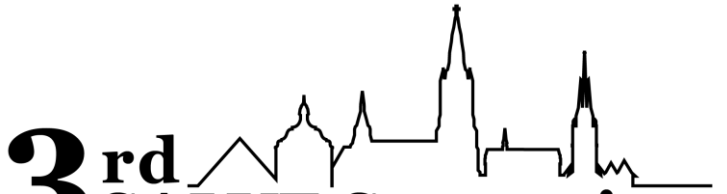
3rd SALVE Symposium

12/2017

Low-voltage research proceedings with contributions from:

U. Bangert, E. Besley, J. Biskupek, F. Börrnert, R. Dunin-Borkowski, X. Feng, B. Freitag, D. Gerthsen, S. Haigh, T. Heine, L. Houben, P. Huang, U. Kaiser, A. Khlobystov, A. Kirkland, C. Koch, M. Kociak, L. Kourkoutis, A. Krasheninnikov, O. Krivanek, T. Latychevskaia, S. Löffler, A. Loiseau, P. Longo, A. Lubk, J. Mayer, J. Meyer, J. (John) Miao, H. Müller, E. Olsson, H. Rose, F. Ross, C. Russo, H. Sawada, M. Schaffer, E. Spiecker, M. Stöger-Pollach, N. Tanaka, R. Tenne, A. Turchanin, T. Weil, M. Willinger, W. Zhou, Y. Zhu



3rd SALVE Symposium

December 12-14, 2017

Program and Abstracts

Sub-Angstrøm Low-Voltage Electron Microscopy

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Scientific Program

Tuesday, December 12th

Session: Advanced Instrumentation I

Chair: U. Kaiser

8:00 - 8:05 am	**Ute Kaiser** *Ulm University, Germany* Opening of the SALVE Symposium
8:05 - 8:35 am	**Harald Rose** *Ulm University, Germany* Correction of aberrations – past – present – future
8:35 – 8:55 am	**Heiko Müller** *CEOS GmbH, Heidelberg, Germany* Optical design of the SALVE Cc/Cs corrector and its benefits for low-kV TEM and EFTEM
8:55 – 9:15 am	**Felix Börrnert** *Ulm University, Germany* Contrast transfer in the SALVE instrument
9:15 – 9:30 am	**Johannes Biskupek** *University of Ulm, Germany* Energy-filtered TEM in the *SALVE* instrument
9:30 – 10:00 am	**Joachim Mayer** *Central Facility for Electron Microscopy, RWTH Aachen, Germany; Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Research Centre Juelich, Germany* Chromatic aberration correction: new methods and applications developed on the PICO instrument
10:00 – 10:30 am	*Coffee Break*

Session: Advanced Instrumentation II

Chair: M. Haider

10:30 – 11:00 am	**Bert Freitag** *ThermoFisher Scientific, Eindhoven, The Netherlands* New capabilities on the Themis Z platform: iDPC imaging, 4D STEM for diffractive imaging and ultra-high resolution EELS
11:00 – 11:30 am	**Hidetaka Sawada** *JEOL Ltd., Tokyo, Japan* High resolution electron microscope developed under Triple C Project, and aberration measurement
11:30 – 12:00 am	**Ondrej L. Krivanek** *Nion R&D, Kirkland, WA, USA* Ultra-high spatial and energy resolution STEM/EELS
12:00 – 12:30 pm	**Paolo Longo** *Gatan, Inc. Pleasanton, CA USA* Latest advances in energy loss spectroscopy detectors: extremely low energy and direct detection
12:30 – 2:00 pm	*Lunch and SALVE visit I*

Session: Low-Dimensional Materials: Preparation, Characterization, Theory I

Chair: E. Olsson

2:00 – 2:30 pm	**Reshef Tenne** *Department of Materials and Interfaces, Weizmann Institute, Israel* Inorganic nanotubes and fullerene-like nanoparticles at the crossroad between materials science and nanotechnology and their applications
2:30 – 3:00 pm	**Tanja Weil** *Max-Planck Institute for polymer Research Mainz, Germany* Emerging nanomaterials for biomedicine and sensing
3:00 – 3:30 pm	**Jannik Meyer** *University of Vienna, Austria* Understanding and exploiting the interaction of electron beams with low-dimensional materials
3:50 – 4:00 pm	**Erdmann Spiecker** *Institute of Micro and Nanostructure Research, FAU, Erlangen, Germany* Exploring extended defects in 2D materials using advanced electron microscopy
4:00 – 4:30 pm	*Coffee Break*

Session: Low-Dimensional Materials: Preparation, Characterization, Theory II

Chair N. Tanaka

4:30 – 5:00 pm	**Rafal E. Dunin-Borkowski** *Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, Germany* Model-based reconstruction of magnetization distributions from optical phase images
5:00 – 5:30 pm	**Axel Lubk** *Advanced Methods of Electron Microscopy, IFW Dresden, Germany* Advanced holographic tomographies for nanoscale materials
5:30 – 6:00 pm	**Xinliang Feng** *Center for Advancing Electronics Dresden & Department of Chemistry and Food Chemistry, Technical University Dresden, Germany* Towards macroscopic organic 2D crystals and beyond
6:00 – 6:30 pm	**Thomas Heine** *Wilhelm-Ostwald-Institute of Physical and Theoretical Chemistry, University of Leipzig, Germany* Rational computational materials design using quantum confinement
7:30 – 8:00 pm	*Visit of the Ulm Cathedral*

Wednesday, December 13th

Session: Advanced Techniques I

Chair: E. Spiecker

8:00 – 8:30 am	**Yimei Zhu** *Brookhaven National Laboratory, Upton, NY, USA* Revealing the origin of charge transfer and charge density wave in layered materials using atomically resolved electron microscopy and spectroscopy
8:30 – 9:00 am	**Jianwei (John) Miao** *Department of Physics and Astronomy and California NanoSystems Institute, University of California, Los Angeles, California, USA* Atomic electron tomography: adding a new dimension to see individual atoms in materials
9:00 – 9:30 am	**Frances M. Ross** *IBM T. J. Watson Research Center, Yorktown Heights, New York, USA* *In situ* growth experiments on 2D materials
9:30 – 10:00 am	**Eva Olsson** *Department of Physics, Chalmers University of Technology, Gothenburg, Sweden* *In situ* electron microscopy studies to link atomic structure to corresponding properties
10:00 – 10:30 am	**Dagmar Gerthsen** *Laboratory for Electron Microscopy, Karlsruhe Institute of Technology (KIT)* Chances and challenges of high-resolution imaging in a scanning electron microscope
10:30 – 11:00 am	*Coffee Break*

Session: Low-Dimensional Materials: Preparation, Characterization, Theory III

Chair: J. Meyer

11:00 – 11:30 am	**Angus Kirkland** *University of Oxford, UK* Recent developments in imaging defects and defect dynamics in low dimensional materials
11:30 – 12:00 pm	**Wu Zhou** *School of Physical Sciences and CAS Key Laboratory of Vacuum Physics, University of Chinese Academy of Sciences; Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA* Low voltage aberration corrected STEM for two-dimensional heterostructures
12:00 – 12:30 pm	**Arkady V. Krasheninnikov** *Helmholtz Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Germany* Electron irradiation-induced defects and phase transformations in two-dimensional materials
12:30 – 2:00 pm	*Lunch and SALVE visit II*

Session: Bridging Biological and Materials Science

Chair: L. Houben

2:00 – 2:30 pm	**Lena F. Kourkoutis** *School of Applied and Engineering Physics, Cornell University, Ithaca, NY, USA; Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, NY, USA* Probing low temperature electronic phases using cryo-STEM
2:30 – 3:00 pm	**Miroslava Schaffer** *Max Planck Institute of Biochemistry, Martinsried, Germany* Cryo-focused ion beam as a game changer in in-situ cryo-electron tomography of frozen hydrated specimens
3:00 – 3:30 pm	**Christopher J. Russo** *MRC Laboratory of Molecular Biology, Cambridge, UK* Determining the energy scaling of some physical phenomenon important in electron cryomicroscopy of biological specimens
3:30 – 4:00 pm	**Christoph T. Koch** *Humboldt-University, Berlin, Germany* Inline electron holography of soft matter
4:00 – 4:30 pm	*Coffee Break*

Session: Low-Dimensional Materials: Preparation, Characterization, Theory IV

Chair: F. Ross

4:30 – 5:00 pm	**Andrey Turchanin** *Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena; Jena Center for Soft Matter (JCSM), Germany* Novel 2D materials by electron beam induced chemistry
5:00 – 5:30 pm	**Pinshane Y. Huang** *Department of Materials Science and Engineering University of Illinois, Urbana-Champaign, USA* Quantitative STEM and EELS of defects and mixing in 2D materials
5:30 – 6:00 pm	**Sarah Haigh** *School of Materials, National Graphene Institute, University of Manchester, Manchester, UK* Exploring structure in 2D crystal hetero-structure stacks
6:00 – 6:30 pm	**Annick Loiseau** *Laboratoire d'Etude des Microstructures, ONERA-CNRS, Université Paris-Saclay, Châtillon Cedex, France* Studying the dielectric function of 2D materials with angular resolved electron energy loss spectroscopy
7:00 – 8:30 pm	*Visit of the Ulm Christmas Market*
9:30 – 10:15 pm	*Valerij Petasch Night Piano Concert in Ulm Theatre*

Thursday, December 14th

Session: Low-Dimensional Materials: Preparation, Characterization, Theory IV

Chair: H. Rose

8:00 – 8:30 am	**Nobuo Tanaka** *Institute of Materials and Systems for Sustainability (IMaSS), Nagoya University, Nagoya, Japan* Past and future prospect of Cs-corrected TEM for nanomaterials
8:30 – 9:00 am	**Elena Besley** *School of Chemistry, University of Nottingham, UK* Electron-beam induced chemistry of organic molecules
9:00 –9:30 am	**Andrei N. Khlobystov** *School of Chemistry, University of Nottingham, UK* Chemistry of single molecules through a TEM
9:30 – 10:00 am	**Tatiana Latychevskaia** *Physics Institute, University of Zurich, Switzerland* Coherent imaging with low-energy electrons (30 – 250 eV)
10:00 – 10:30 am	**Ursel Bangert** *Department of Physics and Energy and Bernal Institute, University of Limerick, Ireland* Atomic scale imaging and spectroscopy: insight into single atom action in 1-D and 2-D materials
10:30 – 11:00 am	*Coffee Break*

Session: Advanced Techniques II

Chair: C. Koch

11:00 – 11:30 am	**Lothar Houben** *Department of Chemical Research Support, Weizmann Institute of Science, Rehovot Israel* Chromatic aberration-Corrected EFTEM
11:30 – 12:00 am	**Stefan Löffler** *University Service Centre for Transmission Electron Microscopy / Institute of Solid State Physics, TU Wien, Austria* Orbital mapping: challenges and prospects
12:00 – 12:30 pm	**Michael Stöger-Pollach** *Technische Universität Wien, Austria* Transition radiation losses in low- and high-voltage EELS
12:30 – 1:00 pm	**Marc Willinger** *Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin; Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany* In situ observation of metal catalyzed CVD growth of graphene
1:00 – 2:30 pm	*Lunch and SALVE visit III*

Session: Advanced Techniques III

Chair: Y. Zhou

2:30 – 3:00 pm	**Harald Rose** *Ulm University, Germany* Advantages of STEM differential phase contrast imaging at low voltages
3:00 – 3:30 pm	**Mathieu Kociak** *LPS, CNRS/Université Paris Sud, 91405 Orsay, France* New directions in nanooptics with fast electrons
3:30 – 4:00 pm	**Ute Kaiser** *Ulm University, Germany* The modern LV-AC-TEM: a view on its transformation
4:00 – 4:30 pm	*Summary and Outcome*

Departure

Abstracts

Correction of Aberrations – Past – Present –Future

Harald Rose

Ulm University, Germany

Aberration correction can be considered as a quantum step in the development of the electron microscope. The correction of spherical aberration, the improved electrical and mechanical stability of the basic instrument, the development of monochromators, detectors, and corrected energy filters have transformed the electron microscope from a crude imaging instrument into a high-performance analytical instrument providing sub-eV spectroscopic information and sub-Angstroem spatial resolution at voltages above about 80kV. The additional correction of the chromatic aberration and the off-axial coma has further improved the performance of the microscope, giving atomic resolution down to 20kV. The requirements necessary for achieving successful aberration correction are illustrated by outlining the evolution of correctors starting from simple systems and ending with the most advanced corrector employed in the SALVE microscope. The improvement of resolution and contrast by means of aberration correction will be documented by experimental results showing the action of different correctors for specific applications at voltages in the range between 10V and 300kV. Perspectives will be suggested to further increase the information on the atomic structure of radiation-sensitive objects and to enable optical sectioning with atomic resolution.

Acknowledgments: The author acknowledges funding from the German Research Foundation (DFG) and the Ministry of Science, Research and the Arts (MWK) of the federal state of Baden-Württemberg, Germany in the frame of the *SALVE* project

Optical Design of the SALVE Cc/Cs Corrector and its Benefits for Low-kV TEM and EFTEM

H. Müller, M. Linck, P. Hartel, F. Kahl, S. Uhlemann, J. Zach, and M. Haider

CEOS GmbH, Heidelberg, Germany

The correction of the chromatic and the spherical aberration in low-kV TEM is useful to image beam sensitive materials consisting of light atoms [1,2]. Within the Sub-Ångstrøm Low-Voltage Electron microscopy (SALVE) project at University of Ulm, we have developed a novel dedicated low-voltage C_c/C_s-corrector. With this instrument at 40 kV an information limit of 90 pm could be achieved. This is only fifteen times the electron wavelength and corresponds to an effective optical aperture of 67 mrad [3]. Compared to the focus-spread defined information limit of the C_s-only corrected system this is an improvement in resolution by more than a factor of three.

Achromatic imaging in low-kV TEM enables the investigation of interface and defect structures with minimized knock-on specimen damage what was not possible before. For energy-filtered TEM it will enable large energy windows without noticeable degradation of optical resolution. This is encouraging for advanced EFTEM applications and in the near future may produce a demand for further improvements also in the area of in-column or post-column imaging energy filters.

[1] Egerton, R. F., P. Li, and M. Malac. Micron **35.6** (2004): 399-409.
[2] Kaiser, U., et al. Ultramicroscopy **111.8** (2011): 1239-1246.
[3] Linck, M. et al. Physical Review Letters **117.7** (2016): 076101.

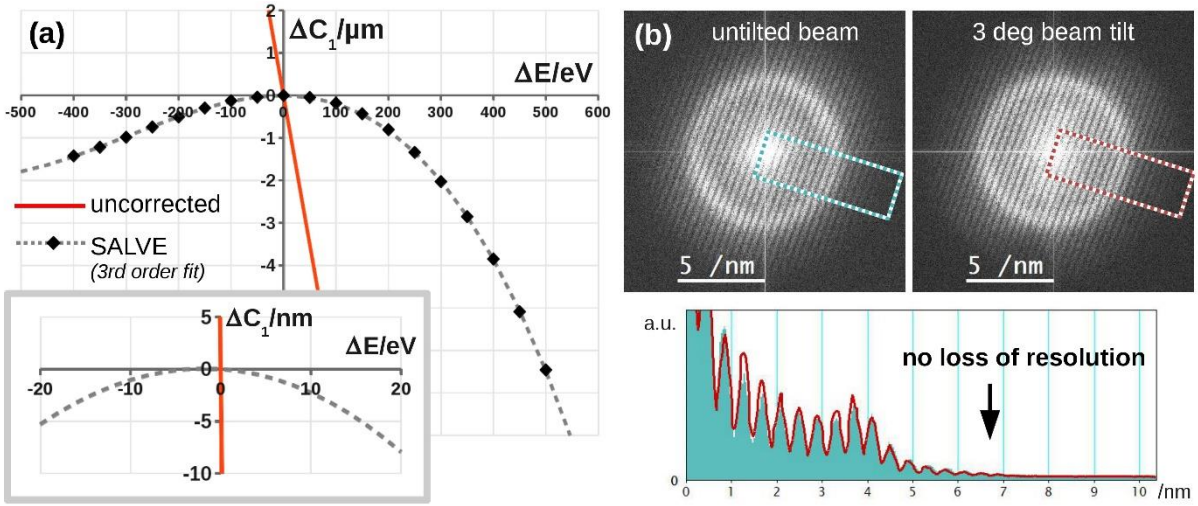

FIG. 1. (a) Change of defocus with energy for the Cc/Cs-corrected SALVE microscope (red line: uncorrected case, black dots: measured, dashed line: third-order fit). (b) Estimation of focus spread: The information transfer under axial illumination (solid profile) does not show any deterioration even under 3° (52.4 mrad) of beam tilt (red line in profile)

Contrast Transfer in the SALVE Instrument

F. Börrnert and Ute Kaiser

Ulm University, Germany

To maintain atomic resolution at low electron energies in transmission electron microscopy (TEM), new aberration correction technology had to be introduced, leading to the SALVE instrument.[1,2] In this new microscope, the heart of the development is the introduction of chromatic aberration correction in addition to geometric aberration correction optimized for low-voltage imaging.

Generally, the use of low electron acceleration voltages in TEM does not itself change the way how to describe the contrast transfer therein. For example, in the information transfer, we consider three main contrast dampening mechanisms, image spread, focus spread, and illumination spread. Due to the new technology, the effect of Johnson-Nyquist noise is now to be considered in the image spread.[3] Also, the traditional description of the focus spread has to be updated.[4] Nevertheless, even without chromatic aberration correction it is necessary to revisit the transfer theory and evaluate some basic implications to the contrast transfer when lowering the electron energy.

We discuss the combined effect of lowering the electron energy and using the new chromatic aberration correction technology on the different information dampening envelope functions as well as on the coherent phase contrast transfer. These effects are demonstrated with on the example of atomically resolved graphene images at 80 kV and 20 kV electron acceleration voltages.

[1] Kaiser, U., et al. Ultramicroscopy 111.8 (2011): 1239-1246.
[2] Linck, M. et al. Physical Review Letters 117.7 (2016): 076101.
[3] Uhlemann, S. et al. Physical Review Letters 111.4 (2013): 046101.
[4] Haider, M. et al. Microscopy and Microanalysis 16 (2010): 393.

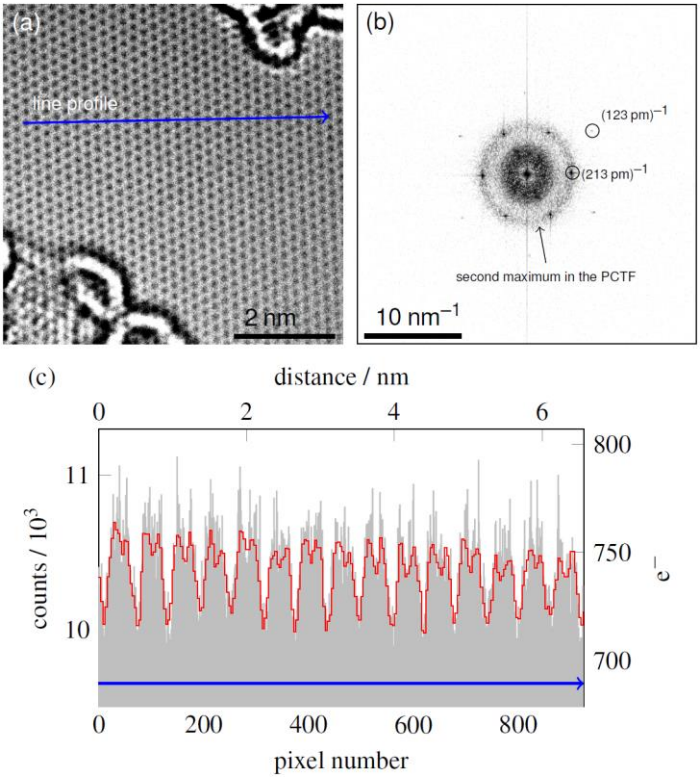

FIG. 1. Transmission electron micrograph of graphene taken with a primary electron energy of 20 keV and positive contrast ("white-atom contrast"). (a) The raw micrograph taken with a dose of 1.4 10^7 e^-/nm^2, (b) Fourier transform of the micrograph featuring a complete set of second order spots indicating an isotropic information transfer up to at least 0.123 nm. (c) The histogram in grey represents an intensity profile along the indicated line in (a), the line width is one pixel. Overlaid in red is an intensity profile along the same line in the same micrograph binned four times that shows a clear separation of the carbon atoms.

Acknowledgments: The authors acknowledge funding from the German Research Foundation (DFG) and the Ministry of Science, Research and the Arts (MWK) of the federal state of Baden-Württemberg, Germany in the frame of the *SALVE* project

Energy-Filtered TEM in the *SALVE* Instrument

Johannes Biskupek[1], Michael J. Mohn[1], Martin Linck[2], Frank Kahl[2], Ute Kaiser[1]

[1]Central Facility of Electron Microscopy, University of Ulm, Germany
[2]CEO*S* GmbH, Heidelberg, Germany

The dedicated *SALVE* (sub-Ångstrøm low voltage electron microscopy) instrument is a TEM were geometric and chromatic aberrations of the objective lens are corrected. It operates voltage tunable between 20 and 80 kV. A point resolution better than 0.14 nm can be achieved even at 20 kV (corresponds to a corrected phase plate of more than 60 mrad) [1]. As many low-dimensional materials have low knock-on damage thresholds, we operate the *SALVE*-TEM below the particular threshold to image the material's structure in its pristine states. The *SALVE-TEM* is also equipped with a Gatan energy filter based on the GIF Quantum 966 for energy filtering and electron energy-loss spectroscopy.

The correction of the chromatic aberrations allows the use of all elastically and all inelastically scattered electrons for image formation, without the loss of beam intensity due to monochromation. Together with an energy filter it is possible to image losses of plasmon or core-state excitations at atomic resolution in an EFTEM image. For atomically resolved energy-filtered TEM not only correction of the chromatic aberration of the objective lens is required, but there are also requirements on the performance of the energy filter. Mainly chromatic distortions and non-isochromaticity have to be very small. We present the evaluation of the Gatan imaging filter attached to the *SALVE* TEM in terms of EFTEM imaging. Fig. 1 shows the plot of the non-isochromaticity at 30 kV and the evaluation between 20 and 80 kV. Fig. 2 shows unprocessed 80 kV EFTEM images (4 seconds exposure time) of a monolayer of graphene, using a 10 eV slit at energy losses of 260, 270 and 295 eV (carbon K edge) together with the zero-loss image for comparison. The image at the K-edge shows lattice fringes while the image before the edge does not. Thus we succeeded to obtain a true inelastic signal at the K-edge for the first time.

[1]Linck, M. et al. Physical Review Letters 117.7(2016): 076101.

Tabulated non-isochromaticity

High tension (kV)	Slit width (eV)	Non-isochromaticity (eV)
20	1	1.0
30	1	0.11
40	1	0.39
60	1	0.23
80	1	0.31

Fig. 1 Non-isochromaticity of the GIF 966 at 30 kVand the evaluation between 20 and 80 kV

Acknowledgments: The authors acknowledge funding from the German Research Foundation (DFG) and the Ministry of Science, Research and the Arts (MWK) of the federal state of Baden-Württemberg, Germany in the frame of the *SALVE* project

Chromatic Aberration Correction: New Methods and Applications Developed on the PICO Instrument

Joachim Mayer[1,2], Juri Barthel[2], Lothar Houben[2], Lei Jin[2], Les J. Allen[2,3] Rafal Dunin-Borkowski[2] and Knut Urban[2]

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[2] Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Research Centre Juelich, 52425 Juelich, Germany
[3] School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia
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We demonstrate the state of the art of Chromatic Aberration Corrected TEM in various application modes. In Cc-corrected HRTEM, resolutions of 50 pm can be reached in suitable samples. A resolution of 0.8 Å could be reached at 80 kV accelerating voltage and even at 50 kV accelerating voltage a resolution of the order of 1.0 Å could be obtained. In EFTEM mode, the resolution which can be reached also approaches 1.0 Å.

In the present contribution we will report on the initial results obtained with the PICO instrument. The application of combined chromatic and spherical aberration correction in high-resolution transmission electron microscopy enables a significant improvement of the spatial resolution down to 50pm. We demonstrate that such a resolution can be achieved in practice at 200kV. Oriented yttrium orthoaluminate was investigated as a model system and to verify the experimental feasibility of close to 50 pm resolution. In a thin section of the sample, the Y atom pairs in [010] projection are successfully imaged together with the Al and the O atoms (Figure 1) [1].

In energy filtering TEM, the newly developed achromatic electron optics allows the use of wide energy windows and makes it feasible to reach atomic resolution in EFTEM images. In systematic work, we have obtained EFTEM images from a range model systems including various oxides and semiconductors. Figure 2 shows an elemental map formed using electrons that have undergone a silicon $L_{2;3}$ core-shell energy loss, exhibiting a resolution in EFTEM of 1.35 Å [2]. This permits elemental mapping beyond the nanoscale provided that

quantum mechanical calculations from first principles are done in tandem with the experiment to understand the physical information encoded in the images.

[1] L. Jin, J. Barthel, C.L. Jia, K.W. Urban, Ultramicroscopy 176 (2017) 99–104.
[2] K.W. Urban, J. Mayer, J. Jinschek, M. J. Neish, N. R. Lugg, L. J. Allen, PRL 110 (2013) 185507.

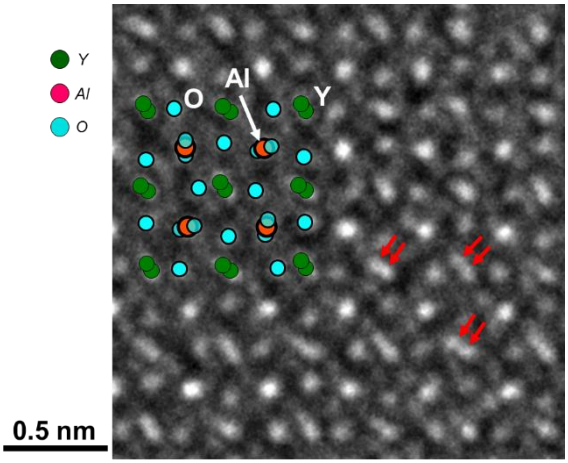

Figure 1: Experimental image of yttrium orthoaluminate along the b axis (unfiltered original). The schematic in the upper left corner depicts the projected atomic structure.

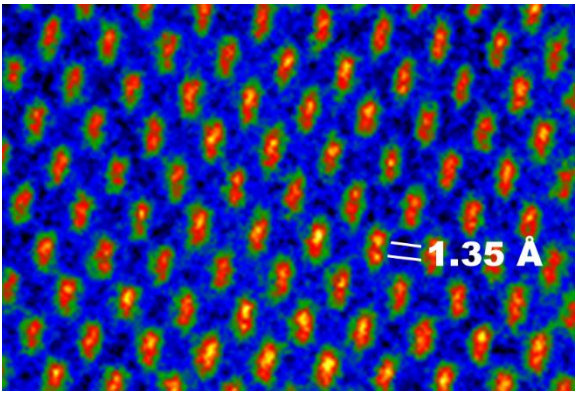

Figure 2: Silicon $L_{2;3}$ elemental map obtained from a thin Si-crystal in <110>-projection. The background was subtracted using the three-window technique.

New Capabilities on the Themis Z platform: iDPC imaging, 4D STEM for Diffractive Imaging and Ultra High Resolution EELS

Bert Freitag, Sorin Lazar, Peter Tiemeijer, Emrah Yucelem, Austin Wade

ThermoFisher Scientific, Achtseweg Noord 5 5651 GG Eindhoven, The Netherlands

Transmission electron microscopy provides via imaging, diffraction and spectroscopy flexible access to morphology, structure, composition and electronic properties of materials down to the atomic level in one instrument. In this presentation new developments on the Themis platform in these three techniques are demonstrate to give an overview of the latest developments.

In imaging the new iDPC method provides access to atomic imaging of not only heavy but also light elements with extreme low doses and high contrast[1]. iDPC requires a segmented STEM detector and examples of different materials are shown proving ultimate resolution in Gallium and nitrogen dumbbell imaging of 63pm and low dose capabilities by damage free imaging of zeolite materials. In diffraction the recording of maps of diffraction pattern instead of single patterns allows for contrast tuning, extraction of complementary information in imaging (Bf,DF,ABF,iDPC,HAADF) using only one acquisition and enables data analysis to obtain quantitative structural information or resolution increase via Ptychography. The benefits of recording the full diffraction pattern with an electron microscope pixel array detector (EMPAD) instead of a integrate the signal with a standard ring or disk detector is illustrated in several examples[2]. Last but not least the latest developments of the ThermoFisher monochromator for EELS spectroscopy with an energy resolution down to 25meV are presented. The new science enabled by this capability is exemplified in low energy loss applications. All these results can be obtained on a highly flexible tool to give the researcher access to the most complete information provided by the interaction of the electrons with their materials.

[1] I. Lazić, E.G.T. Bosch, S. Lazar, Ultramicroscopy 160 (2016) 265-280

[2] MW Tate et al. Microsc Microanal. (2016) 237-49 doi: 10.1017/S1431927615015664

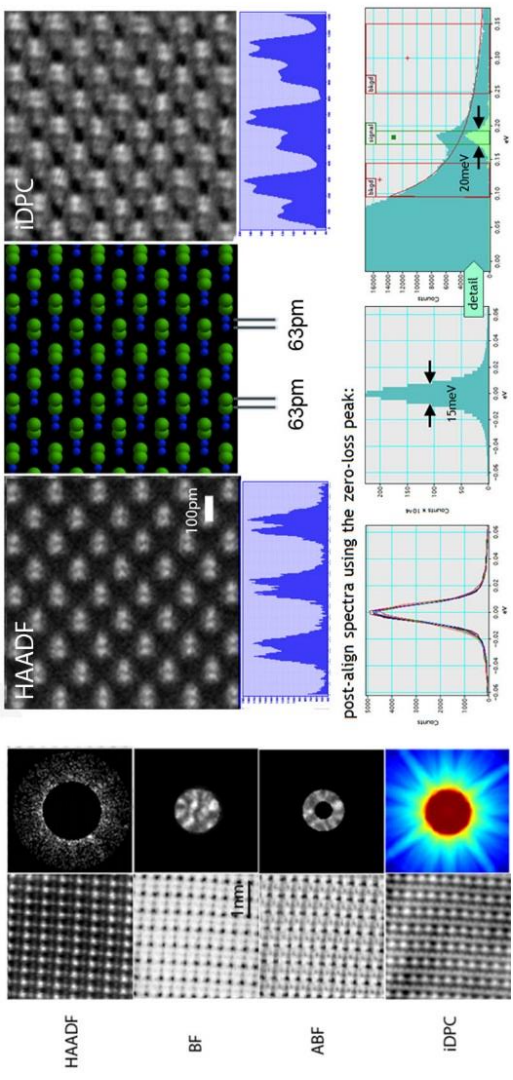

Figure 1: 4D STEM result with extraction of BF,ABF,HAADF&iDPC image of STO (left), comparison of iDPC with HAADF image of GaN[211] projection(upper right) , FWHM zero-loss measurement of monochromator tool with BN low loss spectrum (lower right)

High Resolution Electron Microscope Developed Under Triple C Project, and Aberration Measurement

Hidetaka Sawada [a], Shigeyuki Morishita [a], Takeo Sasaki [a], Masaki Mukai [a], Christopher S. Allen [b,c], Reiner Ramlau [d], Angus Kirkland [b,c], Kazutomo Suenaga [e]

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[b] Electron Physical Science Imaging Centre (ePSIC), Diamond Light Source Ltd, Didcot, Oxford OX11 0DE, UK
[C] Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK
[d] Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, D-01187 Dresden, Germany
[e] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan

In the Triple C project, we have been developing aberration correctors dedicated for use in a low-voltage microscope [1]. The developed Delta aberration corrector, which is equipped with three dodecapoles, compensated for third-order spherical aberration and fifth-order six-fold astigmatism. Triple C microscope #1 had the ability to facilitate atomic resolution imaging on a STEM and a TEM at 15, 30 and 60 kV [2]. For the phase I in Triple C microscope #2, Cc corrector was developed by applying a combination concave-lens effect by magnetic and electrostatic two-fold astigmatism fields produced by dodecapoles with a different dispersion from that for the objective lens. The Triple C microscope # 2 in phase II is equipped with a monochromator, which consists of two Wien filters and a slit between the filters [3]. The instrument was able to obtain atomic resolution image at an ultralow accelerating voltage of 15 kV [4]. UHV-STEM atomic resolution instrument of Triple C microscope #3 [5] at the accelerating voltages of 15, 30, and 60kV has been developed to achieve the vacuum pressure of 9.3 x 10^{-8} Pa at the stage.

The geometric and chromatic aberration coefficients of the probe-forming system in an aberration corrected transmission electron microscope have been measured using a Ronchigram recorded from monolayer graphene [6]. The geometric deformations within

individual local angular sub-regions of the Ronchigram were analyzed using an auto-correlation function and the aberration coefficients for the probe forming lens were calculated. This approach only requires the acquisition of a single Ronchigram allowing rapid measurement of the aberration coefficients. Moreover, the measurement precision for defocus and two-fold astigmatism is improved over that which can be achieved from analysis of Ronchigrams recorded from amorphous films.

Toward further study of three-dimensional reconstruction at atomic-resolution with the geometrical and chromatic aberration correctors, it is important to characterize behavior along the normal (z) direction to the plane of a thin film. We have investigated displacements of a specimen along the z direction using dark field HAADF STEM images of single atoms as a function of specimen tilt [7]. These showed an elongation perpendicular to the tilt axis. Experimental measurements of the contrast of single atoms indicates fluctuations in the film along the z direction with a displacement amplitude of 0.6 nm (FWHM).

[1]Advances in Imaging and Electron Physics (Edited by P. W. Hawkes) **168** (2011) 297-336.
[2]Physical Review Letters **114** (2015) 166102.
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Ultra-High Spatial and Energy Resolution STEM/EELS

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The ground-potential monochromator and highly stable EEL spectrometer developed by Nion are presently reaching <10 meV energy resolution EELS on a routine basis, and < 5 meV resolution appears to be just around the corner. This has extended the capabilities of the electron microscope, especially for vibrational spectroscopy[1], by allowing:

• damage-free identification of different bonds in biological samples[2]

• vibrational spectroscopy using the non-dipole signal, with sub-nm spatial resolution[3]

• probing vibrational modes at surfaces and edges of nano-objects[4]

• mapping phonon dispersion in momentum space with nm-scale spatial resolution[5]

• measuring sample temperature by the energy gain/energy loss ratio[6]

Monochromation can also improve the spatial resolution, which is limited to:

$$d\ probe(C_c) \sim 0.5\ (\lambda\ C_c\ \delta E / E_o)^{0.5}$$

where $d\ probe(C_c)$ is the diameter of the C_c-limited probe, λ the electron wavelength, C_c is the chromatic aberration coefficient, δE the energy spread and E_o the primary energy. Two approaches to overcoming this limit, which is especially severe at low energies (40 keV and below), are possible: correcting C_c, or decreasing δE. The second approach has the advantage that it also provides better EELS energy resolution. We have used it to attain 1.07 Å spatial resolution at 30 keV by monochromating to 100 meV (from 350 meV) and correcting all aberrations as needed for 50 mrad probe half-angle. This has lowered the d/λ figure of merit to 15, and the smaller energy

spread also allowed us to reduce the chromatic “tail” of the probe, leading to improved image signal-to-background ratios.

Nion’s new EEL spectrometer provides high energy stability (instability and energy drift < 10 meV per minute), and aberration correction up to about 50 mrad half-angle (measured at the sample). We have also developed a high dynamic range 2kx2k EELS camera that can detect single electrons (at 30-200 keV) as well as >200 primary electrons/pixel without saturating, and is robust enough to measure an intense Zero Loss Peak without damage.

As we approach sub-5 meV resolution EELS, electron microscopy will enter an era of diffraction-limited EELS, in which the resolution of the energy spectrum will be limited by diffraction effects, and opening up the spectrometer entrance angle (while correcting the spectrometer aberrations) will lead to better energy resolution. The new spectrometer has been designed precisely with this new era in mind.

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Latest Advances in Energy Loss Spectroscopy Detectors: Extremely Low Energy and Direct Detection

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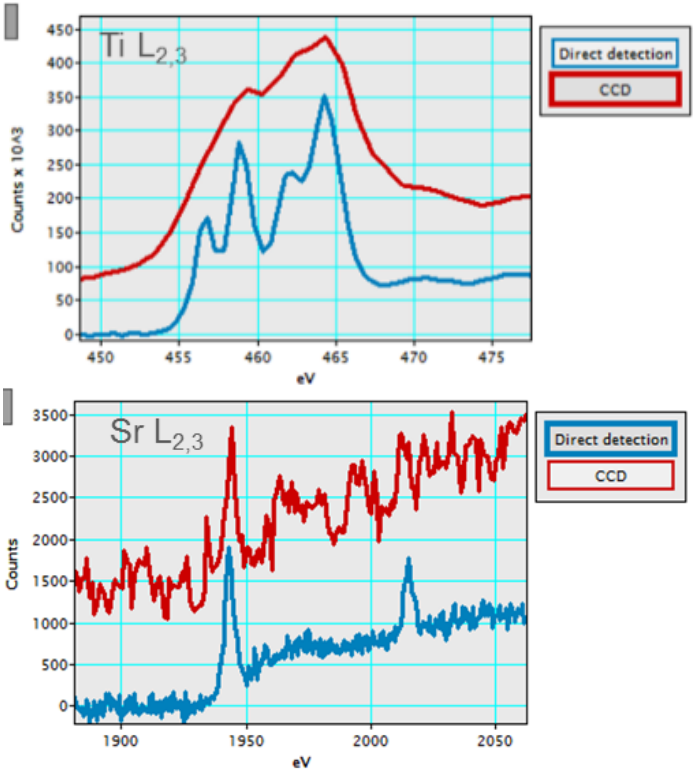
For years, STEM based analysis has been pushing to higher voltages. Initially, 80 and 100 kV STEMs were common, but to improve spatial resolution and microanalysis sensitivity, 200 kV and 300 kV instruments were developed and are now common. However, with the advent of Cs and Cc correction, the effect of lowering the beam energy did not have such a detrimental effect on probe size and many researchers began pushing the energy back down. This greatly reduced knock-on damage and also increases both the elastic and inelastic scattering cross-sections. In order to optimize the acquisition of EELS spectra at low energy to counter the effects of increasing chromatic aberration and reducing energy range we have made some modifications in the optics lens system as well as the detector to increase the efficiency.

In addition to improvements of the EELS spectrometers for the acquisition of low energy EELS spectra, we have witnessed the introduction of direct detection detectors capable to acquire EELS spectra in counting mode. These detectors result in greatly improved point spread function (PSF) and detector quantum efficiency (DQE) in comparison to conventional indirect detection cameras (IDCs). Such direct detection cameras (DDCs) have revolutionized the cryo-TEM field as well as have strong advantages for in-situ TEM in both imaging and diffraction applications. EELS applications can benefit from the improved PSF and the ability to count electrons. The improved PSF allows spectra to be acquired over larger energy ranges while maintaining sharp features and greatly reduced spectral tails. The ability to count electrons nearly eliminates the noise associated with detector readout and greatly reduces the proportional noise associated with detector gain variations. This effectively leaves the shot noise as the limiting noise source present.

In this presentation, we will review the current state of low energy EELS detectors and also electrons counting detectors for electron microscopy with an emphasis on system for EELS measurements.



Figures 1a,b EELS spectra of Ti L- and Sr-edges at 456eV and 1940eV extracted from the same area in the specimen under the same experimental conditions using both the DD and IDC detectors. Both the Ti and Sr L signals are extracted from the same spectrum. The spectra extracted using the DD detector show higher energy resolution as well as much reduced noise that allows the clear observation all the main features in the near edge fine structure.

Inorganic Nanotubes and Fullerene-Like Nanoparticles at the Crossroad Between Materials Science and Nanotechnology and their Applications

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This presentation is aimed at demonstrating the progress with the high-temperature synthesis and characterization of new inorganic nanotubes (INT) and fullerene-like (IF) nanoparticles (NP) from 2-D layered compounds. Two important categories of new IF/INT nanostructures will be discussed in particular: 1. Synthesis of doped IF/INT of WS_2 (MoS_2) by rhenium and niobium; 2. Synthesis of IF and in particular INT from the ternary misfit compounds, like PbS-TaS_2, CaCoO-CoO_2 and numerous others. [1] The synthesis of 1-D nanostructures (nanotubes) from this vast group of layered materials is particularly promising.

Major progress has been achieved in elucidating the structure of INT and IF using advanced microscopy techniques, like aberration corrected TEM and electron tomography. Recent optical, electrical (e.g. superconductivity [2]) and mechanical measurements of WS_2 nanotubes will be discussed. Strong capillary forces were observed upon withdrawal of individual nanotubes from water surface. [3] Applications of the IF/INT as superior solid lubricants and for reinforcement of variety of polymers and light metal alloys was demonstrated. Few recent studies indicate that this brand of nanoparticles is non-toxic and biocompatible. With expanding product lines, manufacturing and sales, this generation of superior lubricants is becoming gradually an industrial commodity.

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Emerging Nanomaterials for Biomedicine and Sensing

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Fluorescent nanodiamonds (FNDs) are emerging as highly promising quantum materials for biomedical applications and precision sensing due to their unique optical and magnetic properties.[1] They are obtained by implementing elemental defects into the carbon lattice, such as the nitrogen vacancy (N-V), giving unconditionally stable fluorescence without bleaching or blinking even after several months of continuous excitation. The emission wavelength of FNDs is not size-dependent and is tuneable from the visible to the near infrared region according to the elemental defects. In addition, the N-V center in FNDs serves as single-spin sensor[2] that locally detects various physical properties offering great potential for atomic resolution imaging under physiological conditions. The advent of diamond quantum sensing promises solving the longstanding goal of single molecule detection with atomic resolution under ambient conditions[1] There is currently no other nanomaterial that would offer such features.

The preparation of high quality N-V diamonds and the chemistry of surface modification with i.e. biopolymers[3-4] and proteins[2] will be discussed that provide the basis for quantum sensing and drug delivery in living biological environments. In addition, functionalization of N-V diamonds with proteins or DNA provides access to precisely assembled diamonds on DNA origami to access sophisticated quantum devices[4].

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Understanding and Exploiting the Interaction of Electron Beams with Low-Dimensional Materials

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Interactions of energetic electrons with materials that result in permanent changes in the structure, often referred to as radiation damage, can be both an obstacle for imaging as well as a useful tool for manipulating matter at the smallest scales. I will discuss both aspects of understanding and controlling the beam-matter interaction especially in the context of 2D materials. The relevant doses for beam-induced structural changes can vary by many orders of magnitude: Radiolysis of organic molecules can happen at doses as low as 10 $e^-/Å^2$ [1], while defect-free graphene in a low-energy (<80 keV) electron beam can be stable up to extremely high doses (10^8 $e^-/Å^2$ in a TEM at 80 kV [2], and even up to 10^{10} $e^-/Å^2$ at 60 kV in ultra-high vacuum). Nevertheless, defects in the lattice such as vacancies or impurities are usually still highly mobile under irradiation [3,4]. In some cases, these dynamics can be induced in a controlled way using the atomically focused electron beam in a STEM: We have achieved a directed displacement of a Si impurity in graphene over several lattice sites [5].

The above-mentioned configurations and their dynamics can be traced because the individual configuration is stable enough for a single atomic resolution exposure, which requires on the order of 10^5 $e^-/Å^2$. For imaging atomic configurations that are less beam-stable, we have redeveloped an approach that has been very successful in structural biology, to the case of defects in a material [6]: Rather than irradiating a single object, we distribute the dose over many identical copies of an object, and use a suited reconstruction algorithm to extract the desired information. We show the first case where this was achieved experimentally for defects in a material and at atomic resolution. We used an automated acquisition of large-area, low-dose data sets that

achieves atomic resolution in nearly all exposures, and a maximum likelihood reconstruction algorithm that can recover effective high-dose views of frequently occurring deviations from the periodic lattice [7].

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Exploring Low-Energy Electron Microscopy for Investigation of Graphene and its Defects: LEND and SEM-STEM

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Current trends in electron microscopy point towards low-voltage applications[1,2]. The reduction of beam energy offers several benefits like reduced beam damage and higher scattering cross sections, especially beneficial for the investigation of light elements. Widely recognized examples of light element-materials are graphene and carbon nanotubes, which have been thoroughly investigated by electron microscopy demanding primary beam energies below 80 keV to exclude knock-on damage. While dedicated low-voltage TEMs are only slowly entering the commercial market, scanning electron microscopes (SEM) already use primary electron energies of 0.5-30 keV and thus offer an easy access to low-voltage microscopy. The SEM is a highly versatile tool for the investigation of novel materials by offering a complex set of applicable techniques, less spatial limitations compared to a TEM, high throughput and the possibilities to use a wide range of available add-on tools (e.g. manipulators, GIS, *in situ* equipment) while still maintaining resolution in the nm-range and high material contrast.

Using a Helios NanoLab 660 FIB-SEM we have carried out detailed microscopic studies on (bilayer) graphene and its defects[3]. A schematic of the ray path is shown in Fig. 1a. Low energy nanodiffraction (LEND) patterns show strong contrast and provide important crystallographic information as demonstrated for rotated bi-layer graphene in Fig. 1b. LEND can furthermore be used to tune diffraction contrast in STEM mode which is key to defect imaging (Fig. 1c). Going one step further micromanipulators have been employed for controlling individual defects *in situ* while studying their mutual interaction at nanometer resolution.

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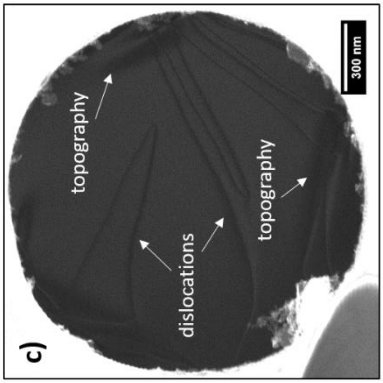

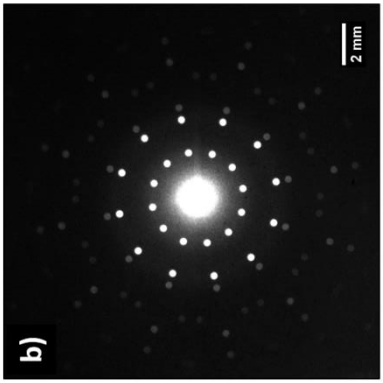

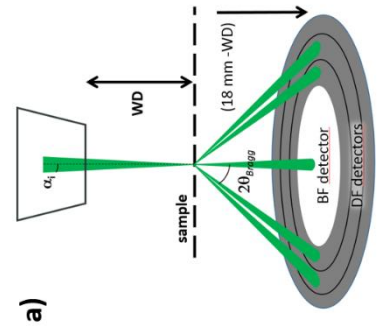

Fig. 1: a) Schematic beam path of electrons in SEM-STEM. b) Low energy nanodiffraction (LEND) pattern of rotated bilayer graphene taken at 30 kV electron energy. Scale bar shows real space distance in detector plane. c) Dark field SEM-STEM image of basal plane dislocations and membrane topography in bilayer graphene.

Model-Based Reconstruction of Magnetization Distributions from Optical Phase Images

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We have developed a model-based approach for the reconstruction of magnetization distributions in nanoscale materials, which involves applying an iterative reconstruction algorithm to one or more magnetic phase images recorded using off-axis electron holography. The advantage of using a model-based approach is that each trial solution satisfies known physical laws. The initially ill-posed problem is replaced by a least-squares minimization problem. First order Tikhonov regularization is applied and a mask is used to localize magnetized objects. All measures are combined into a cost function, whose minimization is facilitated by conjugate gradient methods. Diagnostic tools are used to assess the quality of the reconstruction result. Sources of magnetization outside the field of view are accounted for by introducing buffer pixels. A confidence array is used to exclude other identifiable artefacts from the reconstruction. Figure 1 shows a reconstruction of the three-dimensional magnetization distribution in a magnetized disc that supports a vortex state generated from two tilt series of simulated magnetic phase images. A central slice along the x axis is also shown. The reconstruction is in very good agreement with the original magnetization distribution. Encouraging experimental results have been obtained from the reconstruction of projected magnetization distributions of magnetic skyrmions examined in both extended films and geometrically-confined structures fabricated using focused ion beam milling[1].

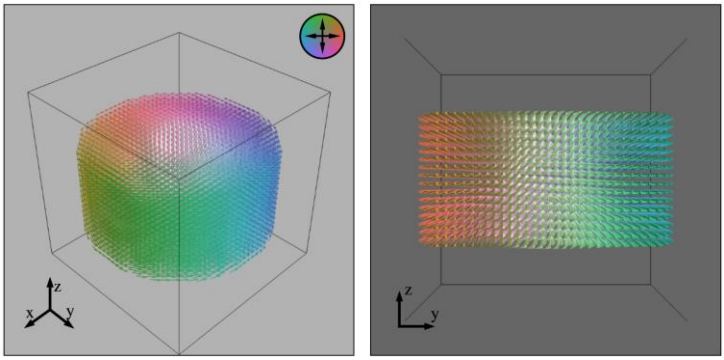

FIG. 1 Reconstructed magnetization distribution of a vortex state in the xy plane calculated from two tilt series of simulated magnetic phase images about the x and y axes for a maximum tilt angle of ±90° and an angular sampling of 5°. The color wheel encodes the magnetization direction in the xy plane, while white arrows point in the positive z direction.

[1]The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013)/ ERC grant agreement number 320832. We are grateful to Z.-A. Li, H. Du, K. Shibata, Y. Tokura, M. Riese, M. Farle, N. Kiselev and S. Blügel for contributions to this work.

Advanced Holographic Tomographies for Nanoscale Materials

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TEM methods reconstructing the beam electrons' phase play a prominent role in material science, and a large number of different phase retrieval setups, such as off-axis and through-focus inline holography or differential phase contrast, in the bright field and dark field mode of the TEM, have been developed, permitting the investigation of a multitude of object geometries and fields. Moreover, the inevitable information loss occurring when projecting a 3D field into a 2D TEM image has been (partly) overcome by combining Electron Holography with Tomography (EHT) [1–4], typically consisting of the acquisition of a set of holograms under different viewing angles (tilt series), followed by a numerical back-projection of the recorded data into 3D space. Here, we report on novel developments in EHT overcoming physical and technological limitations, previously limiting the technique in various important aspects (e.g., spatial resolution, tilt series alignment, and limited tilt range).

In the first part focusing on the reconstruction of electric potentials, we show on the example of a GaAs/AlGaAs core-multishell NW, how functional space charge potentials can be uncovered from materials mean inner potential (MIP) contrast by determining the latter independently from high-angle annular dark-field (HAADF) STEM tomography (solely measuring the material contrast) and subtracting the MIP from the total potential obtained from EHT in a second step. In addition, we will present a novel EHT reconstruction method facilitating the reconstruction of atomic potentials by incorporating dynamic scattering effects.

In the second part we focus on the reconstruction of magnetic vector fields. We present EHT reconstruction all 3 cartesian components of a magnetic vector field in Co/Cu layered magnetic nanowires in 3D from 2 perpendicular tilt series. We discuss the crucial

reconstruction steps including generalizations of tomographic reconstruction algorithms, allowing for a concomitant reconstruction of all electric and magnetic field components in one step. To ease the acquisition of multiple tilt axis EHT and to reduce the missing wedge problem in these we also report on a dedicated tomographic specimen holder development. Additionally, we present tomographic data of the 3D texture in magnetic Skyrmions occurring in thin films of FeGe.

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Towards Macroscopic Organic 2D Crystals and Beyond

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In this lecture, we will present our recent efforts on the bottom-up synthetic approaches towards novel 2D conducting polymers and supramolecular polymers with structural control at the atomic/molecular-level or at the meso-scale. First, we will demonstrate the latest development on the synthetic 2D conjugated polymers including 2D Schiff-base type covalent polymers and 2D metal-dithienene/diamine coordination supramolecular polymers at the air-water or liquid-liquid interfaces. The resulting 2D conjugated polymers exhibit single-layer feature, good local structural ordering and with a size of cm^2. The functional exploration of such 2D single-layer conjugated polymers for the electrical and mechanical properties, as well as serving as efficient electrocatalytic water splitting catalysts will be demonstrated. Second, we will introduce the self-assembly of a host-guest enhanced donor-acceptor interaction, consisting of a tris(methoxynaphthyl)-substituted truxene spacer, and a naphthalene diimide substituted with N-methyl viologenyl moieties as donor and acceptor monomers, respectively, in combination with cucurbit[8]uril as host monomer toward monolayers of an unprecedented 2D supramolecular polymers at liquid-liquid interface. Finally, we will present the supramolecular approaches to synergetic control the multi-component assembly, which results into 2D conducting polymers, such as polypyrrole and polyaniline nanosheets featuring 2D structures and with adjustable mesopores with/without on various functional free-standing surfaces. The unique structure with adjustable pore sizes (5–20 nm) and thickness (35–45 nm), enlarged specific surface area as well as high electrical conductivity make 2D conducting polymers promising for a number of applications. The future perspective and outlook regarding the goal towards highly crystalline organic 2D materials will be provided.

Rational Computational Materials Design using Quantum Confinement

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Quantum confinement is one of the design principles in nanotechnology. Well-known examples are quantum dots, which are nanocrystals whose electronic band gaps depend crucially on their spatial extension. Thus, it is possible to create light emitting devices with the colour defined by the diameter of the quantum dot. Latest applications include large-scale displays and lasers.

In my presentation I will show that quantum confinement is not restricted to quantum dots and optoelectronic applications. I will show how quantum confinement can be exploited as strategy for the rational design of functional nanomaterials.

The first examples are taken from the field of layered materials, where quantum confinement can be used to tailor the band gap, but also the character of the band gap. For example, transition metal dichalcogenides MX_2 (M=Mo, W, X=S, Se) are indirect band gap semiconductors as bulk and multilayer phases, but direct band gap semiconductors with appreciable photoluminescence signal as single-layer material. These ultrathin materials are also called two-dimensional crystals. The exploitation of quantum confinement gets even more interesting if the symmetry of the material is changed by changing the layer number. For example, by the absence (monolayer) or presence (bilayer) of inversion symmetry in two-dimensional crystals strong spin polarization effects are observed. The strongest quantum confinement effect so far we have predicted for PdS_2, a two dimensional crystal that is semiconducting as monolayer, but metallic as bilayer. Similarly, GeP_3 is a semiconductor in mono- and bilayer form, but metallic for trilayers and thicker stacks.

Another way of exploiting quantum confinement is the application of external fields, most notably electric fields, which are

conveniently applied using a gate voltage, and strain fields. I will present various examples where the electronic band gap and/or the density of states are strongly affected by an external gate voltage and by strain fields. For the latter, I will also show some topological phase transitions.

In the final part I will show how quantum confinement can be relieved in molecular crystals, where conjugation can transform local electronic structures to full-featured two-dimensional semiconductors.

Revealing the Origin of Charge Transfer and Charge Density Wave in Layered Materials using Atomically Resolved Electron Microscopy and Spectroscopy

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In this talk I will present our recent studies on the atomic structure and electronic structure of layered materials, in particular the anisotropy of charge density wave (CDW) in 1T-TiSe2, by means of aberration corrected, in-situ atomically resolved electron microscopy at cryogenic temperatures in both reciprocal and real spaces. Using novel coherent nano- and subnano-electron diffraction we developed, we observed short-range coherence of in-plane CDW component while the long-range coherence of out-of-plane CDW component remains intact. The in-plane CDW coherence length of ~10 nm and the out-of-plane CDW coherence length of 17.5 nm were determined. The electron modulation was observed using electron energy-loss spectroscopy (EELS) and verified by orbital-projected density of states. The spatial anisotropic valence charge distribution obtained by Density Functional Theory (DFT) calculations reveals the electronic origin of the anisotropic CDW. Intriguing observations of interfacial charge transfer of monolayer iron selenide (FeSe) films on strontium titanate substrate will also be presented. Integrated approach of combining atomic scale imaging, low temperature (10K) atomic EELS, and ab-initio multiple scattering calculations unraveled the origin of the 7-fold enhanced Tc in the system, compared to its bulk counterpart. Our work illustrates the significance of aberration-corrected electron microscopy and spectroscopy to study materials' emerging behavior in reduced dimensionality in strongly correlated electron systems.

The author would like to thank Q. Qiao, S. Zhou, J-C. Zheng, L. Wu, ST Ciocys, M. Iavarone, DJ. Srolovitz, and G. Karapetrov for their assistance and collaboration. This work was in part supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, and the Center for the Computational Design of

Functional Layered Materials, an Energy Frontier Research Center under DOE-BES Award # DE-SC0012575.

Atomic Electron Tomography: Adding a New Dimension to See Individual Atoms in Materials

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To understand material properties and functionality at the fundamental level, one must know the 3D positions of atoms with high precision. For crystalline materials, crystallography has provided this information since the pioneering work of Max von Laue, William Henry Bragg, and William Lawrence Bragg over a century ago. However, perfect crystals are rare in nature. Real materials often contain crystal defects, surface reconstructions, nanoscale heterogeneities, and disorders, which strongly influence material properties and performance. Here, I present atomic electron tomography (AET) for 3D structure determination of crystal defects and disordered materials at the single-atom level. Using a Fourier based iterative algorithm, we first demonstrated electron tomography at 2.4-Å resolution without assuming crystallinity in 2012. We then applied AET to image the 3D structure of grain boundaries and stacking faults and the 3D core structure of edge and screw dislocations at atomic resolution. Furthermore, in combination of AET and atom tracing algorithms, we localized the coordinates of individual atoms and point defects in materials with a 3D precision of ~19 pm, allowing direct measurements of 3D atomic displacements and the full strain tensor. More recently, we determined the 3D coordinates of 6,569 Fe and 16,627 Pt atoms in an FePt nanoparticle, and correlated chemical order/disorder and crystal defects with material properties at the individual atomic level. We identified rich structural variety with unprecedented 3D detail including atomic composition, grain boundaries, anti-phase boundaries, anti-site point defects and swap defects. We showed that the experimentally measured coordinates and chemical species with 22 pm precision can be used as direct input for density functional theory calculations of material properties such as atomic spin and orbital magnetic moments and local magnetocrystalline anisotropy. More recently, we have applied AET to image the 3D

atomic positions of low-dimensional materials. Looking forward, AET will not only advance our ability in 3D atomic structure determination of crystal defects and disordered materials, but also transform our understanding of materials properties and functionality at the individual atomic level.

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In situ Growth Experiments on 2D Materials

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Graphene is a particularly interesting surface on which to grow nanocrystals since it is now straightforward to transfer a large area of perfect graphene onto many types of substrate. To understand and optimise nanocrystal growth on graphene, we make use of environmental TEM with its ability to explore the dynamic phenomena that underpin growth, catalysis and phase transformations at the nanoscale. We will illustrate the information available from ETEM by showing the nucleation, growth and epitaxy of nanostructured Au and Ge on graphene. The experiments take place in a 300keV ultra high vacuum TEM that has an integrated side chamber with evaporation capabilities. We deposit Au onto samples with suspended graphene membranes then heat and flow the reactive gas digermane. Even though the resolution is low, it is clear that the Au forms epitaxial triangles (Figure 1a). These act as catalysts for the subsequent cracking of digermane to deposit Ge. When the reaction temperature is far enough below the Au-Ge eutectic temperature for the Au to remain solid, the Ge growth is epitaxial (Figure 1b-f). At higher temperatures, we can relate the Ge epitaxy to its nucleation environment in a solid catalyst, a liquid catalyst or with no catalyst present. We can also evaluate the catalytic activities of individual Au islands and correlate with their shapes.

Unsurprisingly, the electron beam has a strong effect on growth processes involving graphene. We will therefore conclude by discussing the opportunities for combining low keV imaging with ETEM capabilities to enhance our ability to extract growth physics during nanoscale materials reactions.

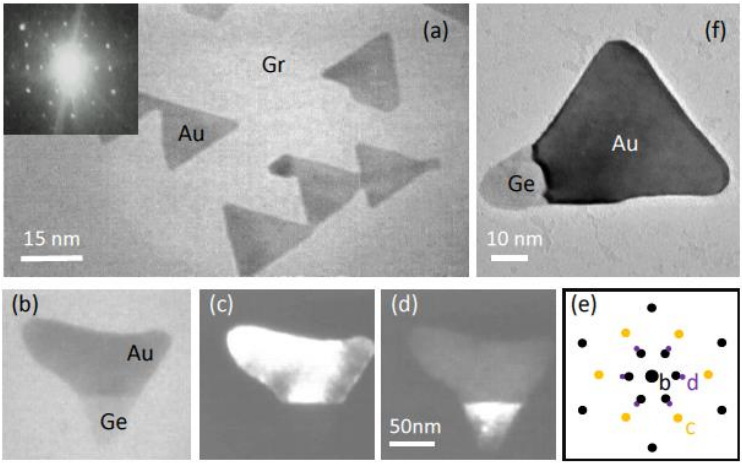

Figure 1. (a) Au triangles that have formed epitaxially on a graphene bilayer suspended across a hole in a microfabricated heater chip. The Au was evaporated in the UHV environment of the TEM. An inset diffraction pattern shows the aligned Gr and Au spots. (b-d) Bright field and two dark field images obtained after exposure of a similar sample to 10^{-5} Torr digermane at only 190°C, far enough below the eutectic temperature that the Au remains solid. The Au catalyses Ge growth that is epitaxial. (c, d) were recorded using, respectively, an Au(220) spot with d=0.144nm and a Ge(220) spot with d=0.199nm. (e) A schematic diagram of the diffraction pattern of the sample in (b-d) with the Ge(220) spots shown in purple, Au(220) in orange and graphene spots in black. (f) A post growth high resolution image showing details of the Au and Ge lattices in another region of the same sample.

In Situ Electron Microscopy Studies to Link Atomic Structure to Corresponding Properties

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In situ electron microscopy enables the direct observation and correlation between material structure and properties on small scales reaching the atomic level. Examples of important mechanisms that can be studied are those of transport properties of charges, heat, liquids and particles in complex structures and also of effects induced by light, mechanical strain and temperature changes.

The direct correlation on the small scale involving individual interfaces, defects and atoms provides access to new information about which microstructural constituents that are active in determining the material properties on the macro, micro, nano and atomic scale. New aspects of material properties and mechanisms not obvious from measurements on the macro scale can also be revealed due to the high spatial resolution. The knowledge is crucial for not only the understanding of the mechanisms that are involved but also for the design or materials and devices with tailored properties.

The need for high spatial resolution imaging and spectroscopy of both surfaces and internal structure can in many cases only be met by transmission electron microscopy (TEM) or a combination of electron microscopy and other techniques. TEM holders for in situ dynamic experiments and manipulation including studies of transport of charges and condensed matter further expand the dimensions of information that can be extracted [1-7]. Simultaneous electron energy loss spectroscopy can also be performed simultaneous with the manipulation and imaging. This talk will address method developments and results of electrical, mechanical, optical and thermal studies of nanoparticles, nanowires and thin films.

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Chances and Challenges of High-Resolution Imaging in a Scanning Electron Microscope

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Transmission electron microscopy with low-energy electrons has been recognized as an important addition to the family of electron microscopies to avoid knock-on damage and increase the contrast of weakly scattering objects. Scanning electron microscopes are in general operated at maximum electron energies of 30 keV but are up to now essentially used as a standard characterization tool for topography imaging of bulk samples. However, the implementation of a scanning transmission electron microscopy (STEM) detector, recent improvements in resolution and the option to install of a charge-coupled-device camera for the acquisition of on-axis transmission electron diffraction (TED) patterns make scanning electron microscopes interesting for enhanced structure analysis of electron transparent specimens (not only beam-sensitive ones), which are traditionally investigated in transmission electron microscopes.

We will show that low-energy STEM in a scanning electron microscope approaches the capabilities of STEM in dedicated (scanning) transmission electron microscopes. A new aspect is correlative scanning electron microscopy (SEM), STEM and TED imaging from the same specimen region in a scanning electron microscope which leads to a wealth of information on the structural properties that cannot been obtained by using SEM and (S)TEM separately and consecutively. The simultaneous acquisition of transmitted electrons and electrons emitted from the sample surface gives comprehensive information on topography, bulk structure, crystal defects and qualitative information on the composition from material contrast.

The benefits of correlative SEM/STEM/TED imaging in a scanning electron microscope will be exemplified by presenting structure analyses from several representative sample classes such as

nanoparticulate and bulk materials. Moreover, low-energy STEM and backscattered-electron intensities can be well modelled by Monte-Carlo simulations and facilitates, e.g., the determination of the composition and local TEM specimen thickness if some pre-information on the sample is available.

Structural Studies of Defects and Defect Dynamics in low Dimensional Materials

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To usefully deploy Graphene and related materials in electronic applications [1-3] it is essential to understand the behavior of defects, which have been the subject of extensive research for decades for silicon devices. High resolution Transmission Electron Microscopy is the ideal characterization tool for studying the formation and evolution of defects in low dimensional materials in real space. Moreover, recent instrumental advances make it possible to image these defects at primary energies below those that cause significant specimen damage whilst retaining sufficient spatial resolution to resolve the local atomic configurations around the defect site [4].

In this paper, I will discuss the controlled formation of several defect types in a variety of low dimensional materials, and will demonstrate that the evolution of these into more complex extended defects that can be controlled by electron beam irradiation [5]. Density functional theory (DFT) calculations have been used to evaluate the energetics of several defect configurations which indicate possible pathways by which these can evolve. In the case of MoS_2 electronic structure calculations suggest that control of line defect lengths and widths can be used for band gap engineering.

I will also report on the development of methods for recovering low signal data from high temporal resolution data sets and early progress in automated pattern recognition of defect structures.

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Low Voltage Aberration Corrected STEM for Two-Dimensional Heterostructures

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Aberration-corrected scanning transmission electron microscopy (STEM) operated at low accelerating voltage can now provide real space imaging and spectroscopy analysis at the atomic scale with single atom sensitivity. This opens new opportunities for quantitative study of the structure and chemistry at the interface of two dimensional (2D) heterostructures. Such studies, especially when combined with first-principles calculations, serve as an important step to correlate the interface structure with their local properties, unveil the atomic growth mechanism for new quantum-structures, and help to create new functionalities in these 2D materials via controlled growth.

Using low-voltage aberration corrected STEM imaging, we presented a systematic study of lateral 2D semiconductor heterostructures with and without lattice mismatch, where quantitative STEM imaging can be applied to perform atom-by-atom chemical mapping and strain analysis at the interfaces. We show that for 2D lateral heterostructures where the two monolayer components have similar crystal structure and negligible lattice mismatch, such as WS_2/MoS_2 or $WSe_2/MoSe_2$, lateral epitaxial growth can lead to

atomically abrupt interface [1]. In contrast, strain relaxation at lateral interfaces with lattice mismatch often lead to misfit dislocation arrays. We demonstrate that such misfit dislocations can induce the formation and growth of sub-2-nm quantum-well arrays in semiconductor monolayers, driven by dislocation climb [2]. Such misfit-dislocation-driven growth can be applied to different combinations of 2D monolayers with lattice mismatch, paving the way to a wide range of 2D quantum-well superlattices with controllable band alignment and nanoscale width.

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Electron Irradiation-Induced Defects and Phase Transformations in Two-Dimensional Materials

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Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN, transition metal dichalcogenides (TMDs) and silica bilayers were manufactured. All these systems contain defects and impurities, which may govern the electronic and optical properties of these materials. Moreover, defects can appear during the characterization of the materials in transmission electron microscope. All of these calls upon the studies on defect properties and mechanisms of their formation under electron beam. In my talk, I will present the results [1] of our first-principles theoretical studies of defects (native and irradiation-induced) in inorganic 2D systems obtained in close collaboration with several experimental TEM groups. I will further discuss defect- and impurity-mediated engineering of the electronic structure of inorganic 2D materials. I will also present the results of our theoretical studies of electron-beam induced phase transformations in 2D TMDs when electric charge, mechanical strain and vacancies are present. Based on the results of our calculations, we propose an explanation for this phenomenon which is likely promoted by charge redistribution in the monolayer combined with vacancy formation due to electron beam and associated mechanical strain in the sample.

The research presented in this paper was possible due to the support from Helmholtz Zentrum Dresden-Rossendorf, Academy of Finland under Project No. 286279, U.S. Army RDECOM via contract No. W911NF-15-1-0606, Deutsche Forschungsgemeinschaft under Project KR 48661, and the Ministry of Education and Science of the

Russian Federation in the framework of Increase Competitiveness Program of NUST “MISiS” (K3-2017-021).

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Probing Low Temperature Electronic Phases using cryo-STEM

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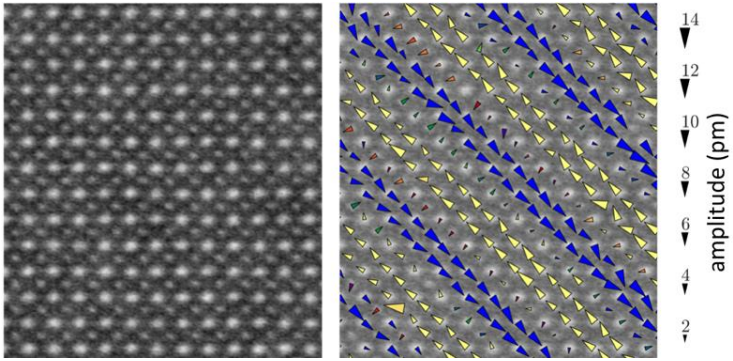
Spectroscopic mapping by STEM/EELS has proven to be a powerful technique for determining the structure, chemistry and bonding of interfaces, reconstructions, and defects. So far, most efforts in the physical sciences have focused on room temperature measurements where atomic resolution mapping of composition and bonding has been demonstrated [1-3]. For many materials, including those that exhibit electronic and structural phase transitions below room temperature and systems that involve liquid/solid interfaces, STEM/EELS measurements at low temperature are required. Operating close to liquid nitrogen temperature gives access to a range of emergent electronic states in solid materials and allows us to study processes at liquid/solid interfaces immobilized by rapid freezing [4-6].

Here, I will demonstrate cryo-STEM imaging at sub-Å resolution and atomic tracking with picometer precision in charge-ordered manganites [6,7]. Using this technique, we measure transverse, displacive lattice modulations of the cations, distinct from existing manganite charge-order models and reveal temperature-dependent inhomogeneities in the stipe order such as shear deformations and topological defects, and the emergence of phase coherence well below T_c (*Figure right*). Correlating the atomic level structure and electronic properties at cryogenic temperatures is an important step in realizing the goal of understanding and controlling emergent phenomena in these materials.



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Cryo-Focused Ion Beam as a Game Changer in *in-situ* Cryo-Electron Tomography of Frozen Hydrated Specimens

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Cryo-electron tomography (CET) has recently become a driving technique in structural biology. Technological advances in detector efficiency, contrast enhancement, and specimen preparation opened whole new possibilities to visualize small macromolecules, such as membrane-bound complexes, within the native cellular environment [1-4]. The molecular structures of specific conformational or assembly states can often be revealed in these *in situ* studies of biological systems, and mapping back classified structures into the cellular volume then gives new insights into biological processes.

A prerequisite for this type of *in situ* CET investigations is the preparation of thin TEM samples from vitreous frozen specimens by cryo-focused ion beam (cryo-FIB) milling. Many biological questions could only be tackled once the production of lamellas from plunge-frozen cells had been developed into a standard technique with highly reproducible results [5].

However, thicker specimens, such as large eukaryotic cells or tissue samples, require vitrification by high-pressure freezing and thus cannot be prepared by this standard technique. Current developments aim at overcoming this sample size limitation by using an alternative cryo-FIB lift-out routine.

In this presentation, we will describe the key aspects of the different sample preparation methods for CET and showcase *in situ* studies of membrane-bound macromolecules, such as photosynthetic complexes, proteasomes and ribosomes.

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Determining the Energy Scaling of Some Physical Phenomenon Important in Electron Cryomicroscopy of Biological Specimens

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Electron cryomicroscopy has undergone tremendous progress in recent years, driven by technological advances in electron detection, microscope optics, specimen supports and image processing algorithms [1]. Still there are several physical phenomena that blur the images of the molecules during irradiation, even before the onset of radiation damage. These include the buildup of static and fluctuating charge on the specimen and the movement of molecules during imaging. In this talk I will outline our efforts to determine the causes of these phenomena, and their relative effects on information content of low-dose electron micrographs. We have recently made several measurements to shed light on these effects. These include experiments to quantify the buildup and fluctuation of charge on the insulating water ice specimen (Fig. 1) and to accurately track the movement of molecules during the onset of irradiation. I will also address how these various physical phenomenon scale with the energy of the incident electron and the implications of this for imaging in cryo-EM. Finally, I will discuss how these efforts to characterise the various physical phenomena in cryo-EM can guide the future development of electron cryomicroscopes and specimen supports for biological structure determination.

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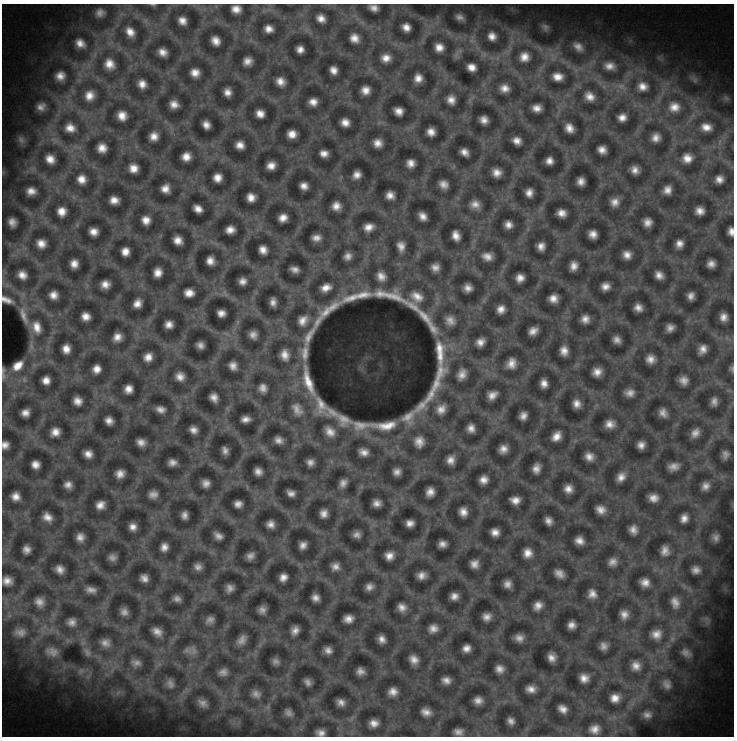

Figure 1. Cryo-EM specimen imaged at –60 mm defocus and 300 keV at ~80K showing the charge buildup on the specimen after low-dose imaging in the electron cryomicroscope. Field of view is 30 x 30 µm and foil contains 1.2 µm holes in a regular square array pattern with thin layers of ice in each hole. Each disk of suspended ice acts like a diverging electrostatic microlens.

Inline Electron Holography of Soft Matter

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High-energy electrons deposit less than one thousandth of the energy per useful elastic scattering event than is being deposited by X-rays [1]. This makes them a favorable type of radiation to study the bulk atomic structure of radiation sensitive materials, such as most soft matter. Another advantage of electrons over X-rays is the possibility to focus them into areas smaller than one $Å^2$. This allows the creation of very fine probes for local scattering or spectroscopy experiments, and also the formation of images with very high spatial resolution. However, the possibility to image with electrons at high magnification also creates the desire to see high-resolution details which, in turn, increases the necessary electron dose.

In most experimental setups, soft matter affects mostly the phase of the transmitted electron beam. Focused TEM images of soft matter, therefore, do not show much contrast. Intentionally introducing aberrations, such as defocus, into the imaging system will, at the one hand delocalize the image information, but also produce interference between differently scattered electrons and thus introduce contrast due to differences in phase of the electron wave that have been imposed on it by the sample. At the same time, partial spatial coherence of the illumination will dampen the transfer of high spatial frequency information. Inline electron holography reconstruction algorithms must be designed such that they take all these effects into account [2,3].

In this talk the application of inline electron holography to hybrid inorganic-organic systems, where the organic phase is very radiation sensitive [4], will be discussed. It will also be discussed how defocus-based inline electron holography compares to recently developed low-dose ptychography, another inline-holographic technique [5].

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Novel 2D Materials by Electron Beam Induced Chemistry

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Low energy electron irradiation of aromatic monolayers and thin films results in their conversion into novel 2D carbon nanosheets (carbon nanomembranes (CNMs) [1], organic semiconductor nanosheets [2]). Similar to graphene or other atomically thin sheets (hBN, MoS_2, etc.) they possess mechanical integrity and therefore can be transferred from their growth substrates onto new substrates, fabricated as suspended sheets or stacked into van der Waals heterostructures with precise control over their thickness. The developed methodology enables lateral stitching of different 2D materials with each other, resulting in engineering of novel heterostructures (e.g. graphene-CNM or MoS_2-CNM) which cannot be prepared by conventional growth techniques. By combining different 2D sheets, organic monolayers and thin films, the heterostructures of both types with tunable physical and chemical properties can be synthesised in this way. In this talk, some examples of these materials including their in detail characterization by complementary microscopy and spectroscopy techniques and device applications will be presented [2-5].

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Quantitative STEM and EELS of Defects and Mixing in 2D Materials

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Transmission electron microscopy (TEM) is a powerful tool to measure local structure, bonding, and electronic properties at sub-angstrom resolution. Applied to two-dimensional (2D) materials such as graphene or thin chalcogenide layers such as MoS_2 or ReS_2, electron microscopy and spectroscopy can reach their ultimate potential: probing structure, bonding, and local electronic structure with single atom precision. Combined with techniques such as electrical transport measurements, photoluminescence, and Raman microscopy, we can measure the properties that emerge when 2D materials are grown, stacked, twisted, and strained into novel structures.

Here, we utilize aberration-corrected scanning transmission electron microscopy (STEM) to map the phase behavior of (Mo/W)Te_2 alloys, a promising system for realizing atomically-thin phase change devices. We observe successful tuning of the crystal structure between a semiconducting 2H and semimetallic 1T' phase as a function of doping, as well as stacking faults and non-equilibrium stacking orders in the 2H structure. These results indicate the potential for phase control of electronic structure in devices a single unit cell thick, and also demonstrate that higher phase complexity exists in transition metal dichalcogenide systems than has been previously understood.

Further, (S)TEM is unique among atomic scale techniques in its ability to access buried interfaces, making it ideal for investigating structure-property relationships in real devices. In these studies, atomic scale imaging and spectroscopy uncover the structures of in- and out-of-plane heterointerfaces that indicate routes towards optimizing 2D device architectures. These studies are critical for exploring the advantages and potential limitations in incorporating 2D systems into applications such as flexible electronics and layered photovoltaic devices.

Exploring Structure in 2D Crystal Hetero-Structure Stacks

S.J. Haigh[1,2], A.P Rooney[1,2], L. Nguyen[1], T.J.A Slater[1], E. Prestat[1], E. Khestanova[1], R.V. Gorbachev[1], R. Boya[2], Y. Cao[2], I. Grigorieva[2], K. Novoselov[2], F. Withers[2], A.K. Geim[2]

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2D crystals can be layered together to create new van der Waals crystals with bespoke properties. However, the performance of such materials is strongly dependent on the quality of the crystals and the interfaces at the atomic scale. Transmission electron microscopy (TEM) is the only technique able to characterize the nature of buried interfaces in these engineered van der Waals crystals and hence to provide insights into the optical, electronic and mechanical properties. I will report the use of TEM imaging technique to aid the development of 2D heterostructures for electronics. Recently it has been shown that confinement between two closely space graphene sheets can have a dramatic effect on the confined material[1,2]. By studying van der Waals structures where encapsulated graphene layers contain channels it is possible to measure the transport behavior of water through such channels. We observe significant enhancement in fluid flow rates for few atomic layer channel heights compared to larger channels[1]. We also observe that confinement in such channels can drive chemical transformations in aqueous salts[2].

Encapsulation with inert 2D crystals (e.g. graphene or hBN) also provides environmental protection from air or vacuum. We have performed mechanical exfoliation of air sensitive 2D materials in an inert argon atmosphere and used hBN or graphene encapsulation to allow the novel electrical properties of air sensitive 2D crystals to be realized[3]. However we find that even when fabricated in an inert atmosphere, $NbSe_2$ monolayers contain point defects that can be observed by high resolution TEM[4]. Furthermore, cross sectional scanning TEM imaging reveals that even comparatively stable materials like $MoSe_2$ and WSe_2 have different interlayer separation

when exfoliated in a glove box compared to fabrication in air[5] (Fig 1). In addition we will demonstrate how this heterostructures platform can be used to fabricate TEM liquid cells with precisely controlled liquid volumes.

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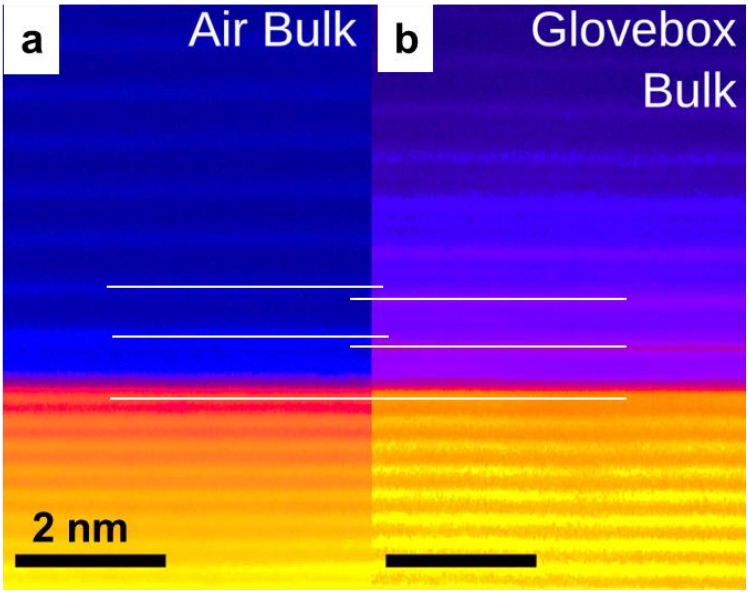

Figure 1: Comparing interlayer separation between WSe_2 (top) and hBN (bottom) when exfoliated (a) in air and (b) in an argon glovebox.

Studying the Dielectric Function of 2D Materials with Angular Resolved Electron Energy Loss Spectroscopy

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2D materials display electronic and optical properties, different from their bulk counterpart and which turn to highly depend on the number of layers and on their environment especially when they are integrated in van der Waals heterostructures. Screening effects may in particular strongly affect electronic features such as band gap, and properties of charge carriers and excitons. It is therefore highly desirable to investigate intrinsic properties of free-standing layers.

Angular resolved Electron energy loss spectroscopy (EELS) implemented in Transmission Electron Microscopy (TEM) offers a unique way to investigate dielectric response of free-standing layers related to valence band and plasmon excitations with the advantage to get access to their q dispersion and their symmetry properties. In this talk, we shall review the capabilities of this technique implemented in a dedicated TEM machine equipped with a monochromator and in column energy filter.

We shall consider applications of the technique to two particular examples: hexagonal boron nitride (h-BN), which is a wide band gap semiconductor (~ 6.5 eV and P(black) thin layers.

In the case of hBN, we will show how the symmetry and angular dependence of the dielectric response is related to excitonic and

plasmonic excitations with the support of ab initio calculations [1]. In the case of Black Phosphorus, we probe the dielectric response of pristine suspended BP down to the monolayer [2] in the range 0.5-40 eV, that include measurements of band gaps threshold and surface/volume plasmons energies. The dispersion of the plasmons as a function of the momentum is also measured and simulated for both in-plane and orthogonal crystallographic directions [3].

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Past and Future Prospect of Cs-corrected TEM for Nanomaterials

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We have been studying aberration corrected TEM/STEM since the beginning of the 21 century under collaboration of JEOL and CEOS[1,2]. The research viewpoints are (1) improvement of point-to-point resolution[3,4], (2) disappearance of Fresnel fringes to observe clearly interfaces and surfaces at atomic resolution[5], (3) realization of ideal Fourier images for z-slicing in TEM[6], (4) non-positional error of selected area diffraction to realize nm-sized diffraction and further diffractive imaging[7], and (5) measurement of wave front and spatial coherence[8]. Samples to be observed are various kinds such as nano-particles and nano-wires including CNT, semiconductor interfaces, catalytic particles, medium range order (MRO) structures of metallic glasses[9] and catalytic porous gold films[10].

In comparison with Cs-corrected TEM imaging, Cs-corrected STEM imaging is more straightforward, where an incident electron probe is minimized to give point-to-point resolution less than 80 pm for oriented crystals at 200kV[2,3]. The second advantage is that probe intensity is larger to make chemical and physical analysis easier, and third advantage is realization of depth-slicing for small clusters embedded in amorphous films. However confocal STEM is still in progress for single crystals at atomic resolution due to dynamical diffraction effects inside the crystals[11]. The recent data of differential phase contrast (DPC) method at atomic resolution are also realized by a small and strong incident probe by aberration correction[11]. The interpretation at atomic resolution is, however, not settled in.

The present challenge is that interaction between electrons and various potential fields of samples is not easy to be localized and well-interpreted[11]. This means that only improvement of electron optics is not linked to new kinds of information in physics and chemistry. A pulsed and spin-polarized incident beam is feasible for the moment in TEM[12], and the study for STEM is expected.

Aberration correction indeed is effective for low voltage high-resolution electron microscopy, where scattered waves at larger angles should be aberration-corrected. German and Japanese national projects have successfully reported interesting data of TEM from Ulm and STEM from Tsukuba.

I would like to thank many collaborators, such as Drs. M. Haider & J. Yamasaki.

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Electron-Beam Induced Chemistry of Organic Molecules

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Transmission electron microscopy (TEM) is traditionally used as a tool to characterise materials, providing atomic resolution imaging of low dimensional nanostructures such as graphene and carbon nanotubes. In this context, damage to materials imaged by TEM (caused by collisions with the highly energetic electrons) is generally considered as something to be avoided or limited. However, with detailed understanding of the effects of the electron beam (e-beam), the energy transmitted from it can be used to drive chemical reactions that would be otherwise unfeasible.

A mechanistic understanding of beam-driven chemical reactions can be achieved with the comparison of experimental TEM images to the results of modelling. The dynamic response of nanotube-encapsulated organic species to the stimulus of the e-beam has been simulated using density functional theory (DFT) molecular dynamics. By combining these results with an accurate analytical model of the interaction of relativistic electrons and atomic nuclei, the experimentally observed behaviour of these systems under the e-beam has been quantitatively characterised.

The elemental dependence of the transfer of energy from the e-beam was shown to play a key role in determining reaction products, and is responsible for the very high susceptibility of carbon-hydrogen bonds to irradiation damage.[1] Deuteration is an effective remedy for overcoming this limitation, increasing lifetimes of organic molecules under electron irradiation and therefore enhancing the accuracy of structural analysis by TEM.[2] A close iterative collaboration between theory and microscopy was used to establish TEM as an effective tool for chemical reaction discovery

and the characterisation of previously unknown reaction mechanisms.[3] This has initially been demonstrated with two example reactions, in which organic molecule precursors are activated by the e-beam, eventually forming novel one-dimensional materials (Figure 1).[4]

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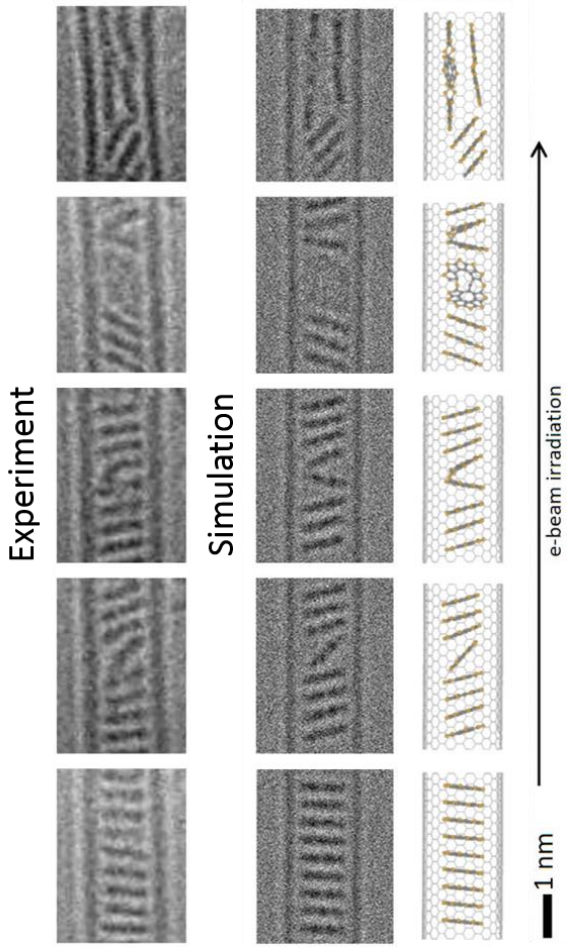

Figure 1. The initial stages of e-beam induced 1D polymerisation of octathio[8]circulene molecules. Experimental TEM images, top; DFT and multislice image simulations, bottom.

Chemistry of Single Molecules Through a TEM

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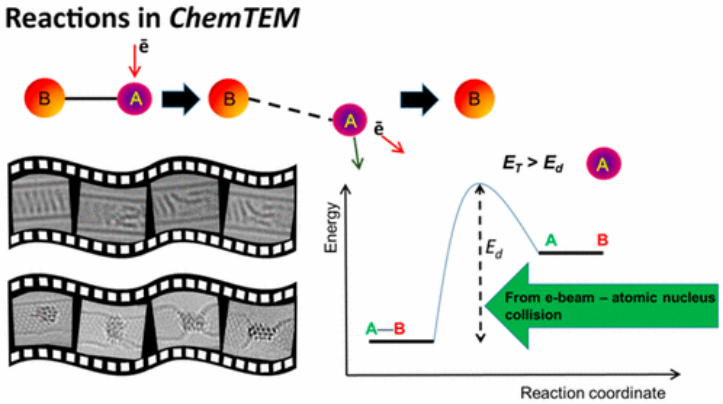
During TEM imaging of an individual molecule adsorbed on an atomically thin substrate, such as graphene or a carbon nanotube, the e-beam transfers kinetic energy to atoms of the molecule, displacing them from equilibrium positions. Impact of the e-beam triggers bond dissociation and various chemical reactions which can be imaged concurrently with their activation by the e-beam and can be presented as stop-frame movies. This experimental approach, which we term ChemTEM, harnesses energy transferred from the e-beam to the molecule via direct interactions with the atomic nuclei, enabling accurate predictions of bond dissociation events and control of the type and rate of chemical reactions. Elemental composition and structure of the reactant molecules as well as the operating conditions of TEM (particularly the energy of the e-beam) determine the product formed in ChemTEM processes, while the e-beam dose rate controls the reaction rate. Because the e-beam of



TEM acts simultaneously as a source of energy for the reaction and as an imaging tool monitoring the same reaction, ChemTEM reveals atomic-level chemical information, such as pathways of reactions imaged for individual molecules, step-by-step and in real time; structures of illusive reaction intermediates; and direct comparison of catalytic activity of different transition metals filmed with atomic resolution. Chemical transformations in ChemTEM often lead to previously unforeseen products, demonstrating the potential of this method to become not only an analytical tool for studying reactions, but also a powerful instrument for discovery of materials that can be synthesized on preparative scale.

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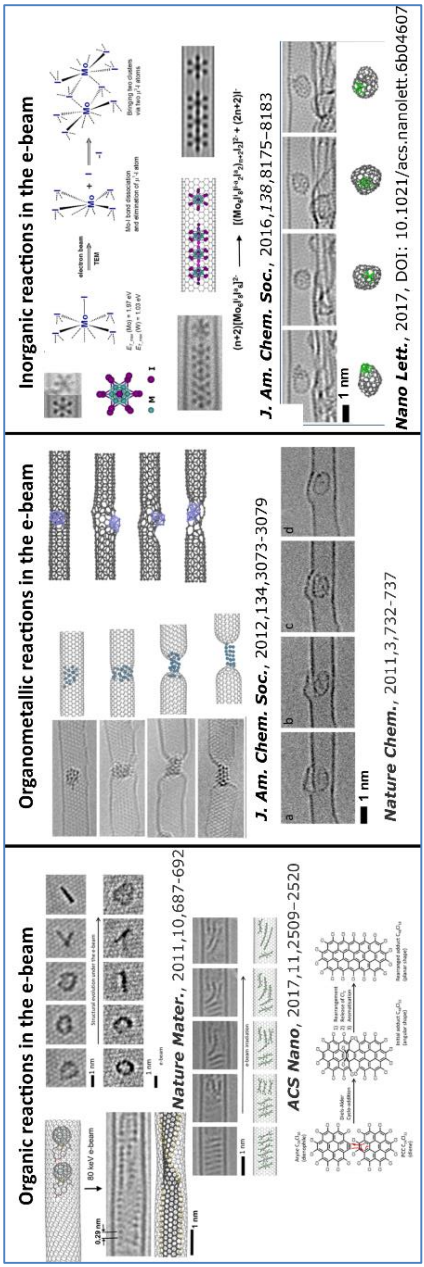
[§] current address: Institute of Process Research and Development, School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom.



Coherent Imaging with Low-Energy Electrons (30 – 250 eV)

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Low-energy (30 – 250 eV) electron in-line holography is realized by placing a sample at a few tens of nanometers in front of an electron point source whereby electrons are extracted by field emission [1], as illustrated in Fig. 1(a). When the electron wave passes through the sample, part of the wave is scattered. The interference between the scattered and unperturbed wave creates an in-line hologram which is acquired at the detector positioned at a few centimetres from the electron source. Two subjects will be discussed: biological imaging and imaging of charged impurities in graphene.

Biological imaging. Low-energy electrons do not damage biological samples in contrast to the case of high-energy electrons. We have demonstrated that individual biomolecules, such as DNA [1, 2], shown in Fig. 1(b), can withstand low-energy electron radiation for hours without detectable radiation damage [1]. The challenges and perspectives in imaging individual biological macromolecules such as proteins with low-energy electrons [3] will be discussed.

Imaging charged impurities in graphene. Some adsorbates on graphene transfer their charge to graphene thus creating a positively charged impurity. Such objects create large local gradients of the electric potential and deflect the passing electrons. Low-energy electrons are extremely sensitive to such local electric fields. A positively charged impurity thus leads to a distinctive signature in the hologram – a bright spot, see Fig. 2. The strength of the charge can be evaluated from the intensity of the bright spot with a precision of a fraction of an elementary charge [4]. Moreover, the projected potential of an individual impurity can be recovered from its in-line hologram by applying an iterative reconstruction routine [5].

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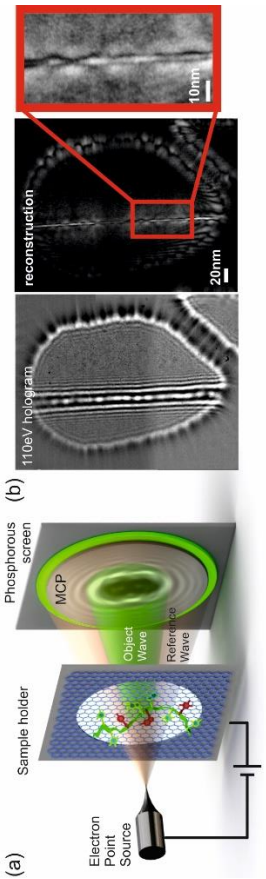

FIG. 1. Principle of in-line holography with low-energy electrons. (a) Sketch of the experimental arrangement. (b) Low-energy electron in-line hologram of a DNA molecule and its reconstruction [2].

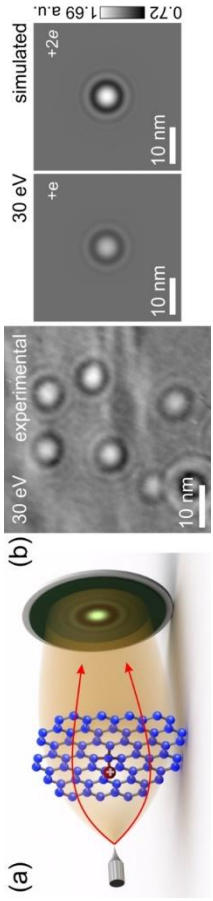

FIG. 2. (a) Sketch of the formation of an in-line hologram from a positively charged impurity. (b) Experimental and simulated in-line holograms of charged impurities [4].

Atomic Scale Imaging and Spectroscopy: Insight into Single Atom Action in 1-D and 2-D Materials

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Recent advancements in transmission electron microscopy (TEM) have made it possible to directly visualise sites of individual atoms in materials as well as reveal their chemical nature and local bandstructure. This talk will focus on TEM investigations of carbon nano-tubes and 2-D materials: graphene, boron nitride and 2-D transition metal dichalcogenides (TMDCs). The latter bear great promise for nano opto-electronics and quantum metrology. The talk will touch upon issues that will be particularly vital for nano- device fabrication and applications of these materials, such as their interaction with metal and dopant atoms, and will present results of a novel way to controllably dope 2-Ds, namely by ultra-low energy ion implantation. Employing ion implantation as a doping method for 2-Ds, together with nanoscale patterning, will enable functionalisation compatible and integratable with large scale semiconductor technologies, and furthermore empower the fabrication of 2-D quantum devices (e.g., single photon emitters).

Monitoring the 'fate' of individual impurity atoms in nanostructured materials, whether unintentionally present or introduced for purposes of electronic functionalisation, is hugely desirable and

essential for controlled design and successful functionalization of these materials. The talk demonstrates that core loss EELS performed in an aberration-corrected scanning transmission electron microscope, in combination with high-angle-annular-dark-field imaging, can be used to pinpoint and identify single atoms of foreign species. Comparison of experimental EEL spectra with density functional theory calculated EEL spectra enables the bonding configuration of single dopant atoms to be ascertained.

Residual impurities on pristine graphene, as well as impurity atoms, introduced via ion implantation as dopants into graphene and carbon nanotubes (CNTs), have been identified, and their precise position (e.g. in-plane or slightly out-off-plane location) and effect on the bandstructure of surrounding atoms been established. Implantation has also been achieved in TMDCs (e.g., implantation of Se into MoS_2) , where, in conjunction with HAADF image simulations the positions of implants could be identified to the point that substitution for the metal or the chalcogene could be identified, and moreover, whether the implant substitutes for the chalcogene in the top or the bottom layer and whether it is neighbored by a chalcogene vacancy above or below.

EEL spectrum imaging and energy filtered imaging was furthermore performed in the low loss regime to monitor spatial distributions and energies of bandgaps and plasmons to show that introduction of foreign species into carbon nanotubes and 2-Ds provides a potential method for modifying their optical response. New plasmons in the vis/uv regime were observed in nanotubes and 2-Ds and their existence confirmed by density functional theory calculations.

Contributions to ion implantation by J. Van den Berg (Salford University, UK) and by and R. Gwilliam (Surrrey University Ion Implantation Centre, UK) are greatly acknowledged

Chromatic Aberration-Corrected EFTEM

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Chromatic aberration-correction is currently available on a handful of TEM instruments yet the promise of further improvements in spatial resolution when compared with spherical aberration correction alone. Chromatic aberration correction is beneficial in particular when studying beam sensitive specimens at lower microscope accelerating voltages, examining thicker specimens and for high-resolution energy-filtered TEM (EFTEM) images using wide energy-selecting windows and large objective aperture sizes. Chromatic aberration correction also allows dose efficient atomic spatial resolution imaging when using wider objective lens pole-piece gaps and thicker biological material.

This contribution focusses on high-resolution EFTEM. The theoretical background for contrast and resolution in chromatic aberration corrected EFTEM will be briefly surveyed. At atomic sampling, when chromatic and spherical aberration become negligible and hence the electron-optical resolution limit, the delocalization of the inelastic scattering process together with the dose dependent resolution become dominant.

Experimental examples of energy-filtered images of complex oxides, thin layered materials and various nanomaterials, all obtained with Jülich's chromatic aberration corrected microscope "PICO", will be presented. EFTEM formed by the inelastic core-loss scattering showing atomic detail is demonstrated, taking benefit of the negligible chromatic focus spread after chromatic aberration correction. The wide-beam setup in EFTEM offers the benefit of fast two-dimensional mapping with wide field of view and atomic resolution. Chemical composition mapping on the atomic scale is achieved, under the constraint of the preservation of elastic contrast.

The detectable limit is a single atom when characteristic energy loss processes with sufficient cross-section and low background are

present. An example will be given for the case of the recognition of dopants in capsule catalyst molecules.

Chromatic aberration corrected EFTEM is therefore attractive route for fast chemical mapping with high-resolution and for chemical imaging of molecules.

Orbital Mapping: Challenges and Prospects

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With the advent of aberration correctors, chemical mapping on the atomic scale has become fairly ubiquitous. The logical next step is the mapping of individual orbitals by selecting particular transitions to those orbitals in EELS. Recently, it was shown both theoretically [1] and in a first proof-of-principle experiment[2] that such an endeavor is indeed possible.

In order to develop the orbital mapping approach into a wide-spread technique, several additional challenges have to be overcome. First of all, the point group symmetry of the scattering atom plays a crucial role in determining whether the directions of orbitals can be made visible in an image or not (see fig. 1). Secondly, the signal to noise ratio, resulting from the intricate interplay of dose, sample stability, instrument stability, and background, must be improved (see fig. 1). Thirdly, the very high spatial resolution required necessitates very good and stable C_s correction to high order, as well as C_c correction.

These technical challenges are very worth to overcome, as the prospects of mapping individual orbitals in solids on the atomic scale are almost countless. From mechanical properties of thin films over optical properties of quantum wells to the binding of molecules on surfaces, most of the world around us is essentially determined by the shape, energy, and interaction between orbitals. Thus, making them directly visible in the TEM is the first step towards a new era of understanding and designing materials.[4]

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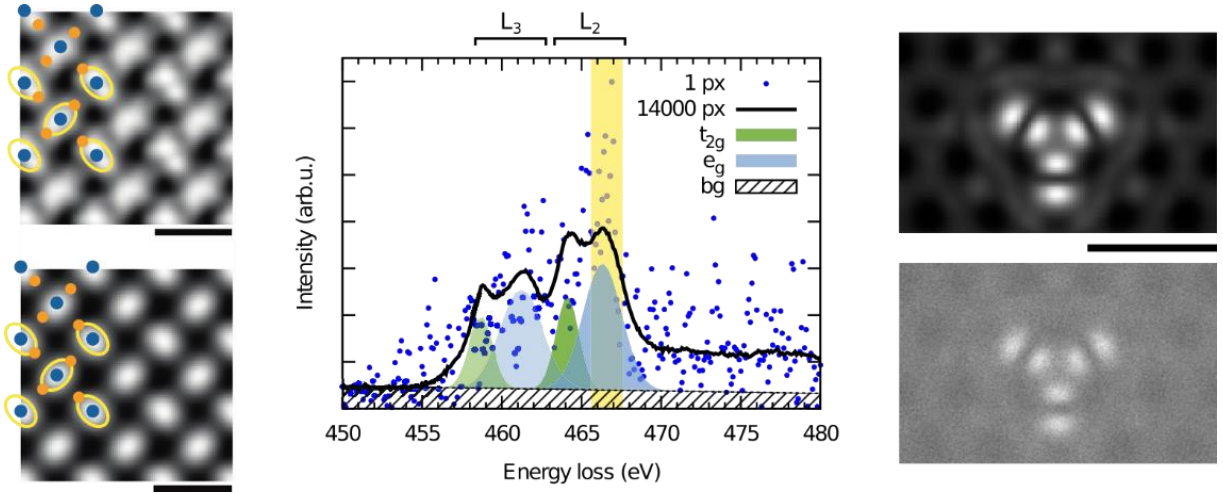

Fig. 1: Left: Smoothed experimental data (top) and simulation (bottom)[2]. Center: EEL spectrum of the experimental Ti L edge[2]. Right: Simulated map around a N dopant in Graphene with infinite dose (top) and with 10^5 e/Å^2 in the image[3]. All scale bars are 5 Å.

[4]Financial support: FWF (I543-N20, J3732-N27).

Transition Radiation Losses in Low- and High-Voltage EELS

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The reduction of beam energy in transmission electron microscopy (TEM) has several more advantages beyond the reduction of knock-on damage. Also for electron energy loss spectrometry (EELS) some benefits can be determined. The most prominent is the prevention of relativistic energy losses, because the speed of the electrons is slow enough, not to excite them at all. Apart of these so-called Čerenkov losses, another electrodynamic effect causes a contribution to the low loss signal in EELS: the excitation of Transition Radiation (TR). Consequently the corresponding losses are called Transition Radiation Losses (TRL). Although they are not caused by a relativistic effect they appear at low beam energies, too. Only their relative intensity is reduced when slower electrons are used.

Transition radiation can be understood the following way: When a charge approximates a metallic surface, a mirror charge is induced and thus forming a Hertz-dipole. While the charge travels downwards to the surface, the mirror charge goes upwards – always in the same distance as the charge, but from the opposite side of the surface. At the moment when the charge hits the surface from above, the mirror charge hits the surface from below. The dipole is annihilated and consequently radiation is emitted. But the emission of radiation means, that energy has to be transferred from the electron to the emitted photon and consequently an energy loss can be observed.

In the present work we study the influence of TRL on the valence EELS (VEELS) signal of Aluminum. We quantify the photon emission probability per electron by employing EELS and cathodoluminescence (CL) with respect to the beam energy in the range from 20 – 200 keV. Additionally we prove that the detected signal is indeed stemming from TRL, because we find it to be independent of the sample thickness, as expected for such a surface effect.

In situ Observation of Metal Catalyzed CVD Growth of Graphene

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We are using a modified scanning electron microscope for *in situ* observation of metal catalyzed chemical vapor deposition (CVD) of graphene.[1.2.3] Since the experiments are performed in the chamber of a microscope, it is possible to follow a complete CVD processes, including substrate annealing, graphene nucleation and growth and, finally, substrate cooling, at nanometer-scale resolution in real-time and without the need of sample transfer.

Direct observation reveals grain orientation dependent surface dynamics of the active metal catalyst during the CVD process at temperatures of up to 1000 °C. Graphene induced surface reconstruction and step bunching during growth, as well as faceting during cooling are observed.[1] Due to the high sensitivity of the secondary electron signal, we are able to visualize different degrees of graphene-substrate coupling.[2] Experiments under well-controlled atmosphere, allow us to investigate the response of the CVD process to changes in the chemical potential of the gas phase. By combining hydrogen etching with graphene growth, we were able to reveal the stacking sequence and interlayer coupling strength in few-layer graphene.[3] Growth and etching dynamics could be related to the substrate structure and inherent properties of graphene. Finally, the *in situ* experiments provide an efficient route to optimized growth of defect-free, large area single-layer graphene.

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Advantages of STEM Differential Phase Contrast Imaging at Low Voltages

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Standard scanning transmission electron microscopy (STEM) employs the high-angle annular dark-field (HAADF) mode for visualizing the atomic structure of objects. However, HAADF images show primarily heavy atoms because the contrast is approximately proportional to Z^2. Aberration correction offers the possibility to visualize the atomic structure of low-Z objects in the STEM by employing differential phase contrast (DPC) methods. Two representative procedures are the annular differential phase contrast (ADPC) mode and the integrated differential phase contrast (IDPC) mode. Both modes enable the use of the elastically scattered electrons located within the cone of the non-scattered electrons beneath the object. The annular ADPC and the IDPC has recently been realized owing to the correction of the third-order spherical aberration (C_3). The ADPC mode is realized by inserting a physical Fresnel phase plate in front of the objective lens and a pixilated detector whereas the IDPC mode is utilizing a quadrant detector configuration. The additional correction of chromatic (C_c) and the fifth-order spherical aberration (C_5) will improve significantly the performance of these methods. The Fresnel phase plate for the DPC can be obtained more flexibly by adjusting the spherical aberration coefficients appropriately. On the condition that Johnson noise is eliminated or sufficiently suppressed, C_c/C_5-correction enables the optical sectioning by the ADPC mode in STEM with atomic resolution and a depth of field shorter than 3Å even at low accelerating voltages required to avoid knock-on damage of radiation-sensitive objects. The ADPC mode allows the investigation of the inner structure of crystalline samples without slicing. Results of image simulations will be presented which demonstrate that the ADPC mode is also appropriate for weak and strong phase objects such as thin crystals.

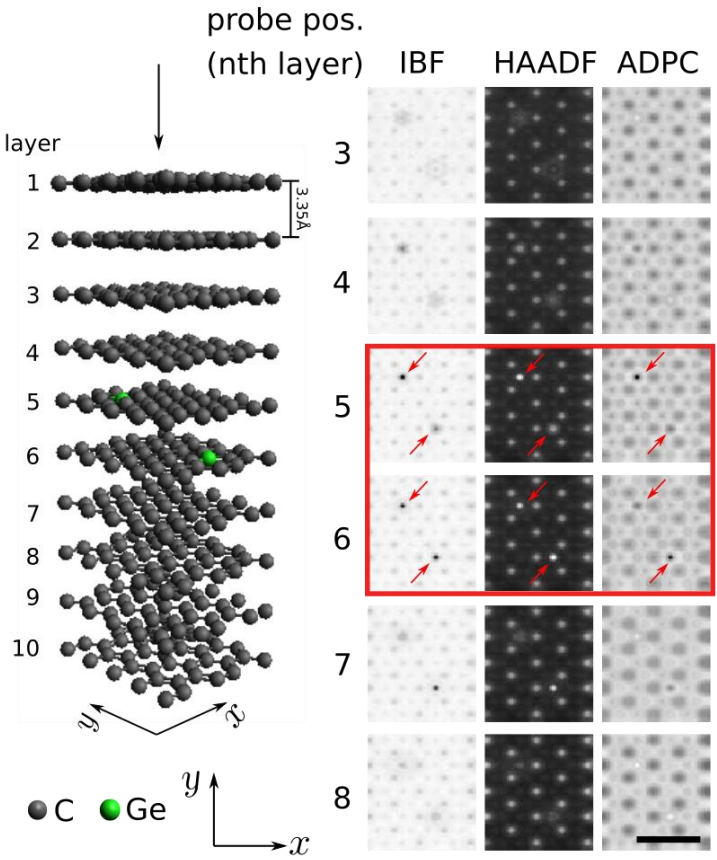

Fig. 1 Focal series of simulated IBF, HAADF and ADPC images of a 3nm thick graphite<110> sample containing 10 atom layers, separated by 3.35Å. In the 5th and the 6th layer, a germanium atom is substituted for a carbon atom. Spherical correction up to C_5, chromatic correction (C_c=0) and an accelerating voltage of 30kV have been assumed. The collection angles are 0-130mrad for the IBF images and 195-390mrad for the HAADF images. Scale-bar: 0.5nm.

Acknowledgments: The authors acknowledge funding from the German Research Foundation (DFG) and the Ministry of Science, Research and the Arts (MWK) of the federal state of Baden-Württemberg, Germany in the frame of the *SALVE* project

New Directions in Nanooptics with Fast Electrons

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Free electrons such as delivered in a scanning electron microscope (STEM) have been demonstrated to be excellent tools for studying nanooptics at high spatial resolution. Indeed, it is now possible to access various optical excitations or effects through electron energy loss spectroscopy (EELS) or cathodoluminescence (CL) in a STEM, from surface plasmon (SP) mapping to the identification of quantum signatures in the emission of single photon emitters[1]. STEM-EELS or -CL have however yet unexpected possibilities that I will try to discuss in this talk.

I will first discuss the use of phase-shaping in the context of probing plasmons properties in the STEM. By shaping the beam of a free electron, we could create a dipolar beam whose symmetries match that of the dipoles that are omnipresent in plasmonics. We have demonstrated that new selection rules, similar to atomic physics, could be deduced for the EELS signal. This makes this technique very appealing for probing arbitrary plasmon symmetries[2].

I will then discuss the possibility to evidence, with a combination of STEM-EELS and CL, an iconic effect in nanooptics, namely the Purcell effect. This effect relies on the decrease of the lifetime of a light emitter close to a plasmonic surface and is a good indicator of the coupling strength between a plasmonic nanostructure and an emitter. We have recently shown that the Purcell effect could be measured at the single nanoparticle level yet with a high statistic[3].

Finally, I will show how the genuine ability of STEM-EELS to probe plasmons in space and energy makes it possible to evidence an unforeseen sort of symmetry breaking. I will indeed show that SP nanoparticles can be seen as a new type of non-hermitian systems. Such systems are usually relying on PT symmetry breaking, and their

study is therefore experimentally delicate. This is not the case of SP systems, where, as I will show, surprising effects related to the non-hermiticity, such as the self-hybridization effect, can be easily observed.

[1]*Ultramicroscopy* 174, 50–69 (2017).
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[3]*ACS Photonics*, in Press (2017)

Modern LV-AC-TEM: a View on Its Transformation

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The term *"low-voltage"* in transmission electron microscopy nowadays refers to accelerating voltages equal or below 80kV, often 60 kV down to 40 and 20kV. One ultimate goal of low-voltage atomic-resolution analytical electron microscopy is the acquisition of data about the structure, the chemical composition, and local electronic states of thin electron-beam-sensitive objects including organic molecules. The latter aim goes back to the late sixties and early seventies of the last century and pioneering work by Otto Scherzer[1] and Albert Crewe[2]. The aim of preventing radiation damage at that time created important discussions about how low should we go in the accelerating voltage[3] and how to calculate and understand the interactions.[4] Today, about 50 years later, the TEM community experiences the realization of aberration-corrected low-voltage electron microscopy—for high-resolution TEM by means of a case-designed low-voltage spherical and chromatic aberration corrector[5-7] and for scanning TEM by means of reducing the chromatic aberration due to monochromated electrons and correcting for the spherical aberration of the condenser lens[8,9]. In my talk I will discuss the potential of the methods and show important applications. These include engineering and imaging of single atomic chains,[10] crystal growth in graphene-encapsulated liquid cells,[11] imaging of the effect of charge re-distribution,[12] imaging of the atomic motion,[13] obtaining single atom core loss signals,[14] and vibrational spectroscopy data,[15] as well as real-time imaging of the effect of chemical reactions,[16] and controlled manipulation of 2D matetrials.[17] With the extended understanding and control of radiation damage processes,[18] including knock-on damage and atomic rearrangements,[19] the progress in understanding the exact image formation process at the low accelerating voltages,[20] improved image processing,[21] and sophisticated specimen preparation methods,[22] the application of LV-AC-TEM/STEM developed enormously, stimulated also by the needs of the fast-developing new field in materials research, the low-dimensional

quantum materials.[23] Today, the interactions between electron beam and the specimen is also utilized to stimulate willingly transformations and shape the property of a material on the atomic level. However, it is still a challenge that avoiding radiation damage poses to the scientific community and still we ask and discuss in my talk how low we should go in the accelerating voltage to image a single molecule without damaging its structure.

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Acknowledgments: The authors acknowledge funding from the German Research Foundation (DFG) and the Ministry of Science, Research and the Arts (MWK) of the federal state of Baden-Württemberg, Germany in the frame of the SALVE project.

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