



L13

HIGH-ENERGY X-RAY DIFFRACTION

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The use of high-energy radiation has increased during the last years with the first high-energy sources on third generation synchrotrons. The high flux and well-collimated beam together with the high penetration depth enable the study of thick samples but nevertheless small gauge volumes. Furthermore, the high-energy diffraction is on forward direction and therefore, the use of flat 2D-detectors is

possible. This has opened new possibilities for many applications including the studies of liquids and amorphous materials, powder diffraction, single crystal studies, diffuse scattering and studies of buried interfaces. Some examples of the use of these properties for studying bulky and heavy samples are given, like, the stress-strain analysis and studies of buried interfaces.

Lectures - Friday, June 23, afternoon

L14

NEUTRON LAUE DIFFRACTION - APPLICATIONS IN MAGNETISM AND HARD CONDENSED MATTER

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Neutron Laue diffraction is a complementary technique to powder and single-crystal neutron diffractometry with possible wide use in magnetism and other areas of hard condensed matter physics. The ILL neutron Laue diffraction instrument VIVALDI (Very-Intense, Vertical-Axis Laue Diffractometer) with its vertical geometry allows for

low-temperature sample environment necessary in most of magnetic structure studies. The power of this technique and the instrument in determining magnetic structures will be shown on the example of several rare-earth intermetallic compounds, in particular NdPtSn, PrCo₂Ge₂ and HoCoIn₅.

L15

STUDY OF FERROELECTRICS BY INELASTIC NEUTRON SCATTERING

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Ferroelectrics, and particularly relaxor ferroelectrics, have been intensively studied for their unusual dielectric, electrostrictive and piezoelectric properties [1, 2]. The majority of ferroelectrics has a cubic perovskite structure in the parent high-temperature phase. However, they exhibit a large variety of phenomena.

The optical methods (infrared, Raman spectroscopy...) are able to provide information about the dynamics only from the Brillouin zone centre. Therefore, in order to inves-

tigate lattice dynamics of single crystals, one has to employ inelastic neutron or X-ray scattering.

In this contribution, we shall describe typical phenomena that can be studied on (nonmagnetic) monocrystalline materials by inelastic neutron scattering. Advantages and difficulties will be demonstrated on:

- determination of dispersion curves [3, 4], in connection with constant-Energy vs. constant -Q scans, and the new FlatCone possibility⁵

- dynamics of phase transitions – diffuse scattering [6], temperature behaviour of soft modes [7].

These properties will be followed by examples from our recent measurements.

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7. M. Kempa, J. Hlinka, J. Kulda, P. Bourges, A. Kania & J. Petzelt, *Phase transitions*, to be published.

L16**NEUTRON DIFFRACTION, INS AND DFT STUDY OF HYDROGEN-BONDING IN TRIS**

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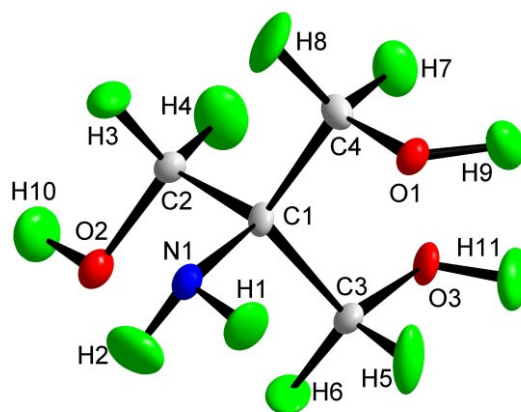
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The proposed project is a part of the study focusing on detailed description of H-bonds in the selected compounds by making a joint use of diffraction, spectroscopy and quantum chemistry methods. The compound tris(hydroxymethyl)-aminomethane, $\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3$, commonly known as TRIS (see the Figure below) can be considered as a good model system for studying the electronic structure of hydrogen bonded-solids. The structure of TRIS can be considered as a layer structure with both intra- and interlayer hydrogen bonds. The individual layers are, except for long range electrostatic forces (dipole moment of the molecule is 2.15D), also connected by weak *interlayer* hydrogen bonds linking N-H...O. Such a structure provides a challenge for theoretical approaches to hydrogen bonded systems since hydrogen bonding can to great extent influence the geometry of a hydrogen bonded molecule and its dynamics.

Accurate structure of TRIS was obtained from low temperature single crystal neutron diffraction. In the molecule of TRIS there are three -OH groups and one -NH₂ group that could act both as donors and acceptors of hydrogen bonds. The INS spectrum of TRIS was measured at 7 K on the HRMECS spectrometer with several incident neutron energies and was interpreted on the basis of a harmonic potential using a variety of models. The models were a single molecule, a molecule in a static field of fragments, and single unit cell with periodic boundary conditions as implemented in VASP program. INS spectrum of TRIS is basically a spectrum of hydrogen motions. Formation of to-

tal of six inter-molecular hydrogen bonds caused significant downshift of OH stretching frequencies and upshift of their bending frequencies. The same trend was observed for NH₂ frequencies but the changes were smaller. This finding goes in agreement with refined structure, which showed that NH₂ participates in the longest hydrogen bond. Hydrogen bonding has almost no influence on CH frequencies. When comparing calculated INS spectra for all models with experimental spectrum the best agreement was reached when considering not only closest hydrogen bonded neighbors but also the periodic character of the crystal structure.





L17

STRUCTURE STUDIES OF MACROMOLECULAR SYSTEMS

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The lecture summarizes briefly results of our laboratory achieved during the last six years. Most of the structure studies are based on our measurements at the X-ray diffraction beam-lines ID14, ID29 in ESRF. Special attention is devoted to future perspectives and to limits of diffraction techniques in solving problems in their complexity to deliver results useful in medicine or technical practice.

Polymer systems – experimental structure determination and applications

Main obstacle of structure determination of synthetic polymers is high structural variability and disorder resulting from the fact that these systems are never in equilibrium state as a rule. Of course, the exact structure determination is meaningful in the cases when some conformations of the polymer chain are markedly preferred. It is in the case of crystalline or semi-crystalline areas in polymer material and also in all instances where the polymer chain specifically interacts with biological material.

- Polymer structure database maintained by our group [1]
- Diffusion and sorption of polymer molecules in protein crystals
- Experimental determination of interactions between synthetic polymers and proteins [2]
- Use of polymers in protein crystallization

Drug design (case study of HIV protease)

- Inhibition of enzymatic processes – optimization of inhibitors for AIDS treatment (inhibitors of HIV protease mutants) [3, 4, 5]
- Binding of inhibitor – enthalpy and entropy of inhibited enzyme system [6]
- Delivery of drugs and controlled release (activation) of drugs in the target tissue
- Removal of products

Modulation of catalytic systems

- Modulation of activity of aspartic proteases
- HIV protease mutants [5]
- Self-inhibition of HIV protease by its own product of enzymatic cleavage [7]
- Coordinated motions in macromolecular systems – motion of HIV protease flaps necessary for inhibitor (substrate) entrance
- Modulation of temperature optimum for enzymatic activity (-galactosidase) [9]

- Diffusion of small molecules in proteins
- 3D design of catalytic systems

Intercellular signaling in immunology – complex systems based on molecular recognition

- Immunoglobulin-like receptors [8]
- Cellular receptors
- Membrane rafting of receptors into clusters of cooperating macromolecules

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L18

PROTEIN-CARBOHYDRATE INTERACTION: STRUCTURAL AND THERMODYNAMIC CHARACTERISATION OF HIGH AFFINITY BINDING BETWEEN LECTINS FROM PATHOGENS AND HOST CARBOHYDRATES

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Carbohydrate-mediated recognition plays an important role in the ability of pathogenic bacteria to adhere to the surface of the host cell in the first step of their invasion and infectivity. Lectin-carbohydrate interactions are usually characterised by a low affinity for monovalent ligands that is balanced by multivalency resulting in high avidity for complex glycans or cell surfaces. Usually, a millimolar affinity is observed for plant lectin binding to monosaccharides. In contrast, bacterial lectins involved in pathogenesis display much higher affinity than that observed for plant or animal lectins [1].

Contribution is focused on bacterial lectins from *Pseudomonas aeruginosa* and their homologues from other

pathogens displaying sub-micromolar range affinity towards their carbohydrate ligands. The combination of X-ray crystallography and isothermal titration microcalorimetry approaches is used to decipher the structural and thermodynamical basis for high affinity binding of these lectins to host carbohydrates. Discovery of a three amino acid motif of the „ligand binding loop” that is responsible for lectin sugar preferences toward different monosaccharides will be discussed.

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Lectures - Saturday, June 24, morning

L19

STRUCTURE OF β -GALACTOSIDASE COMPLEXES

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The unliganded structure of β -galactosidase from the soil bacterium *Arthrobacter* sp. C2-2 isolated in Antarctica (GH family 2) revealed compact hexameric organization of the enzyme [1-2]. It is the first structure of a cold-active β -galactosidase. The structure was determined by single crystal X-ray crystallography with use of synchrotron radiation at the ESRF beamline ID29. The diffraction data were recorded in 1,800 oscillation images at 0.1 λ slicing and the scaled set of intensities contained 577,572 reflections in space group $P2_1$ ($a = 140.1$ Å, $b = 205.7$ Å, $c = 140.5$ Å, $\beta = 102.3^\circ$). Six monomers of the enzyme are arranged with

approximate 32 point symmetry into a sphere-like object and the individual active sites face the internal cavity. The cavity is connected with outer environment mainly by three different types of channels. The hexameric form is present in solution and is assumed to be the relevant biological oligomerization state. Therefore, ligands, substrates, ions and products interacting with the enzyme in the vicinity of the active site must enter and leave through the major openings. *E. coli* β -galactosidase from the same glycoside hydrolase family (a mesophilic counterpart) was extensively studied as for its oligomerization state (tetramer), activity, enzymatic mechanism and the β -complementation