KN-4

High-pressure Crystallography, Weak Interactions and Electron Density. Andrzej Katrusiak. *Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland.*
E-mail: katran@amu.edu.pl

In 2009 the Crystallographic Community celebrates the half-century anniversary of the inception of the diamond-anvil cell (DAC) [1,2] – the ingenious, simple and low-cost device that triggered the structural studies in all high-pressure range from few MPa to hundreds of GPa, higher than at the centre of the Earth (364 GPa). Among several milestones in the development of the high-pressure crystallography were the introduction of gaskets allowing high-pressure studies at hydrostatic conditions [3], development of pressure calibration methods [4], common introduction of automatic diffractometers in the 1970's and 2-dimensional CCD detectors in the 1990's. These greatly facilitated high-pressure experiments. Now the DAC is commonly used for x-ray crystallography in many laboratories all over the world [5,6]. Furthermore, high-pressure is now well established in international and national synchrotron and neutron-source facilities, with numerous beam lines dedicated to high-pressure research.
The scope of high-pressure research is presently very broad, and includes the basic studies on very simple as well as complex systems for geology, physics, chemistry and biology, including several on-going projects on proteins and other biopolymers, and technological applications [6]. The quality of data recorded routinely in laboratories often allows the anisotropic refinements of non-H atoms and location of hydrogens from difference-Fourier maps in most cases, and accuracy of results comparable to those measured for bare crystals. High-pressures are ideal for investigating any structural transformations, as considerable compression of the crystal volume can be readily achieved in the DAC. This allows general description and understanding of thermodynamical processes, the intermolecular interactions and molecular electronic structure and their role for the molecular aggregation and crystal properties [7-9].

[1] Jamieson J.C., Lawson A.W., Nachtrieb N.D. *Rev. Sci. Instrum*. 1959, 30, 1016. [2] Weir C.E., Lippincott E.R., van Valkenburg A., Bunting E.N. J. *Res. Natl. Bur. Stand. Technol*. **1959**, 63A, 55-62. [3] van Valkenburg A. *Rev. Sci. Instrum*. **1962**, 33, 1462. [4] Forman R.A., Piermarini G.J., Barnett J.D.; Block S. *Science* **1972**, 176, 284. [5] Katrusiak A. *Acta Cryst.* **2008**, A64, 135. [6] Katrusiak A., McMillan P.F. (eds.) *High-Pressure Crystallography*, Kluwer Academic Publishers, Dordrecht **2004**.[7] Bujak M., Podsiadlo M., Katrusiak A. *Chem. Commun*. **2008** 4439. [8] Dziubek K., Katrusiak A. *J. Phys. Chem.* **2008**, B112, 12001. [9] Olejniczak A., Katrusiak A. *J. Phys. Chem.* **2008**, B112 7183.

Keywords: high pressure; weak interactions; transitions

KN-5

Modelling of Biomaterials: Molecular Recognition at the Surfaces of Bioactive Glasses. Piero Ugliengo[a], Marta Corno[a], Albert Rimola[a]. [a]*Dipartimento di Chimica IFM and NIS, Torino University, Torino, Italy.*
E-mail: piero.ugliengo@unito.it

Among biomaterials, the Hench Bioglass® 45S5 of 46.1% SiO_2, 26.9% CaO, 24.4% Na_2O and 2.6% P_2O_5 molar composition is of great interest in medical applications since, in the presence of body fluids and depending upon the rate of ion release and re-sorption, it creates chemical gradients which promote the formation of a layer of biologically active bone-like hydroxyapatite at the implantation interface. Osteoblasts can preferentially proliferate on the hydoxyapatite layer, and differentiate to form new bone that binds strongly to the implant surface. Hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] is the main constituent of the mineral phase in mammalian bones and teeth enamel. For this reason, HA is widely applied as an orthopaedic and dental biomaterial, both per se and together with other classes of materials, in the form of coating for metal alloys, in composites with polymers and so on. In this work quantum mechanical simulations carried out at B3LYP level within periodic boundary conditions as encoded in the CRYSTAL06 code to model bulk HA [1] and its main surfaces [2] as well as the Hench Bioglass® will be reported. For bioglass, structure, electronic and vibrational features of the bulk will be discussed [3]. For HA, structure and vibrational features of the bulk as well as the electrostatic features of the most important crystallographic surfaces will be discussed. For these latter, interaction with H_2O [4] and with five aminoacids (Gly, Ser, Lys, Gln and Glu) will be described in terms of most stable adsorbed structures and interaction energies. For the case of glycine [5] a detailed study of the role of co-adsorbed water will be addressed. The above results have allowed us to model the process of conformational stabilization of a short poly-glycine (12 residues) induced by the adsorption on the HA (001) surface as a function of mutations in the chain. This study is believed to be the first attempt to model by an ab-initio approach the interaction of biological relevant molecules with HA being the most important interface at the surface of bioglasses.

[1] Corno M., Busco C., Civalleri B., Ugliengo P., *PhysChemChemPhys*, **2006**, 8, 2464. [2] Corno M., Orlando R., Civalleri B., Ugliengo P., *Eur. J. Mineral.*, **2007**, 19, 757. [3] Corno M., Pedone A., Dovesi R., Ugliengo P., *Chem. Mater*., **2008**, 20, 5610. [4] Corno M., Busco C., Bolis V., Tosoni S., Ugliengo P., *Langmuir*, **2009**, 25, 2188. [5] Rimola A., Corno M., Zicovich-Wilson C.M., Ugliengo P., *J. Am. Chem. Soc.*, **2008**, 130, 16181.

Keywords: ab-initio calculations; surface adsorption; amino acids

KN-6

Phase Transitions in Nano- and Bulk-Materials at Elevated Pressures and Temperatures. Vladimir Dmitriev. *SNBL at ESRF, Grenoble, France.*
E-mail: dmitriev@esrf.fr

Phase transitions induced by the variation of external parameters such as temperature, pressure, crystallite size,

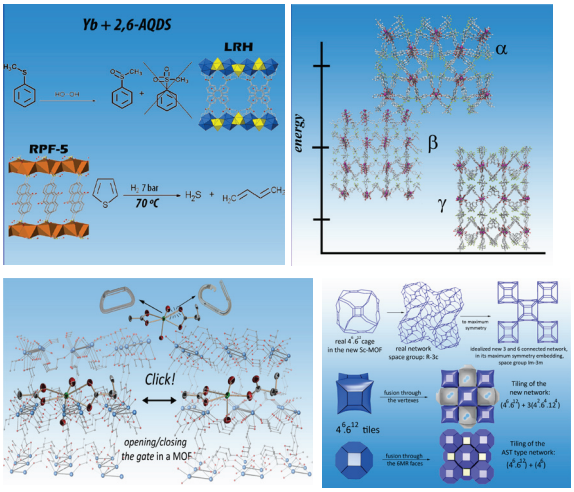
concentration of components etc., are general phenomena typical for condensed matter. Phase transitions can remarkably affect the physical properties of materials, and this behaviour is of great importance both for fundamental science and for materials applications. Establishing relationships between symmetry change at the transition, the mechanism and thermodynamics of a phase transition and the corresponding anomalous macroscopic properties of materials is an important step in understanding the microscopic nature of the effects, and in further developing the rational design of materials with desired properties.
We will consider examples of structural phase transitions in materials particularly interesting due to their perspective properties: elevated hydrogen storage capacity, anomalous negative thermal expansion etc. The related structural features will be analyzed in the framework of a symmetry-based phenomenological theory. It will be shown how the formalism and methods of the theory of phase transitions can be applied to explaining anomalous effects even beyond the transformation region.

Keywords: phase transition; symmetry; transformation mechanism

KN-7

New MOF Materials: Structure-Properties Considerations. M. Angeles Monge. *Instituto de Ciencia de Materiales Madrid CSIC Cantoblanco Madrid, Spain.*
E-mail: amonge@icmm.csic.es

The use of rare earth elements in combination with different ligands has allowed the obtaining of several framework types, whose structural characterization, including the net topology, together with evaluation of their properties will be presented. An overview of the obtained results, on the base of structure-properties relationships allows to extract some conclusions on the properties and features of the new materials. Examples of this research will be presented:
- Controlling the Structure of Rare Earth Arenedisulfonates towards Catalytically Active Materials. All rare earth – anthraquinone-2,6-disulfonate materials show catalytic activity in the oxidation of methyl phenyl sulfide. Among all them, those belonging to the **LRH** family, with a 2D structure with cationic inorganic layers, are very active and selective catalysts in sulfides oxidation. Those belonging to the **RPF** families are also good catalysts for the hydrodesulphurization of tiophene. Structural features explain the differences in the activity among the materials. (Fig 1 up left).
- Polymorphism in Rare Earth MOFs Three Lanthanum MOF polymorphs have been obtained**,** their networks own unusual topologies, the three being uninodal penta-coordinated, two of them unknown up to now and the other named as hxg-d-5-Imma. They will be described and compared. DFT calculations of the relative energies for the three polymorphs show that the most often obtained structure is a metastable phase, which appears next to others thermodynamically more stable. Optical properties will be commented. (Fig 1 up right).
- Reversible breaking and forming of metal-ligand coordination bonds. A temperature triggered single-crystal-to-single-crystal fase transformation in a Metal–Organic Framework , makes this material an intersting heterogeneous catalyst. (Fig 1down left).
- A new Scandium Metal Organic Framework built up from Octadecasil zeolitic cages as heterogeneous catalyst. Zeolitic cages of the AST type are found in the novel scandium-squarate MOF, and the joining of them gives rise to a new binodal network with a unique topology. This new material is an efficient heterogeneous Lewis acid catalyst (Fig 1down right).



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Complementarity of Magnetic Neutron and X-ray Scattering. Thomas Brueckel. *Forschungszentrum Juelich GmbH / Institut fuer Festkoerperforschung / Juelich-Germany.*
E-mail: t.brueckel@fz-juelich.de

While the phenomena of magnetism is known to mankind since nearly 3 millennia, research on this macroscopic quantum phenomena is very topical as witnessed by the Nobel Prize in physics in the year 2007 awarded to Albert Fert and Peter Grünberg for their groundbreaking work in thin films magnetism. Understanding the magnetism of nanostructures paves the way to possible applications in information technology. Spintronics labels information storage, information transport and information processing using the spin of the electron and not its charge. In complex highly correlated electron systems, such as transition metal oxides, mag-netism competes with other degrees of freedom leading to novel ground states and a high sen-sitivity to external disturbances and thus possible novel functionalities. In the quest to control functionalities in these complex materials and materials systems, it is essential to relate them with microscopic information on magnetic structures, magnetisation densities, magnetic exci-tations and fluctuations, which is a realm of scattering methods, namely neutron scattering complemented by magnetic synchrotron X-ray scattering.