

available as single crystals, thus making the determination of the full elastic tensor possible at high pressure.

The electronic and magnetic properties of minerals under extreme conditions of pressure or temperature can also be studied through X-ray emission spectroscopy (XES) in the fluorescence regime. We measured the spin state of iron in the main constituent of the Earth's lower mantle, *i.e.* the iron-bearing magnesium silicate perovskite (Mg,Fe)SiO₃, by studying the K β emission line to pressures exceeding 140 GPa. Geophysical implications for both the anisotropy of propagation of acoustic waves in the Earth's core and the physical properties of the lowermost mantle will be discussed.

Keywords: geophysics, inelastic X-ray scattering, high-pressure

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Phonon Dispersions in fcc δ -Pu-Ga by High Resolution Inelastic X-ray Scattering

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The phonon spectra of plutonium and its alloys have been sought after in the past few decades following the discovery of this actinide element in 1941, but with no success. This was due to a combination of the high neutron absorption cross section of ²³⁹Pu, the common isotope, and non-availability of large single crystals of any Pu-bearing materials. We have recently designed a high resolution inelastic x-ray scattering experiment using a bright synchrotron x-ray beam at the ESRF, Grenoble and mapped the full phonon dispersion curves of an fcc δ -phase polycrystalline Pu-Ga alloy[1]. Several unusual features including, a large elastic anisotropy, a small shear elastic modulus C', a Kohn-like anomaly in the T₁[011] branch, and a pronounced softening of the [111] transverse modes are found. These features can be related to the phase transitions of plutonium and to strong coupling between the lattice structure and the 5f valence instabilities. Our results also provide a critical test for theoretical treatments of highly correlated 5f electron systems as exemplified by recent dynamical mean field theory (DMFT) calculations for δ -plutonium[2]. Recent work on imaging phonons in Pu-Ga alloys with thermal diffuse scattering[3] will also be discussed.

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[1] Wong J., et al., *Science*, 2003, **301**, 1078. [2] Dai X., et al., *Science*, 2003, **300**, 953. [3] Wong J., et al., *Appl. Phys. Lett.*, 2004, **84**, 3747.

Keywords: lattice dynamics, inelastic X-ray scattering, phonon softening

MS17 NON-COVALENT INTERACTIONS IN CRYSTALS OF SMALL MOLECULES AND MACROMOLECULES

Chairpersons: Gautam R. Desiraju, Mariusz Jaskolski

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Multipolar Interactions in Structural Chemistry and Biology

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The past decades of molecular recognition studies have greatly enhanced our knowledge on apolar, ion-dipole, and H-bonding interactions. However, much less attention has been given to the role that multipolar interactions, in particular those with orthogonal dipolar alignment, adopt in organizing a crystal lattice or stabilizing complexes involving biological receptors.

In a recent fluorine scan of thrombin inhibitors to map the fluorophilicity/fluorophobicity of an enzyme active site, we discovered favorable C–F_(ligand)...C=O_(protein) interactions, with the F-atom approaching the electrophilic C-atom in a nearly orthogonal way, along the pseudotrigonal axis of the carbonyl unit. The attractive nature of such contacts was subsequently established in model studies.

Using Cambridge structural database (CSD) and protein database (PDB) mining tools, we now have established the generality of these previously rather overlooked interactions. A number of illustrative examples of these interactions found in X-ray crystal structures of small molecules and protein-ligand complexes will be shown to demonstrate their propensity and thus potential importance for both, chemical and biological molecular recognition processes. [1]

[1] Paulini R., Müller K., Diederich F., *Angew. Chem. Int. Ed.*, 2005, *in press*.

Keywords: nonbonded interactions, databases, X-ray crystal structure analysis

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Carbonyl...Carbonyl Interactions are Structurally Ubiquitous and Important

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Recent years have seen an increasing interest in intermolecular interactions that are *not* mediated by hydrogen. An early analysis [1] of the Cambridge Structural Database (CSD) identified the isosteric nature of nitro and carbonyl groups in molecular design applications. This prompted further work on dipolar carbonyl-carbonyl interactions that will be reviewed and extended in this talk. In *small organic molecules* it has been shown that CO groups in simple ketones and trans-amides form three main interaction motifs, and that the most frequent sheared-antiparallel arrangement has an attractive interaction energy of ca. -22kJ mol⁻¹, competitive with medium-strength H-bonds. In *proteins*, PDB analyses show that CO...CO interactions stabilise α -helices, β -sheets and β -strands, including the stabilization of the partially allowed Ramachandran conformations of asparagine and aspartic acid. In *organometallics*, we are now studying CO...CO interactions using the CSD. Although compromised by steric hindrance, very significant numbers of CO...CO interactions are observed in M-C=O systems. The antiparallel motif again predominates, and C...O distances are usually shorter than in organic systems, indicative of the stronger dipole in the M-C=O case. Preliminary DFT calculations indicate attractive energies of -20 to -30 kJ mol⁻¹ for the predominant motif, similar to or stronger than the attractive energies in organic systems.

[1] Taylor R., Mullaley A., Mullier G.W., *Pestic. Sci.*, 1990, **29**, 197-213.

Keywords: intermolecular interactions, crystallographic databases, ab initio energy calculations

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Small Molecules and Macromolecules make Contact: Messages from Protein Structures to Atomic Resolution

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Atomic and ultra-high resolution macromolecular crystal structure determination and *ab initio* quantum chemical calculations have become indispensable tools for comprehensive structure interpretation, as they permit acquiring snapshots along the reaction pathway and the assignment of function to the residues involved in catalysis. Fine electronic detail can be visualised and yield valuable information on protein function. The assessment and description of intra- and intermolecular contacts reaches a degree of accuracy which in the past was considered impossible for macromolecules.

The release of geometric restraints and the low coordinate error in atomic resolution protein structures allow the identification of deviations from standard stereochemistry which, at lower resolution, might not have been accounted for. These deviations may occur in intramolecular interactions as well as in intermolecular (protein-ligand) contacts. Quantum chemical calculations, or direct multipole refinement, on these accurate model templates complement the structural data with information beyond the analysis of contact distances. The charge distribution which one can obtain determines the chemical properties and hence characteristics such as substrate

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,