IUCr/DGK Summer School 2020, Bayreuth, Germany

"Introduction to Novel Methods of Atomic and Electronic Structure Studies at High Pressures"

Lecture Outlines

I. SINGLE CRYSTAL DIFFRACTION AT HIGH PRESSURES

Basics of DACs, pressure determination, equation of states (LSD)
Pressure generation, fundamentals of the diamond anvil cell, types of DACs, fastening of diamonds, alignment of diamonds, diamonds types, anvil cuts, seat types and materials, DACs for single crystal X-ray diffraction studies, gasket materials, gasket preparation, pressure transmitting media (PTM), PTM hydrostaticity, methodology of loading PTM, pressure metrology, fluorescence sensors, Raman sensors, stress of the diamond anvils as pressure sensor, equation of states, determination of EOSes.

Introduction to crystal symmetry (LSD)
Definition of symmetry, crystal systems, symmetry operations and point groups, Bravais lattices and space groups, space group symbols, graphical symbols of crystallographic symmetry elements, symmetry diagrams, coordinates and special positions, equivalent points, definition of the cell origin, the asymmetric unit cell, subgroups and supergroups, reflection conditions.

Introduction to X-ray diffraction (DL)
Defining diffraction, constructive/destructive interference, why employ X-rays, Bragg's Law, Miller indices, intensity of the diffraction peaks, structure factors, atomic form factors, systematic absences and examples for the cubic case, the phase problem, Fourier transformation into electronic density, phase solving methods, R-factors (R_1, wR_2, GoF), advantages of single-crystal X-ray diffraction (Ewald sphere, peak overlapping).

Heating (LSD) and cooling (KG) in DACs
Heating in DACs: electrical external heating, laser-heating setups, temperature determination in laser-heated DACs, single-crystal diffraction in laser-heated DACs, cryogenic cooling with applications to single crystal X-ray diffraction in DACs.

Historical overview and perspectives of HP crystallography (ND)
Diamond history by period; development of DAC design and HP crystallography; double-stage DACs and crystallography at ultra-high pressures

Strategies to acquire good X-ray diffraction SC data in DACs (DL)
Obtaining single crystals (laser heating, direct growth, loading), importance of beam size, importance of the DAC opening, high precision *w*-motor, detector position (large 2θ range), powder calibration (LaB_6/CeO_2), single-crystal calibration (enstatite), sample alignment (gasket or sample), collection strategy (sample mapping, wide scans, step-scans, time per step), data quality verification (intensity, centering, sufficient reflections).

PETRA III facility, the P02.2 beamline and the SC crystal data setup (KG)
The lecture will provide an overview of capabilities of P02.2 beamline (Extreme Conditions Beamline) of Petra-III facility (DESY, Hamburg) with application to single crystal x-ray diffraction of materials compressed using diamond anvil cells. We focus to single crystal x-ray diffraction measurements at ambient temperature, low and high temperature conditions (laser heating and resistive heating). In particular, we will cover the capabilities of 2-circle diffractometer with simultaneous laser heating and the recently commissioned motor stack dedicated to studies of sub-micron crystallites with a sub-micron beam.

Introduction to the CrysAlis^{Pro} software (LSD)
CrysAlis^{Pro} software package, starting and operating the software, images and data types, data conversion, creating an instrument model (calibration), peak search and indexing, reciprocal space viewing (Ewald explorer), data filtering, unit cell verification, unwarps, summation, background evaluation, profile fitting and intensity extraction (integration and additional filtering, outlier rejection), multiple domains and twinning, algorithm parameters, DAC-specific options, data finalization and absorption correction, final integration.

Crystal structure visualization and building blocks of HP crystallochemistry (LSD)
Single crystal databases, ICSD, software for crystal structure visualization, DIAMOND, connectivity and filters, exploring unknown crystal structures, VESTA, close-packed structures, polyhedra, Pauling's rules, bond valence method, deformation of polyhedra, tilting of polyhedra and Glazer's notation, flexible and decorated nets, rod description of structures, building units and descriptions of structures, structural relations.

Introduction to Jana2006 - Crystallographic Computing System (KG)
This lecture gives an overview of Jana software package conventionally used for powder and single crystal data treatment (solution and refinement). The following information would be covered: installation of Jana, configuration of external programs, overview of the most important functionality related to the single crystal data. In particular, we will look at simulation of existing compounds (powder and single crystal), solution and refinement of data and etc. At the moment the most popular version of Jana in the community is Jana2006. In a case Jana2020 would be released by the time of the workshop, we will try our best to cover the functionality of the latest version.

The diamond anvil cell program at GSECARS (APS, Chicago, USA) (SC, VP)
APS facility, GSECARS at Sector 13 mission, capabilities of the 13IDD, BMD and BMC beamlines, experimental techniques currently available to users, double-sided laser heating system operating in various modes (continuous, burst, pulsed) for time-resolved experiments, on-line optical spectroscopy (in-situ Raman, fluorescence, Brillouin), high resolution micro-XRD and XES, multichannel collimator for non-crystalline and low Z materials, well isolated Cryostat system for low T measurements, offline high-resolution Raman spectroscopy system, standard single-crystal and multigrain measurement procedures, the hardware and software involved in single-crystal experiments with DACs, how to apply for an experiment and what to expect as a first-time user at GSECARS and/or first-time single-crystal XRD experimenter at 13IDD.

Application case - materials science (SO)
Application of a single-crystal X-ray diffraction to solve complex problems of Materials Science; new outlook at the long-standing problems; charge-ordering-related phase transitions and phenomena; interrelation of crystals structure and physical properties; examples of mixed-valence iron oxides; Verwey transition in magnetite; using high-pressure methods for modification and comprehension of properties of materials

Handling twinned crystals data (EB)
Definition of a twin, classification of twins (racemic, non-merohedral, pseudo-merohedral, merohedral, by reticular merohedry), integration of a twin in CrysAlis^{Pro}, tests for twinning, twin refinement, warning signs of twinning, examples.

Getting the maximum out of your data (MB)
Common problems arising in high-pressure datasets, guidelines for extracting the maximum reliable information from intrinsically poor datasets, tips and tricks for working with highly mosaic crystals, weakly scattering crystals and crystals featuring weak superlattice reflections, the advanced features of CrysAlis^{Pro} and Jana2006/2020: advanced indexing (manual peak search, scan width adjustment, advanced peak filtering algorithm), adjustment of integration parameters (integration mask size, cutoff resolution), merging datasets, constraints and restraints in the crystal structure refinement, the relationship between the quality of a dataset and the level of the information that one can reliably extract from it (from lattice parameters and chemical composition to electron density distribution).

Processing HP data: problems and helpful tools for their solution (KF)
Sources of error in HP data, scaling of datasets, internal R-value, redundancy, usage of symmetry in data reduction, parameter to data ratio, restricting parameters, influence of limited resolution on ADPs and standard deviations, influence of falsified intensities, using options in Jana to identify outliers, role of pseudosymmetry, Fobs/Fcalc plots, evaluation of different structural models (Hamilton test), resonant scattering, (non)centrosymmetric structures and inversion twins from HP data.

SC data validation (EB)
Refinement indicators (R_1, wR_1, chemical and crystal-chemical consistency), IUCr Checkcif website (working with the site, explanation of alerts), typical alerts that appear in the high-pressure data and how to deal with them, typical "red flags" that should be checked before submission of the cif file (missing atoms, wrong atom assignments, bad initial data integration, bad ADPs, residual density peaks *vs* Fourier truncation errors), submission of the final cif file to the CCDC database.

Application case: high-pressure nitrides (MB)
Modern HP chemistry in DACs, synergy of structure predictions and powder X-ray diffraction in HP chemistry, introduction to HP polynitrides, polymeric nitrogen at HP, novel transition metal polynitrides: how crystallography helps to understand chemistry and properties, HP crystallography at multimegabar conditions at the nanofocus beamlines, mapping the compositional space in a single DAC experiment, increasing complexity: from binary to ternary systems.

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II. NMR AT HIGH PRESSURES

Introduction to NMR (TM)
Introducing the general working principle, nuclear spin interactions, chemical and Knight shift, dipole-dipole interaction, quadrupole interaction, nuclear spin relaxation.

Technical aspects of HP-NMR (TM)
Signal-to-noise ratios and spin sensitivity, HP NMR resonators, Lenz lenses, HP-NMR probe heads, challenges of HP-NMR investigations.

HP-NMR methods (TM)
Broadband single pulse excitation for ultra-wideline NMR, melting and freezing phenomena, pressure-induced electron delocalization, electronic properties of metallic systems, hydrogen bond symmetrisation, laser-heating in DACs, outlook: superconductivity.

Combination of NMR and SC data for Materials Science (TM)
Difference between X-ray and NMR crystallography, high resolution methods in HP-NMR, average Hamiltonian theory, homonuclear spin decoupling in DACs, combining SC data with NMR based electronic structure investigations, high resolution HP-NMR of nominally anhydrous minerals.

Lecturers

ND - Natalia Dubrovinskaia, **DL** - Dominique Laniel, **TM** - Thomas Meier, **KG** - Konstantin Glazyrin, **SK** - Saiana Khandarkhaeva, **AS** - Achim Schaller, **VP** - Vitali Prakapenka, **SC** - Stella Chariton, **SO** - Sergey Ovsyannikov, **EB** - Elena Bykova, **MB** - Maxim Bykov, **KF** - Karen Friese, **LSD** - Leonid Dubrovinsky

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