

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

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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:  $\mu$ -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

#### MS10.24.4

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#### 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

of molecular structures for  $C_{70}Br_{10}$  or  $C_{60}Cl_{24}$ , which have been later confirmed by X-ray crystallography (partially with the use of synchrotron radiation). For the mixture of two compounds with known X-ray structures,  $C_{60}Cl_{28}$  and  $C_{60}Cl_{30}$ , the experimental IR spectra were interpreted by comparison with the calculated ones using subtle differences for compounds possessing very similar structures. For the mixture of isomeric molecules in the same crystal (examples:  $C_{70}Cl_{28}$  [1],  $C_{60}F_{48}$ , and  $C_{78}Br_{18}$  [2]), theoretically predicted structures were helpful in the search for suitable disordering model in LS refinements.

Thus, simultaneous use of X-ray crystallography, IR spectroscopy, and theoretical calculations resulted in obtaining highly valuable structural information for many halogenated fullerenes.

[1] Troyanov S.I., Shustova N.B., Ioffe I.N., Turnbull A.P., Kemnitz E., *Chem. Commun.*, 2005, 72. [2] Troyanov S., Kemnitz E., *Eur. J. Org. Chem.* 2003, 3916.

**Keywords:** fullerene halides, molecular structure, DFT

#### MS10.24.5

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**The Nature of the HB. 3. Towards a Comprehensive HB Theory**  
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Communications 1 and 2 have shown that the *empirical laws* governing HB strength can be reduced to two main points: (i) The PA/pK<sub>a</sub> Equalization Principle; and (ii) The Six Chemical Leitmotifs. Much more difficult is the formulation of a *HB theory*, that is a complete explanation of the two empirical laws in terms of basic chemical bonding theory. Our method relies on what we have called “*The Transition-State HB Theory*” according to which any X-H...Y bond can be considered as a proton-transfer (PT) reaction  $X-H...Y \leftrightarrow X...H...Y \leftrightarrow X...H-Y$  which is bimolecular in both directions, proceeds *via* the X...H...Y transition state (the activated complex) and differs from ordinary reactions only because reactants and products are pre-bound by the HB, so that rather small PT-barriers are to be expected. This method is applied to the study of O-H...O and N-H...O/O-H...N RAHBs by quantum-mechanical DFT emulation with full geometry optimization of the three stationary points or of the complete PT-pathway profile. Analysis of the data was performed, in a VB logic frame, by the Marcus rate-equilibrium relationships, extrathermodynamic LFER Hammett parameters and avoided crossing (state correlation) diagrams. Results show that HB strength, single or double-well shape of the PT-pathway and height of the PT-barriers are completely determined, for any R<sub>1</sub>X-H...YR<sub>2</sub> HB, by the ability of the R<sub>1</sub> and R<sub>2</sub> substituents to achieve the condition of PA/pK<sub>a</sub> matching between the HB donor and acceptor molecules. The theory is used to interpret accurate variable-temperature X-ray crystallographic data.

**Keywords:** hydrogen bond theory, proton transfer, variable-temperature X-ray crystallography

#### MS11 INSTRUMENTATION AT NEXT GENERATION X-RAY SOURCES

**Chairpersons:** Thomas Tschentscher, John Arthur

#### MS11.24.1

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##### Roles of X-ray Optics in the Next Generation X-ray Source

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X-ray optics for x-ray free-electron lasers (XFEL) are very important for beam handling/diagnostics, and, potentially, for FEL generation. In particular, special characters of XFEL such as high spatial coherence, short pulse, and peak brightness, should be well considered in the design work.

For beam handling (*i.e.*, monochromatization, focusing, filtering, *etc.*), conventional optical components are still important. However, higher qualities are required to avoid unwanted speckles under coherent illumination [1,2] and to keep high brightness. Diagnostics of coherence properties, temporal profile, and photon statistics [3] give

crucial information for accelerator operation as well as for user applications. Shot-by-shot and non-destructive methods are highly desirable. X-ray monochromator is a key issue to realize a seeded XFEL such as the two-staged configuration [4].

In order to meet these severe requirements, several R&D programs utilizing presently available synchrotron sources are in progress. Achievements and current problems are discussed.

[1] Mori Y., et al., *Proc. SPIE*, 2001, **4501**, 30. [2] Goto S., et al., *AIP Conf. Proc.*, 2004, **705**, 400. [3] a) Yabashi M., Tamasaku K., Ishikawa T., *Phys. Rev. Lett.*, 2001, **87**, 140801; b) Yabashi M., Tamasaku K., Ishikawa T., *Phys. Rev. Lett.*, 2002, **88**, 244801; c) Yabashi M., Tamasaku K., Ishikawa T., *Phys. Rev. Lett. A*, 2004, **68**, 023813. [4] Feldhaus J., Saldin E. L., Schneider J. R., Schneidmiller E. A., Yurkov M. V., *Opt. Commun.*, 1997, **140**, 341.

**Keywords:** X-ray optics, free electron lasers, synchrotron X-ray instrumentation

#### MS11.24.2

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##### Ultrafast X-ray Studies of Structural Dynamics

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The physical and chemical transformation of matter on the atomic scale typically occurs in many femtoseconds to a few picoseconds and involves the motion of atoms on the Ångström length scale. The unique capabilities of linac based light sources match the natural time and length scale of structural dynamics and provide scientists with an outstanding opportunity to better understand the chemical and physical transformations of matter. Results from the recently commissioned Sub-picosecond Pulse Source (SPPS) at the Stanford Linear Accelerator Center (SLAC) will be utilized to highlight the unique capabilities and challenges of linac based ultrafast light sources. The projected capabilities of the Linac Coherent Light Source (LCLS) and a brief description of the science it will enable will also be discussed.

**Keywords:** time-resolved structural studies, femtosecond X-ray sources, X-ray free electron lasers

#### MS11.24.3

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##### Imaging of Single Molecules

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The path toward imaging single molecules with a free electron laser presents several challenges: from the particle injection and partial physical orientation to the ability to produce x-ray pulses that are short and intense. From short pulses required to the collection of the data with the appropriate detectors. From the classification of the orientation of millions of images to their phasing. Some of these problems will have to wait for the available sources, while others can be studied now by simulations or experiments. We will present some of these experiments, and discuss experimental requirements.

**Keywords:** non-crystallographic phase retrieval, biological molecules, instrumentation

#### MS11.24.4

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##### Parabolic Refractive X-ray Lenses

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Parabolic refractive x-ray lenses are novel optical components for the hard x-ray range from about 5 keV to about 120 keV. They are compact, robust, and easy to align and to operate. They can be used like glass lenses are used for visible light, the main difference being that the numerical aperture is much smaller than one (of order 10<sup>-3</sup> to 10<sup>-4</sup>) [1-3]. They have been developed at Aachen University and are made of aluminium and beryllium. Their main applications are in