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_a 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 ↔ X…H…Y ↔ 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_1X-H…YR_2 HB, by the ability of the R_1 and R_2 substituents to achieve the condition of PA/pK_a 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

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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

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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^{-3} to 10^{-4}) [1-3]. They have been developed at Aachen University and are made of aluminium and beryllium. Their main applications are in micro- and nanofocusing, in imaging in absorption and phase contrast. They are excellently suited in crystallography to match the beam size to the size of the sample and to control the divergence of the beam.

[1] Lengeler B., et al., *Journal of Synchrotron Radiation*, 1999, **6**, 1153-1167. [2] Lengeler B., et al., *Journal of Synchrotron Radiation*, 2002, **9**, 119-124. [3] Lengeler B., et al., *Journal of Physics D*, 2005, *accepted for publication*.

Keywords: X-ray optics, microtomography, X-ray microscopy

MS11.24.5

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Solid State Detectors for Present and Future X-ray Sources

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At the Paul Scherrer Institut, solid state detector development for the Swiss Light Source SLS is successfully done since several years. Results of these efforts are two large area detector systems: The MYTHEN detector is an array of microstrip detectors installed at the powder diffraction station of the material science (MS) beamline X04SA. It covers an angle of 60^o and has a resolution of 0.005^o. Powder patterns can be recorded in a fraction of a second, which opens a new field of experiments. The PILATUS 1M detector is a large area pixel detector with more than 10^6 pixels. Experiments benefit from the properties of the single photon counting detectors: No background from dark current, no read-out noise, very good efficiency in the energy range of 6-15 keV and readout-times below 10ms. Examples of some experiments are given.

In order to improve the pixel detector, a new read-out chip was designed, with much improved performance. It has a 20-bit dynamic range, a count rate capability per pixel of 1MHz and a pixel size of 0.172 x 0.172 mm^2. Based on these components, the new PILATUS 6M detector for the protein crystallography beamline will be built.

For future applications, we have started a development program for a high speed digital X-ray imaging system. The system operates in single photon counting mode and should work at frame-rates of up to 1 KHz. The pixel-size will be approximately 50 x 50 um^2, the system should have about 1000 x 1000 pixels.

Keywords: pixel detectors, powder diffraction, protein crystallography

MS12 DISORDER DIFFUSE SCATTERING

Chairpersons: Reinhard Neder, Thomas Proffen

MS12.24.1

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Diffuse Scattering and Monte Carlo Studies of Relaxor Ferroelectrics

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A renewed interest in the field of ferroelectricity has taken place in recent years since the finding of exceptional piezoelectric properties in the lead-oxide class of relaxor ferroelectric (RF) materials typified by the disordered perovskites $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $PbZn_{1/3}Nb_{2/3}O_3$ (PZN) [1-5].

Although PMN, PZN and numerous related materials have been extensively studied over a long period a detailed understanding of the exact nature of their polar nanostructure has still not emerged. In this paper we describe experiments in which full three-dimensional diffuse neutron scattering data have been recorded from a single crystal of PZN using the time-of-flight (tof) Laue technique on the SXD single crystal instrument at ISIS.

Monte Carlo simulation has been used to demonstrate that the observed diffuse patterns are due to planar nano-domains oriented normal to the six ⟨110⟩ directions. A simple model has been developed which explains the observed scattering. This is based on the fact that Pb atom possesses a lone-pair of electrons, which gives it directionality.

[1] Gehring P.M., Park S.E., Shirane G., *Phys. Rev. B*, 2001, **63**, 224109. [2] Hirota K., Ye Z.G., Wakimoto S., Gehring P.M., Shirane G., *Phys. Rev. B*, 2002, **65**, 104105. [3] Gehring P.M., Ohwada K., Shirane G., *Phys. Rev. B*, 2004, **70**, 014110. [4] Xu G.Y., Shirane G., Copley J.R.D., Gehring P.M., *Phys. Rev. B*, 2004, **69**, 064112. [5] Takesue N., Fujii Y., You H., *Phys. Rev. B*, 2001, **64**, 184112.

Keywords: diffuse scattering, monte carlo treatment, ferroelectric materials

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Order and Disorder in Lysozyme Crystals Caused by the Phase Transition

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Some lysozyme crystals transform to low-solvent crystals by dehydration-induced phase transition [1], [2]. The transition took several hours and the change of X-ray diffraction was recorded to monitor the process [2]. Strong diffuse streaks were observed in the intermediate state where the crystal contains two types of micro-crystals, one with the native lattice and the other with the transformed lattice. At the end of the transition, the transformed micro-crystals were re-ordered as indicated by disappearance of the diffuse streaks. However, the relatively large mosaicity and distinct diffuse scattering indicated that the order of the micro-crystal as well as the crystal packing was not fully recovered.

The structures of native and transformed crystals were determined at resolution 1.13-1.16 Å. They shared essentially the same backbone structure between native and transformed crystals. In the triclinic crystal, however, a conformational change in the main chain was observed in the large loop region of Ser60-Leu75, where a sodium ion was bound in the transformed crystal in place of water molecules in the native crystal. The peptide plane linking Arg73 and Asn74 was rotated 180° in the transformed crystal. In contrast, a sodium ion bound in the monoclinic crystal was removed in the transformed crystal where the corresponding loop region showed a water-bound structure.

[1] Kodandapani M.R.,Vijayan M., *Acta Cryst.*, 1993, D**49**, 234. [2] Harata K., Akiba T., *Acta Cryst.*, 2004, D**60**, 630.

Keywords: phase transition, lysozyme crystal, dehydration

MS12.24.3

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X-ray and Neutron Diffuse Scattering by Cation and Anion Deficient Zirconia

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Zirconia, ZrO_2 doped with cations (e.g. Y^{3+}, Sc^{3+}, Ca^{2+}), is a technologically important material, e.g. with respect to its high ionic conductivity based on oxygen vacancies. An alternative route to create the vacancies is the doping with anions (e.g. nitrogen). To understand the properties of these materials it is necessary to know both long-range and short-range ordering effects of cations, anions and vacancies as well as relaxations of atoms surrounding the defects. The diffuse scattering of zirconia with different types of cation dopants with or without co-doping with nitrogen has been investigated by neutron and X-ray scattering. The typical neutron diffuse scattering of cubic stabilized zirconia shows diffuse maxima being part of global features, such as diffuse bands perpendicular ⟨111⟩, whose distance corresponds to the smallest Zr-O distance. This can be described by a defect model based on statistically distributed vacancies surrounded by radially displaced ions [1], ascribed to rhombohedral short-range order. The parameters of this model, i.e. the various amounts of the displacements of the ions, are obtained by fitting them to the experimental data and are compared to theoretical (ab initio) predictions.

[1] Kaiser-Bischoff I., Boysen H., Frey F., Hoffmann J.-U., Hohlwein D., Lerch M., *J. Appl. Cryst.*, 2005, **38**, 139-146.

Keywords: zirconia, diffuse scattering, defect structures