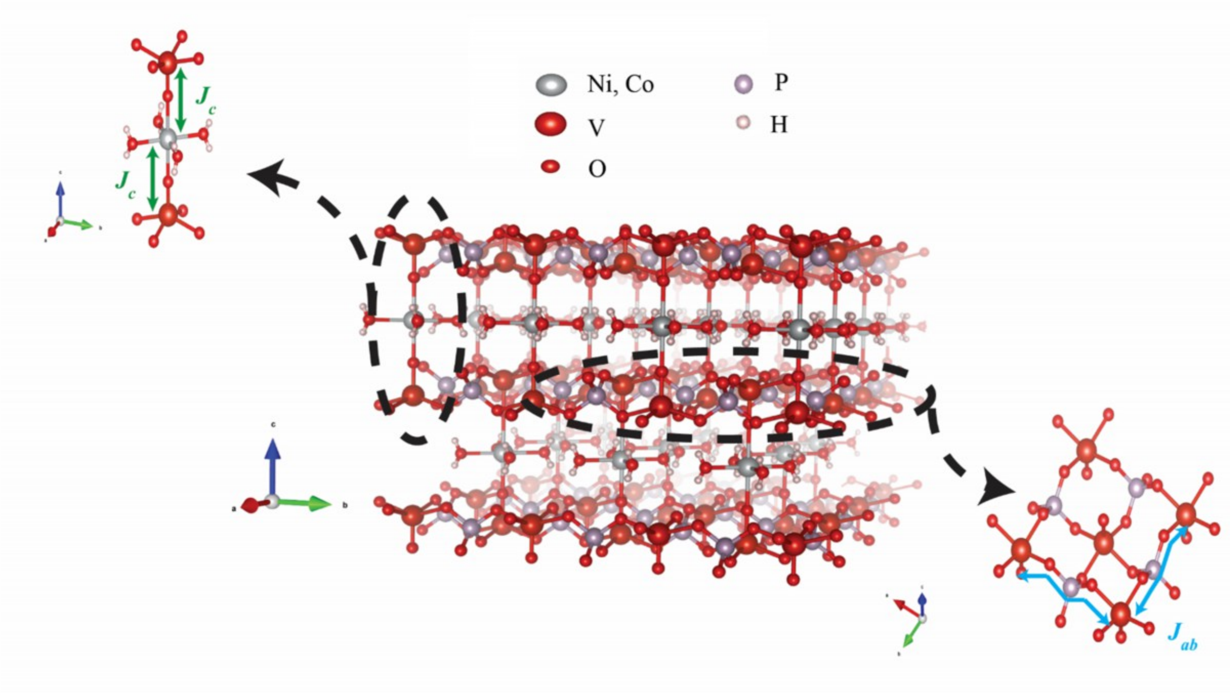
2D layered vanadyl phosphates and their metal-intercalated derivatives have long attracted interest due to their catalytic, optical, and magnetic properties [1]. When intercalated with 3d transition metals, they serve as model systems for studying geometrical frustration, low-dimensional magnetism, and anisotropy. This work focuses on two isostructural tetragonal compounds, $Ni(VO)_2(PO_4)_2{\cdot}4H_2O$ and $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ (space group I4/m), comprising V^{4+} square pyramids connected via phosphate tetrahedra into layers in the ab-plane. These layers are linked along c by linear V=O–M–O=V (M = Ni^{2+}, Co^{2+}) trimers, with M in octahedral $MO_2(H_2O)_4$ coordination (Figure 1).

Earlier models proposed bulk ferromagnetic coupling via an isotropic trimer spin Hamiltonian, assuming orthogonal e_g d-orbitals [2]. However, inverse susceptibility data suggest antiferromagnetic interactions. To clarify this, we combined oriented magnetic measurements on single crystals, DFT+U calculations, and X-ray charge density analysis.

Magnetic susceptibility measurements reveal anisotropic behavior: ferromagnetic along c, antiferromagnetic within the ab-plane, with partial moment cancellation. Long-range ordering emerges at 4 K, as confirmed by heat capacity data, with dominant low-dimensional antiferromagnetic correlations preceding 3D ordering.

Our interpretation of the exchange mechanisms is complemented by DFT+U calculations using CP2K code [3] and X-ray charge density measurements at 100 K, analyzed via Multipole Modelling (WINXD2024) [4], with a two-fold purpose of chemical bonding analysis and as comparison with theoretical transition metal d-orbital populations.



Layered structure of M(VO)2(PO4)2*4H2O compounds, showing trimer linker motifs (upper right) and Vanadyl phosphate layers (lower right), with magnetic super-exchange interaction pathways (green and blue arrows indicating interplane and intraplane pathways respectively)

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Discovering Vitrification Pathways in Zr-Based Metallic Glasses: Structural Insights from Microgravity Experiments

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Bulk metallic glasses (BMGs) offer a compelling route in materials discovery, enabling the design of new non-crystalline metallic alloys with exceptional strength, elasticity, and corrosion resistance.**[1]** These properties stem from their disordered atomic structure, which deviates from traditional crystalline metals and opens new frontiers for applications in extreme environments such as aerospace, energy, and defense.

This study investigates the structural evolution and glass-forming behavior of the Zr-based alloy Vit106a ($Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$) under varying processing conditions. Emphasis is placed on containerless electromagnetic levitation (EML) experiments conducted aboard the International Space Station (ISS), where microgravity enables the elimination of heterogeneous nucleation and gravity-driven segregation. Complementary thermophysical measurements, including viscosity, surface tension, and specific heat, were combined with structural analysis via X-ray diffraction (XRD) and wide-angle X-ray scattering (WAXS) on samples processed both terrestrially and in space.

Key findings reveal that Earth-based processing introduces Nb segregation and premature crystallization, hindering vitrification (see **Figure 1**). In contrast, containerless microgravity conditions facilitate deeper undercooling and reduced nucleation, enhancing amorphous phase formation. Remarkably, thermal modulation in the supercooled liquid state led to an 85 K drop in crystallization onset, suggesting a reversible liquid structural transition that alters nucleation kinetics. Viscosity measurements further confirmed a strong-to-fragile transition in the liquid, underscoring significant rearrangements in atomic mobility. These insights demonstrate the importance of liquid-state control in advancing the discovery and fabrication of new metallic glass materials.

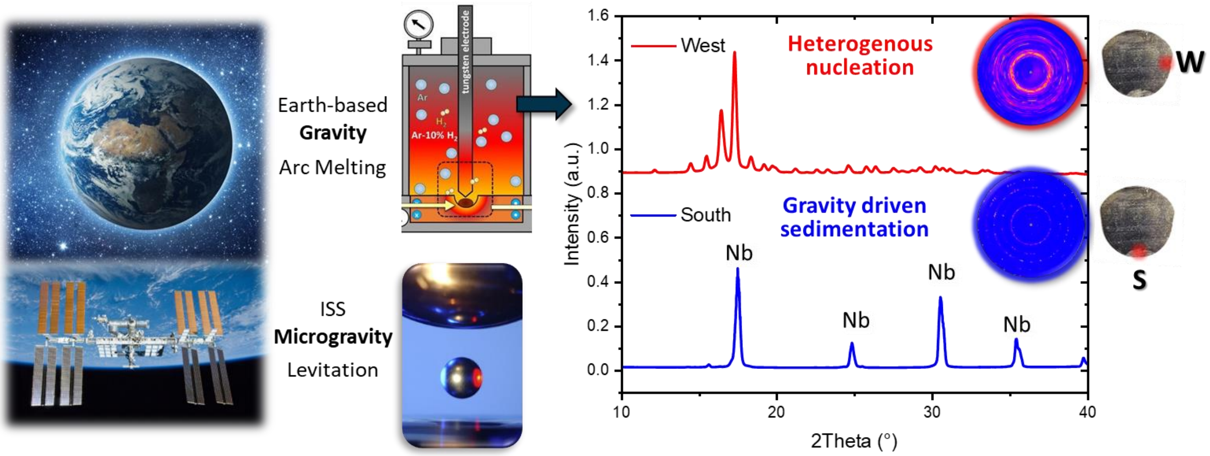

Figure 1- *Comparison of Zr-based bulk metallic glass (BMG) Vit106a processed on Earth via arc melting and under microgravity using electromagnetic levitation aboard the ISS. The WAXS patterns obtained in transmission mode for the Earth-processed sample reveal signs of heterogeneous nucleation at the edges (red curve) and Nb-rich phase segregation due to gravity-driven effects (blue curve), both of which hinder the formation of a fully homogeneous amorphous structure.*

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Collaborative Crystallography: Accelerating Discovery with DECTRIS CLOUD

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DECTRIS CLOUD is a web-based platform that reimagines how scientists collaborate, process data, and generate insight. Built around secure, real-time collaboration, the platform enables researchers to share datasets, software, and compute environments across global teams. Whether co-developing workflows or reviewing structural results, scientists can work together through browser-based access with no need for local setup or configuration.

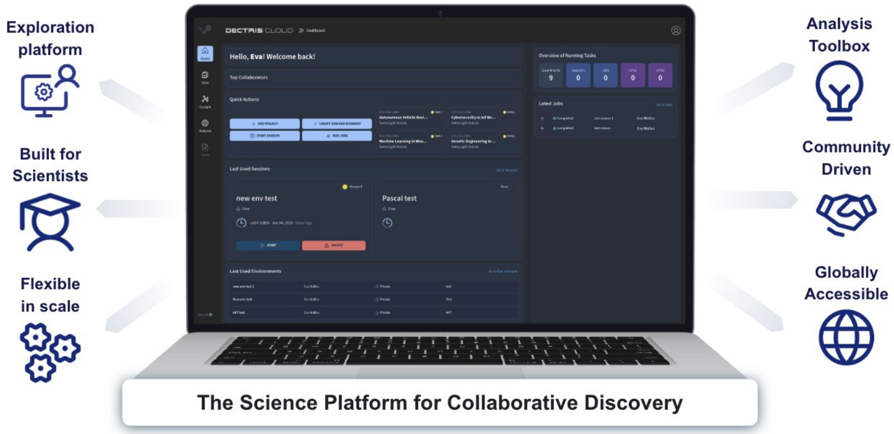

Figure 1- The DECTRIS CLOUD web application, an open platform for scientific discovery and real-time collaboration.

For crystallography, DECTRIS CLOUD brings together a comprehensive suite of community-curated software. These tools are available through ready-to-use, academic-licensed environments, while researchers can also create fully custom workspaces tailored to specific project needs with full control over the environment. The platform supports the entire crystallographic pipeline, from raw diffraction data to refined structures. Automated workflows support researchers through indexing, integration, structure solution, refinement, and analysis. Built-in virtual machines, Jupyter notebooks, visualization tools, and metadata curation features help document insights, support reproducibility, and strengthen data governance.

By eliminating computational barriers and reducing setup time, DECTRIS CLOUD allows scientists to concentrate on scientific challenges and discovery. The ability to collaborate effortlessly, adapt environments flexibly, and scale resources on demand makes it an ideal platform for advancing structural research.

Structural Evolution of $Sm_2Pt_{0.1}Ce_{1.9}O_7$ Solid Solution During Reductive Exsolution of Pt

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Exsolution is a promising approach for the synthesis of supported nanoparticle catalysts that maintain stable catalytic activity under harsh reaction conditions — such as dry reforming of methane (DRM) — in contrast to catalysts prepared by conventional approaches, such as impregnation.[1] The enhanced stability of exsolved catalysts is commonly attributed to the stronger interaction between the support and the highly dispersed metallic nanoparticles (NPs) (anchoring of the exsolved NPs), arising during the reductive treatment of the initially doped host oxide solid solution.[1] In this study, we have developed catalysts for DRM by exsolution of Pt NPs from $Sm_2Pt_{0.1}Ce_{1.9}O_7$ solid solutions synthesized via a sol-gel method. To gain a deeper understanding of the exsolution mechanism, we employed synchrotron X-ray powder diffraction (XRD), pair distribution function (PDF) analysis of X-ray total scattering data, and in-situ scanning transmission electron microscopy (STEM) to characterize the structural and morphological changes that $Sm_2Pt_{0.1}Ce_{1.9}O_7$ undergoes during the exsolution process. Our findings show that Pt is initially incorporated into the oxide structure, forming a random fluorite-type (*Fm-3m*) solid solution ($Sm_2Pt_{0.1}Ce_{1.9}O_7$) (Figure 1a). Upon a reductive treatment, Pt NPs of ≈ 2 nm in size (Figure 1b) emerged on the surface of the host oxide, while the host undergoes a structural transformation into a C-type (*Ia-3*) structure. This C-type structure is a superstructure of the fluorite phase, distinguished by the ordering of oxygen vacancies and displacement of cations from the initial fluorite lattice positions.[2] The results presented in this study provide mechanistic insights into the reductive exsolution from ceria-based materials, highlighting a relationship between structural changes in the host oxide and the formation of exsolved NPs.

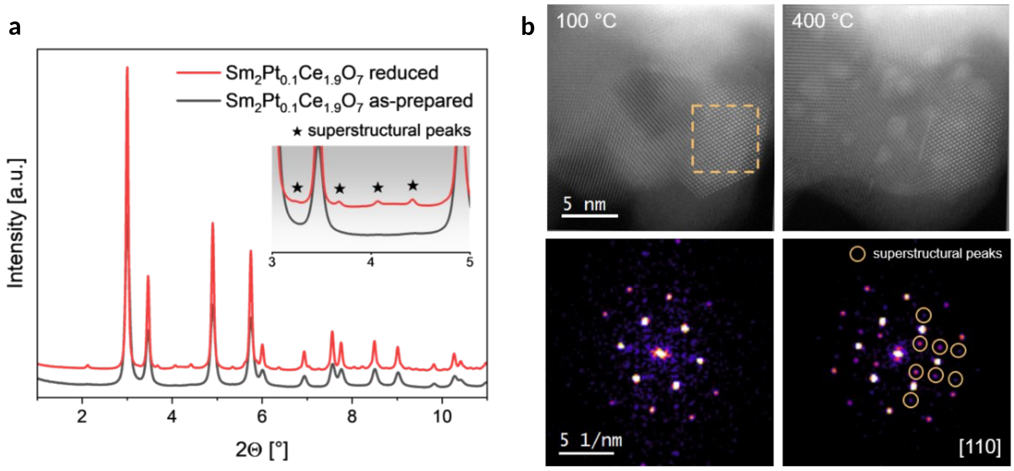

Figure 1. (a) XRD patterns of as-prepared fluorite-type $Sm_2Pt_{0.1}Ce_{1.9}O_7$ vs. reduced C-type $Sm_2Pt_{0.1}Ce_{1.9}O_7$, (b) HAADF STEM images of $Sm_2Pt_{0.1}Ce_{1.9}O_7$ at 100 °C vs. 400 °C with corresponding FFT patterns of a host oxide particle (in the dashed square) oriented along [110] zone axis.

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Structure determination from complex powder mixtures

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The search for novel material increasingly employes the use of combinatorial synthesis. Simultaneously, structure solution from powder diffraction data has become a more mature field. However, structure solution usually requires single phase diffraction patterns [1], while combinatorial synthesis typically yields complex diffraction patterns of mixtures. So far, only serial rotation electron diffraction [2] offers a good way to structure determination in such cases.

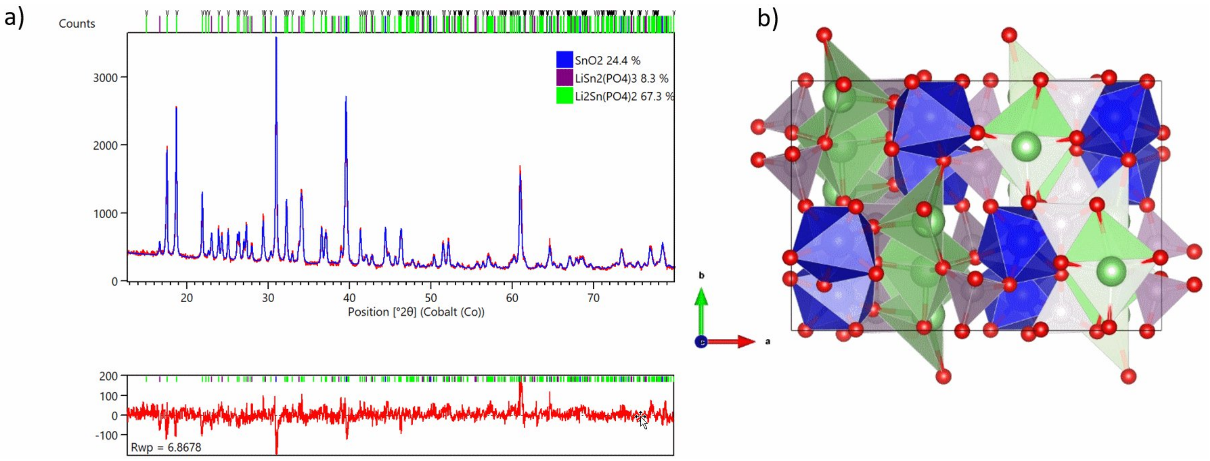

Figure 1 (a) Rietveld quantification and (b) crystal structure of the new ionic conductor $Li_2Sn(PO_4)_2$

We present an alternative way to obtain structure solutions from complex mixtures where we deconvolute the various contributions from different phases and solve these structures individually. This approach was first used during the exploration of new hydrates and layered materials [3, 4] using powder diffraction data of mixture data. Finally, it enabled us to report 2 new candidates, $A_2Sn(PO_4)_2$ (A = Li, Na), for battery electrodes which were found during our investigation of the system Li/Na-Sn-P-O and were solved from 5-minute scans on an Aeris compact XRD. Both constitute a new type with in the $A_2M(PO_4)_2$ series (A= Alkali ion, M = Zr, Ti, Sn). The accuracy of the structure solution has been verified by DFT calculations.

The reported method unlocks the full potential of powder X-ray diffraction for structure determination in combinatorial chemistry.

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Understanding and tuning the electronic structure of covalent organic frameworks

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Covalent organic frameworks (COFs) are crystalline, porous materials composed of light elements connected by strong covalent bonds. Their extended π-conjugation and tunable topologies make them promising for electronic and optoelectronic applications. However, understanding and predicting their electronic structure remains challenging due to the interplay between local building block chemistry and extended topology. This challenge is reinforced by the limited number of experimentally realized COFs and the difficulty of synthesizing well-ordered single crystals, which complicates structural characterization.

I will present two recent studies, in which we applied computational methods to rationalize and tune the electronic properties of COFs.

The first part will focus on how far the electronic structure of a COF can be understood from its molecular building blocks. While fragment-based approaches are well established for metal-organic frameworks, they are harder to apply to COFs, where covalent bonds form a continuous network and electron delocalization is not easily confined to individual subunits. We developed **deCOFpose**, an **automated fragmentation algorithm that identifies chemically meaningful units using a set of graph-based rules**. Applied to over 300 experimentally reported COFs, this approach enables large-scale analysis of the **relationship between fragment frontier orbital energies and full-framework band gaps**. The analysis shows that fragment electronic properties alone do not capture the electronic structure of the periodic COF. Improved correlations emerge when the dataset is restricted to chemically similar subsets, highlighting the combined influence of local chemistry and extended topology.[1]

The second part will address how **hydrostatic pressure and metal intercalation** change **the band structure** of COF-1, a prototypical two-dimensional framework. Compression up to 10 GPa results in a continuous band gap reduction of approximately 1 eV, which is larger than typically observed in other two-dimensional materials. Metal intercalation induces even more pronounced effects, and, in some cases, a transition to metallic behaviour. These findings demonstrate that pressure and intercalation are effective strategies for tuning the electronic structure while preserving the overall framework connectivity.[2]

Together, these studies illustrate different routes toward a deeper understanding and more systematic control of electronic properties in COFs, relevant to their application in electronic, sensing, and energy-related technologies.

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[2] Ernst, M., Hutter, J., Battaglia, S. (**2025**). Preprint: ChemRxiv (doi: 10.26434/chemrxiv-2025-4vprm)

An all-order phonon approach to thermal diffuse scattering

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In scattering experiments, phonons manifest themselves as Thermal Diffuse Scattering (TDS). Recent research has focused on phonons due to their role in various properties. This includes interactions like phonon-electron coupling in superconductivity and phonon-spin coupling, which finds application in spintronics, among other significant interactions. Understanding phonons and detecting phonon anomalies in materials is crucial in determining the material properties and their phase stabilities. Phonons are particularly important in elastic properties, with applications spanning from geology, where they aid in discerning planetary composition and temperature through the analysis of seismological wave propagation, to research in quantum phase transitions exploring their formation in crystals and interaction with other quasi-particles [1]. However, regular TDS, predominantly from acoustic phonon modes, often masks anomalies in phonons. While software exists for one or two-phonon processes, higher-order contributions are significant in certain systems. We are currently developing software capable of describing these higher-order contributions.

TDS arises from the scattering of X-rays by phonons and is present in all crystals. It contains valuable insights into phonon dispersion relations and the crystal elastic properties. Moreover, in many crystals static displacements give rise to intensity around the Bragg peaks which is very similar in shape to TDS, and thus can also be efficiently modelled using a similar approach. Currently, there are several programs available for modelling TDS, such as TDS2EL [2] and AB2TDS [3], however they have some limitations. In particular, TDS2EL allows to extract elastic constants from the TDS, but it can only model limited regions near Bragg peaks, while AB2TDS can cover all reciprocal space, but it utilizes single or two-phonon scattering approximations. In this work we propose a method to derive joint atomic displacement parameters which are used in conjunction with YELL [4] to model and fit real-space 3D-ΔPDF TDS signals efficiently. This approach avoids the need for large real-space models and offers good computational efficiency. Joint atomic displacement parameters are calculated based on the crystal's dynamical matrix, which can be derived using various methods, including universal potentials [5], DFT-based [6] approaches, or, in an approximated fashion, from the elastic constants of the material.

Our objective is to develop user-friendly software capable of describing TDS and TDS-like static disorder. Our approach offers faster computation compared to existing software and will be a valuable tool in the suite of 3D-ΔPDF software. It will facilitate the extraction of elastic constants from diverse materials and has the potential to be extended to extracting the portion of dynamical matrix responsible for high-amplitude soft phonons.

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pgtrainer : a classroom tool and 3D models for teaching point group symmetry

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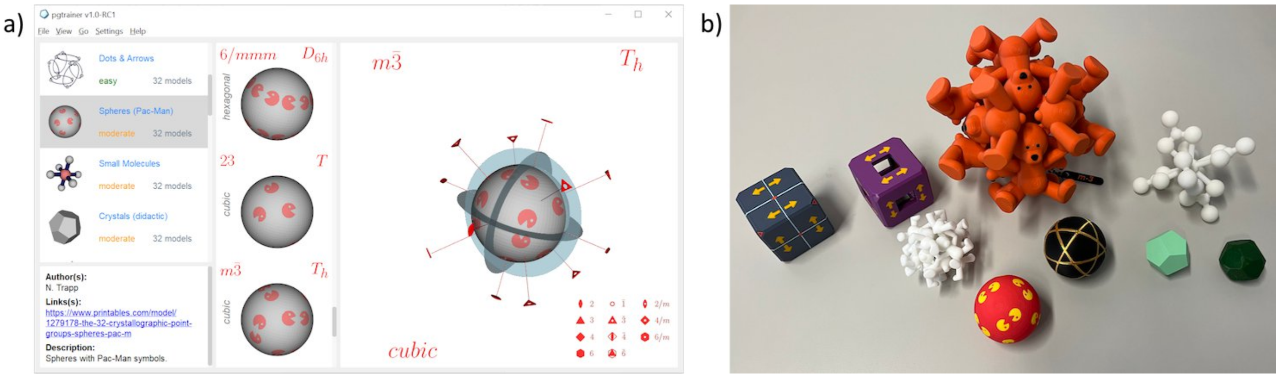
pgtrainer is a simple viewer program designed to assist with teaching point group symmetries, specifically the 32 crystal classes. It comes bundled with hundreds of different 3D models arranged in themed sets, such as crystal shapes, molecules or objects from daily life, with the intention of lowering the barriers for self study. The program has a simple & uncluttered interface, making it suitable for both projection in a lecture setting and practicing at home. Included models can be downloaded individually, and most are suitable for 3D printing.[1,2]

Models can be navigated by mouse, keyboard or presenter, and rotated/scaled/moved manually or automatically. Point group symmetry elements can be projected on the models. The user interface and displayed information are configurable and can be controlled with hotkey commands. This is a work in progress, i.e. more features will be added to the program. Installers for Windows and MacOS are available to download.[3]



Author(s):
N. Trapp
Links(s):
https://www.printables.com/model/1279178-the-32-crystallographic-point-groups-spheres-pac-m
Description:
Spheres with Pac-Man symbols.

Figure 1- Screenshot of the main *pgtrainer* program window with all GUI elements activated (a) and physical models representing point group $m\bar{3}$ (b). White models were produced by an online 3D printing service (resin), colored models were printed on a hobby-level FDM printer.

Implementing more models into the program is relatively easy if they exists in .stl or .obj format. If you have your own and are interested in sharing them under a free license, please get in touch with the authors.

[1] https://www.printables.com/@ntdesign/collections/2283402
[2] https://www.thingiverse.com/aarono/designs
[3] https://gitlab.ethz.ch/trappn/pgtrainer

How Different Can Water Be?

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The distribution of O-H bond lengths in water molecules within crystalline hydrates reported in the Cambridge Structural Database (CSD) demonstrated a significant discrepancy between the dataset of structures measured using both X-ray and neutron diffraction, and those determined exclusively by neutron diffraction. While neutron structures exhibited a mean bond length of 0.959 Å ± 0.033 Å, the combined neutron and X-ray dataset showed an artificially shortened mean covalent bond length (0.861 Å ± 0.070 Å). The reason for the disagreement between the two datasets was primarily found in the standard refinement model, the Independent Atom Model (IAM), which systematically underestimates hydrogen positions. It was estimated that 60,000 of the 90,000 hydrate structures in the CSD may contain incorrect bond parameters, and require re-refinement using Hirshfeld Atom Refinement (HAR).

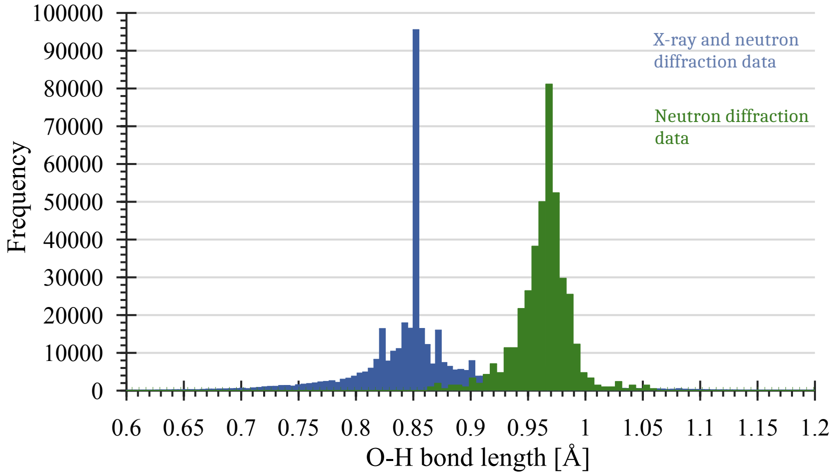

Figure 1- O-H bond length distribution of water in crystalline hydrates reported in the Cambridge Structural Database (CSD). In blue, hydrates measured with X-ray and neutron diffraction. In green, hydrates measured with neutron diffraction.

The presence of outliers in both datasets was attributed to the low energetic penalty associated with H-O-H bond angle deformations in isolated water molecules, as indicated by a potential energy scan in the gas phase. Thus, in the crystalline environment, such a small energy cost may be offset by favorable intermolecular interactions, allowing for a broader distribution of bond angles.

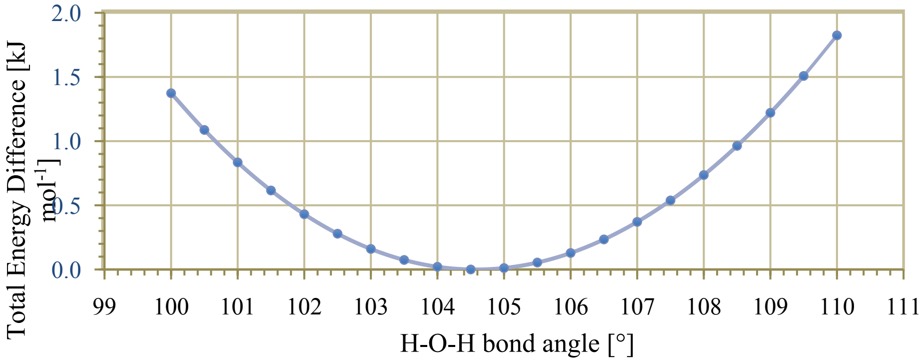

Figure 2- Potential energy scan of the H-O-H bond angle deformation in an isolated water molecule, calculated at the CCSD/def2-QZVP level of theory. The energy minimum occurs at 104.56°, with deviations of ±5° requiring less than 2 kJ mol^{-1}, indicating a low energetic cost for moderate bond angle distortions.

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Efficient Soft-Chemical Synthesis of Large van-der-Waals Crystals of the Room-Temperature Ferromagnet 1T-$CrTe_2$

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We herein report on a fast and convenient soft-chemical synthesis approach towards large 1T-$CrTe_2$ van-der-Waals crystals. 1T-$CrTe_2$ is a metastable room-temperature ferromagnetic van-der-Waals material with a Curie temperature of $T_C \sim 320$ K, which was first mentioned by Freitas *et al.* in 2015.[1] This compound is formed X-ray diffraction pure, with a complete conversion within just over 2 h from flux-grown $LiCrTe_2$ crystals [2] using diluted acids. Deintercalation of $LiCrTe_2$ using iodine, previously reported for the deintercalation of $KCrTe_2$ [1,3,4], was significantly slower and yielded partially deintercalated crystals. Due to the availability of high-quality single crystals, we have confirmed the crystal structure for the first time by single-crystal X-ray diffraction experiments. For the acid deintercalated 1T-$CrTe_2$ crystals, we find long-range ferromagnetic order with a Curie temperature of $T_C = 318$ K. We further revealed the magnetic structure of 1T-$CrTe_2$ using low-temperature neutron powder diffraction experiments. X-ray diffraction experiments of postannealed crystals suggest a thermal stability of 1T-$CrTe_2$ up to at least 100 °C. Our findings expand the synthesis methods for 1T-$CrTe_2$ crystals, which hold promise for integrated room-temperature spintronics applications. [5]

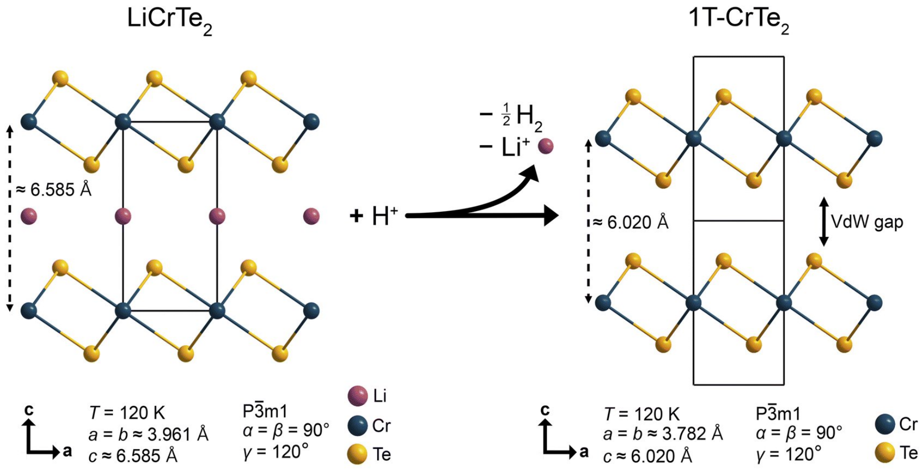

Figure 1: Acid-assisted synthesis of 1T-$CrTe_2$: Scheme of the deintercalation reaction of $LiCrTe_2$ with an acid and the respective cell parameters of $LiCrTe_2$ an 1T-$CrTe_2$.

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Stabilizing Metastable l-V_2O_5 via Pillaring: Single–Crystal to Single–Crystal transformations for Advanced Lithium–Ion Cathodes

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Email: *sarbajeet.chakraborty@psi.ch* **Please name your file Name-SSCr2025-Title.docx**

The growing demand for high-performance lithium-ion batteries necessitates cathode materials with enhanced stability and energy density. Vanadium pentoxide (V_2O_5) has emerged as an enticing candidate, offering high theoretical capacities (~441 mAh/g), but the structural degradation experienced by the thermodynamically stable polymorph, α-V_2O_5, during cycling precludes it from application. Instead, we are exploring the metastable polymorphs of V_2O_5 and utilizing pre-intercalation strategies to improve the host's structural resilience, using single-crystal electrochemistry to probe ion diffusion at the atomic scale. This approach is particularly effective in layered frameworks, where the strategic insertion of cations expands the host's interlayer spacing as means towards mitigating ion diffusion bottlenecks and suppressing shear transformations. We are currently investigating single crystals of a metastable, double-layered l-V_2O_5 polymorph synthesized via topochemical routes. Its wide (~8.5 Å) interlayer spacing enables the pre-intercalation of Na^+ and K^+, producing a pillared structure with enhanced structural rigidity. The single crystals were subsequently topochemically treated to insert Li^+ ions and subsequently *ex situ* single-crystal X-ray diffraction provided the exact crystallographic positions of the Na^+ and K^+ ions, as well as the topochemically inserted Li^+ cations. Notably, the l-$K^xV_2O_5$ phase exhibits significantly reduced lattice distortions compared to the empty l-V_2O_5, underscoring the stabilizing effect of the inserted pillaring ions. This enhanced stability is also reflected in the electrochemical studies, which show that l-$K_xV_2O_5$ achieves superior capacity retention and cyclability. Galvanostatic Intermittent Titration Technique (GITT) measurements reveal Li^+ diffusion coefficients several orders of magnitude higher than those in conventional l-V_2O_5 phases. Ergo, single-crystal-to-single-crystal topochemical transformations reveal ion-specific responses. For example, Li^+ intercalation induces Na^+ rearrangement but does not affect the K^+ ions, demonstrating the nuanced role of the pre-intercalated ions in governing transport kinetics and rate performance. By leveraging structural insights at the atomic scale, our work elucidates ion coordination environments and lattice dynamics in layered oxides. These findings lay the foundation for the rational design of next-generation cathodes with improved performance metrics.

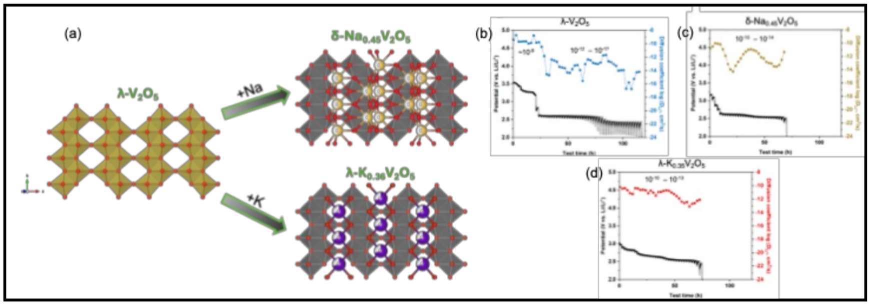

Figure 1. (a) Topochemical insertion of double-layered V_2O_5. The depicted crystal structures were obtained from single crystal diffraction of the herein synthesized for the empty l-V_2O_5, d-$Na_{0.45}V_2O_5$, and l-$K_{0.36}V_2O_5$, viewed down the *b*-axis. (Color key: Na, yellow; K, purple; polyhedral, VO_6). Li-ion diffusivity of (b) l-V_2O_5, (c) d-$Na_{0.45}V_2O_5$, and (d) l-$K_{0.36}V_2O_5$ measured by GITT. Black empty circles represent potential variation as a function of discharge/charge. Solid marker with solid line represents Li-ion diffusivity.

High Pressure Research at Swiss Neutron Source

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The Swiss neutron source SINQ at Paul Scherrer Institute has recently undergone an extensive upgrade improving the versatility of several instruments as well as increased neutron flux. The increased performance opens up more opportunities for advanced-sample-environment research, such as experiments involving high pressure. In this contribution, we will present the current status of high-pressure sample environment at SINQ and will discuss our future plans.

[1] https://www.psi.ch/en/lin/high-pressure-experiments

Uniaxial Control of Cuprate Superconductors

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Quantum matter is characterised by competing and intertwined orders. Here I will present our recent advances in using uniaxial pressure as a clean “surgical” tool to tune quantum phases while simultaneously obtaining microscopic insights via scattering experiments. The realizations of the experiments are achieved through technical developments by minimizing the background and enabling the tuning in-situ [1]. First, we study spin order in cuprate superconductors characterized by small moments, which remains challenging for pressure studies. We overcome this challenge by designing a low-background uniaxial strain cell, optimizing the experiment based on neutron-tracing simulations and using aggressive focusing and energy analysis. We show that the spin order parameter in cuprates is uniaxial and coupled to the charge channel [2]. We further show how superconducting transition temperature is affected by uniaxial pressure applied in different directions by combining uniaxial pressure and polarized neutron scattering [3]. To achieve the fine-tuning in-situ, we have designed a new in-situ uniaxial device for largescale facility research based on an actuator-motor mechanism, efficient feedback loops and the sample-holder design enabling rapid exchange of the samples [4]. I will demonstrate the advanced capabilities of this device by reporting the control of charge and structural degrees of freedom as studied by X-rays in an archetypical cuprate [5,6].

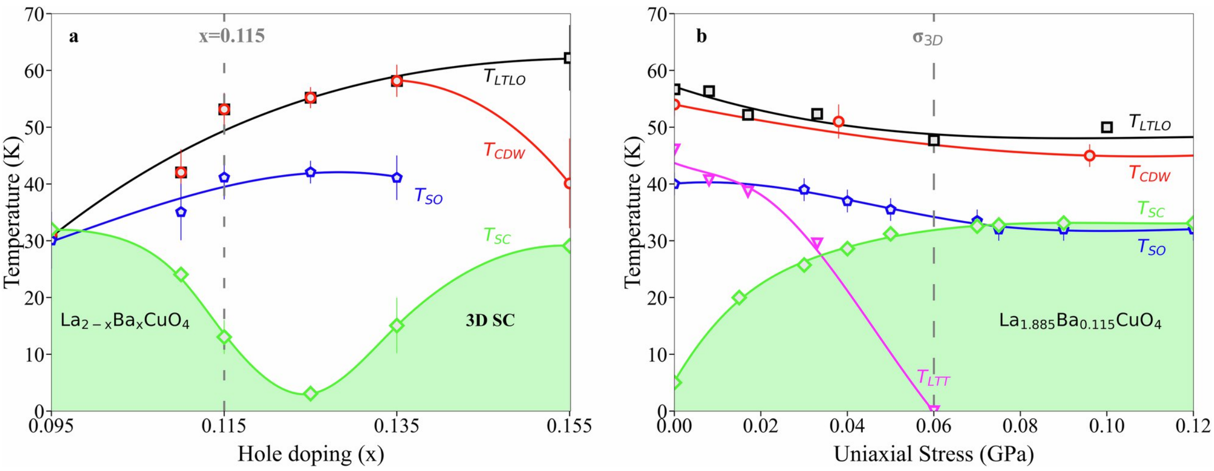

Figure 1- Phase diagram of a La-based cuprate, showing the multiple electronic and structural phases and indicating with a gray dashed line the part of the slice of a phase diagram that was explored using uniaxial tuning. The green area represents phase space where three-dimensional superconductivity (3D SC) is established and the solid lines are guides to the eye of the onset temperatures of charge density wave (TCDW), spin order (TSO) and low-temperature less-orthorhombic (TLTLO) crystal structure. b The complete phase diagram as a function of uniaxial stress, around the doping of x = 0.115, where the multiple degrees of freedom and corresponding phases are modified. As superconducting temperature is increased with stress, the transition temperatures of charge density wave and spin order are suppressed, together with the reduction of macroscopically occupied volume fraction. Notably, the structural low-temperature tetragonal (LTT) phase is completely suppressed at moderate stress, yet the electronic stripe order persists throughout the studied pressure range, albeit with a reduced volume fraction. All changes saturate above the meager stress of σ3D ≈ 0.06 GPa [6].

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The role of magma mixing in the petrogenesis of melilite-bearing nephelinite from southeast China

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Magma mixing is widely acknowledged as a prevalent magmatic mechanism [1], yet its significance in the formation of coexisting nephelinite and melilitite has frequently been overlooked. This oversight stems from the conventional assumption that nephelinite forms either through fractional crystallization from melilitite or directly sources from the mantle and rapidly traverse the crust [2, 3]. To bridge this knowledge gap, we provide a comprehensive petrological analysis of melilite-bearing nephelinite in Southeast China, which serves as a compositionally transitional facies between nephelinite and melilitite. This lava exhibits a distinctive mineral assemblage, including olivine, nepheline, clinopyroxene, titanomagnetite, melilite, perovskite, monticellite, cancrinite, and sodalite—a combination first documented in nephelinitic lava flows. Crystals within this assemblage commonly display disequilibrium textures and intricate zoning patterns. Based on mineral textures and coexisting mineral phases, we infer that the unique mineral assemblage in the Yongquan melilite-bearing nephelinite results from the mixing of pre-existing nephelinitic magma with a recharged melilititic magma (Figure 1). Thermodynamic calculations outline a two-stage petrogenetic process for this rock type. The initial stage involved the crystallization of olivine-nephelinite melt at depths of approximately 18 km under moderate undercooling conditions. Subsequently, a hydrous (3.97–4.40 wt.% H_2O), high-temperature (> 1060 °C) melilitite melt was emplaced into shallower (~11 km) magma conduits, initiating mixing with the resident magma. Thus, we conclude that mixing processes are pivotal in the petrogenesis of coexisting melilitite and nephelinite, rather than a straightforward evolution from melilitite magma. The groundmass zoning and phenocryst characteristics in nephelinite magmas reveal short-timescale dynamics, highlighting the necessity of integrating textural data with bulk-rock compositions for precise source signature interpretation.

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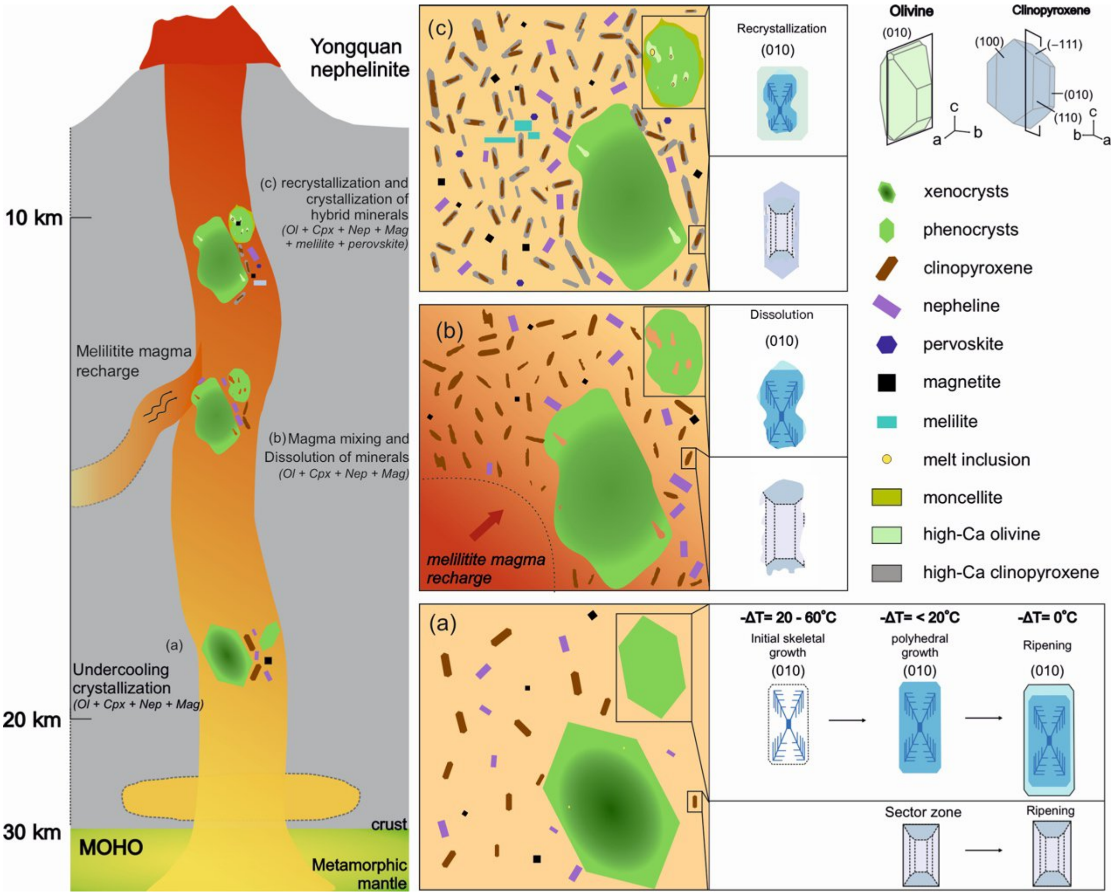

Figure 1-Schematic evolution model of magma mixing between nephelinite and melilitite magma resulting in the formation of the Yongquan nephelinite. (a) During rapid ascent, the low water content olivine nephelinitic melt underwent kinetically controlled crystallization at moderate-to-low undercooling, sequentially forming dendritic to polyhedral olivine phenocrysts with P-rich zoning, sector-zoned clinopyroxene, nepheline and magnetite at 1010–1050 °C. (b) The injection of a high-temperature, H_2O-rich melilititic melt (> 1060 °C; 3.97–4.40 wt. % H_2O) into magma conduits at ~11 km depth prompted mixing with the resident olivine-nephelinite melt. The resulting thermodynamic disequilibrium dissolved pre-existing olivine and clinopyroxene, producing resorption textures. (c) The ensuing disequilibrium promoted reactive growth of monticellite and high-Mg$^{\#}$ clinopyroxene rims. Continued cooling then initiated fractional crystallization, sequentially precipitating diopside, melilite, nepheline and perovskite.

Crystal Growth and Characterization of Ytterbium-Based Silicate Materials

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The family of rare earth (RE) based silicate materials is quite vast, not only in terms of possible chemical compositions, but also in terms of the available crystal structures. In particular, the RE_2SiO_5 (monosilicate), $RE_2Si_2O_7$ (disilicate) families have attracted a lot of attention, mainly due to their polymorphic behavior as well as their peculiar physical and chemical properties. For example, the disilicate phase has at least seven known polymorphs that can be obtained based on the composition and temperature shown in figure 1 [1]. Meanwhile, the monosilicate system has two possible polymorphs referred in the literature as either X1 or X2. The X1 polymorph is always obtained with larger RE ions (La – Gd), however, in the case of smaller RE ions (Tb – Lu) X2 can be stabilized by using a relatively low calcination temperature between 900 and 1100 °C [2]. The natural abundance of the crystal structures as well as broad chemical composition ranges of rare-earth silicates led to an investigation of potential applications as either host materials for luminescence or for their scintillation properties. More recently, the silicates are being investigated as thermal barrier coating due to their thermal conductivity [3]. At the same time, their magnetic properties largely remain unexplored.

However, while promising the RE based silicates suffer significantly due to the lack high-quality single phase samples. The main reason for this is that the different phases, be it RE_2SiO_5, $RE_2Si_2O_7$ or even the apatite ones are quite close in stability. As such, when preparing bulk samples, one often obtains a mixture of all or some of the phases. To further and unambiguously investigate the fundamental properties of the RE silicate materials, high-quality crystal samples are required. In this work we present the synthesis and crystal growth of Yb_2SiO_5 and $Yb_2Si_2O_7$ using a laser diode optical floating zone furnace. We also investigate their crystal structure and quality by means of powder and single crystal X-ray diffraction as well as Laue diffraction.

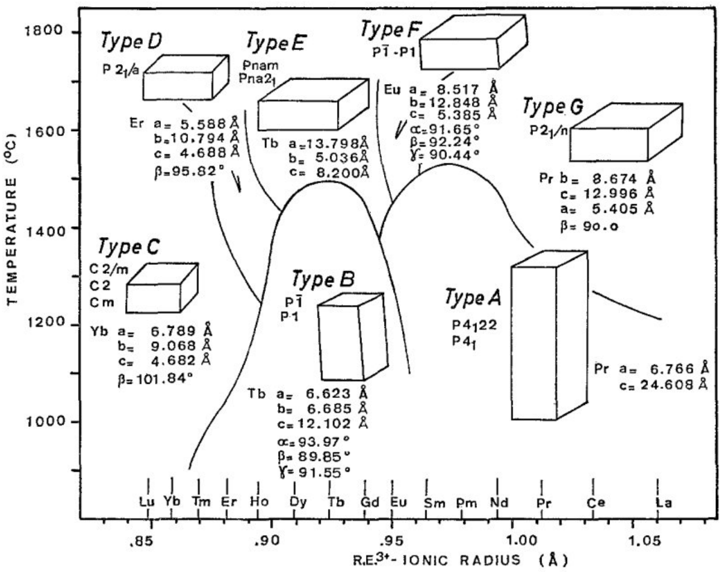

Figure 1- Graphical representations of the molecular structures of possible crystal structure of the rare earth disilicate compounds [1].

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SAXS-guided Design of Responsive Microemulsion

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Microemulsions are mixtures of water, oil, surfactant, and co-surfactant that spontaneously self-assemble into nanostructures depending on composition and environmental conditions.[1] They are thermodynamically stable and, depending on the curvature of the surfactant/co-surfactant layer can exist as oil-in-water coexisting with excess oil, water-in-oil with excess water, or bicontinuous systems with oil and water dissolved in a single phase. While the phase behavior of these systems have been studied for decades, typically varying composition, temperature or ionic strength, the formation of food-grade, stimuli-responsive microemulsions that can switch reversibly between these states remains a challenge.[2]

In this presentation, we demonstrate the formulation and characterization of novel, pH-responsive microemulsions using food-grade, polar lipids.[3] The interfacial tension between oil and water in these microemulsions is studied with spinning drop tensiometry, and their nanostructures in solution and as thin films coated onto surfaces are analyzed using Small-Angle X-ray Scattering (SAXS) and Grazing-Incidence SAXS (GISAXS) combined with numerical data modelling. These techniques enable a detailed understanding of how self-assembly and interfacial behavior are influenced by compositional and pH changes. Finally, we examine how these findings contribute to understanding phase transitions in complex fluids and how such systems hold potential for applications in nutrient extraction.

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The $CaSO_4$-antibiotic system: Structural insights into the uptake and release mechanisms for infection treatment

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The discovery and development of new materials are crucial for overcoming the existing challenges in infection management, particularly in orthopedic and trauma surgery.[1] Local antibiotic therapy enables the delivery of antibiotics directly to bone and joint infections, while minimizing systemic toxicity.[2] Calcium sulfate ($CaSO_4$) has gained attention as a promising osteoconductive carrier for antibiotics, such as vancomycin,[2] ceftriaxone,[3] and tobramycin[4] due to its biocompatibility and biodegradable properties. This study aims to investigate the molecular interactions and controlled uptake mechanisms of antibiotic-loaded $CaSO_4$ carriers.

We employed powder X-ray diffraction (PXRD) as the primary technique for in-situ kinetic studies of drug-carrier interactions at the molecular level. PXRD was used to track in real-time the polymorphic transition from hemihydrate to gypsum,[5] a process intrinsically linked to the hydration state of the $CaSO_4$ matrix loaded with various antibiotics (Fig. 1). Kinetic analysis revealed distinct transformation rates: 0.040 ± 0.015 min^{-1} for $CaSO_4$_Ceftriaxone, 0.045 ± 0.005 min^{-1} for $CaSO_4$_Vancomycin, and $0.002 \pm 5\times10^{-4}$ min^{-1} for $CaSO_4$_Tobramycin. Understanding of drug-carrier interactions is supporting the advancement of local antibiotic delivery, improving infection management and clinical outcomes in orthopaedic and trauma surgery.

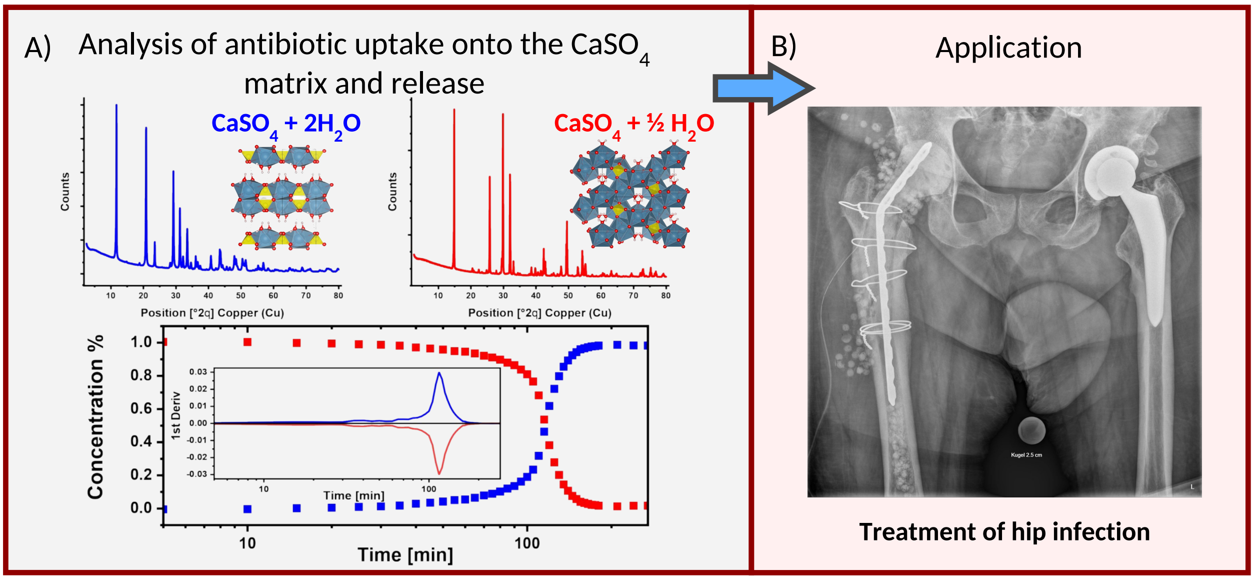

Fig. 1: Summary of analysis and application of the studied materials

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Disorder structure determination by 3DΔPDF analysis of a Dy-based metal–organic framework

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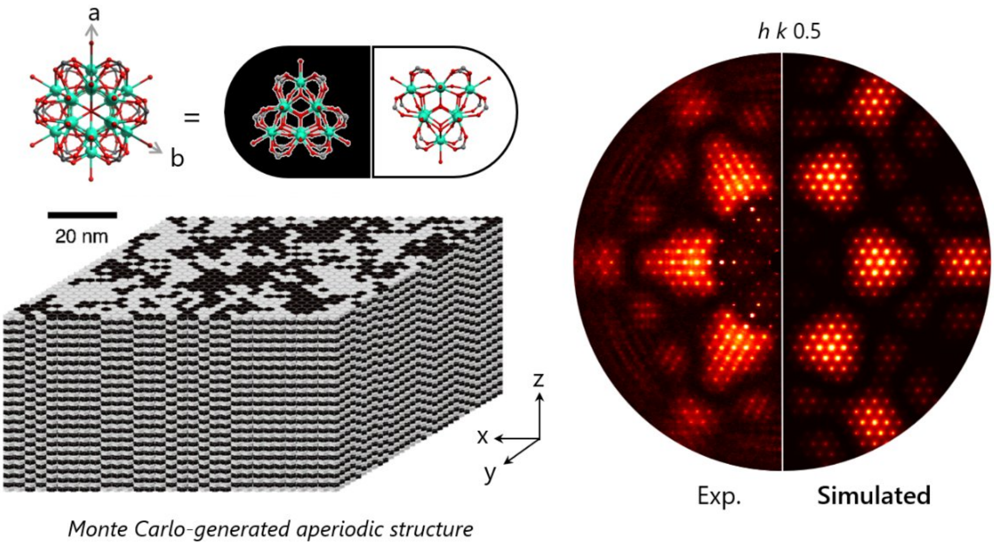
A novel lanthanide MOF, UoB-100, containing Dy based metal nodes was found disordered in its average crystal structure. Inspection of the diffraction planes reconstructed from laboratory single crystal X-ray diffraction data revealed structured broad intensities containing information on the local arrangement of cluster disorder. A combination of single crystal 3D delta pair distribution function [1] and Monte Carlo simulations afforded a realistic nonperiodic model for the atomic structure of UoB-100, which reproduces the total scattering observed in diffraction experiments [2]. This case study exemplifies the power of 3D total scattering analysis for the combined structure determination of average and real structure of MOFs, thereby providing essential information for tuning distribution of species, defects and disorder towards finer control over their complex emergent properties [3].



Igure 1. Simulated realistic distribution of cluster orietations in the disordered UoB-100 (left), and resulting diffuse scattering pattern, side by side with the experimentally observed one (right).

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Hydrogen storage in ice matrices at high pressure

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Hydrogen hydrates are promising functional materials for clean energy storage and offer alternative to the current cryo-compressed hydrogen storage technology, insuring low production and operational costs, environmentally benign nature, and lower risk of flammability. Hydrogen hydrate clathrate sII phase transitions into to the so-called “filled ice” forms above 0.8 GPa. In filled ice, the water frame assumes one of the known ice phases, and hydrogen occupies definite positions in the ice channels. Up to ~3 GPa, five different phases have been reported (C_{-1}, C_0, C_1, C_1’, and C_2 respectively), with increasing hydrogen-to-water ratio [1-2]. Recently, a new C_3 phase with a hydrogen-to-water ratio of 2:1[2] forming above 40 GPa, upon laser heating (~1200 K), and being stable up to 90 GPa, has also been observed.

It has been shown that the C2-form of hydrogen hydrate ($H_2O{\cdot}H_2$/ $D_2O{\cdot}D_2$), which is constituted by an ice I_c skeleton, transforms into pure cubic ice Ic releasing molecular hydrogen upon decompression at 100 K [3]. However, the mechanism and kinetics of C2 hydrogen loss is not well-defined. It was suggested to progress through sample amorphization, though no evidence of an amorphous intermediate state was observed by neutron diffraction. We have recently determined, via high-pressure neutron powder diffraction experiments, that the unit cell volume of the C2 phase-produced in a Paris-Edinburgh (PE) cell at 3 GPa, and then recovered at ambient pressure and 78 K - continuously decreases upon heating above 100 K at ambient pressure. This indicates, at least partial, controlled hydrogen release without loss of crystallinity up to 130 K and the capability of C2 to store hydrogen up to 100 K at ambient pressure. Additionally, we present insights into structural deformation, phase boundaries, hydrogen content and mechanisms of formation of C2 under extreme pressure and/or low-temperature conditions. [4].

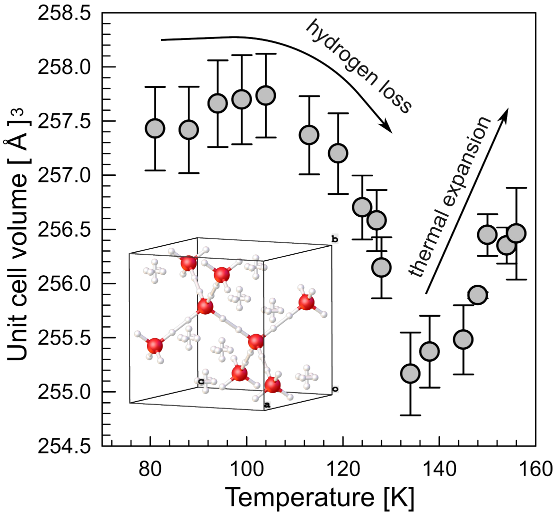

Figure 1- Unit cell volume variation during thermal decomposition of C2 hydrogen hydrate tracked with neutron powder diffraction (D20 at ILL). Inset: contents of the unit cell of C2 (oxygen in red)

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Effect of Deuteration on Glycine Crystallization: In Situ Raman Spectroscopy Insights into Non-Classical Nucleation and Polymorph Stability

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Crystallization from the liquid phase is a central process in materials synthesis, purification, and pharmaceutical formulation. A key challenge in this domain lies in understanding and controlling polymorphism—the ability of a compound to form multiple crystalline structures—which can significantly impact solubility, stability, and functionality of the final product. The effect of deuteration on crystallization behavior has been discussed in several occasions, because the use of deuterated solvents is essential for some characterization techniques. Some recent studies have reported the effect of deuteration on nucleation rates and polymorph outcomes, but the mechanisms underlying these differences remain elusive.

Glycine, a simple amino acid with three well-characterized polymorphs (α, β, and γ), serves as a model system for investigating such effects. Under ambient conditions, α-glycine typically forms in H_2O. In contrast, in D_2O, there are many literatures reporting the observation of γ-glycine—thermodynamically the most stable polymorph. However, some also reported no difference between H_2O and D_2O. The discrepancies in literature motivated us to explore the effect of isotopic substitution on glycine polymorphs by using in situ Raman spectroscopy as a main tool.

In this work, we combined Single Crystal Nucleation Spectroscopy (SCNS) [1,2] and bulk crystallization characterization methods. SCNS enables one to monitor the Raman spectral evolution of polymorphic transitions at the single crystallization level. Our results show that in both H_2O and D_2O, glycine undergoes a non-classical crystallization process: formation of prenucleation aggregates leads first to β-glycine, which rapidly transforms into α-glycine. While a slight longer stability of β-glycine was observed in D_2O, γ-polymorph was never observed. To compare the two systems at bulk crystallization level, we performed the measurement of crystallization induction time at 20 ℃. Using the histogram of induction time, the nucleation rate and critical nucleus size were extracted. These values were, however, found similar between H_2O and D_2O, with about three times slower nucleation rate in D2O. We characterized the polymorph of glycine crystals formed in the vials used for induction time measurement. Only α-polymorph was observed.

The puzzle of searching γ-polymorph was solved when we widened the crystallization condition further: crystallization from high degree of supersaturation ($SS > 2.0$) or crystallization at low temperature. These conditions were achieved by either rapid solvent evaporation or cooling. Rapid solvent evaporation revealed that γ-glycine formed only from D_2O and not in H_2O. Under rapid cooling conditions, it was found that γ-polymorph appeared in both H_2O and D_2O. Remarkably, the stability of β-glycine in D_2O appeared higher and it persisted for longer than 30 min in many conditions. DSC measurements confirmed the enhanced thermal stability of the deuterated glycine compared to glycine.

Collectively, we conclude that major effect of deuteration in the glycine crystallization is on the stability of β-glycine, which increases the probability of forming γ-polymorph in D_2O. The effect of deuteration at the molecular level as well as the microscopic picture of how polymorph stability is altered will be discussed. This work contributes to the broader effort of rationally controlling polymorphism in molecular solids.

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Synthesis and Crystallography of a Tetranuclear Copper Cluster with μ₃-Methoxy Bridge Featuring Vacant Coordination Sites for Biomimetic Reactions

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In this study, a dinuclear copper complex was synthesized using the salt $[Cu(CH_3CN)_4]PF_6$ (containing Cu(I)) and the tridentate Schiff base ligand H_3L. The precipitate obtained from the reaction was dissolved in methanol, and upon diffusion of n-hexane into the methanolic solution, under aerial oxidation, two dinuclear subunits connected via triply bridging methoxy groups (μ_3-OMe, derived from methanol) to form a tetranuclear Cu(II) copper cluster. In this cluster, each copper ion exhibits a distorted square pyramidal geometry and provides a vacant coordination site for catalytic reactions. This complex, inspired by the dinuclear active site of the catechol oxidase enzyme, can be utilized in biomimetic reactions such as catechol oxidations and phenoxazinone synthase.

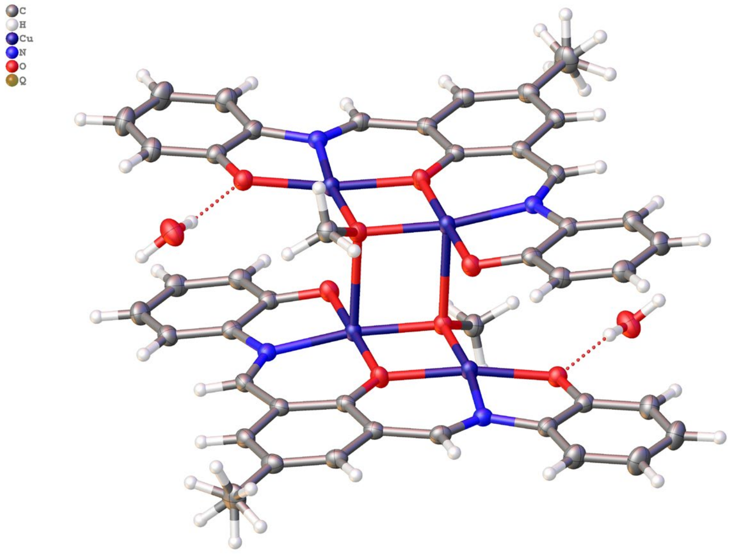

Figure 1- Molecular structures of $[Cu_4L_2(\mu_3\text{-}OMe)_2].2H_2O$ in the crystal.