$\Delta T$ dependencies [3] need to be fitted by least squares minimization. JANA2006 has recently with success implemented this new approach to rigorously refine these parameters for calibration purpose. This presentation will compare the approach between JANA2006, Fullprof [4] and also GSAS.

In the second part of the presentation we will discuss the advantage of the new approach using magnetic superspace groups introduced into the JANA2006 software. Such tool is adequate with high resolution data which highlights more complex magnetic ordering.

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**Keywords: software, time-of-flight, neutron**

## MS.69.4

**Fitting a square peg into a round hole: Simulating a modulated protein crystal**

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We are interested in solving a protein crystal structure that contains an incommensurate modulation in one direction, a so-called (3+1) dimensional modulation. Several roadblocks in this structure determination have been found and will be solved by simulating this type of crystal and diffraction data. In the world of small molecules, modulated datasets are handled in a routine fashion. The existing software supplied with most X-ray systems can index the satellite reflections with the associated q-vectors, predict, integrate and scale the data. Then the Jana software suite can refine and solve the modulated small molecule structure. The resulting data can be neatly stored into a CIF file and submitted for archival and publication.

For protein crystallography it is an entirely different situation. Great strides have been made in processing modulated macromolecular diffraction data. Most protein data processing software cannot handle satellite reflections but the recently released EVAL15 software can process incommensurately modulated data for both protein and small molecules. Then SADABS can be purchased as standalone software to scale the resulting indexed and integrated values from EVAL15 producing an HK6 file. The HK6 format contains up to 6 indices (HKL + 3 q-vectors). It is at this point that there is currently no pathway for solving an incommensurately modulated protein crystal. Incommensurate protein models cannot be fit to 4D electron density maps, these structures cannot be refined against the modulated diffraction data and even if they could it would not possible to store the structure in existing mmCIF or PDB formats. Thus significant modifications of existing tools are required to enable the solution of the first incommensurately modulated protein structure.

As a first step we are in the process of creating a (3+1)D training set that can be used to test approaches for modeling and refining a modulated protein structure against the corresponding diffraction data. The procedure to create the training dataset is backwards from normal data processing. First a modulated structure is generated and then the

resulting main and satellite reflections are simulated. The reflections are represented in (3+1)D indexing. Then everything needs is written into a CIF-type format that can be read in and used by protein crystallographic software. The problems we have encountered as well as the solutions we have selected will be presented and evaluated. The overall result was that each step of the process was much more challenging than we had initially envisioned.

**Keywords: modulation, CIF, simulation, incommensurate**

## MS.69.5

**Higher-dimensional crystallography of n-fold quasiperiodic tilings (n=7-15)**

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The study of periodic average structures gives periodic lattices which closely correspond to the quasiperiodic tilings. This concept is of particular interest for the study of geometrical aspects of quasicrystal-to-crystal phase transformations [1], formation and understanding of quasicrystal-crystal interfaces [2], as well as the intrinsic band-gap behavior of phononic or photonic quasicrystals [3], [4]. For a general overview, see e.g. [5]. A detailed discussion on the periodic average structures of the Penrose and Ammann tiling (pentagonal, resp. icosahedral symmetry), as well as the Fibonacci sequence, can be found in [6].

We studied two-dimensional quasiperiodic tilings with heptagonal, octagonal, enneagonal, decagonal, hendecagonal, dodecagonal, triskaidecagonal and pentakaidecagonal symmetry with regard to their periodic average structures. By identifying the best (most representative) periodic average structures for each case, we have found that quasiperiodic tilings with different symmetries can show significantly different degrees of average periodicity.

The complexity of the periodic average structures and the degree of average periodicity depend on the minimum dimensionality and topological constitution of the hypersurfaces. The distribution of deviations from periodicity is given by the projected volume function of the higher-dimensional hypersurfaces upon physical space. The octagonal, decagonal and dodecagonal tilings show the smallest deviation from their periodic average structures. They have two-dimensional hypersurfaces, and the distribution of deviations can be described by simple sep-functions.

In the 7-, 9-, 11-, 13- and 15-fold tilings, the dimensionality of the hypersurfaces is greater than two, and is therefore reduced in the projection upon a two-dimensional space. This results in a non-homogeneous distribution of deviations from the periodic average lattice, and therefore in a higher complexity of the periodic average structures. But while the 7- and 9-fold tilings can still be described reasonably by at least one periodic average structure, the 11-, 13-, and 15-fold cases show a very low degree of average periodicity. A representation of the infinite tilings by their periodic average structures is generally unfavorable for systems of such high dimensionality. The concept of a periodic average structure can here best be used on finite systems like in photonic and phononic quasiperiodic crystals. The infinite systems on the other hand, show deviations from the periodic lattice that densely fill the unit cell of the later. However, the distribution of deviations is highly inhomogeneous. The study of periodic average structures gives therefore still information about which periodic lattices match the quasiperiodic ones best.

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**Keywords: quasicrystal, tiling, periodic average structure**

## MS.70.1

### Radiation Damage and Mn Metalloproteins

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Manganese complexes play critical roles in the metabolism of oxygen that is important in many biological systems. Among these systems, one of the most important is the photo-induced oxidation of water to dioxygen by the photosynthetic membrane protein complex, Photosystem II (PS II). This reaction is catalyzed by a $Mn_4CaO_5$ cluster located in the PS II membrane complex. One other system is a catalase that contains a binuclear Mn cluster, that disproportionates peroxide to water and dioxygen.

We have shown previously by X-ray spectroscopy that the $Mn_4Ca$ cluster is highly susceptible to the X-ray radiation damage, particularly under the condition that the diffraction data have been commonly collected [1]. We have detailed XAS studies as a function of dose, temperature, energy, and time. We have also completed a similar X-ray damage study using XAS of the oxidized and reduced Mn catalase.

Recently, the crystal structure of PS II isolated from thermophile was reported at a resolution of 1.9 A [2] by collecting the data at much lower X-ray dose than that has been used for the earlier PSII crystallography studies. The electron density map clearly shows the geometry of the four metals and one Ca. Their study for the first time gives us a starting point to think about the detailed chemical structure of the $Mn_4CaO_5$ cluster in the dark state $(S_1)$ and also the consequence of specific radiation damage to the redox-active Mn site. The crystal structures of the Mn catalase have also been reported with high resolutions (~ 1 A) [3,4].

We have compared the effect of X-ray radiation damage on the two major Mn metalloprotains, PS II and Mn catalase. We discuss possible differences between these two cases. The study also gives us an insight into the unique effect of radiation damage to individual metalloproteins and the importance of the combination of the spectroscopic techniques and crystallography in order to obtain intact forms of the catalytic complexes [1,5].

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**Keywords: photosynthesis, manganese, xanes**

## MS.70.2

### Radiation Damage to Protein Crystals is Reduced with a Micron-sized X-ray Beam

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The small, intense X-ray beams available at $3^{rd}$ generation light sources have been exploited by structural biologists to determine the structure of increasing larger or more complex macromolecules. The crystals of many of these macromolecules may have a largest dimension of only 5-10 microns, and may diffract poorly due to lack of internal order. Obtaining data of high signal-to-noise requires exposing the crystal to a beam of high flux density, resulting in increased absorbed dose and radiation damage. Although cryo-cooling of protein crystals significantly reduces X-ray induced radiation damage, it does not eliminate the damage.

The predominant mechanism of interaction of an X-ray with a low-Z atom in the crystal is the emission of a photoelectron, which carries away most of the energy of the incident X-ray. When the emitted photoelectron scatters off another atom, it loses energy to the atom resulting in local damage. As the photoelectron energy decreases, the probability of interacting with yet another atom increases causing more frequent interactions until finally the photoelectron is recaptured. Thus, if the X-ray beam size is small compared to the distance the photoelectron travels from its point of emission, then deposition of photoelectron energy outside the beam footprint may reduce radiation damage inside the beam footprint. Monte-Carlo simulations predict that a photoelectron of typical energy could travel $4 - 5$ µm from the point of emission before being absorbed. We studied radiation damage to lysozyme crystals by monitoring the diffracted intensity of 18.5-keV X-rays as a function of dose and beam size $(0.86 - 15.6$ µm) at beamline 23-ID-B at the Advanced Photon Source. We observed a 3-fold reduction of damage per dose within the footprint of the smallest compared to the largest beam. In addition, the spatial extent of radiation damage was mapped using both 15.1- and 18.5-keV X-rays and a ~1-µm beam. The damage profiles displayed spatial anisotropy with greater damage occurring along the direction of the X-ray polarization, as expected. The spatial extent of the damage was limited to about 4 µm.

**Keywords: radiation, damage, microcrystallography**

## MS.70.3

### The Role of Hydrogen in Radiation Damage

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Radiation damage of biological samples is a major impediment to the success of experiments using ionizing radiation. In a recent study