

MS09 Combined XAS and XRD Techniques in Physics Chemistry and Materials Science**Chairpersons:** Settimio Mobilio, Joaquin Garcia-Ruiz**MS09.24.1***Acta Cryst.* (2005). A61, C18**XAS and XRD: Complementary Tools to Explore Matter under Extreme Pressure**Alfonso San Miguel, *Laboratoire de Physique de la Matière Condensée et Nanostructures, Université de Lyon-I and CNRS, Villeurbanne, France.* E-mail: sanmiguel@lpmcn.univ-lyon1.fr

The study of matter under extreme conditions introduces strong experimental constraints that, in many cases, ask for the use of complementary techniques for structural characterization. These constraints can include the presence of a complex sample environment with different absorbing and/or scattering elements, a reduced k-space domain or the presence of non isotropic constraints.

I will present here a condensed review of examples where the successful combination of X-ray absorption spectroscopy and X-ray diffraction has contributed to the understanding of the structure and physical properties of matter under extreme conditions of pressure and/or temperature.

Emphasis will be given to those cases where the actual local structure is different from that obtained from the long range order structural analysis and/or when crystallography does not succeed in getting the full structure of a system.

Examples will range from simple molecular crystals with only 4 atoms in the unit cell to the silicon clathrate case with more than fifty atoms in the Bravais lattice. The study of the local compressibility combining both techniques constitutes a further example of the complementarity of both techniques that will be illustrated in the case of pseudobinary alloys and lamellar systems.

Keywords: high pressure research, absorption spectroscopy experimental, high-pressure X-ray diffraction**MS09.24.2***Acta Cryst.* (2005). A61, C18**Element- and Site-specific Study of the Atomic Origin of Magnetic Hardness in Modern Magnets***Daniel Haske, *Advanced Photon Source, Argonne National Laboratory, Argonne IL 60439, USA.* E-mail: haskel@aps.anl.gov

We combined resonant diffraction and absorption of circularly polarized x-rays to probe the atomic origins of magnetic hardness, or coercivity, in permanent magnetic materials. Modern permanent magnets gain both intrinsic stability against demagnetizing fields and large magnetization through alloying of rare-earth and transition metal ions. The resultant complex crystal structures not only feature more than one magnetic element type but also elements of the same species in inequivalent crystal sites, making it difficult for even state-of-the-art probes of magnetism to pinpoint the atomic origins of the desirable magnetic properties of these materials. The element specificity of x-ray magnetic circular dichroism, combined with the site selectivity of resonant magnetic diffraction allow for a more thorough understanding of the rare-earth role. We show that the magnetic hardness of currently the best permanent magnet has its atomic origin predominately at one of the two inequivalent Nd crystal sites.

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Keywords: resonant diffraction, xmc, permanent magnets**MS09.24.3***Acta Cryst.* (2005). A61, C18**X-rays to Elucidate the Structure of Catalysts: Probing the Local and the Crystalline Structure by XAS and XRD**Jan-Dierk Grunwaldt, *Alfons Baiker, Department of Chemistry and Applied Biosciences, Swiss Federal Institute, ETH Hönggerberg, Zürich, Switzerland.* E-mail: grunwaldt@chem.ethz.ch

Both X-ray diffraction and X-ray absorption spectroscopy are widely used in heterogeneous catalysis, since the synthesis of heterogeneous catalysts often aims at high surface area materials. Hence, the materials are often at least partly X-ray amorphous and X-ray absorption spectroscopy is an ideal complementary tool to XRD to monitor the local structure. Recent examples in the field of heterogeneous catalysis and the field of nanomaterials are discussed, where novel synthesis methods, such as flame spray pyrolysis, were used to produce high surface area materials.

An important advantage of the use of X-rays is that the solid catalysts can be studied in situ. Recently, we studied the formation of MoO₃ nanorods from MoO₃·2H₂O by XAS, monitoring both the liquid phase and the solid phase. XAS uncovered the formation of soluble species as soon as the transformation to MoO₃ started. No evidence for an intermediate product was found, which is supported by in situ XRD results. Another key field is the identification of the active species under reaction conditions [2-4]. Also here X-ray based techniques are powerful, as will be illustrated using recent examples.

[1] Michailovski A., Grunwaldt J.-D., Baiker A., Kiebach R., Bensch W., Patzke G.R., *submitted*. [2] Clausen B. S., Topsøe H., Frahm R., *Adv. in Catal.*, 1998, **42**, 315. [3] Sankar G., Thomas J. M., Catlow C. R. A., *Topics Catal.*, 2000, **10**, 255. [4] Grunwaldt J.-D., Clausen B. S., *Topics Catal.*, 2002, **18**, 37.

Keywords: EXAFS, XRD, catalysis**MS09.24.4***Acta Cryst.* (2005). A61, C18**Structural Properties of Semiconductor Nanostructures Determined via X-ray Anomalous Diffraction (DAFS) and Absorption (EXAFS)**Maria Grazia Proietti², Johann Coraux¹, Hubert Renevier¹, Vincent Favre-Nicolin¹, Cristele Monaf³, Michel Gendry³, Bruno Daudin¹, ¹CEA, DRFCM-SP2M, Grenoble, France. ²Dep. Física de la Materia Condensada-ICMA, CSIC-Universidad de Zaragoza, Spain. ³LEOM, UMR-CNRS 5512, Ecole Centrale Lyon, France. LENAC, Université Lyon I, France. E-mail: Hubert.Renevier@cea.fr

We will report novel results on the structural properties of encapsulated semiconductor nanostructures obtained by an ultimate application of anomalous diffraction combined with ray absorption spectroscopy. We have been studying InAs/InP Quantum Sticks (Qs) and GaN/AlN Quantum Dots (QDs). Reciprocal space mapping and fixed-Q anomalous diffraction, measured as a function of energy, in grazing incidence, gives access to the the partial structure factor of the embedded nanostructures (Qs or QDs), allowing to determine their size, strain and atomic composition. Quantitative analysis of the Grazing Incidence Diffraction Anomalous Fine Structure (GIDAFS) oscillations above the resonant edges, gives strain accommodation and coordination at a local atomic scale for the diffraction-selected iso-strain region inside the nanostructures. On the other hand EXAFS measurements provide a comparison with the average atomic environment in the whole island. These methods have been applied successfully both to InAs sticks and to the GaN dots.

[1] Létoublon A., et al., *Phys. Rev. Lett.*, 2004, **92**, 186101. [2] Létoublon A., et al., *Physica B*, 2005, **357/1-2**, 11-15.

Keywords: nanostructures, EXAFS, GIDAFS**MS09.24.5***Acta Cryst.* (2005). A61, C18-C19**The Power of the Multi-disciplinary Approaches to the Study of Minor and Trace Element Incorporation in Geo- and Technological Materials**Simona Quartieri¹, R. Oberti², M. C. Dalconi³, F. Boscherini⁴, G. Iezzi⁵, M. Boiocchi⁶, ¹Dip. di Scienze della Terra, Messina, Italy. ²CNR, Istituto di Geoscienze e Georisorse, Pavia, Italy. ³Dip. di Scienze della Terra, Ferrara, Italy. ⁴INFN and Dip. di Fisica, Bologna, Italy. ⁵Dip. di Scienze della Terra, Chieti, Italy. ⁶Centro Grandi Strumenti, Pavia, Italy. E-mail: simonaq@unimo.it

Much of our knowledge of the origin and differentiation of the terrestrial planets arises from the study of trace elements behaviour.

Interpreting and modelling trace element data requires quantitative information on how elements partition between coexisting mineral and melt phases, which in turn requires understanding of the mechanisms of trace-element incorporation. This goal can be achieved combining various experimental (X-ray diffraction, spectroscopic methods, microbeam analysis) and computational techniques. This combined multidisciplinary approach allows integration of structural information at both short- and long-range scale, and provides greatly enhanced interpretative and modelling tools for geochemistry and, in general, for material sciences. In fact, a correct model of the incorporation and local environment of dopants is crucial to interpret many technological properties and to design innovative materials. A number of case studies (mainly based on electron microprobe analyses, single-crystal and powder X-ray diffraction, XANES and EXAFS spectroscopy applied to natural and synthetic garnets) will be discussed. They mainly concern: i) changes in the local environment of cations along solid solutions; ii) multiple mechanisms of incorporation and partitioning of minor and trace elements in mineral structures with multiple sites with different coordination geometries.

Keywords: XRD, absorption spectroscopy, trace elements

MS10 INTEGRATED CRYSTALLOGRAPHIC, SPECTROSCOPIC, AND COMPUTATIONAL APPROACHES

Chairpersons: Andreas Roodt, Santiago Alvarez

MS10.24.1

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Time-resolved Photocrystallography of Short-lived Molecular Excited States

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Time-resolved photocrystallography is capable of providing atomic-resolution information on the nature of very short-lived transient species [1]. In its comprehensive application diffraction studies are combined with absorption and emission spectroscopy and parallel theory calculations. Several recent single-crystal results on triplet excited states, including large contractions up to 0.85 Å in a binuclear Rh-Rh complex and in a Cu(I) pyrazolate crystal, the latter leading to excimer formation through transient intermolecular Cu...Cu bonding, will be presented. Parallel theoretical calculations give insight into the electronic nature of the excitations. It is evident from the completed studies that the effect of the crystalline environment has a constraining influence when large shape changes are predicted, but is much less severe when intramolecular contractions occur. As may be expected, the crystal structure becomes the determining factor when intermolecular excitations are taking place.

The field is to be extended to include study of excited singlet states with nanosecond lifetimes and monitoring of irreversible chemical reactions in crystalline materials. Modifications in the techniques needed to accomplish such studies will be discussed.

[1] Coppens P., *Chem. Commun.* 2003, 1317. [2] Coppens P., Gerlits O., Vorontsov I. I., Kovalevsky A. Yu., Chen Y.-S., Graber T., Novozhilova I. V., *Chem. Commun.*, 2004, 2144. [3] Coppens P., Vorontsov I. I., Graber T., Milan Gembicky M., Kovalevsky A. Yu., *Acta Cryst.*, 2005, A61, 162-172.

Keywords: time-resolved diffraction, photochemistry, theoretical chemistry

MS10.24.2

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Crystal Structure Prediction with WIEN2k

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The ground state properties of solids are calculated within density functional theory (DFT) using the WIEN2k code [1] that is based on the full-potential augmented plane wave (APW) method. From the total energy the relative stability of different structures can be compared. By minimizing the forces acting on the atoms we can optimize the atomic positions. For the relaxed geometry the electronic

structure is known, from which properties and spectra can be calculated. Phonons can be obtained with a direct method, in which the dynamical matrix is derived from a set of forces that are created when a single atom is displaced along a symmetry-adapted direction in a supercell containing 60-100 atoms. From a limited number of such displacements the complete phonon spectrum can be derived.

Such calculations will be illustrated for $Y_2Nb_2O_7$ that (based on powder diffraction) was proposed to crystallize in the pyrochlore structure and experimentally was found to be an insulator [2]. DFT calculations would make it metallic but the phonons indicate an instability that leads to a significant distortion of the structure, in which it is an insulator. Another example is the ferroelectric phase transition that occurs in the Aurivillius compound $SrBi_2Ta_2O_9$. In this case three phonons, a combination of 1 hard and 2 soft phonon modes, are needed to describe this unconventional ferroelectric phase transition.

[1] Schwarz K., Blaha P., Madsen G.H.K., *Comp. Phys. Commun.*, 2002, 147, 71. [2] Blaha P., Singh D.J., Schwarz K., *Phys. Rev. Lett.*, 2004, 93, 216403.

Keywords: DFT, computation, band structure

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Correlation of Structures and Reactivity of Bispidine Coordination Compounds

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Bispidine-type ligands are relatively easy to synthesize, and a large number of tetra-, penta- and hexadentate ligands, including chiral and dinucleating ligands with a variety of donor groups are available (shown in the Figure is a tetradentate ligand and the simplified structure of the corresponding metal complex with two monodentate co-ligands).



The very rigid ligand structures and the elasticity of the coordination sphere, as well as the enforced octahedral geometry with two electronically and structurally distinct sites for substrate coordination lead interesting molecular properties: μ -peroxodicyclopentadienyl-copper(II) complexes with dinucleating bispidine ligands are among the most stable examples known today, four coordination modes of catechol to copper(II) have been observed, structurally characterized and found to exhibit catechol oxidase activity, "Jahn-Teller isomers" have been observed and analyzed in detail, the iron(II)/ H_2O_2 system is an efficient oxidation catalyst and various mechanistic pathways have been found and analyzed in detail. These and other properties are interpreted on the basis of X-ray data, DFT, MM and ligand field calculations, and the molecular properties are found to strongly correlate with specific structural parameters.

Keywords: catalysis, oxygen activation, structure correlation

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Acta Cryst. (2005). A61, C19-C20

Structure of Halofullerenes Using Experimental and Theoretical Approaches

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Halogenated fullerenes are compounds of profound fundamental and practical importance. Investigation of these fullerene derivatives is complicated by the formation of compound and/or isomer mixtures. Theoretical calculations at the DFT level of theory allow a reliable prediction of relative energy, geometry, and spectroscopic properties of halofullerene molecules containing more than 100 atoms.

In the absence of experimental crystallographic data, a comparison of experimental and calculated IR spectra was indicative for a choice