$_xSm_xSe_3$ system. Comparisons will be made with quantitative chemical analyses obtained through the use of inductively coupled plasma (ICP) analyses.

Finally, the compound $Ba_4Fe_2I_5S_4$ will be used to illustrate the structural challenges posed by the unexpected in solid-state syntheses.

Keywords: metal chalcogenides, chemical crystallography, physical properties structure relationships

KN20.27

Acta Cryst. (2005). A**61**, C5

The Importance of Structure in the Design of Lithium Battery Materials

Michael Thackeray, *Argonne National Laboratory, Argonne, Illinois 60439, USA*. E-mail: thackeray@cmt.anl.gov

Since 1990, rechargeable lithium batteries have made a huge impact in powering consumer electronic devices such as cell phones and laptop computers [1]. The need for new insertion electrode structures that will provide additional energy, power and a superior cycle life to satisfy the increasing demands for reliable and safe high-energy/high power batteries by the transportation, medical, space, and defense sectors will ensure that lithium battery research will continue for many more years to come. This presentation will review the progress that has been made over the past 15 years and it will highlight the critical role that structure plays in the design and operation of lithium battery electrodes. Recent advances that have been made in designing two-component, structurally-integrated materials to achieve performance objectives will be discussed [2, 3]. The presentation will be made in the context of the advantages and limitations of other battery systems.

[1] Tarascon J.M., Armand M., *Nature*, 2001, **414**, 359. [2] Kim J-S., Johnson C. S., Vaughey J. T., Thackeray M. M., Hackney S. A., Yoon W., Grey C. P., *Chem Mater*., 2004, **16**, 1996. [3] Thackeray M. M., Johnson C. S., Vaughey J. T., Li N., Hackney S. A., *J. Mater. Chem*., 2005, *in press*.

Keywords: lithium battery, insertion electrode, structure

KN21.28

Acta Cryst. (2005). A**61**, C5

Pore-Forming Toxins

Michael W. Parker, *Biota Structural Biology Laboratory, St. Vincent's Institute of Medical Research, Melbourne, Victoria 3065, Australia*. E-mail: mparker@svi.edu.au

Pore-forming protein toxins (PFTs) are one of Nature's most potent biological weapons. They are produced by a variety of living organisms, particularly bacteria, certain insects, poisonous reptiles and stinging marine invertebrates. As offensive weapons these toxins can aid digestion or degeneration of the host whilst as defensive weapons they can protect by killing invaders. Of the more than 300 protein toxins characterized to date, at least a third act by disrupting membranes. In order for these water-soluble proteins to insert into membranes they must undergo a series of conformational changes to expose or generate new hydrophobic surfaces that can penetrate the core of cell membranes.

We have determined the crystal structures of a number of microbial pore-forming toxins. Although the structures are quite different they reveal common features that have been implicated in the mechanism of membrane insertion into cells. Two of these toxins belong to the family of cholesterol-dependent cytolysins (CDCs). CDCs exhibit a number of unique features amongst pore-forming toxins including an absolute dependence on the presence of cholesterol-rich membranes for their activity and the formation of very large oligomeric transmembrane pores greater than 15 nm in diameter. The crystal structures of these toxins suggest how they recognise cholesterol and provide the basis, together with available cryoelectron microscopy data, for modelling their pores.

Keywords: toxins, channel proteins, membrane associated proteins

KN22.28

Acta Cryst. (2005). A**61**, C5

Pressure Induced Complexity in the Elements

Malcolm McMahon, *School of Physics and Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh EH9 3JZ, U.K.* E-mail: mim@ph.ed.ac.uk

At ambient pressure, the metallic elements typically adopt high-symmetry crystal structures such as bcc, fcc and hcp. However, on compression, many of these simple structures undergo a series of structural transitions to phases characterised by considerable structural complexity, and it is only with recent advances in high-pressure single-crystal and powder-diffraction techniques that many of them have been determined. In the group 1, 2, and 15 elements, we have found a number of incommensurate "hotel" structures comprising interpenetrating host and guest structures [1]; transitions between these composite structures [2]; modulations of the host and guest structures; a transition to a composite structure with a "liquid" guest component [3]; and a number of surprisingly complex commensurate structures. And in the group 16 elements, we have found a number of incommensurately modulated structures that are stable over a remarkably wide range of pressures and temperatures [4]. I will review all the recent results on these "simple" metals, and discuss possible explanations for the existence of this complexity.

[1] McMahon M. I., Degtyareva O., Nelmes R. J., *Phys. Rev. Lett*.,2003, **85**, 4896. [2] Nelmes R. J., Allan D. R., McMahon M. I., Belmonte S. A., *Phys. Rev. Lett.*, 1999, **83**, 4081. [3] McMahon M. I., Nelmes R. J., *Phys. Rev. Lett*., 2004, **93**, 055501. [4] Hejny C., McMahon M. I., *Phys. Rev. Lett.*, 2003, **91**, 215502.

Keywords: incommensurate phases, high pressure physics, metals

KN23.28

Acta Cryst. (2005). A**61**, C5

Electrostatic and Related Properties from Accurate Charge Density Analyses

Mark Spackman, *Chemistry - M314, University of Western Australia, Crawley WA 6008, Australia.* E-mail: mas@cyllene.uwa.edu.au

Properties of atoms and molecules in crystals are now commonly extracted from a combination of X-ray diffraction experiments and theoretical results from a variety of approaches. Modern quantitative charge density studies typically involve use of CCDs and/or synchrotrons, *T* below 120 K and frequently nearer 10 K, careful data reduction and correction for systematic effects, and detailed modelling of atomic motion. Multipole refinement yields topological properties of the electron density in almost all studies, while valuable electrostatic properties are seldom reported. Yet there is a wealth of such properties accessible from the X-ray experiment: electrostatic potential, electric field and field gradient, atomic charges, electric moments of molecules in the crystal, and even intermolecular interaction energies.

If we accept that "theory is a good thing but a good experiment is forever" [1], we must ask: Are we maximizing the information that can be obtained from charge density data sets? If not, why not, and how might this be redressed? This presentation will seek answers to these questions from a discussion including results from a selection of recent studies. Limitations of some of the common approaches will be highlighted, and some solutions will be proposed, along with comments on related properties that might be explored.

[1] Kapitza P.L., *Experiment*, *Theory*, *Practice*, (D. Reidel, Boston),1980, 160.

Keywords: charge density studies, electron density studies, electrostatic properties

KN24.28

Acta Cryst. (2005). A**61**, C5-C6

Structural and Functional Studies of Large Macromolecular Assemblies

Nenad Ban, *Department of Molecular Biology and Biophysics ETH Honggerbery, CH-8093 Zurich, Switzerland*. E-mail: ban@mol.biol.ethz.ch

The main goal of the research in my laboratory is to study structure and function of large macromolecular assemblies involved in central cellular processes. Although most of our work focuses on

complexes involved in protein synthesis, recently we have expanded our studies to investigate structure and function of large eukaryotic multienzyme complexes such as the fatty acid synthase, a giant multifunctional enzyme that contains seven catalytic domains and catalyses all steps of fatty acid synthesis. We are using crystallography as the primary method in combination with electron microscopy and biochemical experiments.

Keywords: cellular processes, fatty acid synthesis, macromolecular assemblies

KN25.28

Acta Cryst. (2005). A**61**, C6

Microbeam Diffraction using High Energy Synchrotron Radiation

Lawrence Margulies[ab], Henning Poulsen[b], Dorte Juul Jensen[b] , [a]*European Synchrotron Radiation Facility, Grenoble, France.* [b]*Risoe National Laboratory, Roskilde, Denmark.* E-mail: margulie@esrf.fr

The possibility of micron and sub-micron X-ray beams at High Energies (50-100keV) has opened up a wealth of new experimental possibilities. At the Materials Science beamline (ID11) of the European Synchrotron Radiation Facility (ESRF) a dedicated instrument, the three dimensional X-ray diffraction microscope (3DXRD), has been developed in collaboration with Risoe National Lab. Beam sizes ranging from 1 mm to 1 micron are available, and the combination of high flux and fast detectors allows for time resolved measurements. A number of examples will be presented to demonstrate the range of possible applications. The focus here will be on materials science applications, although these techniques are applicable to a large range of fields.

Among the applications presented will be the kinetics of recovery of sub-micron cells in highly deformed metals. The technique for constructing 3D maps of the full microstructure of materials (grain boundary morphology, grain orientation, elastic strain tensor) will be described, and a time resolved measurement of nucleation and growth of an imbedded grain within a highly deformed bulk metal will be shown in 4D.

Finally, the potential of achieving micron spatial resolution without micro focusing, that is using large beams, will be discussed with the obvious advantage of greater time resolution. Specifications for the current nanoscope project (an extension of the ID11 beamline due for completion in 2007) will be briefly described.

Keywords: microbeams, X-ray diffraction, materials science

KN26.28

Acta Cryst. (2005). A**61**, C6

New Possibilities for Structure Determination of Biomolecular Complexes

Dmitri Svergun, *EMBL, Hamburg Outstation, Germany and Institute of Crystallography RAS, Moscow, Russia.* E-mail: Svergun@EMBL-Hamburg.DE

New possibilities to analyse the structure of macromolecular complexes using small-angle scattering (SAS) of X-rays and neutrons are presented. SAS allows one to study the overall structure of native particles in solutions and to analyse structural changes in response to variations in external conditions. Recent progress in instrumentation and data analysis [1] significantly enhanced resolution and reliability of structural models provided by the technique and made SAXS a useful complementary tool to high resolution methods, especially powerful in the analysis of complex macromolecules. The latter mediate most of fundamental biological processes and the focus of modern structural biology is rapidly shifting towards their study.

Advanced approaches to analyze macromolecular complexes in solution using SAS will be presented including: *ab initio* low resolution structure analysis, rigid body refinement and addition of missing fragments to high resolution models, analysis of equilibrium mixtures and the use of contrast variation and specific deuteration in neutron SAS Practical applications of the methods will be illustrated by recent examples.

[1] Svergun D. I., Koch M. H. J., *Rep. Progr. Phys.*, 2003, **66**, 1735.

Keywords: small-angle scattering, rigid-body analysis, biomacromolecular structures

KN27.29

Acta Cryst. (2005). A**61**, C6

Bound Ligands to Probe the Activity of Type 2 Copper Sites in Proteins

Michael E.P. Murphy, *Department of Microbiology & Immunology, University of British Columbia, Vancouver, Canada.* E-mail: Michael.Murphy@ubc.ca

Nitrite reductase (NiR) is a type 2 copper-containing enzyme that reduces nitrite to nitric oxide as part of the global nitrogen cycle. Type 2 copper sites are found in a variety of versatile oxidoreductases that mediate reactions involving oxygen or nitrogen oxides and are found throughout all branches of life. Crystal structures of (NiR) to beyond 1.4 Å resolution with bound nitrite and nitric oxide have given insight into the catalytic mechanism which differs from that of heme cd_1 NiR. Mutagenesis studies of copper NiRs show that an aspartate – histidine pair in the active site is found to control binding of copper ligands and largely define the chemical reactivity of NiR. Unexpectedly, nitrite and nitric oxide are bound in an almost face-on and side-on coordination to the copper. In contrast, the inhibitor azide binds end-on to the type 2 copper. Also, acetate and nitrate coordinate through both oxygens (bidentate), whereas nitrite is coordinated by a single oxygen that forms an H-bond to the active site aspartate, an interaction that is likely to be essential for efficient catalysis.

Interestingly, NiR is able to reduce oxygen to hydrogen peroxide in vitro, eventually leading to enzyme inactivation. The NiR type 2 copper site shares a similar coordination sphere to those of superoxide dismutase and amine oxidases suggesting the possibility of common mechanistic features with respect to reactivity of these sites with oxygen and nitrogen oxides.

Keywords: structures of metalloproteins, copper complexes, nitric oxide

KN28.29

Acta Cryst. (2005). A**61**, C6

Crystallochemical Basis of Synthetic Mineral Immobilisation

Tim White, Madhavi Srinivasan, Jean Kim, *MSE-NTU, 639798 Singapore.* E-mail: tjwhite@ntu.edu.sg

Designing contemporary methods for immobilising pollutants is underpinned by crystal chemical and mineralogical principles [1], with the selection of a ceramic or synthetic mineral immobilisation matrix governed by several considerations. First, toxic metals should be incorporated in their least toxic chemical states. For example, substances that eschew As^{3+} and Cr^{6+} in favour of less dangerous As^{5+} and Cr^{3+} are preferable. Second, as this illustration indicates, it is sometimes necessary to simultaneously accommodate the oxidized and reduced species of different metals, restricting the suite of mutually compatible minerals that can be selected. Third, crystal structures are preferred that have multiple cation and/or anion acceptor sites as this minimizes the number of phases required to crystallise simultaneously, and allows greater flexibility to respond to variations in waste stream composition. This in turn limits the chance of undesirable compounds forming. Finally, phases with large numbers of appropriate cation acceptor sites are advantageous, as they result in higher waste loadings and less 'bulking' of the waste product through the introduction of inert additives. These matters will be illustrated by reference to the zirconolites [2], already being used for nuclear waste treatment, and the apatites [3,4] that are potential materials for the fixation of hazardous waste.

[1] Haggerty S.E., *Ann. Rev. Earth Planet. Sci*.,1983, **11**, 133. [2] Grey I.E., Mumme W.G., Ness T.J., Roth R.S., Smith K.L., *J. Solid State Chem.*, 2003, **174**, 285. [3] Ioannidis T.A., Zouboulis A.I., *J. Hazardous Materials*, 2003, **B97**, 173. [4] Dong Z.L, White T.J., *Acta Crystallogr.*, 2004, B**60**, 138.

Keywords: waste management, environmental chemistry, environmental affairs