

# **Local 3D atomic and electronic structure imaging of functionally active sites (VUVX-2016 satellite workshop)**

**Friday 01 July 2016**

**University of Zurich, Irchel campus**

## **Programme**



**Chairs:** **Fumihiko Matsui** (Nara Institute of Science and Technology, Japan)  
**Matthias Kurt Muntwiler** (Paul Scherrer Institut, Switzerland)  
**Juerg Osterwalder** (University of Zurich)  
**Hiroshi Daimon** (Nara Institute of Science and Technology, Japan)  
**Secretary:** **Carmelina Genovese** (University of Zurich)

**Sponsored by**

**Paul Scherrer Institut, VUVX2016 conference**  
**Japanese Society for the Promotion of Science, 3D active-site science project**  
**University of Zurich, Institute of Physics**

# Friday 01 July 2016

## **Registration - Theatersaal (08:30-09:00)**

### **Imaging with Photoelectrons - Theatersaal (09:00-10:25)**

- Conveners: Prof. Osterwalder, Juerg (University of Zuerich)

time	title	presenter
09:00	3D active-site science – 3D atomic structure analysis around local active-site atoms by holography (00h25')	Prof. DAIMON, Hiroshi (Nara Institute of Science and Technology (NAIST))
09:25	Keynote lecture: Looking Into Complex Quantum Materials and Multilayer Heterostructures with Holographic-, Standing Wave-, and Resonant- Photoemission (00h35')	Prof. FADLEY, Charles S. (University of California, Davis)
10:00	PEARL – Photoelectron Diffraction and Atomic Imaging at the Swiss Light Source (00h25')	Dr. MUNTWILER, Matthias Kurt (Paul Scherrer Institut)

## **Coffee Break - Cafeteria (10:25-10:45)**

### **Imaging with Photoelectrons - Theatersaal (10:45-12:10)**

- Conveners: Prof. Daimon, Hiroshi (Nara Institute of Science and Technology (NAIST))

time	title	presenter
10:45	Keynote lecture: X-ray standing waves: a 'simple' method of adsorbate site determination at surfaces (00h35')	Prof. WOODRUFF, D. Phil (University of Warwick)
11:20	Photoelectron diffraction study of topological insulators and doped graphene (00h25')	Prof. YASHINA, Lada V. (Lomonosov Moscow State University)
11:45	Diffraction Spectroscopy as an alternative way of using photoelectron diffraction (00h25')	Dr. MATSUI, Fumihiko (Nara Institute of Science and Technology)

### **Poster Presentations & Photo - Theatersaal (12:10-12:40)**

- Conveners: Dr. Kinoshita, Toyohiko (Japan Synchrotron Radiation Research Institute)

## **Lunch Break - Cafeteria (12:40-13:25)**

### **Poster Session - Theatersaal (13:25-14:25)**

### **Imaging with Fluorescent X-Rays - Theatersaal (14:25-15:50)**

- Conveners: Dr. Matsui, Fumihiko (Nara Institute of Science and Technology)

time	title	presenter
14:25	Keynote lecture: Solution of the phase problem using inside sources (00h35')	Prof. FAIGEL, Gyula (Research Institute for Solid State Physics, Budapest)
15:00	Applications of X-ray fluorescence holography –Lattice distortions and dopants- (00h25')	Prof. HAYASHI, Kouichi (Institute for Materials Research, Tohoku University)
15:25	X-ray Single Molecular Observations from Nanomaterials to Membrane Proteins (00h25')	Prof. SASAKI, Yuji (The University of Tokyo)

**Coffee Break - Cafeteria (15:50-16:10)****Molecular Structure and Properties: Future Opportunities - Theatersaal (16:10-18:00)****- Conveners: Dr. Muntwiler, Matthias Kurt (Paul Scherrer Institut)**

time	title	presenter
16:10	Time-resolved X-ray absorption spectroscopy of molecular systems and materials (00h25')	Prof. CHERGUI, Majed (Ecole Polytechnique Fédérale de Lausanne)
16:35	Endofullerene nanomagnets in reduced dimensions: From Bulk to one-dimensional chains (00h25')	Dr. WESTERSTRÖM, Rasmus (Lund University)
17:00	Orbital Imaging by ARPES: From Basic Principles to High Resolution Experiments (00h25')	Dr. SCHÖLL, Achim (Universität Würzburg)
17:25	Ambient Pressure X-ray Photoelectron Spectroscopy for In-Operando Studies of Solid-Gas and Solid-Liquid Interfaces (00h25')	Dr. SHAVORSKIY, Andrey (MAX IV Laboratory, Lund)
17:50	Concluding Remarks (00h10')	Prof. OSTERWALDER, Juerg (University of Zuerich)

**Poster presentations:**

Dr. KINOSHITA, Toyohiko

P-1 Time-Resolved Atomic Imaging of 3D Active Site by Micro-Photoelectron Holography at SPring-8

Mr. KLIUIEV, Pavel

P-2 Phase problem in photoemission-based imaging of molecular wave functions

Prof. TAGUCHI, Munetaka

P-3 Electronic Structure and Local Structure Study of Active-Site in Functional Materials by Photoelectron Diffraction

Dr. DE LIMA, Luis Henrique

P-4 X-ray photoelectron spectroscopy and tunneling microscopy from very dilute systems: Rb nanotents

Dr. SATO-TOMITA, Ayana

P-5 Visualization of iron environments in hemoglobin using X-ray fluorescence holography

Dr. SHOJI, Mitsuo

P-6 Electronic structures of the synthetic model of the photosynthetic oxygen-evolving complex

Mr. FUKAMI, Shun

P-7 Temperature Dependence of Atomic Structure Around Doped W atom in ZnO thin film studied by photoelectron diffraction

Mr. WALTAR, Kay

P-8 Investigations on the adsorption geometry of CO adsorbed on Pt(111)

Mr. IDEGUCHI, Yuki

P-9 X-ray fluorescence holographic study on valence fluctuating material YbInCu<sub>4</sub>P-10 X-ray fluorescence holographic study on high-temperature superconductor FeSe<sub>0.4</sub>Te<sub>0.6</sub>

Mr. OTA, Hiroshi

P-11 Characterization of photocatalytic active sites of rutile (110) surface by circular dichroism of resonant Auger electron diffraction

*Welcome to the satellite workshop "Local 3D atomic and electronic structure imaging of functionally active sites" of the VUVX2016 conference!*

*Core-level and valence band holographic imaging techniques have been extensively developed recently owing to constructions of new light sources and developments of new analysis programs and high performance detectors. This workshop will focus on new science opened by such new analysis methods. Keynote lectures by the Maestri of photoelectron and x-ray fluorescent diffraction as well as X-ray standing wave techniques, and various cutting-edge presentations by invited researchers will be arranged. A poster session is also planned for young researchers.*

*We thank the supports by Paul Scherrer Institut, VUVX2016 conference, Japanese Society for the Promotion of Science "3D active-site science project", and University of Zurich, Institute of Physics.*

*We hope all attendees will be inspired by a new science of "Local 3D atomic and electronic structure imaging".*

*July 1st, 2016*

*Organizers*

# Lectures



### 3D active-site science

#### – 3D atomic structure analysis around local active-site atoms by holography

Hiroshi Daimon

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An active-site atom plays an important role in a functional material, such as a dopant boron atom in a p-type Si semiconductor. However the 3D atomic structure analysis around this kind of specific atom has been impossible by a standard structure analysis method such as an x-ray diffraction because this kind of active site has no translational symmetry. Several methods to analyze the 3D atomic structure around this kind of specific atoms with no translational symmetry have been developed around 1990's such as "photoelectron holography"<sup>1,2)</sup>, and "fluorescent x-ray holography"<sup>3)</sup>. Their accuracy to reproduce the atomic positions, however, has not been enough to investigate their structure in detail. Recently their accuracy improved dramatically by the development of analysis code<sup>4)</sup> and sensitive detectors for fluorescent x-ray holography<sup>5)</sup>. A new technique of direct 3D atomic structure analysis method "stereo-photography of atomic arrangement" has also been developed<sup>6)</sup>. These techniques received renewed attention recently because of its theoretical interest and potential technological applications. Hence we started a project of "3D active-site science" supported by JSPS Grant-in-Aid for Scientific Research on Innovative Areas: Grant Number 26105001 in order to open a new field of local 3D active-site science. Main subjects in this project are ranging from inorganic materials to bio-materials, such as the dopant in semiconductor or oxides, the active-center in catalysis, the interface structure in organic devices, the photochemical center of photosynthesis proteins and so on.

One example of recent "stereo photograph of atomic arrangement"<sup>8)</sup> is shown in Fig. 1, which is a direct 3D image of atomic arrangement around emitter atom. The accuracy is improved by "photoelectron diffraction/holography" because the diffraction pattern can be commonly used.

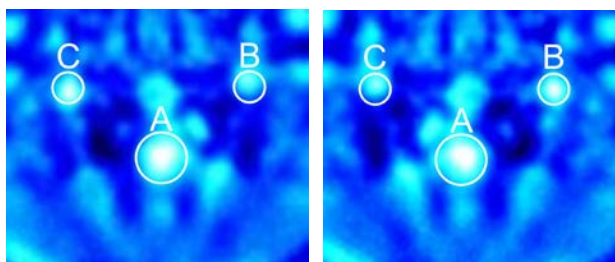


Fig. 1 Stereo-photograph of atomic arrangement around In atom in InP crystal. <sup>8)</sup>

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# Looking Into Complex Quantum Materials and Multilayer Heterostructures with Holographic-, Standing Wave-, and Resonant- Photoemission

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In this talk, I will discuss several emerging aspects of imaging atomic and magnetic structure, as well as element-specific contributions to electronic structure, using photoemission. These make use of techniques whose exploitation has become more and more possible through the development of better x-ray sources spanning the soft x-ray and multi-keV regimes, and improved spectrometer and detector instrumentation: holographic analysis of photoelectron angular distributions including spin resolution [1], the excitation of photoelectrons with Bragg-reflection x-ray standing waves [2], the full exploitation of variable-polarization radiation [2], and the tuning of photon energy so as to enhance the influence of different atoms or interfaces in the sample [3].

## Acknowledgements:

This work was supported by the U.S. Department of Energy, Contracts DE-AC02-05CH11231 at LBNL and DE-SC0014697 at UC Davis, and through the LDRD Program of LBNL.

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- [3] “Energetic, spatial and momentum character of a two-dimensional electron gas at the buried interface between GdTiO<sub>3</sub> and SrTiO<sub>3</sub>”, S. Nemšák et al., Phys. Rev. B, to appear, <http://arxiv.org/abs/1508.01832>



# PEARL – Photoelectron Diffraction and Atomic Imaging at the Swiss Light Source

M. Muntwiler<sup>1</sup>, J. Zhang<sup>1</sup>, R. Stania<sup>1,2</sup>, F. Matsui<sup>3</sup>,  
T. Glatzel<sup>4</sup>, E. Meyer<sup>4</sup>, T. A. Jung<sup>1,4</sup>, P. Aebi<sup>5</sup>, R. Fasel<sup>6</sup>, T. Greber<sup>2</sup>

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The Photo-Emission and Atomic Resolution Laboratory (PEARL) is a new synchrotron-based user laboratory for studies of surface structure at the Swiss Light Source (SLS). The main experimental methods are photoelectron diffraction in angle and energy scanned modes, as well as low-temperature scanning tunnelling microscopy (LT-STM). The experimental setup at PEARL also supports high-resolution XPS and Auger electron spectroscopy. Valence band spectroscopy and circular dichroism measurements are possible with limited performance.

The soft X-ray beamline delivers smoothly tunable X-rays in the energy range from 60 eV to 2000 eV at a resolving power up to  $E/\Delta E \approx 7000$ . The main polarization mode of the bending magnet is linear, but can be switched to partial circular polarization. The focal spot size of  $200\ \mu\text{m} \times 100\ \mu\text{m}$  can alternatively be detuned to approximately  $1\ \text{mm} \times 1\ \text{mm}$  for radiation-sensitive samples.

The experimental station consists of three parts which are connected by sample transfer under ultra-high vacuum: a state of the art angle- and energy-resolved photoelectron spectrometer with a  $60^\circ$  acceptance angle, a low-temperature scanning tunnelling microscope, and a surface preparation chamber with standard surface cleaning, organic evaporators, and accessory ports.

As a scientific example, we present a study of the atomic details, in particular the adsorption height, of a monolayer of hexagonal boron nitride on Ni(111) measured with sub-Ångström resolution using angle-scanned and energy-scanned photoelectron diffraction. The distance is determined by a multi-dimensional R-factor optimization of multiple scattering cluster calculations.

The beamline is open to external users in the regular user facilities programme of the Paul Scherrer Institut.

## **X-ray standing waves: a 'simple' method of adsorbate site determination at surfaces**

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The X-ray standing wave technique, when applied in the normal incidence geometry (NIXSW) relative to the Bragg scattering planes of a crystalline substrate, provides a particularly simple method to determine the local adsorption site of adsorbates on surfaces in an element-specific and chemical-state-specific fashion. The experimental data can be fitted in a model-independent fashion with just two parameters, the coherent position (CP) and the coherent fraction (CF), and for occupation of single high-symmetry sites the interpretation of these parameter values in terms of the adsorption site is trivial. For low-symmetry sites or coadsorption in multiple sites simple modeling is required. The basic principles of the NIXSW technique will be describe and illustrated with a number of examples.

As the CF and CP values correspond to the amplitude and phase of individual Fourier components of the real-space structure, the XSW technique overcomes the well-known 'phase problem' of X-ray diffraction methods. NIXSW measurements taken in several different geometries can therefore provide sufficient components to produce a direct image of the structure, and one example exists of the application of this approach to determine the adsorption structure at a solid-electrolyte interface. The strengths and limitations of this approach will be discussed, along with some remarks regarding the complementarity of the NIXSW and scanned-energy photoelectron diffraction (PhD) methods for adsorbate structure determination.

# Photoelectron diffraction study of topological insulators and doped graphene

Lada V. Yashina<sup>1</sup>, Dmitry Yu. Usachov<sup>2</sup>, Ilya Ogorodnikov<sup>3</sup>, Mikhail V. Kuznetsov<sup>3</sup>

<sup>1</sup>Moscow State University, Moscow, Russia, <sup>2</sup>St. Petersburg State University, 7/9 Universitetskaya nab, St. Petersburg, 199034, Russia, <sup>3</sup>Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia<sup>SEP</sup>

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X-ray photoelectron diffraction is a unique tool and the only choice to probe local atomic structure of 2D materials and buried interfaces. Both graphene and topological insulators (TIs) present a fundament for future electronics and spintronics. Using photoelectron diffraction and spectroscopy we have demonstrated a selective incorporation of boron impurities into only one of the two graphene sublattices. We have shown that in the well-oriented graphene on the Co(0001) surface the carbon atoms occupy two nonequivalent positions with respect to the Co lattice, namely top and hollow sites. Boron impurities embedded into the graphene lattice preferably occupy the hollow sites due to a site-specific interaction with the Co pattern. Our theoretical calculations predict that such boron-doped graphene possesses a band gap that can be precisely controlled by the dopant concentration. B-graphene with doping asymmetry is, thus, a novel material, which is worth considering as a good candidate for electronic applications.

We characterized the atomically precise interface between Fe, Co, Ni and the topological insulators Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> using chemical state specific full hemisphere photoelectron diffraction and holography, STM, valence band and core level photoemission and DFT modeling as well. Our ab-initio calculations show that such hidden order at the interface leads to a suppression of the coupling between neighboring magnetic moments. The intact interface properties revealed by our experiments are suitable for devices based on spin-transfer torque effects between TIs and ferromagnetic layers.

## Reference

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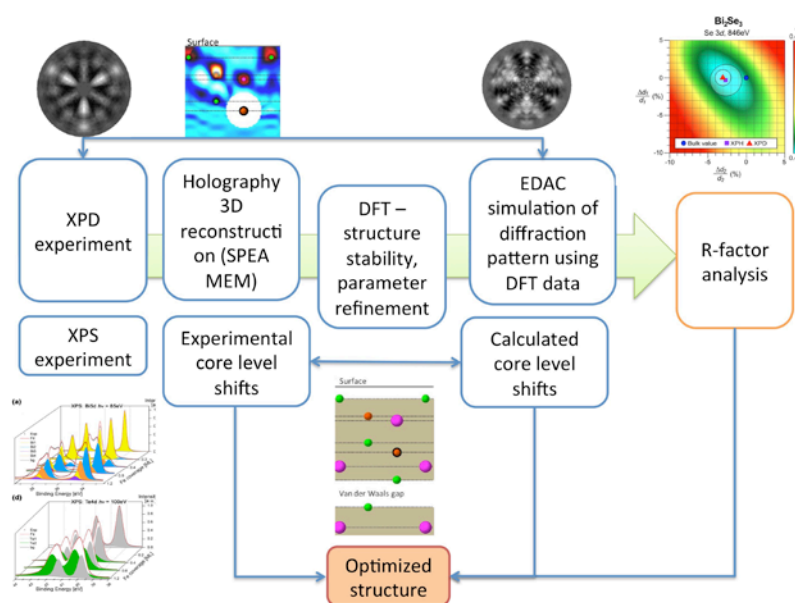


Fig. 1. A scheme illustrating a paradigm for local structure determination.

## Diffraction Spectroscopy as an alternative way of using photoelectron diffraction

Fumihiko Matsui<sup>1</sup>, Tomohiro Matsushita<sup>2</sup>, Hiroshi Daimon<sup>1</sup>, Matthias Muntwiler<sup>3</sup>, Thomas Greber<sup>4</sup>

<sup>1</sup> Nara Institute of Science and Technology, Japan, <sup>2</sup> JASRI/SPring-8, Japan, <sup>3</sup> Paul Scherrer Institut, Switzerland, <sup>4</sup> University of Zürich, Switzerland

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The photoelectron from a localized core level is an excellent probe for element-specific atomic structure analysis. Photoelectron diffraction provides information on the surrounding atomic configuration, which is recorded as forward focusing peaks (FFPs) at local interatomic directions and diffraction patterns in the photoelectron intensity angular distribution (PIAD). We developed a new holographic reconstruction algorithm based on iterative cycles of scattering pattern fitting and diffraction pattern simulating.<sup>1)</sup> We succeeded in reconstructing atomic arrangement images of graphite and intercalated compounds.<sup>2)</sup> Since PIAD differs by different surrounding atomic arrangement, emitter atom sites can be specified by their characteristic diffraction patterns. By combining this diffraction technique with various spectroscopies -- we call it *diffraction spectroscopy*, the electronic property information of each atomic site structure can be investigated individually.

We have applied this method to study the electronic and magnetic structures of Ni thin film.<sup>3)</sup> X-ray absorption and magnetic circular dichroism (XAS/XMCD) spectra for each atomic layer were separated. Surface and interior core-level shifts and magnetic moments were determined for each atomic layer individually around the spin reorientation transition. Furthermore, by probing the rotational circular dichroism of FFPs which also appears in resonant Auger electron angular distribution pattern, site specific and magnetic quantum number ( $m_l$ )-resolved XMCD spectra can be obtained.<sup>4,5)</sup>

In the valence PIAD at high kinetic energy, the quantum phenomena in initial states (*band dispersion*) and final states (*photoelectron diffraction*) are both well observed. Making use of the site-specific photoelectron diffraction, we succeeded in measuring the valence band spectra from graphene edge region.<sup>6)</sup> Element-resolved density of state (DOS) for compound crystals such as InSb can be obtained analyzing corresponding FFP intensities from different sites.

### 2D-measurements: Order is important!

#### Spectro-diffraction

Resolve different states  $\Rightarrow$  state-specific structures



Can cook separately

Initial shape preserved



#### Diffraction spectroscopy

Resolve different sites  $\Rightarrow$  site-specific properties

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## Solution of the phase problem using inside sources

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Traditionally, the atomic order in crystalline substances is determined by x-ray diffraction. Measuring diffraction peaks we obtain the magnitude of the scattered waves, but the phase information is lost. However, for direct structure determination both the magnitude and the phase of the structure factors should be known. In practice the loss of phase information is compensated by additional knowledge, such as atomicity, positivity of electron density, known part of the structure, composition etc. Clever algorithms, like direct [1], Patterson [2], dual space [3] methods, have been developed to incorporate and use our extra knowledge. Beside the theoretical solutions there are experimental approaches. The best known is the controlled variation of the structure factor. However, in this case special sample has to be prepared, which limits applicability. Another approach is the three-beam diffraction, where three reflections are simultaneously excited [4,5]. Although it was shown that this method works, the practical application is not widespread, due to experimental difficulties. Another possibility is atomic resolution holography using inside sources or detectors [6,7,8]. This method can give the average local atomic arrangement in orientationally ordered samples by a direct transformation of the holographic pattern. However, the measurement of x-ray holograms are technically complicated, time consuming and only relatively simple structures (10–100 atoms) can be determined. An other approach, which gives the phase, is the Kossel pattern analysis. Lately, it was experimentally demonstrated that the phase of several structure factors can be simultaneously measured [9,10]. In this talk the basics of inside source techniques is given with a comparison of holography and the Kossel technique. Outlook for future development is also presented.

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## Applications of X-ray fluorescence holography –Lattice distortions and dopants-

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X-ray fluorescence holography (XFH) can provide atomic arrangements around a specific element without any prior knowledge of structures. From the viewpoint of structural analyses, such a novel feature of the XFH has a great possibility to pioneer new fields in the solid state physics. Actually, to date, using the XFH we have produced quite new information of the structures in some advanced materials. We call this feature of the XFH “3D medium-range local structure”. Nowadays, there are many applications of XFH particularly for disordered systems and dopants. Among them, we will show the recent topics about high- $T_c$  diluted magnetic semiconductors (DMS).

Figure 1 shows atomic images the  $\text{ZnSnAs}_2/\text{InP}$  thin film, which is the host material of a high- $T_c$  DMS  $\text{Mn:ZnSnAs}_2$ . Comparing the Zn/Sn images in Fig.1 (a) and (c), the As images in Fig.1 (b) are very weak. This feature reflects larger lattice distortion of As layer, because the intensity of atomic image is inversely proportional to the atomic fluctuation. This indicates that As layer served as a buffer, which relaxed the strain caused by random occupations of Zn and Sn atoms in sphalerite-type stricture. These results could lead to further understanding and controlling of the growth of highly Mn-doped  $\text{ZnSnAs}_2$ .

Another topic of the high- $T_c$  DMS is the local structure around Co doped into  $\text{TiO}_2$  thin films. Currie temperature of the  $\text{Co:TiO}_2$  exceed to 600 K, which is highest among various DMS materials. We measured Co K X-ray fluorescence holograms of the  $\text{Co:TiO}_2$ . The reconstructed atomic images and XAFS data revealed a suboxide nanocluster around Co. Possible atomic configurations of the suboxide network were investigated by first-principles calculation, which justified the reason why the clusters appear only at a high Co concentration. Furthermore, the suboxide network might be the source of the strong exchange interaction leading to the high  $T_c$  in Co-doped  $\text{TiO}_2$ .

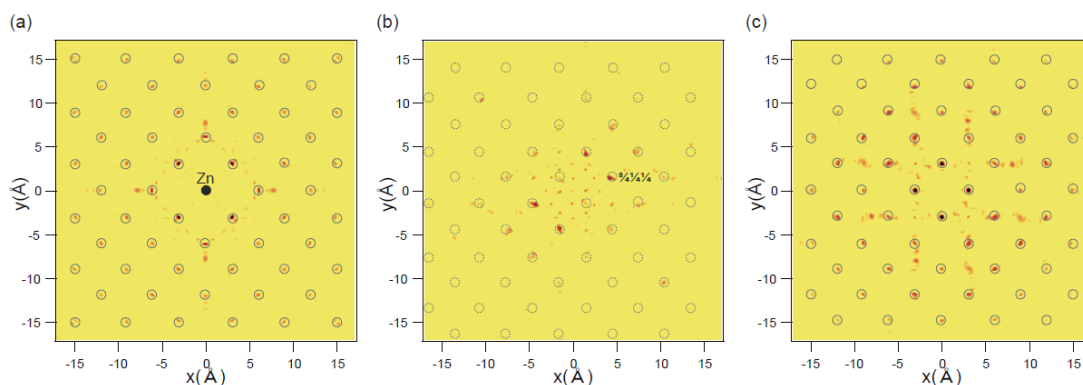


Fig. 1. Atomic images around Zn obtained from the X-ray fluorescence holograms. (a): Zn/Sn images at  $z = 0 \text{ \AA}$ . (b): As images at  $z = 1.4 \text{ \AA}$ . (c): Zn/Sn images at  $z = 2.8 \text{ \AA}$ .

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## **X-ray Single Molecular Observations from Nanomaterials to Membrane Proteins**

Yuji C. Sasaki<sup>1,2</sup>, Keigo Ikezaki<sup>1</sup>, Yufuku Matsushita<sup>1</sup>, Hiroshi Sekiguchi<sup>2</sup>

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Diffraction X-Ray Tracking (DXT) using normal synchrotron orbital radiation source has been developed for obtaining the information of the 3D internal motions of single protein molecules with both high time-resolution (micro-seconds) and high precision (nm/1000)<sup>1)-8)</sup>. Recently, we succeeded in observing picometer-scale Brownian motions of individual functional membrane protein channels (bR, KcsA, KvAP, nAChR, AChBP,  $\alpha 7$ -nAChR), antigen-antibody interactions, peptide/MHC complexes, ATP ligand proteins (Myosin, Chaperonin), structural fluctuations of intrinsically disordered proteins (IDP; Tau protein and  $\alpha$ -Synuclein), and monitoring super-weak force field (pN) under super-saturated solutions.

We have proposed single molecule techniques using short wavelength probes, such as X-rays, electrons, and neutron. Especially, Diffraction X-Ray Tracking (DXT) using normal synchrotron orbital radiation source has been developed for obtaining the information of the 3D internal motions of single protein molecules with both high time-resolution (micro-seconds) and high precision (nm/1000). DXT is a method to obtain three-dimensional (3D) dynamics through trajectories of the Laue diffraction spots from the labelled individual gold nanocrystals. DXT can be used to trace functional motions of proteins at single molecule level in two rotational axes, tilting and twisting views. This concept can be applied to utilize also with electrons or neutrons<sup>9)</sup>.

Additionally, we have applied DXT method as a high time resolution (100ns-10 $\mu$ s) and high positional accuracy ( $\pm$ pm) detection system for the time-resolved dynamical interactions between a single gold nanocrystal and super-saturated molecule networks<sup>10)-11)</sup>. This method is able to direct observation of nano-scale dynamics for super-saturated protein molecules by detecting angular rotational displacement of a coexisted single gold nanocrystal. For target samples, we choose a crystal precursor metastable state of lysozyme solution. The weak point in DXT is to use labelling technique. The size of the labelled gold nanocrystal influences movement inside the molecule and material systems. Recently, we succeeded to estimate size effect quantitatively. From now, DXT would expand sample systems into many materials and molecules.

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## **Core-level Photoelectrons to visualize Structural Dynamics**

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The advent of femtosecond (fs) laser technology some twenty five years ago opened a whole new era in Science because of its ability to probe in “real-time” nuclear motion in molecules, crystals, liquids and proteins. In the past fifteen years, huge efforts have been deployed aimed at combining the high time resolution of fs lasers with the high spatial resolutions of structural techniques, such as X-ray and electron diffraction and X-ray spectroscopies. This has been made possible thanks to the advent of sources of ultrashort electron or X-ray pulses, such as the X-ray free electron lasers. In parallel, lab-based sources of ultrashort vacuum ultraviolet and soft X-rays based on the process of High Harmonic Generation reach the sub-fs domain, which make it possible to study the underlying electronic structure changes which drive the actual structural dynamics of systems. Ultrafast core-level spectroscopies (X-ray absorption and emission and photoelectron spectroscopies) are emerging as the ideal tools to probe structural dynamics in matter. The talk will focus on describing the tools and demonstrating their power at probing the structural dynamics of solution chemical and biological systems and solid materials.



# Endofullerene Nanomagnets in Reduced Dimensions: From Bulk to One-Dimensional Chains

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Endofullerene nanomagnets [1] belong to the group of single-molecule magnets (SMMs), a class of molecules that exhibits an intrinsic magnetic bistability at low temperatures and are particularly promising for molecular spintronic applications [2]. A fascinating example is the dysprosium-scandium-nitrogen based  $\text{Dy}_n\text{Sc}_{3-n}\text{N}@\text{C}_{80}$  ( $n = 1-3$ ) series, where the entrapped cluster combines diamagnetic  $\text{Sc}^{3+}$  and/or paramagnetic  $\text{Dy}^{3+}$  species at the corners of a triangle with a central  $\text{N}^{3-}$  ion. The ligand fields, mainly from the  $\text{N}^{3-}$  ion, results in an axial anisotropy where the magnetic easy axis is directed along the corresponding Dy-N bonds. Additionally, for the polynuclear Dy clusters ( $n=2,3$ ), the central  $\text{N}^{3-}$  ion mediates a superexchange coupling that, in combination with the dipolar interactions, leads to a ferromagnetically coupled ground state with blocking of the magnetization ( $n=2$ ), or frustration ( $n=3$ ) [3]. Here I will present an X-ray study of endofullerene nanomagnets in the bulk phase, on surfaces, and one-dimensional chains encapsulated in carbon nanotubes, so-called peapods. The studies were performed using X-ray magnetic circular dichroism and scanning transmission X-ray microscopy.

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# Orbital Imaging by ARPES: From Basic Principles to High Resolution Experiments

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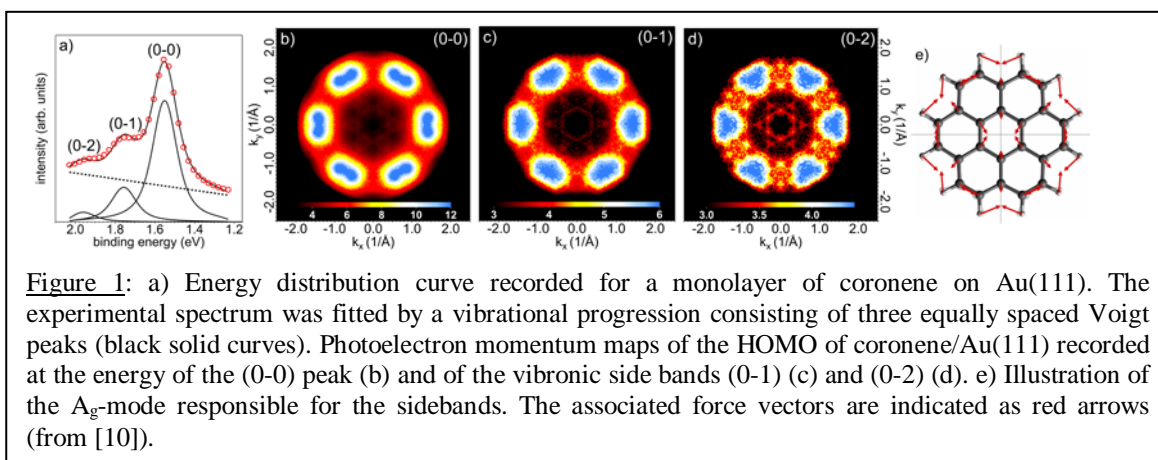
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In recent years angle-resolved photoelectron spectroscopy (ARPES) has emerged as a particularly powerful tool for the imaging of orbital densities [1,2]. In this talk I will briefly introduce this technique and discuss its prospects and main limitations.

The imaging of orbitals in momentum space by ARPES has been applied in several instances, e.g. to show hybridization at interfaces [3], the resulting band dispersion [4] and many particle effects [5,6]. By retrieval of the phase information, which can be done by mathematical algorithms [7] or by experiments with circular light polarization [8] orbitals can also be reconstructed in real space and in three dimensions [9].

In particular by using state-of-the-art momentum microscopes with high energy resolution in combination with synchrotron radiation orbital imaging by ARPES can provide unprecedented insight into the properties of molecular materials. For example, photoelectron momentum microscopy with high energy resolution allows imaging of molecular orbitals with resolution of vibronic modes. I will demonstrate that the intensity patterns of photoelectrons derived for the vibronic sidebands of molecular states show characteristic changes due to the distortion of the molecular frame in the vibronically excited state (see Figure 1). By a comparison to the simulated patterns derived from calculations, an assignment of the specific vibronic mode that preferentially couples to the electronic excitation is possible, which in the example of the highest occupied molecular orbital (HOMO) of coronene is a  $b_{2u}$  inplane mode with an energy of 0.2 eV [10]. Orbital imaging by photoelectron momentum mapping with vibronic resolution thus provides unique information for the analysis of the coupling between electronic and vibronic excitation.



**Figure 1:** a) Energy distribution curve recorded for a monolayer of coronene on Au(111). The experimental spectrum was fitted by a vibrational progression consisting of three equally spaced Voigt peaks (black solid curves). Photoelectron momentum maps of the HOMO of coronene/Au(111) recorded at the energy of the (0-0) peak (b) and of the vibronic side bands (0-1) (c) and (0-2) (d). e) Illustration of the  $A_g$ -mode responsible for the sidebands. The associated force vectors are indicated as red arrows (from [10]).

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## **Ambient Pressure X-Ray Photoelectron Spectroscopy for in-operando Studies of Solid-Liquid and Solid-Gas Interfaces**

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Ambient Pressure X-Ray Photoelectron Spectroscopy (AP-XPS) is an emerging technique, which has already demonstrated its ability to reliably and quantitatively measure chemical composition of the interfaces between solids, gases, and liquids under realistic conditions.<sup>1</sup> It combines a set of power tools provided by conventional XPS, such as chemical specificity, surface sensitivity, non-contact probe nature, with the recent technical developments of the differentially-pumping electrostatic lenses, and, thus, allowing experiments in the areas and in environments not possible before – high humidity, ambient pressures, multiple components and phases. This makes AP-XPS a great tool for studies of Catalysis, Bio- and Geo- Chemistry, Solar and Energy Sciences, Atmospheric Chemistry, and many others. In recent years several new developments in AP-XPS have taken place, bringing focus of the technique into time and space domain, as well as increasing complexity of studied samples. Thus, it has been demonstrated that by using specifically designed samples (i.e. multi-layer mirror) AP-XPS is capable of quantitatively probing spatial distribution of solvated ions within Helmholtz layer at a solution-solid interface with 1 Å resolution.<sup>2</sup> It has also been demonstrated that AP-XPS can monitor distribution of electron energy levels (band bending) at the electrolyte-semiconductor interface during light-assisted water splitting reaction.<sup>3</sup> In this paper we will discuss in details these examples, and demonstrate how such spatial resolution capability allows better understanding fundamental principles governing composition and reactivity of the interfaces.

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# Posters



# Time-Resolved Atomic Imaging of 3D Active Site by Micro-Photoelectron Holography at SPring-8

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We have organized a research group to investigate “3D active site” by using photoelectron holography method [1]. The purpose on this project research is to perform photoelectron holography measurements for a variety of materials, in which impurity sites of dopants, active sites of catalysis, and local structures of interfaces fulfil their important functions. Schematic image of the purpose of the project is shown in the figure. Most of the studies are undergoing at the two soft-x-ray beamlines BL07LSU & 25SU at SPring-8. We consider that the off-line measurements without using synchrotron radiation are also very important to get good quality of the data before starting the online measurements at the above beamlines. In this project, we will realize the followings.

1. Distinguished imaging of active sites depending on chemical bonding conditions by using high-energy resolution apparatus.
2. Pinpoint analysis by using micron-size beam.
3. Time-resolved dynamical analysis under applying outer field.

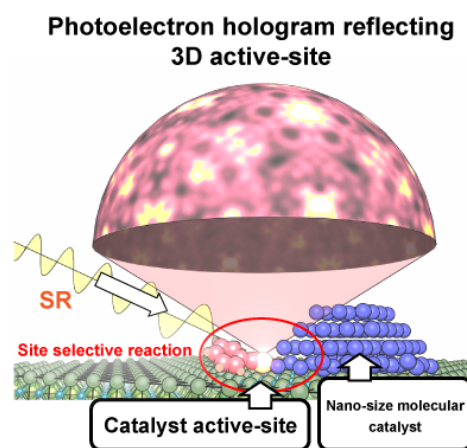
In the fiscal year 2015, we have collaborated with many members in and out of the “3D active site” projects. Throughout the collaboration and discussion, some outside members have attended to the projects group.

Some of the successful examples are introduced together with the apparatus used in the project. We are using the two-dimensional photoelectron spectrometer Display-type Spherical Mirror Analyzer (DIANA) and a hemispherical analyzer (DA30). Some developments of apparatus towards realizing a micro-focus beam are performed. Studies using the display-type ellipsoidal mesh analyzer (DELMA) [2-4] at BL07LSU are also undergoing. Another type of compact display type analyzer PESCATORA works well.

For the time-resolved measurements, we have almost finished to set experimental apparatuses, such as pump laser branch lines, soft-x-ray choppers and so on.

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Schematic image of the 3D active site research using photoelectron holography.

## Phase problem in photoemission-based imaging of molecular wave functions

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Much information about the structure of molecular wave functions can be inferred from angular-resolved photoelectron spectroscopy of well-ordered molecular layers on single-crystalline metal substrates [1-3]. For large planar molecules, final state scattering can be neglected and the photoelectron final state can be approximated with a plane wave [1]. As a result, the measured ARPES intensity is proportional to the squared modulus of the Fourier transform of the initial state wave function. This situation is directly analogous to the phase problem in coherent diffraction imaging (CDI) [4]. Although the phase of the complex-valued photoelectron distribution in the detector plane is lost in the measurement, both the magnitude and the phase of the wave function can be reconstructed from the experimentally available modulus of its Fourier transform, provided the intensity in the detector plane is measured at the oversampling condition and some *a priori* knowledge about the object is available [5,6]. We draw an analogy between the phase problem in molecular orbital imaging via ARPES and of that in optical coherent diffraction imaging, and we present the reconstructed molecular wave functions from simulated and experimental ARPES data as well as the micrometer-sized structures from an analogue optical experiment. Fig. 1 shows amplitude and phase of the HOMO of PTCDA reconstructed by applying the phase retrieval algorithms [5-8] to the data simulated by density functional theory (DFT).

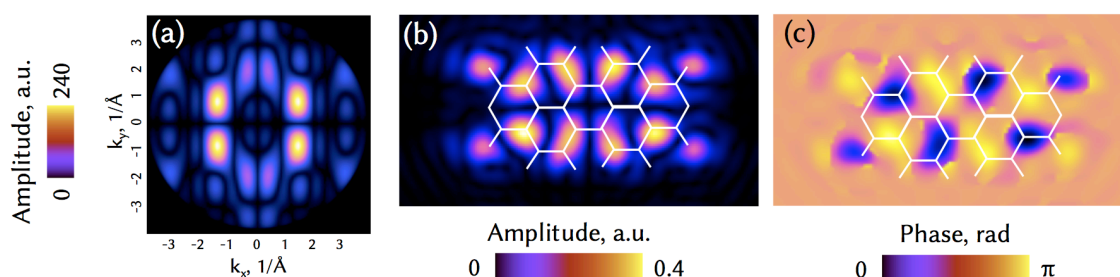


Fig. 1: Reconstruction of simulated HOMO of PTCDA. (a) Amplitude of DFT-simulated ARPES of PTCDA HOMO at 50 eV photon energy. (b) Reconstructed amplitude of PTCDA HOMO. (c) Reconstructed phase of PTCDA HOMO.

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# Electronic Structure and Local Structure Study of Active-Site in Functional Materials by Photoelectron Diffraction

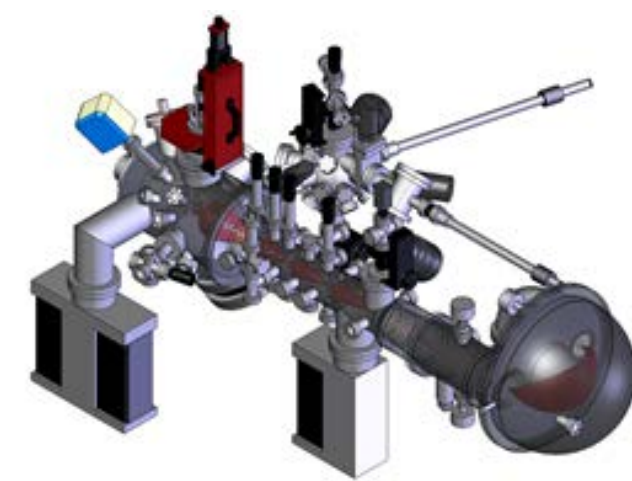
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## Summery

We have been developing a two-dimensional display-type ellipsoidal mesh analyzer (DELMA), which is composed of a wide acceptance angle electrostatic lens (WAAEL) unit, a transfer lens system and a high energy electron analyzer (VG SCIENTA R4000) at SPring-8 BL07LSU in Japan [1]. DELMA is a photoelectron spectroscopy device that has the photoelectron emission microscope function, spatial resolution about 100  $\mu\text{m}$  now, which allows us to measure two dimensional photoelectron intensity angular distribution of the individual small regions in the sample microscopically. The acceptance angle of the photoelectron angular distribution pattern is  $\pm 45^\circ$ , and the total energy resolution  $\Delta E/E$  of DELMA combined with a concentric hemispherical analyzer is 0.2% at kinetic energy around 700 eV. While DELMA was originally designed for soft x-ray energy region, we plan to experiment with the hard x-ray photoelectron diffraction by using synchrotron light at BL13XU and BL39XU SPring-8. Since hard x-ray photoelectron spectroscopy (HAXPES) is now being used in various fields as powerful method for the research of bulk electronic properties of materials, the main purpose of our project is to reveal the bulk electronic and local atomic structure using microscopic photoelectron diffraction spectroscopy with hard x-ray. In present poster, we will show the details of the development of DELMA and some typical results, which we have measured very recently.



**Figure 1:** DELMA is a photoelectron diffraction and spectroscopy device, which is composed of PEEM's lens system and high resolution electron spectrometer (VG SCIENTA).

## Acknowledgments

This work was supported by KAKENHI (Grants No. 26105001).

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# X-ray photoelectron spectroscopy and tunneling microscopy from very dilute systems: Rb nanotents

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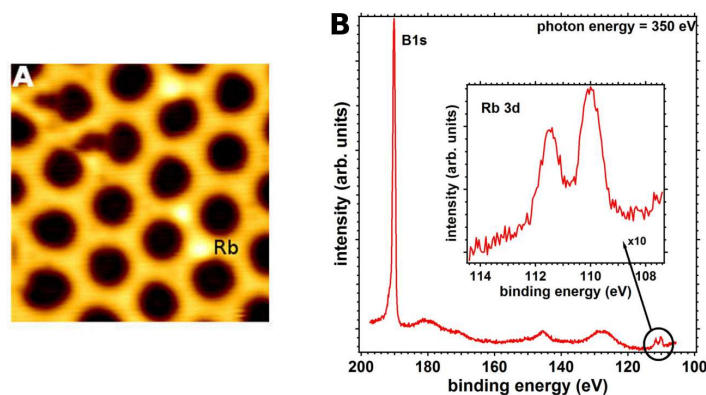
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## Summary

Exposure of a single layer of boron nitride on Rh(111) to low energy argon ions leads to the formation of stable atomic structures [1]. Here we show that these “nanotents” may also be formed with Rb atoms [2]. For this purpose an alkali-metal ion source was constructed and will be presented. The electronic and atomic structure of the Rb-nanotent is being investigated by x-ray photoelectron spectroscopy/scanning tunneling spectroscopy and x-ray photoelectron diffraction/scanning tunneling microscopy, respectively, at the PEARL beamline of Swiss Light Source.

## Alkali-metal Ion Source

For the Rb implantation an alkali-metal ion source was constructed. It allows the acceleration of the Rb ions to an energy that enables the penetration through the h-BN single layer and also graphene. The Rb atoms are sublimated from an alkali-metal dispenser and ionized by a hot surface with high work function. The ion current was demonstrated to be easily controlled by the temperature of ionizer. Figure 1A shows an STM image with three nanotents as produced with Rb atoms.



**Figure 1:** A) Low temperature (4K) STM image ( $V = 0.1$  V;  $I = 50$  pA)  $14 \times 14$  nm<sup>2</sup> of the h-BN nanomesh, with the 3.2 nm superstructure with 2 nm pores (dark areas) and wires (bright network-areas) with 3 implanted Rb atoms that stop at wire crossing sites. B) XPS spectrum measured with 350 eV photon energy showing the B 1s and Rb 3d peaks (normal emission).

## Photoemission experiments

High-resolution x-ray photoelectron spectroscopy (XPS) and x-ray photoelectron diffraction (XPD) were carried out at PEARL beamline of Swiss Light Source - SLS. The XPS measurements confirm the identity of the protrusions as can be seen in Figure 1B.

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## Visualization of iron environments in hemoglobin using X-ray fluorescence holography

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X-ray fluorescence holography (XFH) is a powerful tool that can visualize the three-dimensional atomic structures around specific elements<sup>1-2</sup>. An advantage of XFH is the capability of model-free imaging of atomic environments by a simple Fourier transform-like procedure. So far, XFH has generally been applied to inorganic materials to investigate the microscopic environments of trace metals. However, the application of XFH to the crystals of biomolecules is still challenging, since biomolecular crystals contain less metals and show a high susceptibility to radiation damages. To overcome these difficulties, we have re-designed an experimental system of XFH to be able to obtain X-ray fluorescence hologram of biological samples<sup>3</sup>. In this study, hemoglobin, an  $\alpha_2\beta_2$  tetrameric oxygen transport protein that binds gaseous ligands such as O<sub>2</sub> and CO cooperatively at the four heme irons (Fig. 1), has been chosen as a sample, because its very large crystals can be obtained.

Using our developed experimental setup, XFH measurements of CO-bound hemoglobin crystals were carried out at the beamlines BL6C (KEK-PF, Japan) and BL39XU (Spring-8, Japan). The data in Fig.2 show, for the first time, the hologram patterns for a protein crystal, and will provide the three dimensional atomic images around the central iron atoms of the individual hemes. However, the reconstruction of such images needs special consideration of orientationally different hemes resulting from the hemoglobin quaternary structure (Fig. 1, right) and crystallographically related four locations of the tetramer. The analysis to resolve these complexities is now under way. We will present our latest data and share with you the results and discussion of this work.

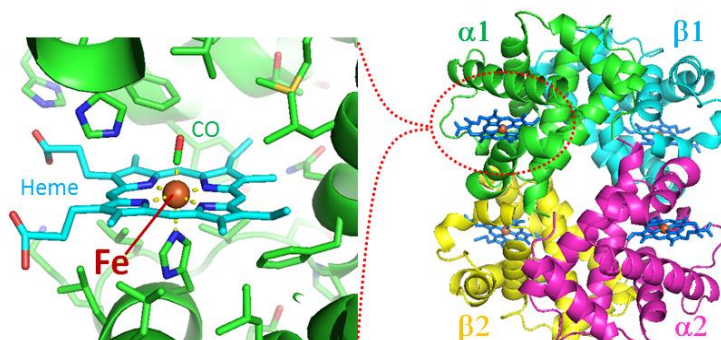


Fig. 1 Tetrameric quaternary structure (right) and the heme iron active site (left) of hemoglobin (PDB ID: 2DN3).

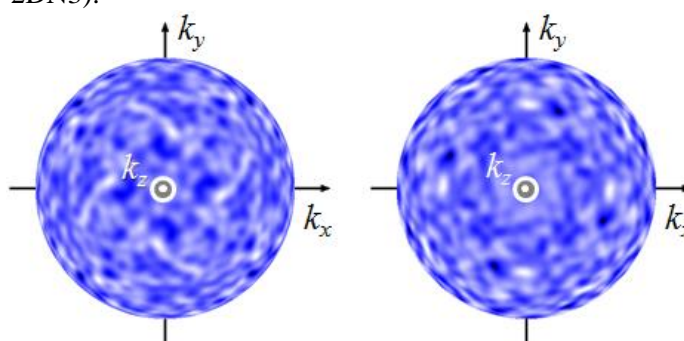


Fig. 2 Hologram patterns obtained from hemoglobin crystal using X-ray energies of 7750 eV (left) and 9750 eV (right).

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## Electronic structures of the synthetic model of the photosynthetic oxygen-evolving complex

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Photosynthetic water oxidation sustains all aerobic life on the earth, and is catalyzed by the  $\text{Mn}_4\text{CaO}_5$  cluster embedded in the protein complex photosystem II. A synthetic model complex,  $\text{Mn}_4\text{CaO}_4(\text{Bu}^t\text{COO})_8(\text{Py})(\text{Bu}^t\text{COOH})_2$  ( $\text{Bu}^t$ , tert-butyl, Py, pyridine) (**1**) closely mimicking the Mn cluster has been reported by C. Zhang et al. recently (Fig. 1).<sup>1</sup> In the present study, the geometric, electronic and spin structures of **1** for all of the four oxidation states ( $S_0 - S_3$ ) were examined at the density functional theory level. The inherent natures of the  $\text{Mn}_4\text{Ca}$  cluster were investigated in comparison with the native OEC. We showed that the geometric structure of **1** can be accurately reproduced by the theoretical calculations, and revealed many similarities in the ground valence and spin states between **1** and the native OEC. We also clarified that two different valence states exist in the one-electron oxidized state of **1** (corresponding to the  $S_2$  state), which lie in the lower and higher ground spin states ( $S = 1/2$  and  $S = 5/2$ ), respectively. There are many similarities between **1** and the native OEC with respect to the Mn valences, total spin states and Jahn-Teller axes, however, one remarkable difference between **1** and the native OEC is the presence of a non-negligible antiferromagnetic interaction between the Mn1 and Mn4 sites, which slightly influenced their ground spin structures (spin alignments). The major reason causing the difference can be attributed to the short Mn1–O5 and Mn1–Mn4 distances in **1**. Theoretical introduction of the missing O4 atom and the reorientation of the Ca coordinating ligands improved the Mn1–O5 and Mn1–Mn4 distances comparable to the native OEC. We expect that these modifications will therefore be important for the synthesis of further advanced model complexes more closely mimicking the native OEC beyond **1**.<sup>2,3</sup>

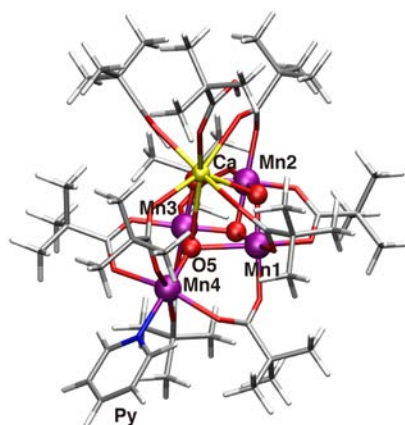


Fig. 1. Molecular structure of the synthetic model (**1**).

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# Temperature Dependence of Atomic Structure Around Doped W atom in ZnO thin film studied by photoelectron diffraction

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W-doped ZnO (W-ZnO) has been found to be very active for a gas sensor. In the present study, we analyzed a local structure around doped W atom in W-ZnO by using the two-dimensional photoelectron diffraction. Figure 1 shows Zn 3*p* and W 4*f* Photoelectron Intensity Angular Distributions (PIADs) after annealing at 600°C and 1000°C. The kinetic energy of the photoelectron was set to  $E_k=800$  eV. In Zn 3*p* PIAD after the 600°C annealing, the FFPs at the polar angle of  $\theta=65^\circ$  (dotted red circle) were observed. This FFP disappeared after the annealing at 1000°C. We also observed W4*f* patterns in both 600°C and 1000°C annealed samples, where the FFP became clearer after annealing at 1000°C. The direction of this FFP is along [12-30] which correspond to the direction of first nearest O atoms viewed from the second layer Zn atoms. This observation indicates that, the doped W atoms, segregated to the surface by annealing, substituting the Zn site in the second layer, corresponding to previous ion scattering results by Suzuki *et al* [1]. Figure 2 shows polar angle dependence of PIAD of W 4*f* and Zn 3*p* around [12-30] direction. The FFP peak positions are almost the same in both Zn 3*p* and W 4*f* PIADs. The W 4*f* peak positions ( $\theta=65.2^\circ$ ) in 600 °C annealed sample is completely the same as that in 1000°C annealed one. We found about 2.5° peak shift of FFPs between Zn 3*p* and W 4*f*, which corresponds directly to the directional change between scattered atoms and the emitter atom. This peak shift suggests that the direction of first nearest neighbor O from W is  $2.5^\circ \pm 0.5^\circ$  different from that from first nearest neighbor O and Zn at the top most surface.

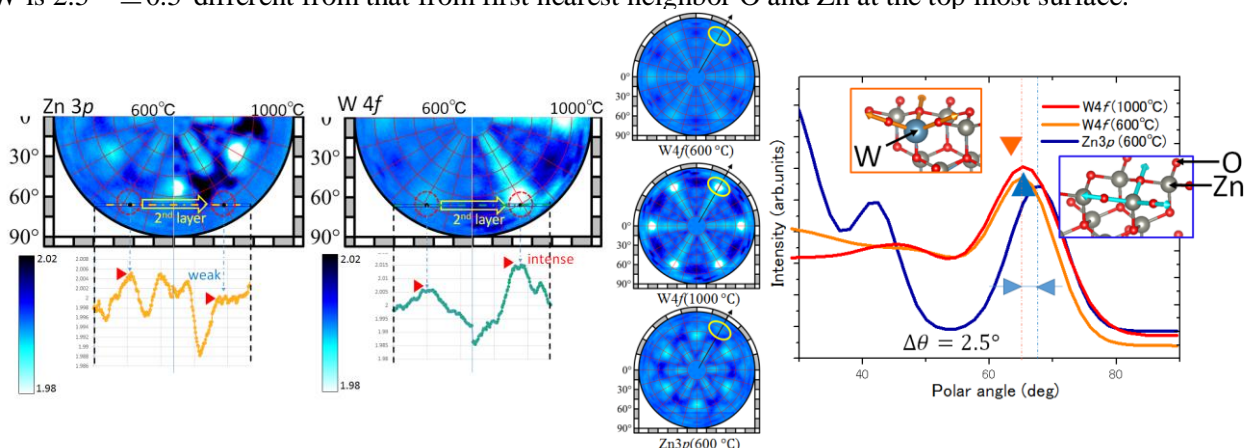


Figure1. PIADs after annealing (600K and 1000K).

Figure2. Comparison of line profile of W 4*f* and Zn 3*p* PIAD along [12-30] direction.

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## Investigations on the adsorption geometry of CO adsorbed on Pt(111)

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High-resolution x-ray photoelectron spectroscopy (XPS) and x-ray photoelectron diffraction (XPD) is used to investigate the adsorption behaviour of CO on Pt(111) at 150 K. The chemical shift between atop and bridge CO-binding sites is well resolved. XPD maps at each site were recorded at photon energies between 400-500 eV where backscattering is more pronounced and provides information about the adsorption geometry. The presented investigations of the CO adsorption geometry at low photon energies are in view of a planned time-resolved XPD experiment at a free electron laser facility. CO is known to adsorb on Pt(111) surfaces in a non-dissociating fashion at several different adsorption sites, namely atop, bridge and hollow position [1,2]. In the present study the adsorption behaviour of CO on Pt(111) is investigated by high-resolution XPS. While dosing CO onto the sample surface at low pressures of  $3 \cdot 10^{-9}$  mbar and a surface temperature of 150 K XPS spectra were recorded continuously. Thereby, it was possible to show that CO resides at two distinct adsorption sites at saturation coverage, atop and bridge, which are separated by 0.7 eV in binding energy. Furthermore, the XPS spectra reveal that for low doses of below 1 L CO molecules almost exclusively adsorb at atop sites. This is an important result in view of any pump-probe experiment with the presented system. For atop and bridge sites the dipole moment is known to be of opposite sign [2] which in turn has an influence on the coupling of electromagnetic waves to the adsorbed COs molecular dipole moment [3]. In photoelectron diffraction an emitted photoelectron wave of a specific atomic orbital coherently scatters off neighbouring atoms and produces a diffraction pattern due to interference of the scattered and unscattered photoelectron waves [4]. In case of molecular adsorbates, information about the molecular adsorption geometry, including bond lengths and angles, with sub-Angstrom resolution can be retrieved [5]. Among the undisputed strengths of this method are its chemical sensitivity due to the possible selection of individual atomic orbitals as emitters and its sole dependency on the local atomic environment [4]. In the present study photoelectron diffraction experiments were performed at photon energies of 400 and 500 eV employing the C1s orbital of CO as the emitter. We were able to deconvolve the resulting C1s XPD signal at saturation coverage into the respective components belonging to CO molecules in both atop and bridge position. Even at the relatively low photon energies employed all diffraction patterns are dominated by the C1s photoelectron waves forward scattering off the oxygen atom along the molecular bond axis. In addition, a pronounced backscattering at substrate atoms reveals differences between CO molecules at atop and bridge sites. The backscattering features in both cases are of sixfold symmetry but show an azimuthal rotation angle of 30° with respect to each other.

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# X-ray fluorescence holographic study on valence fluctuating material YbInCu<sub>4</sub>

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Yb-based metallic alloys often exhibit the valence fluctuating phenomenon, where the average oxidation number of Yb atoms varies with temperature [1]. The temperature dependence of the averaged valence number of YbInCu<sub>4</sub> is estimated by the high energy x-ray photoelectron spectroscopy (HXPES) data [2], and the averaged Yb valence rapidly changes from 2.90 to 2.74 at about 42K. In accordance with this valence transition, abrupt changes in lattice volume, electrical resistivity, magnetic susceptibility, etc. are observed without changing the crystal structure type [3]. The lattice expansion at low temperatures is believed to originate from the ionic radii of smaller Yb<sup>3+</sup> and larger Yb<sup>2+</sup>, and correspondingly a Curie-Weise type paramagnetic transforms to a Pauli type one.

X-ray fluorescence holography (XFH) provides three-dimensional atomic images around a specific element emitting its own fluorescent x-ray [4]. Recently, we have found that XFH is electronic state sensitive by choosing the incident x-ray energy near the absorption edge of the observing element. Figure 2(a) and (b) show atomic image of YbInCu<sub>4</sub> obtained by XFH at incident x-ray energies at XANES spectra indicating Yb<sup>3+</sup> (8949 eV) and Yb<sup>2+</sup> (8942 eV) absorption, respectively. As clearly seen in the figures, atomic images are very different from each other. Detailed analyses are now in progress.

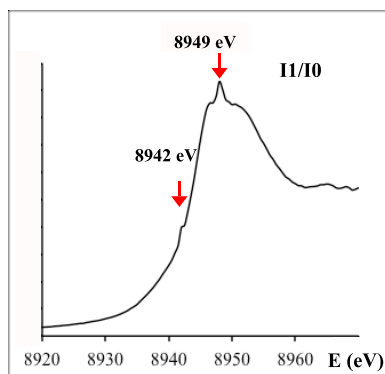


Figure 1 : XANES spectra indicating Yb<sup>3+</sup> (8949 eV) and Yb<sup>2+</sup> (8942 eV) absorption

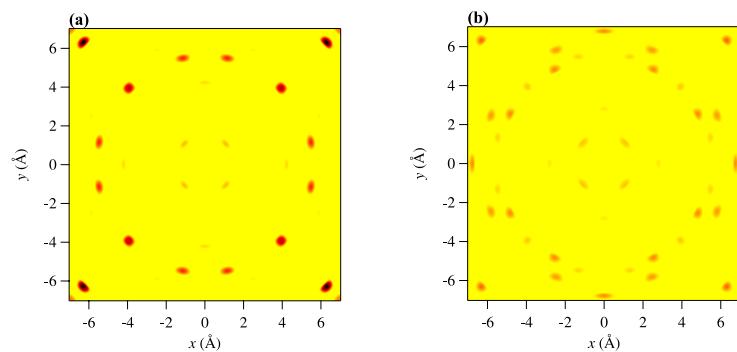


Figure 2 :Atomic images of YbInCu<sub>4</sub> single crystal on the (111) plane around the Yb atom at (a) 8942 eV and (b) 8949 eV

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## X-ray fluorescence holographic study on high-temperature superconductor $\text{FeSe}_{0.4}\text{Te}_{0.6}$

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$\text{FeSe}_x\text{Te}_{1-x}$  is one of the simplest Fe-based superconductors, and has intensively been studied concerning the interplay between structural or magnetic degrees of freedom and superconductivity. It is widely accepted that magnetic fluctuations play a very important role for their superconducting nature.  $\text{FeSe}_{0.4}\text{Te}_{0.6}$  is a layered structure that the layers of Fe atoms and Se/Te atoms overlap alternately [1]. To understand the superconductivity of  $\text{FeSe}_{0.4}\text{Te}_{0.6}$ , it is necessary to reveal the local structure of the around the Fe atom.

The x-ray fluorescence holography (XFH) is a newly developed technique that enables one to draw three-dimensional (3D) atomic images around a specific element emitting fluorescent x-rays [2]. We have performed Fe  $K\alpha$  XFH measurements on a  $\text{FeSe}_{0.4}\text{Te}_{0.6}$  single crystal at 100 K. Figure 1 shows the reconstructed atomic images on the (001) plane at the Fe, Se, and Te layers. Previously, we performed XFH measurements at 300 K, and show the local structures of around the Se and Te atoms [3]. In this paper, we report atomic images of neighboring atoms around the central Fe atom at low temperature and compared with those at 300 K. Additionally, we will show results of extended x-ray absorption fine structure (EXAFS) measurements to confirm the XFH data.

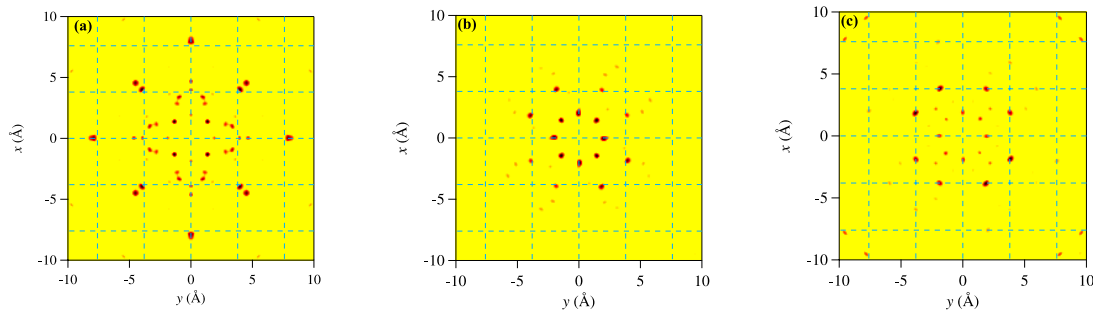


Figure 1 : Atomic image of the  $\text{FeSe}_{0.4}\text{Te}_{0.6}$  single crystal on the (001) plane at  $z =$  (a) 0 Å (Fe layer), (b) 1.478 Å (Se layer), (c) 1.718 Å (Te layer)

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# Characterization of photocatalytic active sites of rutile (110) surface by circular dichroism of resonant Auger electron diffraction

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**Introduction** Oxygen vacancy at the rutile surface induces a photo-catalytically active electronic state in the TiO<sub>2</sub> band gap. The state of Ti atoms in the second layer was assigned to be responsible for such electronic state<sup>1)</sup>. We investigated the atomic orbital character of this electronic state by Ti *LV* resonant Auger electron diffraction. The results of this observation suggest that the initial electronic states of emitted electrons are localized at the 2<sup>nd</sup> layer Ti atom sites and has the 3d atomic orbital character.

**Experimental detail** The measurement was performed at the PEARL beamline (X03DA) at SLS. The clean rutile(110) 4° off single crystal surface was obtained by annealing at 500°C in O<sub>2</sub> gas flow (1 atm, 1 hr and 4.0 × 10<sup>-4</sup> Pa, 30 min). We measured Auger electron spectra to confirm the cleanliness of the surface. The emission angle  $\theta_{out}$  relative to the X-ray incident axis was fixed at 60°. The resonant Auger electron diffraction at Ti *L*<sub>3</sub> *t*<sub>2g</sub> absorption edge ( $h\nu=457.9$  eV) was measured.

**Results and Discussion** Firstly, we measure a series of X-ray photoelectron spectra at the Ti *L*<sub>3</sub>, and *L*<sub>2</sub> absorption edges regions. Photon energy integrated Auger electron spectrum was obtained from this series of XPS. The kinetic energy (*E<sub>k</sub>*) of Auger electrons were 375 eV (*LMM*), 407 eV (*LMV*), and 446 eV (*LV*). Then, we measured a full hemispherical resonant Ti *LMM* Auger electron diffraction (AED) pattern. In this AED pattern (not shown), we observed a FFP at the [223] direction of neighbouring O atoms seen from the second layer Ti atoms. Finally, we investigated the circular dichroism of resonant AED<sup>2)</sup>. Circular dichroism contrast did not appear in the case of Ti *LMM* and *LMV* Auger transitions. This is because the angular momentum does not change upon 3p → 2p core hole decay process in these cases. On the other hand, we succeeded in detecting the circular dichroism contrast in the case of Ti *LV* Auger transition. Angular momentum was transfer to Auger electron during 3d → 2p core hole decay process in this case. According to analysis of the atomic orbital of [223] FFP by curve fitting, components of magnetic quantum number of  $m=\pm 3$  from Ti 3d orbital were not observed in this FFP. Angular momentum of light transferred to components of magnetic quantum number of  $m=\pm 2$  in Ti 3d orbital. From this results, the atomic orbital Ti 3d<sup>1</sup> electronic state was induced by oxygen vacancy at the rutile surface. Components of  $m=\pm 2$  in Ti 3d orbital related to photocatalytic activity of rutile(110) surface.

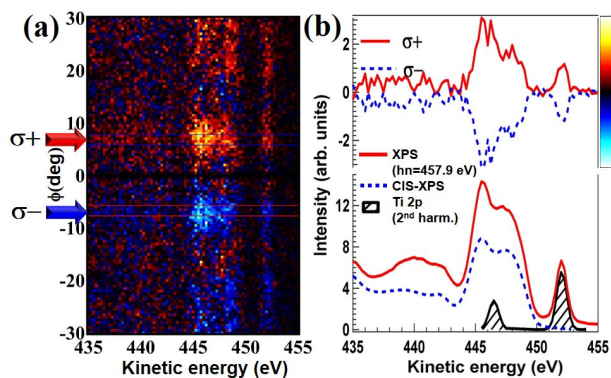


Fig. 1 (a) CD image of circular dichroism of Ti *LV* Auger decay, (b) CD spectra, CIS-XPS and XPS.

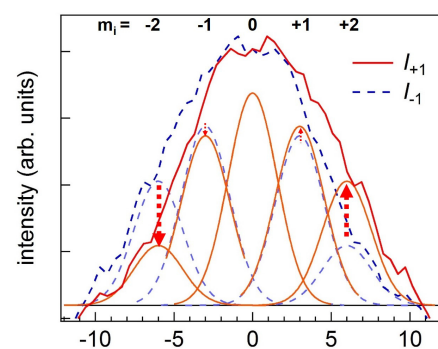


Fig. 2 The circular dichroism of FFP for [223] direction of resonant AED.

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