

specificity and binding energies.

The availability of atomic resolution X-ray data allows refinement of anisotropic displacement parameters (ADPs) that complement the 3D coordinates. The information extracted from the ADPs gives insight into the mobility and the presence of ligand induced directional motion in the protein. Together with the change of contact distances and the occurrence of multiple conformers they reflect spatial rearrangement or steric strain. Thus, the analysis of the ADPs complements the time-averaged structural picture with dynamics, revealing subtleties of protein function which may not be attainable if a structure is analyzed only on the basis of the atomic coordinates.

A thorough analysis in terms of accessible conformational states deduced from the directional motion, may provide insight into the energetics of complex formation and the driving forces for allosteric mechanisms.

Examples for application of these analysis methods and their implication for protein structure interpretation will be given.

Keywords: intermolecular contacts, intramolecular contacts, protein structure

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Protein-Protein Interactions in the Cyanobacterial KaiABC Circadian Clock

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Circadian clocks are self-sustained biochemical oscillators. Their properties include temperature compensation, a time constant of approximately 24 h, and high precision. These properties are difficult to explain by known biochemical reactions. The ultimate explanation for the mechanism of these unusual oscillators will require characterizing the structures, functions, and interactions of their molecular components. We are analyzing the biological clock in the simplest cells that are known to exhibit circadian phenomena, the prokaryotic cyanobacteria, whose basic clock is composed of three essential genes, *kaiA*, *kaiB* and *kaiC* [1]. The structures of all three Kai proteins have recently been reported ([2], reviewed in [3]), along with phosphorylation sites in KaiC that are crucial for sustaining the oscillation [4]. Very recent research has demonstrated that the KaiABC clock keeps time in the absence of a transcriptional-translational oscillatory feedback loop [5] and that the circadian oscillation of KaiC phosphorylation can be reconstituted *in vitro* [6]. This means that the clock made up of recombinant KaiC, KaiA and KaiB proteins in the presence of ATP and Mg²⁺ ticks in an Eppendorf tube! The presentation will summarize the status of structural work on Kai proteins and efforts to begin to understand their complexes.

[1] Ishiura M., et al., *Science*, 1998, **281**, 1519. [2] Pattanayek R., et al., *Molec. Cell*, 2004, **15**, 375. [3] Johnson C.H., Egli M., *Nature Struct. Mol. Biol.*, 2004, **11**, 584. [4] Xu Y., et al., *Proc. Natl. Acad. Sci. U.S.A.*, 2004, **101**, 13933. [5] Tomita J., et al., *Science*, 2005, **307**, 251. [6] Nakajima M., et al., *Science*, 2005, *in press*.

Keywords: protein-complexes, protein-crystallography, protein-phosphorylation

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Unusual Ion Coordination in Membrane Channels and CH Hydrogen Bonds in Enzyme Catalysis

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Non covalent interaction play a critical role in ion transport by the membrane channel forming antibiotic gramicidin A and in the mechanism of catalysis in short chain oxidoreductase (SCOR) enzymes. Gramicidin A, a pentadecopeptide composed of alternating d and l residues, form a nanotube long enough to extend across a lipid bilayer and large enough to allow an unsolvated monovalent cation to

move through the membrane. The inner surface of the nanotube is lined by π orbitals associated with peptide bonds and conjugated carbonyl groups. Ion coordination with these π orbitals are the driving force in ion transport. A pattern of strong C-H...O=C hydrogen bonds between carbon atoms on the nicotinamide ring of the NAD cofactor and the backbone carbonyl is of a Pro-Gly sequence in SCOR enzymes indicates that these interactions facilitate hydride transfer in the enzymes. Funded in part by NIH grant No. DK26546.

Keywords: cation-II interaction, C-H hydrogen bonds, natural nanotube

MS18 POWDER DIFFRACTION ON MICRO- AND MESOPOROUS MATERIALS

Chairpersons: Christian Baerlocher, Sergey Krivovichev

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Structure Determination of Zeolites: Making all the Pieces Fit

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In recent years new powder diffraction programs such as FOCUS [1] and EXPO [2] and simulated annealing techniques [3] have been developed to help solve zeolite structures, since these microporous materials are typically synthesized with crystal sizes too small for conventional single crystal structure determinations. Auxiliary techniques are usually employed to assist the researcher in solving a new framework structure. A correct unit cell and space group determination can be aided by electron diffraction, and the number of unique T-atoms and their connectivity can be determined by MQMAS and MQ-HETCOR NMR techniques. Gas absorption measurements indicate the size of the micropores and the dimensionality of its channels, while crystal density gives information about the total number of tetrahedral atoms in the unit cell.

A successful structure determination should not only ensure that the calculated diffraction pattern closely matches the experimental pattern, but also that *all the pieces fit*, i.e., all the characterization data support the proposed model. The above-mentioned and other techniques were used to elucidate the structures of zeolites ECR-34 and SUZ-4 and the aluminophosphates ECR-40 and EMM-3. The supporting characterization data were found to be essential for determining these new structures from powder diffraction data.

[1] Grosse-Kunstleve R., McCusker L.B., Baerlocher Ch., *J. Appl. Cryst.*, 1997, **30**, 985. [2] Altomari A. et al., *J. Appl. Cryst.*, 1999, **32**, 339. [3] Falcioni M., Deem M.W., *J. Chem. Physics*, 1999, **110**, 1754.

Keywords: X-ray powder diffraction, zeolites, NMR spectroscopy

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Structural Characterisation and Properties of New Microporous Materials

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Zeolites are crystalline, hydrated aluminosilicates with open three-dimensional structures built of SiO₄ and AlO₄ tetrahedra linked to each other by sharing all the oxygens to form regular intracrystalline cavities and channels of molecular dimensions. These materials possess remarkable physical and chemical properties, such as selective adsorption, ion exchange and catalytic activity.

Mixed octahedral-pentahedral-tetrahedral (heteropolyhedra) microporous (OPT) framework silicates are zeolite-type materials synthesised and comprehensively studied since the early 1990s [1]. Examples include silicates of Ti and other metals, such as Zr, Nb, V and Sn and Cu. With the advent of the nanotechnology era, and the increasing interest in the use of molecular sieves for device applications, the constituent elements of OPT materials have been further extended to the lanthanide metals, exploring properties like photoluminescence [2].

OPT materials are often prepared in the form of microcrystalline powders (sometimes with considerable degree of disorder) and, thus,

single-crystal X-ray diffraction (XRD) is not generally used. Here, we wish to show how a combination of powder XRD and advanced solid-state NMR (among other) techniques allow the resolution of the crystal structures of these materials. A brief account of some of the materials properties will also be given.

[1] Rocha J., Anderson M. W., *Eur. J. Inorg. Chem.*, 2000, 801. [2] Rocha J., Carlos L. D., *Curr. Opin. Solid State Mater. Sci.*, 2003, 7, 199.

Keywords: zeolites, structure, lanthanides

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Direct Localization of Atoms in Nanoporous Powders by Resonant Contrast Diffraction

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Based on the experimental improvement of data collection achieved for DAFS spectroscopy and applied using the MAD principles, a methodology has been developed for powder sample analysis in order to optimise the use and the interpretation of anomalous information. By using a zeolite example^[1] our aim was to validate the resonant scattering method for contrast studies in complex powders with mixed occupancy sites. On one hand we show that even in powder samples with considerable reflection overlap and with a basically known framework the use of “*dispersive difference*” electron density maps allows an easy localisation of resonant atoms. On the other hand, the use of “*anomalous difference patterns*” enables good agreement factors to be achieved for accurate localisation. These two specific difference tools can also be used in powders containing several phases. The application of these methods can be extended to materials in geology, industry, environmental studies to localize transition metals or RE atoms. It can also give their valence by the use on powders of Diffraction Anomalous Near Edge Structure spectra. The extension of resonant contrast diffraction to in situ measurements can be foreseen to analyse the evolution of atomic order during chemical reactions.

[1] Palancher H. et al., *Angew. Chem. Int. Ed.*, 2005, 117, 1753.

Keywords: anomalous diffraction, resonant scattering, zeolites

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Structural Characterisation of Encapsulated Nanoparticles Inside Mesoporous MCM-48 with XRD, TEM and EXAFS

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Mesoporous silica-MCM-48 has been synthesized making use of the liquid crystal templating technique. In the synthesized form the organic amphiphil occupies the pores of the silica framework. Because of the amorphous structure of silica in the framework wall, diffraction experiments only show the periodic order of the wall/pore system, i.e. the diffraction contrast, which has cubic symmetry and has been assigned to space group I a3d. Depending on the wall thickness and the periodicity of the silica framework diffraction signals only up to 8 °2θ for copper radiation can be observed. After calcination the pore space becomes open and accessible for sorbate molecules.

Using dip impregnation methods metal organic salts have been introduced inside the pore system of MCM-48 which is ca. 30 Å in diameter. Subsequent calcination has transformed the salt into the oxide and furthermore, the oxides were reduced to the elementary metal. The contribution will discuss the structural characterization of ZnO, CuO, Cu, TiO₂, and Au deposited as nanoparticles inside the

pore system using TEM, XAS, and PXRD and discuss their specific nature.

Keywords: mesoporous MCM-48, nanoparticles, EXAFS

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Zeolite and MCM Nano- and Mesoporous Structures

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Ordered micro- and mesoporous materials are well known for their catalytic and highly selective adsorbent properties. However they also offer a wealth of possibilities for creating materials with additional functionality.

Detailed X-ray diffraction interpretation of mesoporous materials is hampered by their large unit cell, the variable stacking and the limited crystal size. Electron microscopy combined with electron diffraction is therefore a more powerful technique to determine the structure of mesoporous materials on a local scale.

A crystalline silica material “Zeolite”, with two levels of porosity and a clear structural order can be produced by tiling nanoslabs with the Silicalite-1 structure type. They can be tiled in various ways into materials with a well-defined mesoporosity. Microscopy of Zeolite-1 shows two types of pores: hexagonal and triangular with sides of 2.0 nm and 2.6 nm, respectively. In Zeolite-1, nanoslabs are forced into face sharing, double units, and then linked to form a pattern with hexagonal symmetry. Zeolite-2 is built from very similar (double) units as Zeolite-1, but has a body centred cubic symmetry (SG Ia $\bar{3}$ d). Hexagonal MCM-41 can be turned into cubic MCM-48 and finally into spherical particles (SSP) by the addition of alcohol to the synthesis of a mesoporous silica material. XRD suggests that the structure of these spherical particles is of the MCM-41 type. However, TEM reveals that the structure of mesoporous SSP consists of a core in the form of a truncated octahedron with the MCM-48 cubic structure and radial pores grown on the surfaces of the truncated octahedron. Spherical MCM particles therefore have a mixture of cubic and hexagonally arranged pores.

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Keywords: zeolite, mesoporous materials, electron microscopy

MS19 NEWS FROM INCOMMENSURATE CRYSTALS

Chairpersons: Sander Van Smaalen, Sven Lidin

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Nowotny Chimney Ladders and Giant Cubic Structures: Electron Driven Interfaces

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Sometimes intermetallic phases can adopt bewildering structures with hundreds or thousands of atoms per unit cell, or no detectable 3-dimensional periodicity. Using quantum mechanical calculations as a guide to view these structures, we will see one reason that such structures form: many complex intermetallics are, at heart, simple structures that have made room for extra electrons through the formation of interfaces. The Nowotny chimney ladder phases are an example: these are beautiful examples of two component composite crystals, in which the two incommensurable components form helical motifs. Electronic structure calculations reveal that the complex chimney ladder structures each chimney ladder consists of slabs of TiSi₂ structure type. The interfaces between the slabs act as electron sinks to achieve electron counts optimal to the TiSi₂ structure. The same thing happens in giant cubic intermetallic phases based on Friauf polyhedra, such as NaCd₂. This phase the NaCd₂ structure, with over 1000 atoms per unit cell, is also built from blocks cut from a simple structure type, this time the MgCu₂ type. Extra electrons are accommodated by the interfaces between MgCu₂-type blocks. While