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משרד המדע והטכנולוגיה

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Titles & Abstracts

Introduction to Picometer Transmission Electron Microscopy (CTEM and STEM)

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During the nineteen nineties, it has at last become possible to realize aberration-corrected electron optics [1,2]. This has revolutionized electron microscopy. The Rayleigh resolution increased to better than 50 picometers, and it has been demonstrated that individual atom displacements in the order of 1 picometer can be measured. This means genuine atomic resolution [3]. On this basis the electron microscope has become a unique high-precision measurement tool allowing the direct correlation of macroscopic physical properties with atomic position measurements.

But, in contrast to common believe, optical resolution is just one of the pre-requisites of atomic resolution work [4]. In quantum physics the term 'image' loses its conventional meaning. The electron waves sent through a crystal in order to provide us with information on the object are subject to quantum-mechanical interaction with the atom potential as described by a relativistically corrected Schrödinger equation. The resulting complex wave function at the exit plane of the specimen does not lent itself to an intuitive interpretation. In order to understand the images and to push the frontiers of electron microscopy to picometer precision it is therefore unavoidable that the highly non-linear quantum-mechanical imaging process is inverted numerically on a computer.

The lecture concentrates on a description of the quantitative background of both Conventional Transmission Electron Microscopy (CTEM) [5,6] and Scanning Transmission Electron Microscopy (STEM) [7,8] with respect to structure-related ultra-high resolution atomic studies. The spectroscopic and other special aspects of CTEM and STEM will be treated in subsequent lectures of the school.

[1] Haider, M. et al. (1998). Electron microscopy image enhanced, *Nature* 392, 768.

[2] Haider, M. et al. (1998). A spherical-aberration-corrected 200 kV transmission electron microscope, *Ultramicroscopy* 75, 53.

[3] Urban, K. (2008). Studying Atomic Structures by Aberration-Corrected Transmission Electron Microscopy, *Science* 321, 506.

[4] Urban, K. (2009). Is science prepared for atomic resolution electron microscopy? *Nature Materials* 8, 261.

[5] Jia, C. L., et al. (2013). Atomic-scale measurement of structure and chemistry of a single-unit-cell layer of $LaAlO_3$ embedded in $SrTiO_3$. *Microsc. Microanal.* 19, 310.

[6] Jia, C.L. et al. (2014). Determination of the 3D shape of a nanoscale crystal with atomic resolution from a single image, *Nature Materials* 13, 1044.

[7] Forbes, B.D. et al. (2010). Quantum mechanical model for phonon excitation in electron diffraction and imaging using a Born-Oppenheimer approximation, *Phys. Rev. B* 82, 104103.

[8] Pennycook, S.J. and Nellist, P.D. (2011). Scanning Transmission Electron Microscopy, Springer.

Energy Dispersive Spectroscopy and its Application Towards Understanding Thermodynamic Transitions at Interfaces

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Energy dispersive spectroscopy (EDS) used during transmission electron microscopy (TEM) has unique quantitative advantages over EDS used during scanning electron microscopy in the characterization of local chemical distributions. When EDS is incorporated into scanning TEM (STEM), interface excess at unprecedented detection limits can be achieved. At the same time, full quantification requires a careful approach and an understanding of the method. This presentation will review the use of EDS in S/TEM for full quantitative analysis, and will focus on the measurement of interface (surface) excess.

The issue of interface excess will then be addressed from a fundamental point of view, and expanded to include structural transitions in addition to chemical transitions, where interfaces can go through two dimensional transitions between thermodynamic states (sometimes termed *complexions*) in order to minimize the interface energy. First order interface transitions from a chemical and structural point of view will be described, focusing on Ni-YSZ fully equilibrated interfaces as a model system. The equilibrium atomistic structure correlated with measured interface energy will be explored, as well as how Cr adsorption affects the interface structure. These results will show how the concept of coherent-incoherent interfaces as a means for describing interface atomistic structure is over simplified, where the concept of interfacial reconstruction is more complete, and serves to connect the atomistic structure to a thermodynamic description of the equilibrium interface state.

Electron Energy Loss Spectroscopy, Energy Filtering TEM and Impact of Correcting Chromatic Aberration

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Electron Energy Loss Spectroscopy (EELS) and Energy Filtering TEM (EFTEM) are powerful techniques which make it possible to characterize the chemical distribution and the bonding state of individual elements in the investigated samples [1, 2]. The lecture will introduce the basics of the inelastic scattering processes which provide the EELS and EFTEM signals. Furthermore the required spectrometers and filters, detectors and procedures for the analysis of the signals will be introduced.

EELS and EFTEM greatly benefit from the correction of chromatic aberration. At the Ernst Ruska-Centre [3] we have recently installed the FEI Titan 60-300 PICO. PICO is a fourth-generation transmission electron microscope capable of obtaining high-resolution transmission electron microscopy images approaching 50 pm resolution in the C_C- and C_S-corrected mode at 300 keV. It is currently one of only three microscopes in the world capable of chromatic aberration correction [4].

In the second part of the contribution we will report on the EELS and EFTEM experiments and the results obtained with the PICO instrument. The benefits of chromatic aberration corrected imaging are particularly large for HRTEM imaging at low accelerating voltages and for energy filtered (EFTEM) imaging with large energy window width [5]. In the present contribution we will focus on new applications and resulting challenges for data acquisition and analysis.

References:

[1] R.F. Egerton, Electron Energy Loss Spectroscopy in the Electron Microscope, Plenum Press
[2] L. Reimer (Ed.), Energy Filtering Transmission Electron Microscopy, Springer Series in Optical Sciences
[3] http://www.er-c.org
[4] B. Kabius, P. Hartel, M. Haider, H. Müller, S. Uhlemann, U. Loebau, J. Zach, and H. Rose, J. Electron Microsc. 58, 147 (2009).
[5] K. Urban, J. Mayer, J. Jinschek, M. J. Neish, N. R. Lugg, and L. J. Allen, PRL 110, 185507 (2013)

"Electromagnetic field mapping at the nanoscale in the TEM"

In this talk, I will describe how electron microscopy can be used to obtain quantitative information about not only local microstructure and chemistry in materials but also electromagnetic fields with close-to-atomic spatial resolution. When combined with model-based iterative reconstruction, electron tomography and *in situ* techniques, this information can be obtained quantitatively, in three dimensions, as a function of temperature and in the presence of applied fields and reactive gases. I will present results obtained from materials that include individual magnetic nanocrystals and electrically biased field emitters. I will conclude with a personal perspective on directions for the future development of transmission electron microscopy, which may require radical changes to the design of electron microscopes, longer experiments, quantitative comparisons of experimental measurements with both complementary techniques and advanced simulations, and new approaches for data handling and storage.

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Ultrafast Electron Diffraction and Microscopy with High-Coherence Beams

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Time-resolved electron imaging, diffraction and spectroscopy are exceptional laboratory-based tools to trace non-equilibrium dynamics in materials with a sensitivity to structural, electronic and electromagnetic degrees of freedom. The capabilities of these approaches are largely governed by the quality of the beam of electrons used.

This talk will introduce the basic experimental and conceptual principles of ultrafast electron microscopy and diffraction, followed by a discussion of recent advances. Specifically, employing high-coherence ultrashort electron pulses from nanoscale field emitters is shown to substantially enhance the achievable image resolution in both real and reciprocal space.

Two complementary developments with ultimate surface sensitivity and spatial resolution, respectively, will be presented, namely Ultrafast Low-Energy Electron Diffraction (ULEED; Fig. 1, left) and Ultrafast Transmission Electron Microscopy (UTEM, Fig. 1, right). Recent examples of applying these methods to the observation of phase-ordering kinetics, the real-space imaging of phase transitions, the excitation of strongly-coupled fluctuation modes and the control of metastable states will be given.

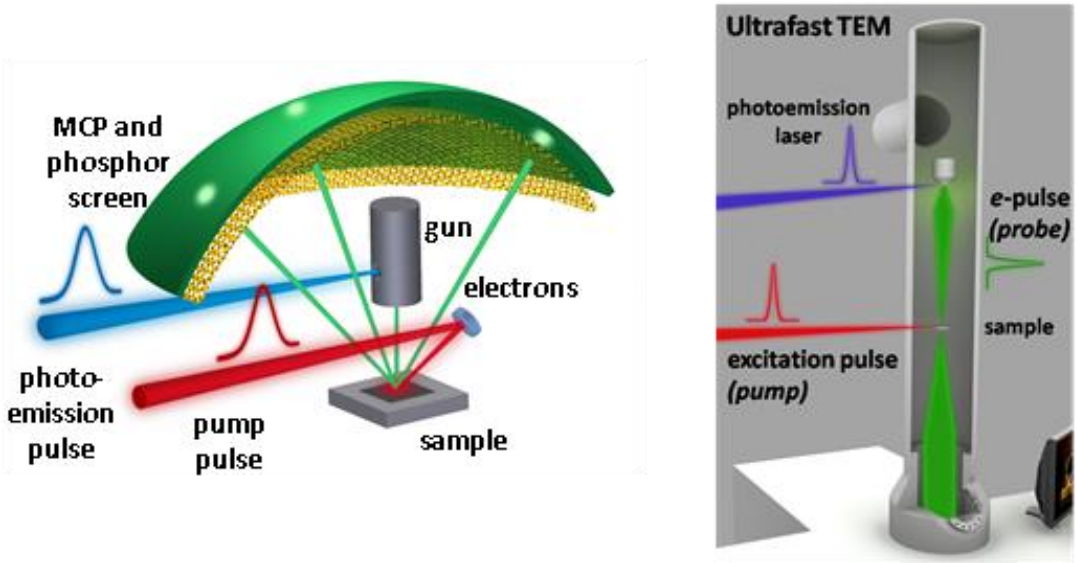

Fig. 1: Two complementary approaches to the study of ultrafast dynamics in solids, at surfaces and nanostructures: Ultrafast Low-energy electron diffraction (ULEED, left) probes structural dynamics at surfaces with electron pulses at kinetic energies of 20-200 eV. Ultrafast transmission electron microscopy (UTEM, right) allows for ultrafast imaging, diffraction and spectroscopy of thin films and nanostructures using high-energy electron pulses (100-200 keV).

Russell-Berrie: Advanced Characterization

From real to reciprocal space: spectromicroscopy with synchrotron radiation

The ongoing progress in information and energy technology and materials science asks for sophisticated analytical tools. These should combine high lateral resolution with chemical specificity and magnetic sensitivity. They should also permit *in-operando* studies with an ultimate time resolution in the femtosecond regime. In recent years, spectromicroscopy using synchrotron radiation has matured into a very versatile tool, matching many of the above requirements. Synchrotron light can be tuned over a wide range of photon energies, provides polarization selection and a picosecond time structure. Used as illumination in a photoelectron microscope it provides a multitude of contrast mechanisms for imaging in real and reciprocal space. In my contribution I will first cover the basics of photoemission and full-field photoelectron spectromicroscopy. In the 2nd part I'll discuss selected applications in the field of information science.

Prof. Dr. C.M.Schneider

Director

Peter Grünberg Institute PGI-6| Faculty of Physics

Forschungszentrum Jülich GmbH

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The Last Nanometer – Hydration Structure of DNA and Solid Surfaces Probed by Ultra-High- Resolution AFM

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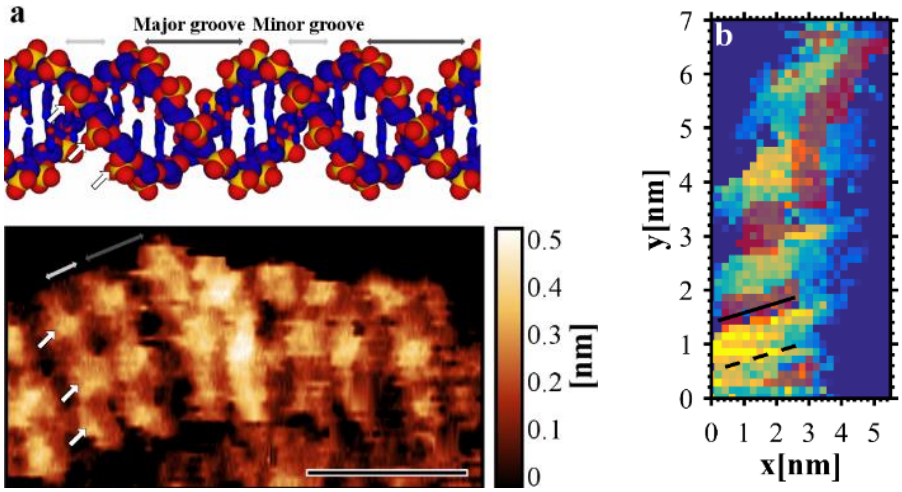
Recent advancements in atomic force microscopy facilitate atomic-resolution three-dimensional mapping of hydration layers next to macromolecules and solid surfaces. These maps provide unprecedented information on the way water molecules organize and bind these objects. Since the hydration structure governs the energetics of solvation and interactions between objects immersed in solution, the new data are invaluable when trying to resolve fundamental questions such as identification of molecular binding sites and interaction mechanisms.

The first part of my presentation will focus on the theory of three-dimensional atomic force microscopy in liquids and practical considerations that lead to ultra-high-resolution. These principles will be demonstrated using our home-built microscopes. In the second part I will use three examples to demonstrate the type of data obtainable with state-of the art microscopes. The first example will disclose ordering of individual water molecules next to crystalline mica (water epitaxy growth on mica). I will then move to atomic resolution imaging of DNA and 3d maps of its hydration structure (e.g., figure below). The last example will disclose resolution of one of the oldest puzzles in physical chemistry – the way water orders next to hydrophobic surfaces and the source of hydrophobic interactions.



An ultra-high-resolution image of DNA with a reference model of B-DNA. The major grooves, minor grooves and top-facing phosphates are highlighted with gray and white arrows on the model and the scan. Scale bar, 5nm. (b) Hydration of double stranded DNA. Red shaded pixels mark the position of labile water molecules.

Scanning tunneling microscopy

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The talk provides an introduction to scanning tunneling microscopy and spectroscopy featuring, in particular, modern applications at low temperature and in high magnetic fields. Besides the method to map the local density of states, i.e. wave function properties of single electrons, I will discuss the abilities to probe other types of excitations via inelastic tunneling spectroscopy, to access energetic dispersions in k-space via Fourier transformation, and to get access to the dynamics of solids via time-resolved pump-probe techniques down to the picosecond regime. Insights from more conventional scanning tunneling microscopy into topological materials, confinement properties or the Kondo effect will also be discussed.

SYNCHROTRON BASED HARD X-RAY MICROSCOPY: STATE OF THE ART AND APPLICATIONS

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Over the past three decades, interest in X-ray microscopy has been revived, nurtured by several major advances in X-ray sources and X-ray optics. X-ray imaging techniques largely benefit from the high brilliance of X-ray beams produced by third generation, and soon fourth generation, synchrotron sources which offer a control of the brightness, spectrum, geometry, polarization and coherence of the beam. Driven by these unprecedented properties of X-ray beams, concomitant progress has been made in X-ray optics and X-ray detectors.

In the overall context of the dramatic growth of nanoscience and nanotechnologies, which is currently fostering the development of high spatial resolution and high sensitivity analytical techniques, synchrotron based analytical techniques (diffraction, imaging and micro-spectroscopies) play an important role by offering unique capabilities in the study of complex systems. Ultimately, this complexity can be envisioned in three dimensions: composition, time and space. Furthermore, the possibility of *in-situ* or *operando* experiments remains a unique attribute of synchrotron-based analytical methods. The photon penetration depth of hard X-rays enables specific sample environments to be developed to study realistic systems in their near-native environment rather than model systems.

This lecture aims at giving an overview of the main development trends of synchrotron-based X-ray microscopy and spectro-microscopy. Following a brief introduction on the principles and characteristics of synchrotron radiation, the second part of the lecture will discuss the strengths and weaknesses of imaging and spectro-microscopy techniques while the third part will focus on examples of applications in various fields of applied research.

‘High resolution imaging with coherent X-rays’.

‘For the last 20 years synchrotron sources have produced brighter and more coherent X-ray beams. This has allowed the development of Coherent X-ray Imaging techniques which yield a resolution which is neither limited by the X-ray beam size, nor by the pixel size on the detector. In this lecture I will present the different techniques (including phase contract imaging, coherent diffraction imaging and ptychography), and show selected applications.'

Vincent Favre-Nicolin

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Modern Cryogenic-Temperature Electron Microscopy in the Nanostructural Study of Soft Matter

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Cryogenic-temperature transmission electron microscopy (cryo-TEM) is now accepted as an almost standard tool in the study of complex liquids, i.e., liquid systems with aggregates or building blocks on the nanometric scale. Methodologies have been developed to capture the nanostructure of liquid systems, while preserving their original state at a given concentration and temperature. Cryo-TEM is now widely used to study synthetic, biological, and medical soft matter. Originally developed for aqueous systems, it has been also applied successfully in the study of non-aqueous systems. Recent developments in TEM include highly-sensitive cameras that allow imaging with very few electrons, thus reducing electron-beam radiation-damage, a main limitation in electron microscopy of soft matter. Recent introduction of the analog to light microscopy "phase-plate", enhances image-contrast in low-contrast specimens, another major limitation in microscopy of soft matter.

However, cryo-TEM cannot be used to study highly viscous systems, or those containing objects larger than several hundreds of nanometers. Recent developments in high-resolution scanning electron microscopy (HR-SEM) have made it an ideal tool for the study of nano-aggregates in viscous systems or in systems containing large objects hundreds of nanometers and larger, in which small (nanometric) features are to be imaged. Improved field-emission electron guns, electron optics and detectors have made it possible to image nanoparticles down to a few nanometers. Liquid nanostructured systems can now be studied by cryo-SEM, using much-improved cryogenic specimen holders and transfer systems. In recent years we have developed and improved a novel specimen preparation methodology for cryo-SEM specimens that preserves the original nanostructure of labile complex liquids, at specified composition and temperature, quite similarly to what had been done in cryo-TEM.

In my presentation I will describe the state-of-the-technology of cryo-TEM and cryo-SEM, and demonstrate the application of the combined methodology in nano- and bio-technology. I will also describe some new observations in low-voltage SEM and cryo-SEM. Among others, I will describe applications in the study of polyelectrolytes and their interaction with oppositely-charged amphiphiles, biological system, such as extracellular vesicles, and carbon nanotubes dispersed in super-acids.

Overview of Atom Probe Tomography

Thomas Kelly

Steam Instruments, Inc. (formerly of CAMECA Instruments, Inc.)

Atom probe tomography (APT) will be reviewed for the beginner. A brief history of the technique will be given to set the stage for understanding the current state of the art. The instrumentation used to record atom probe tomographs will be described. The entire process from making specimens to collecting data to analyzing data will be covered without assuming prior knowledge of the technique. The strengths and limitations of the technique will be presented. There will be some discussion of artifacts and errors that can occur in the technique. A review of a variety of applications will be used to illustrate the utility of atom probe tomography. The lectures will conclude with a look toward anticipated future developments.

Imaging Dynamic Materials Processes by (Scanning) Transmission Electron Microscopy (STEM)

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Many processes in materials science, chemistry and biology take place in a liquid environment – such as chemical conversions, the synthesis of nanoparticles, the operation of Li-ion or next generation batteries, and biological cellular functions. In many of these cases, the final desired outcome is a result of a series of complicated transients, where a change in the order, magnitude or location in each of the steps in the process can lead to a radically different result. Understanding and subsequently controlling the final outcome of the process therefore requires the ability to directly observe the transients as they happen. Aberration Corrected (Scanning) Transmission Electron Microscopy ((S)TEM) has the spatial resolution to directly visualize these transient processes on the atomic scale. However, the increased current densities caused by the correctors have made beam damage more prevalent and the limitation to imaging in many cases is now the sample rather than microscope. Similar constraints are implicit during *in-situ* or *operando* TEM experiments involving liquids (and gases), where the goal of the experiment is to observe a transient phenomenon without the beam altering the process. The aim now is therefore to more efficiently use the dose that is supplied to the sample and to extract the most information from each image. Optimizing the dose/data content in non-traditional ways (i.e. not just simply lowering the beam current) involves two main strategies to achieve dose fractionation – reducing the number of pixels being sampled in STEM mode, or increasing the speed of the images in TEM mode. For the case of the STEM, inpainting methods allow a dose reduction of an order of magnitude or more, allowing data to be automatically recorded in a compressed form. For the TEM mode of operation, an increase in speed increases the number of images and means that compressive sensing and automated methods of tracking changes in the structure need to be developed so that only the important changes need to recorded. In this presentation, the basic approach to dose control using both conventional and unconventional sampling methods will be described. Results showing the use of *in-situ* liquid stages to study nanoscale dynamic processes involving electrochemical driving forces will be presented and the potential insights gained by increasing the image acquisition speed and/or decreasing the electron dose for future research projects will be described.

This work was supported in part by the Chemical Imaging Initiative under the Laboratory Directed Research and Development Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated by Battelle for the U.S. Department of Energy (DOE) under Contract DE-AC05-76RL01830. A portion of the research was performed using the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at PNNL.

Lecture 1:

Basics of Electron Backscatter Diffraction (EBSD)

The lecture will give an introduction into the fundamentals and basic applications of EBSD analyses in the SEM. Topics to be discussed will include:

- Formation of EBSD patterns (EBSPs)
- Information content of an individual EBSP
- Automatic collection and Hough-transform based indexing of EBSPs
- Spatial and angular resolution
- Parameters to control the quality/reliability of the automatic indexing
- Fundamental evaluations of EBSD datasets: Pattern Quality Maps, Orientation Maps, Microtexture evaluations

Lecture 2:

EBSD-based analysis of lattice deformations/defects in the SEM

The high spatial and good angular resolution of EBSD make it an ideal tool to analyze lattice deformations/defects in the SEM. The lecture will give an overview on standard as well as advanced techniques including:

- Parameters assessing local orientation gradients
- Orientation gradients as cumulative measure of geometrically necessary dislocation densities
- High (angular) resolution EBSD: Improvement of the angular resolution of EBSD by cross correlation of individual EBSPs and its application to the measurement of lattice strains
- EBSD-based optimization of orientation contrasts in the SEM for imaging of individual lattice defects: Controlled Electron Channeling Contrast Imaging (cECCI)

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