

**KY.NT.10 THE STRUCTURE OF BOVINE MITOCHONDRIAL F1-ATPASE - AN EXAMPLE OF ROTATIONAL CATALYSIS ?** A.G.W. Leslie, J.P. Abrahams, M. van Raaij, R. Lutter, J.E. Walker, MRC Laboratory of Molecular Biology, Hills Road, Cambridge CB2 2QH, UK

ATP is the energy currency of all living cells. It is generated by the enzyme ATP synthase, a complex oligomeric assembly found in mitochondria, chloroplasts and bacteria. This enzyme uses a trans-membrane proton gradient (established by respiration in mitochondria or photosynthesis in chloroplasts) to generate ATP from ADP and inorganic phosphate. There is a high level of sequence homology between the enzymes from these various sources and it is likely that they share a common tertiary structure and catalytic mechanism.

The intact ATP synthase consists of a membrane bound segment (Fo) and a soluble component (F1) linked by a stalk. Fo contains the proton channel, while the catalytic sites are located on F1. In isolation, F1 displays ATPase activity, and is therefore known as F1-ATPase. It consists of five different subunits, with stoichiometry  $\alpha_3\beta_3\gamma\delta\epsilon$ . In the crystal structure of bovine mitochondrial F1-ATPase, the  $\alpha$  and  $\beta$  subunits are arranged like the segments of an orange around a central spindle formed by two long  $\alpha$  helices from the  $\gamma$  subunit. The three catalytic sites are on the  $\beta$  subunits, but lie at the interface with the adjacent  $\alpha$  subunit. The three catalytic interfaces are quite different in nature, and may represent different conformational states on the catalytic pathway. The structure supports the binding change mechanism of catalysis as proposed by P. Boyer, in which the three catalytic sites alternate cyclically between three different states. Several aspects of the structure suggest that during catalysis the interconversion of the catalytic sites is achieved by a relative rotation of the  $\alpha_3\beta_3$  assembly and the  $\gamma$  subunit. The structures of two enzyme-inhibitor complexes lend support to this hypothesis.

**KY.NT.11 MODERN POWDER DIFFRACTION IN MATERIALS SCIENCE.** Daniel Louër, Laboratoire de Cristallographie, CSIM (URA CNRS 1495), Université de Rennes, 35042 Rennes cedex, France

The powder diffraction method offers a wide spectrum of applications to materials scientists. Most modern applications have benefited, in the recent years, from substantial advances in high resolution instrumentation and modelling of diffraction patterns, to overcome the line overlap problem, and from high-intensity X-ray synchrotron and neutron sources (see Langford and Louër, *Rep. Prog. Phys.* 1996, 59, 131). The development of new materials, e.g. high Tc ceramics, carbon-cage molecular compounds or in general zeolites, and the investigation of powder materials, in terms of structural and microstructural properties, in solid state chemistry or mineralogy, are widely based on the use of powder diffraction.

Modern powder diffraction applications include (i) analytical characterization, such as the improved identification of unknown materials from crystallographic databases using storage media, the introduction of fast search/match algorithms and quantitative determination of phase abundance using the Rietveld method; (ii) the extraction of 3-dimensional structural and microstructural information from 1-dimensional data and (iii) the use of dynamic and non-ambient diffraction to study the behaviour of materials subjected to external perturbation.

The most significant advance in the recent years has probably been the determination of crystal structures *ab initio* from powder data. More complex structures can be studied (e.g. up to 29 atoms in the asymmetric unit) by combining X-ray and neutron diffraction. New classes of compounds are being studied, such as coordination, organic or pharmaceutical compounds and new strategies for solving the phase problem have been introduced (e.g. entropy maximization, simulated annealing, atom-atom potential methods, direct methods,...).

Although the frontiers of powder diffraction have been extended by high-intensity radiation sources, most applications can be carried out with conventional sealed-tube X-ray sources, preferably by using monochromatic radiation.

**KY.NT.12 APPLIED PHYSICS OF QUASICRYSTALS AND APPLICATIONS.** Jean Marie Dubois, Laboratoire de Science et Genie des Matériaux Metalliques, CNRS URA 159 et GDR CINQ, Ecole des Mines, Parc de Saurupt, F54042 Nancy

Despite a small fraction of its atomic positions cannot be fully specified, the structure of quasicrystals is now well understood with the help of high-dimensional crystallography techniques. The interest of (quasi)crystallographers therefore turns at present towards exploring the physical, mechanical and chemical properties.

This task is made easier by the availability of stable quasicrystals and of single "grained samples the quality of which competes with that of the best crystalline specimens. The result of all such measurements is rather outstanding: quasicrystals, basically made of seventy atomic percent of aluminum and of transition metals, are heat insulators, they show a very weak electronic conductivity which furthermore increases with temperature. Their optical properties dramatically depart from those of a free electron metal. They produce surprisingly low friction as compared to usual metallic alloys, they exhibit catalytic properties and good corrosion resistance. Altogether, their electronic structure proves to be different from that of their elemental constituents. This picture can be understood by reference to the hierarchy of atomic clusters which characterizes this specific structure.

The purpose of the lecture will be to review the most significant applied properties discovered in recent years with stable quasicrystals. The fields of potential technological applications that follow will be evoked such as thermal barriers, low wear coatings, thin quasicrystalline films sandwiched between dielectric layers for solar light absorption, weak adhesion surfaces, hydrogen storage or the reinforcement of metal-matrix composites.

**KY.NT.13 CRYSTALLIZATION & CRYSTAL STRUCTURE OF BEEF HEART CYTOCHROME C OXIDASE.** S. Yoshikawa K. Shinzawa-Itoh, R. Nakashima, R. Yaono, Department of Life Science, Himeji Institute of Technology, Kamigohri Akoh, Hyogo 678-12, Japan; T. Tsukihara, H. Aoyama, E. Yamashita, T. Tomizaki, H. Yamaguchi, Institute for Protein Research, Osaka University, 3-2 Yamada-oka, Suita 565 Japan

Crystals of bovine heart cytochrome c oxidase, which diffract X-rays to 2.5 Å resolution, have been obtained in the presence of decyl maltoside. Three dimensional structure of the enzyme, determined at 2.8 Å resolution with an R value of 20.4 % reveals that the monomer of the enzyme is composed of 13 subunits, different from any other, five phosphatidyl ethanolamines, three phosphatidyl glycerols and two cholates, two hemes A, and three Cu, one Mg, and one Zn. Each structure of all the residues of the monomer (1780 in total) except for 23 residues has been converged to a reasonable structure by structural refinement. A dimeric structure in the crystal in which the two monomers are bridged by one of the subunits in each monomer suggests the stability of the dimer under physiological conditions. Essentially all the transmembrane part of the protein moiety is folded to  $\alpha$ -helical conformation and contains many alcoholic amino acids, serine and threonine. A concaved surface which could accept cytochrome c is located very near one of the copper site, Cu<sub>A</sub>, suggesting that the initial electron acceptor from cytochrome c is Cu<sub>A</sub>. A hydrogen bond system including a propionate of a heme A (heme a), peptide unit and an imidazole bound to Cu<sub>A</sub> could provide much faster electron transfer between Cu<sub>A</sub> and heme a than between Cu<sub>A</sub> and the other heme A at the oxygen reduction site (heme a<sub>3</sub>), though the Cu<sub>A</sub>-heme a distance (20.6 Å) is only 2.6 Å shorter than the Cu<sub>A</sub>-heme a<sub>3</sub> (23.2 Å)

Two structures likely to serve as proton transfer path, which include hydrogen bonds and internal cavities likely to contain water molecules are spanned from the matrix surface to the cytosolic. The O<sub>2</sub> reduction site is equipped with a possible proton transfer path from the matrix surface to produce H<sub>2</sub>O from O<sub>2</sub> and a structure likely to be a water channel to the cytosolic surface. The crystal structure shows three possible O<sub>2</sub> paths to the O<sub>2</sub> reduction site which are composed of hydrophobic amino acid side chains loosely packed.