

**KY.NT.06 DESIGNER CRYSTALS: INTERMOLECULAR INTERACTIONS, NETWORK STRUCTURES AND SUPRAMOLECULAR SYNTHESIS.** Gautam R.Desiraju, School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

Crystal engineering attempts an understanding of the packing of molecular solids towards the design of new materials with desired aesthetic or functional properties. The Cambridge Structural Database can be used to identify patterns of intermolecular interactions that control crystal packing. Strong O-H...O and N-H...O hydrogen bonds are generally used for crystal design but weaker, polarisation-induced interactions, such as say, C-H...O, O-H... $\pi$ , Br...Br and O...I may often be reliable. Still, a major concern in crystal engineering is that the interactions which control crystal packing are weak and numerous. The same molecular structure could be associated with several crystal structures and this problem of polymorphism is not very helpful.

The growth and development of supramolecular chemistry has led to the consideration of a crystal as the ultimate supermolecule. Going further, crystal engineering becomes the supramolecular equivalent of organic synthesis and like any other form of synthesis, it is characterised by target definition, methodology and strategy. The crystal is a supermolecule and so, a target in crystal engineering should be defined supramolecularly, that is as a network. Synthetic methodology corresponds to interaction properties while strategy invokes the concept of supramolecular synthons. These are robust combinations of interactions that incorporate geometrical and chemical recognition features of molecules. As in traditional synthesis, retrosynthetic analysis is of value, because it permits general design strategies leading to an identification of several molecular structures which could crystallise in the same target network. Such an intertwining of crystallography with organic chemistry has the promise of leading to new vistas in property-driven and goal-oriented crystal engineering.

**KY.NT.07 LESSONS FROM THE HIGH-RESOLUTION CRYSTALLOGRAPHY OF PROTEIN-DNA COMPLEXES.** Stephen C. Harrison, HHMI and Department of Molecular and Cellular Biology, Harvard University, Cambridge, MA

Proteins recognize specific DNA sequences and DNA conformations. Crystal structures of protein/DNA complexes, particularly those of transcription factors bound to specific regulatory sites, have yielded high-resolution images of protein/DNA interfaces. End-on stacking of DNA fragments often dominates molecular packing in crystals of protein/DNA complexes, so that variation of the lengths and terminal sequences of synthetic DNA fragments facilitates crystallization. Use of halogenated bases rationalizes the search for isomorphous derivatives. *Local recognition* of short DNA sequences often involves small, distinct, DNA-binding domains of larger proteins. There are a number of stereotypical recognition motifs, frequently with an  $\alpha$ -helix that lies in the DNA major groove. Side chains (e.g., from this "recognition helix") have extensive non-covalent interactions with the edges of bases; van der Waals complementarity is as important as hydrogen bonding. There is no recognition "code", but there are noteworthy regularities. Positioning contacts to sugar-phosphate backbone are important for presenting a recognition motif to DNA bases. *Extended specificity*, for recognition of longer sequences, can involve homo- or hetero-dimerization, concatenation of domains in a longer polypeptide, and heterologous interactions with other proteins. All these points will be illustrated with specific structures.

**KY.NT.08 CRYSTALLOGRAPHY OF EARTH AND PLANETARY INTERIORS.** Russell J. Hemley, Geophysical Laboratory and Center for High-Pressure Research, Carnegie Institution of Washington, Washington, D.C. 20015, USA

Recent developments in diamond-anvil cell x-ray diffraction methods have ushered in a new era for structural study of Earth and planetary materials at the high pressure-temperature conditions that prevail deep within the planets. These methods include single-crystal and polycrystalline diffraction with both polychromatic and monochromatic synchrotron radiation for in situ determination of crystal structures, phase transitions, equations of state, and elasticity of materials. Structural variations with pressure, temperature, and composition of silicates and oxides form the key for understanding the composition and global properties of the Earth's mantle (to 135 GPa or 1.35 Mbar). These studies have recently been complemented by x-ray crystallography of natural mineral inclusions in diamonds brought up from the deep mantle. Experiments on iron and iron alloys to pressures above 300 GPa elucidate the nature of the Earth's core. Recently, these studies have been combined with new laser heating techniques for x-ray diffraction at simultaneous high pressures and temperatures above 100 GPa, and with new methods to determine directly the effects of hydrostatic and uniaxial stress on crystal structures at these pressures. Finally, these methods have been applied to the structural properties of the solidified gases and ices relevant to bodies of the outer solar system. This includes x-ray diffraction of solid hydrogen above 100 GPa, new high-density H<sub>2</sub>-bearing compounds, and H<sub>2</sub>O-ice at very high pressures.

**KY.NT.09 NEW OPPORTUNITIES IN X RAY CRYSTALLOGRAPHY AT THIRD GENERATION SYNCHROTRON SOURCES.** Carl-Ivar Bränden, ESRF, BP 220, F-38043 Grenoble Cedex

Undulators at third generation Synchrotron sources produce parallel, narrow X-ray beams of very high brilliance even at energies as high as 70 keV. These beams open up new opportunities for diffraction and some examples will be presented from recent experiments at ESRF. Conventional optical elements are used to produce a monochromatic beam with as high flux as possible for macromolecular crystallography. Excellent data have been collected from virus crystals with cell dimensions 1110\*1110\*1547Å and from needle-shaped protein crystals 10 micrometers thick. Circular Bragg-Fresnel lenses have been used to produce beams with focal spot size in the micron or sub-micron range. Such beams have been used in diffraction experiments using diamond anvil cells to study solid hydrogen and oxygen as well as ice at very high pressure. Capillary optics was used in a combined microfluorescence and microdiffraction experiment to study the composition and structure of individual grains of micron size in fly-ash particles. Diamond crystal monochromators are now used in combination with multilayer mirrors to build four independent protein crystallography stations on one beamline for high data collection throughput.

Time-resolved experiments have been made both by multi-bunch energydispersive diffraction and by single bunch Laue diffraction. The early process of hydration of cement was studied by energy-dispersive diffraction using high energy to penetrate the 10 mm thick sample and fast data acquisition in the subsecond range. It was found that a previously unknown intermediate phase appears seconds after mixing and disappears again after 2-3 minutes. Photolysis of CO-myoglobin was studied by single bunch Laue diffraction in the pico and nanosecond range. Excellent electron density maps were obtained from a dataset collected by single bunch exposures which last about 50 picoseconds.