Poster Session 1

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Department of Materials, University of Oxford, Oxford, UK

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Imperial College London, UK

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¹ Université de Poitiers/CNRS, Futuroscope-Chasseneuil, France.
² IMEC, Leuven, Belgium.

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F. Pailloux¹, S. Camelio¹, V. Mauchamp¹, D. Lantiat¹,¹², L. Simonot¹ and D. Babonneau¹
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N. Geuquet¹, J. Nelayah²,³, M. Kociak², O. Stéphan², and L. Henrard¹
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M. Stöger-Pollach¹, E.L. Shirley², P. Schattschneider¹,³
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² Universidade de Vigo, Madrid, Spain
³ Tamkang University, Taipei, Taiwan
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² Institut für Materialphysik, WWU Münster, Münster, Germany

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B.G. Mendis¹,², M. MacKenzie¹ and A. J. Craven¹,²
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² SuperSTEM, Daresbury Laboratory, Daresbury, UK

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C.T. Schamp¹
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A. Gloter¹, M.-W. Chu², M. Kociak¹, C.H. Chen²,³, C. Colliex¹
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² National Taiwan University, Taipei, Taiwan
³ National Taiwan University and Academia Sinica, Taipei, Taiwan
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² Universidad de Cádiz, Puerto Real, Spain

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Kasim Sader¹,², Bernhard Schaffer¹, Gareth Vaughan², Peng Wang¹*, Andrew Bleloch¹, Andy Brown², Rik Brydson²
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K. Riegler¹ and G. Kothleitner¹
¹ Institute for Electron Microscopy, Graz University of Technology, Graz, Austria

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E. Essers¹, G. Benner¹, T. Mandler¹, D. Mittmann¹, and R. Hoeschen²
¹ Carl Zeiss NTS GmbH, Oberkochen, Germany
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B. Schaffer^{1,2}, K. Sader^{1,3} and A. Bleloch^{1}
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Ø. Prytz^{1}, E. Flage-Larsen^{1}, L. Gu^{2}, W. Sigle^{2}, and J. Taftø^{1}
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Understanding the features in the low-loss $Y_2O_3$ EELS spectrum

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Yttrium-rich oxide nanoparticles are used in oxide dispersion strengthened reduced activation ferritic/martensitic steels. These steels are being considered as structural materials in fusion reactors. Characterisation of the composition of the nanoparticles using Energy Filtered Transmission Electron Microscopy (EFTEM) is important in understanding the evolution during the alloy processing which could affect the mechanical performance. Recent papers have used the Yttrium $M_{4,5}$ edge to construct EFTEM maps [1]. The Yttrium $N_{2,3}$ edge would produce a better signal to noise ratio but lies very close to the plasmon peaks and, in order to use it to map Yttrium, it must be established that this feature is associated with the Yttrium only.

In order to understand the origin of the features in the low-loss part of the spectrum, we have simulated spectra from both monoclinic (Fig.1a) and cubic (Fig. 1b) $Y_2O_3$ using the pseudopotential density functional theory code CASTEP [2]. Plasmon and core-loss edges can both be simulated using dielectric theory and so the loss function includes both the plasmon excitations and any core-loss edges in the same energy range. One of the advantages of using pseudopotentials is that it is possible to choose which electrons are treated as core and which as valence electrons. Two simulations were carried out for each $Y_2O_3$ phase, one where the Yttrium pseudopotential treated the 4s and 4p electrons as valence electrons (shown in both cases as spectrum i) and one which treated them as core electrons and essentially froze them for the loss function calculation (shown in both cases as spectrum ii). The resulting loss functions show a feature around 35eV when the Yttrium 4s and 4p electrons are treated as valence electrons which is absent when they are treated as core-electrons indicating that this feature is an Yttrium N-edge. These simulations allow an understanding of the observed features in the spectrum and enable confident EFTEM mapping using the Yttrium N-edge.

![Simulated loss functions for monoclinic (a) and cubic (b) $Y_2O_3$](attachment:loss_functions.png)

**FIG. 1.** Simulated loss functions for monoclinic (a) and cubic (b) $Y_2O_3$

EELS Investigations of Surface Plasmons in Noble Metal Nanostructures: Influence of Beam Damage and Mapping of Dark Modes

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To realize the potential applications [1-3] related to surface plasmon polaritons (SPPs) [4-6], one needs to understand their associated near-field electromagnetic interactions and correlate them to their structure. SPPs can be generated using high-energy electron beam and can be studied with nanometer spatial resolution using a scanning transmission electron microscope (STEM) equipped with an electron energy loss (EEL) spectrometer. Excitation via electron impact also constitutes a particularly promising way for the investigation of inherently dark modes, which only weakly couple to the radiation continuum.

This talk describes our recent efforts to investigate the spatial distribution of bright and dark modes in noble metal nanostructures. We will also provide a critical assessment of the influence on beam damage on the plasmon spectra. We believe that this effect has been overlooked in parts of the recent scientific discussions within the plasmonic community.

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FIG. 1. HAADF STEM image of dimer and EEL spectra at positions A to E. Shifts in plasmon peak energies were observed at these positions.

Dielectric properties of $\text{Co}_5\text{Ge}_7$ and $\text{CoGe}_2$ investigated by VEELS experiments and DFT calculations.

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Because of its high carrier mobility, Ge is considered as an attractive material for future CMOS technologies. One of the key processes is the formation of a low-resistive germanide layer above the substrate that reduces the source/drain series resistance [1]. Cobalt germanides, and in particular $\text{CoGe}_2$, are good candidates for such an application, as low-resistive phases can be formed at low temperatures without metal diffusion into the substrate [2]. Up to now, most of the studies concerning these compounds have been achieved at a macroscopic scale (ellipsometry, dc electrical resistivity measurements, …) and thus the microstructure of the systems (grain boundaries, interface roughness…) has not been considered. Local investigation techniques can then be used to analyse such samples. Transmission electron microscopy coupled with valence electron energy-loss spectroscopy (VEELS) is a technique of choice to probe the dielectric function at a nanometer scale and then to determine the local resistivity [3].

In this paper, VEELS experiments were performed on two cobalt germanide compounds: $\text{Co}_5\text{Ge}_7$ and $\text{CoGe}_2$ using a JEOL 2200 FS TEM (200kV, FEG, in-column $\Omega$-filter, point-to-point resolution = 0.23 nm). After Fourier-log deconvolution and Kramers-Kronig analysis, the real and imaginary parts of the dielectric function were extracted and fitted according to the Drude-Lorentz model. Nevertheless, crucial parameters such as the possible presence of interband transition before the plasmon energy are needed for accurate determination of the Drude-Lorentz parameters. Thus, in addition, electronic band structures calculations and energy-loss function simulations are obtained from the WIEN2k code. This approach would allow us to extract precisely the resistivity of each compound.

Silver nanoparticles embedded in dielectric matrices: impact of morphology and organization of particles on the surface plasmon excitation

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Nanocermets based on noble metal nanoparticles embedded in a dielectric matrix exhibit a characteristic surface plasmon resonance (SPR) phenomenon. The use of such nanostructures for plasmonic applications requires a precise monitoring of the amplitude and spectral position of the SPR.

In this study, silver nanoparticles have been grown and capped with various dielectric matrices (BN, Al\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}) by using physical vapor deposition routes. On flat substrates, it is shown that the shape of the particles is strongly affected by the nature of the matrix; their optical response is modified as well [1]. The spatial organization of Ag particles on nanostructured surfaces also leads to specific optical responses.

On such systems, transmission electron microscopy provides data obtained at the nanometer scale which can be used either as input parameters for macroscopic optical models and/or compared to data obtained at a macroscopic scale.

The HAADF-STEM imaging is particularly well-suited to investigate the morphology of the buried nanoparticles. A quantitative analysis of the HAADF contrast shows that the aspect-ratio of the particles (considered as truncated spheres or hemispheroids) decreases with their in-plane diameter, this behavior being uncorrelated from the total amount of deposited silver.

EELS can also be performed at the same scale and allows probing the changes in the low-loss signature close to the surface of the silver particles. Experimental data are then compared to ab initio calculations performed with the WIEN2K code.

How can the DDA be an approach for the surface plasmon mapping on metallic nanoparticles

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Surface plasmon excitations have applications in several fields of nanotechnology. Besides optical measurements, such electromagnetic response can be investigated by low-loss EELS. In such experiment plasmonic modes are imaged with a subwavelength resolution [1].

From the theoretical point of view, the main numerical methods to describe the EELS of metallic nanostructures are the Boundary Element Method (BEM) [2] and the Discrete Dipole Approximation (DDA). In the second approach a discrete mesh of punctual dipoles describes the nanoparticle, in order to simulate the low-loss EELS response [3]. In this poster we compare simulated and experimental image-spectra for several metallic nanoparticles, notably for a gold nanodecahedron (see FIG. 1), and emphasize the relations with surface plasmon excitations and the optical active modes, too. Finally, we focus on the way the spectra are affected by the environment of the nanoparticle.

FIG. 1. Left, HAADF-STEM image of a nanodecahedron. Center, modeling. Right, map of the energy of the localized surface plasmon mode.

Investigating the Dielectric Properties of Silicon by means of Valence EELS in a TEM

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The main difficulty in determining dielectric properties by means of EELS is the influence of relativistic effects giving rise to Čerenkov losses of the probe electron \cite{1}. As a consequence, standard Kramers-Kronig analysis is not appropriate for calculating the dielectric function from the valence energy loss spectrum (VEELS). We give an introductory overview of the methods developed so far to overcome such effects \cite{2,3}.

We then compare the results of VEELS experiments on Silicon using an acceleration voltage of 20 kV – in order to avoid Čerenkov losses – with \textit{ab initio} calculations performed using the valence NBSE code \cite{4} and the data of Palik’s \textit{handbook of optical constants of solids} \cite{5}.

For the experimental work a conventional TECNAI G20 with a LaB\textsubscript{6} electron source was used. Careful tuning of the GATAN GIF 2001 allows achieving an energy resolution of 0.35 eV full width at half maximum in the zero loss peak. The samples are 5 nm and 9 nm free standing poly-crystalline Silicon thin films from TEMwindows.com cleaned from surface oxide by using a 1\% HF-acid dip.

The \textit{ab initio} calculations were done using plane-wave/pseudopotential technique with a He-like core. Bloch functions for the silicon L and M electrons were expanded using a 400 Ry cutoff and the dielectric function was well reproduced to beyond the L2,3 edge, beyond which the core NBSE code \cite{6} can be used to calculate core edges. These calculations include electron-state lifetime damping and the effects of the mutual electron-hole attraction.

\begin{thebibliography}{9}
\bibitem{1} M. Stöger-Pollach et al., \textit{Micron} 37 (2006) 396.
\bibitem{7} The Hochschulfjubiläumsfond of the Municipality of Vienna, contract # H-01585/2007, is acknowledged for funding.
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Surface Exciton Polaritons in Individual Au Nanoparticles in the Far-UV Spectral Regime

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Interests in surface excitations of Au are mainly focused on the well-known surface plasmon (SP) in the visible spectral regime [1]. The existence of surface exciton polaritons (SEPs) is believed to be pristine to the spectral regimes showing strong excitonic absorptions [2]. The presence of SEPs in far-UV in Au (≥ 10 eV), where the optical and electronic properties of Au are dominated by broad interband transitions that display characters of weak and diffused excitonic oscillator strengths, is not expected and has never been discussed. Reexamining Ref. 2 and using electron energy-loss spectroscopy (EELS) with a 2-Å electron probe in aloof (optical near-field) setup and energy filtered mapping (FIG. 1), we firmly establish the existence of SEPs in individual Au nanoparticles in the far-UV spectral regime [1]. These results indicate that SEPs indeed can be excited in weak excitonic onsets in addition to their general believing for the sharp excitonic oscillations. Our experimental observations are further confirmed by the theoretical calculations of EELS spectra. The unmatched spatial resolution (2 Å) of the electron spectroscopy technique enables an investigation of individual nanomaterials and their surface excitations in aloof setup. The SEPs in individual Au nanoparticles thus represent an example of surface excitations of this type beyond the visible spectral regime and could stimulate further interests in SEPs in various materials and applications in novel plasmonics and nanophotonics at high energies via manipulations of the associated surface near fields.

FIG. 1. (a) EELS mapping of SP near fields in an individual Au nanoparticle (radius, 13 nm; dotted circle, the projected surface of the nanoparticle). The intensity maximum encircling the surface is well known to signify the surface-excitation nature, which is also observed in (b) and (c) for SEP excitations in Au in the far-UV spectral regime (10.0 and 15.0 eV, respectively). Reproduced from [1].

Surface Exciton Polariton in Monoclinic HfO$_2$: Electron Energy-Loss Spectroscopy Study

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We have recently revisited the conventional understanding in surface exciton polaritons (SEPs) and established their excitations in materials displaying an otherwise weak excitonic oscillator strength [1]. The existence of SEPs is thus not limited to materials with a sharp excitonic absorption [2], and the collective nature of SEPs upon weak excitonic absorption originates from oscillations of loosely defined delocalized excitons, which are correlated with broad interband transitions in materials (e.g., FIG. 1). The weak excitonic absorption and the associated interband transitions can be observed in practically all semiconductors and insulators above the band gap, suggesting the existence of SEPs in the materials. Using scanning transmission electron microscope (STEM) in conjunction with electron energy-loss spectroscopy (EELS) with an ultimate spatial resolution of 0.2-2 nm, we have firmly established the existence of SEP (~7.5 eV) in monoclinic, insulating HfO$_2$ upon the weak excitonic excitation, ~6.2 eV, above the optical band gap (~5.1 eV), FIG. 1. Interband transitions can be found in almost all semiconductors and insulators above the band gap, and this work could stimulate future interests in SEPs in various materials, where the SEP excitations may find unexpected optics applications via manipulations of their surface wave fields analogous to surface plasmons for plasmonics.

FIG. 1. The real ($\varepsilon_1$) and imaginary parts ($\varepsilon_2$) of the complex dielectric function of monoclinic HfO$_2$, displaying a broad, weak excitonic absorption (maximum in $\varepsilon_2$) at ~6.2 eV above the optical band gap. SEP onset at ~7.5 eV and that for surface plasmon (SP) at ~13.4 eV are indicated by dashed lines. Gray, STEM-EELS excitations of SEP and SP taken at 4 nm from the surface of an HfO$_2$ bulk ceramic.

Crystal structure determination and band gap measurement of PbSe nanoparticles

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One way to form superlattices is by self-assembled colloidal nanocrystals (NCs) with controlled features. Superlattices combine unique properties of individual NCs with new collective properties arising from interactions between contiguous NCs. After each elaboration stage, shape, size, crystal structure, electronic and dielectric properties have to be fully characterized. High Resolution Transmission Electron Microscopy and HR-STEM combined with HR-EELS, in state of the art instruments, can provide such information from the level of individual nanoparticles down to atomic scale.

In this work, colloidal PbSe NCs were investigated using a FEI TITAN 80-300 equipped with a monochromator as well as a probe and an image Cs correctors. From HREM and HAADF image series, particle size distribution, shape, crystal structure and crystal orientation relations of NCs have been determined. Crystal orientation relations were obtained using ASTAR software [1] (www.nanomegas.com). From the analysis of low energy loss spectra, the NCs electronic transitions were deduced using the procedure in reference [2]. Results were then discussed on the basis of theoretical calculations [3] and density of states function measurement using resonant shell-tunneling Spectroscopy experiments [4].

FIG. 1.  a) PbSe nanoparticles: FCC crystal structure of space group Fm3-m.  
   b) Histogram of nanoparticles size distribution (mean diameter: 6 ± 0.5 nm).  
   c) Single Scattering Distribution spectrum of a 6 nm PbSe nanoparticles

Electron spectroscopy and imaging of experimental ilmenite alteration.

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Ilmenite is the major raw material for the production of TiO₂, used in pigment industries. The production process typically involves acid treatment, which oxidises and removes the Fe and impurities, leaving behind a TiO₂-rich phase (generally rutile). The kinetics of ilmenite leaching in acid solutions has been well studied [1]. However detailed information of the ilmenite alteration mechanism is still not available. In nature ilmenite initially undergoes weathering through oxidation and removal of Fe to form an apparently continuous series of compositions from ilmenite to pseudorutile (ideally Fe₂Ti₃O₉) as a transitional phase [2]. The Fe is assumed to diffuse out through the unaltered oxygen lattice. In the second stage, pseudorutile undergoes incongruent dissolution, resulting in the formation of rutile, hematite, and goethite [3].

We have carried out an experimental study of ilmenite alteration with 0.1 molar hydrochloric and sulphuric acids at 150 °C for 31 days in Teflon©-lined autoclaves. The resulting products were studied by electron microprobe, scanning and transmission electron microscopy.

The alteration begins at the original ilmenite crystal surface and has also taken place along fractures in the ilmenite. However, the fracture pattern did not exist before the reaction and appears have to been generated by the reaction. Element distribution maps and chemical analyses of the reaction products within the fractures show marked depletion in Fe and Mn and a relative enrichment of Ti. However the results of these bulk chemical analysis, do not correspond to any stoichiometric composition, and may represent mixtures of TiO₂ and Fe₂O₃. Transmission electron microscopy is used to clarify the nature of these product phases. Characterization of the fractures with HRTEM is underway. Electron energy loss spectroscopy (EELS) is used to investigate the starting material and the distribution of elements and phases in the resulting alteration products.

A new method for extracting ELNES information at a rough interface

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The near edge fine structure (i.e. ELNES) in EELS gives information on site-specific, atomic bonding environments. In many materials, such as high-k gate stacks, an interface has considerable projected width when viewed in cross section. An EELS spectrum will therefore contain information from the rough interface and neighbouring matrix phase(s), thereby obscuring the true interfacial bonding.

We have developed a new analytical method for extracting the change in EELS edge intensity at a rough interface with respect to the matrix phase using a concept proposed in Ref [1]. The method analyses a series of spectra from regions of varying interface to matrix volume fraction \( (V_i/V_M) \), the regions being extracted from a single spectrum image. Regions with high \( (V_i/V_M) \) are more ‘interface-like’ and conversely more ‘matrix-like’ for regions with low \( (V_i/V_M) \). By extrapolating to the two extremes it should be possible to determine the true interface and matrix EELS edges. However, since the volume of a rough interface is not known, a more detailed analysis shows that only the change in EELS edge intensity at the interface with respect to the matrix phase can be determined (rather than the interfacial EELS edge itself).

The technique has been applied to a rough, TiN/ poly-Si interface in a HfO\textsubscript{2} based high-k gate stack containing oxygen impurities introduced during processing. Figure 1 shows the change in Si-L edge intensity at the interface with respect to the poly-Si matrix (dark curve). This spectrum was calculated using the method described in the previous paragraph; experimental data from a spectrum image that was acquired across the TiN/ poly-Si interface was used for the calculation. Also shown in figure 1 is the \((\text{SiO}_x\text{-Si})\) difference spectrum (light curve) which was derived by subtracting the experimentally measured Si-L edge for bulk Si from that of bulk SiO\textsubscript{x} (the Si-substrate and SiO\textsubscript{x} amorphous layer in the high-k gate stack were used as the bulk phases). The intensity of the \((\text{SiO}_x\text{-Si})\) difference spectrum is negative since for material of constant thickness the Si-L edge intensity measured from Si is larger than that from SiO\textsubscript{x}. The two spectra in figure 1 have similar gross features indicating the presence of a large number of Si-O bonds at the TiN/ poly-Si interface. A more detailed analysis shows that the difference between the two spectra is due partly to a smaller fraction of interfacial Si-N bonds.

[2] This work was supported by EPSRC grants GR/S44280 and EP/D040205; the authors would like to thank Mr. B. Miller for specimen preparation.
Using EFTEM SI to Visualize and Identify Embedded Poly-Crystalline Si Bump Defects Invisible in Conventional TEM

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In the manufacture of Si-based semiconductor devices, polycrystalline Si (also called poly-Si) thin films are often utilized, but occasionally exhibit bumps as detected through in-line inspection tools. These bumps are routinely cross-sectioned for Transmission Electron Microscopy (TEM) analysis and typically no obvious defect is found [1]. The analysis usually involves bright field imaging which is conducive to enhancing contrast between regions of differently diffracting grains. However, when imaging poly-Si thin films, a small grain of similar mass contrast will not be readily revealed through bright field TEM imaging as seen in figure a.

In the present work, three Energy Filtered TEM (EFTEM) spectral images (SI) were acquired from -5eV to 650eV, spatially aligned to correct sample drift, rebinned in energy to a common 5eV resolution and stitched together to form a composite EFTEM SI. By scrolling through the EFTEM SI, one finds that in the region between roughly 50eV and 100eV, the contrast between a contaminant particle and the surrounding poly-Si matrix is strongly enhanced as seen in figure b where a composite of 4 EFTEM images is summed together to form an effective 20eV slit width image at 72.5eV energy loss.

By extracting composite EEL spectra from the region of the particle and from the poly-Si film [2], one can identify bulk plasmon peaks for each phase and ratio the images of those peak energies as shown in figure c. In this case, the diffraction contrast is nearly eliminated and the particle is readily observed and found to be of circular cross-section. Extracting relative quantification maps for Si, N, O, and C indicate that the particle is nearly stoichiometric SiO$_2$, and also show “wings” on the particle as is also seen in figure b. This is attributed to the particle being of a rod shape with circular cross-section and the TEM lamella being prepared such that it cuts the rod at an angle to the long axis.

[2] This data will be shown in the presentation.
High spatial resolution EELS with StripeSTEM

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For the investigation of atomic-scale chemistry e.g. at interfaces, defects or narrow layers spectroscopic data with an adequate spatial resolution is required. Lately, atomic-scale electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) benefits from the rapid progress in aberration-corrected optics, which provides small and intense probes. In principle a STEM has the advantage to simultaneously collect spatially resolved high-angle annular dark-field (HAADF) signal and EELS data. It is, however, common that the HAADF image acquisition is interrupted for spectrum acquisition. This is the case e.g. for the line profile method with drift correction via cross-correlation of reference images. The disadvantage of such sequential recording techniques is that there is a limited control of the measurement location during processing dead times and the EELS acquisition time, brought about by the frequently uncontrollable specimen and beam drift in a practical experiment.

To address this problem for atomic scale spectroscopy, we propose a variant of the simultaneous acquisition of HAADF images and EELS spectra, which is well suited for the high-resolution study of two-dimensional interfaces and defects or one-dimensional nanomaterials under low electron dose. This variant, called StripeSTEM, collects a sequence of EELS data while a conventional HAADF image is taken line-wise. By this means each EEL spectrum is linked to a number of HAADF scan lines. The measurement dead time is minimized by abandoning spatial synchronization. Drift corrections to the quantitative EEL data can be done post-acquisition, since the beam and specimen drift are recorded in the HAADF image, unlike for example in the line profile and spectrum imaging method.

This contribution discusses capabilities of the StripeSTEM approach. The application to the reference case of SrTiO₃ [100] and single atomic layers of In in ZnO demonstrates monolayer resolution for EEL core loss spectroscopy.

Further application examples are given, e.g. to the study of twin boundaries in barium titanate, the intermixing at the polar/non-polar perovskite interface between dysprosium scandate and strontium titanate and the study of single tungsten disulfide nanotubes.

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We demonstrate that d-d excitations in NiO can be measured by electron energy-loss spectroscopy in transmission electron microscopes. Strong excitations from $^3A_{2g}$ ground states to $^3T_{1g}$ excited states are measured at 1.7 and 3 eV when transferred momentum are beyond 1.5 Å⁻¹. Such a result can be seen in the figure 1. We also show that these d-d excitations can be collected with a nanometrical resolution in a dedicated scanning transmission electron microscope by setting a good compromise between the convergence angle of the electron probe and the collected transferred momentum. This work opens new possibility for the study of strongly correlated materials on a nanoscale.

FIG. 1. a) Schematic representation of the NiO [111] zone axis electron diffraction pattern. Arrows indicate positions of collected spectra along the [22-4] and [20-2] directions. The grids along the directions indicate the value of the transferred momentum (one mark per Å⁻¹). The numbers indicate the q-space positions of the presented spectra. The shaded areas indicate the q domain where d-d excitations are easily visible in the EELS spectra. b) Electron energy loss spectra corresponding to the different q positions numbered in figure 1a. Spectrum 1 is centred at q = 0 Å⁻¹, spectrum 2 is centred at q = 0.53 Å⁻¹ (along [000]-[20-2]), spectrum 3 is centred at q = 1.59 Å⁻¹ (along [000]-[22-4]), spectrum 4 is for 2.12 Å⁻¹ < q < 3.18 Å⁻¹ (along [000]-[20-2]), spectrum 5 is for 2.94 Å⁻¹ < q < 4.50 Å⁻¹ (along [000]-[22-4]). The contributions of the intense zero-loss peak have been removed. Bars and letters indicate remarkable features (H, I, J are d-d excitations).
Elemental and Chemical State Mapping in 3D using STEM-EELS Tomography

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EELS spectroscopy, when coupled with the STEM spectrum-imaging approach [1], has become the de-facto method of choice for the acquisition of elemental, chemical and physical information at the nano-scale. However, information obtained via this acquisition modality is projected in one physical dimension, providing only 2D maps of the three dimensional object of interest. Recently, the technique of tilt series tomography has been utilized widely in transmission EM to resolve the dimension that is typically projected [2]. Once the tilt-series data has been acquired and tomographic reconstruction performed using a suitable signal, the object can be viewed and manipulated as a three-dimensional object using visualization software, allowing the sample morphology to be much better understood.

In this work, these two techniques are combined in a complementary manner to perform STEM EELS spectrum-image tomography. This approach involves acquiring a tomographic tilt-series of STEM-EELS spectrum-images, generating a four dimensional data-set $I(x, y, E, \theta)$. Any monotonically varying signal in the EELS spectrum can be extracted and used for tomographic reconstruction, allowing element or even chemical state specific maps to be generated over the 3D sample volume. Details of this technique will be presented with reference to results from a semi-conductor example, and future developments discussed.

FIG. 1. Color composite image of a W to Si contact from a failed semiconductor device. Volumetric elemental distribution maps for Ti, N, Co and Si were obtained by tomographic (SIRT) reconstruction from the corresponding elemental map tilt-series.

Model-less Spectrum Image quantification by Independent Components Analysis

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Principal Components Analysis has proven to be useful in data analysis of spectrum-images (SIs) [1] for denoising and number of components estimation. However, the components obtained by this method are not in general physically interpretable. In contrast, Independent Components Analysis (ICA) [2] can identify the physical components of an SI under the assumption that they are mutually statistically independent. Therefore, ICA has the potential to enable model-less quantification.

We have successfully applied this method to the quantification of an atomic-resolution SI acquired in the Orsay Nion UltraSTEM 100™ from a CeZrO_{2-x} catalyst. Furthermore we show that in this case it surpasses PCA in signal denoising because it is able to filter a “ghost” background present in our microscope [3].

FIG. 1. (left) Original spectrum and reconstructed spectra by PCA and ICA. (right) Independent components maps corresponding to Ce (red) and Zr (green).

[3] This work was supported by Project MAT2008-00889/NAN and the European Community Marie Curie Action (No. MEST-CT-2004-514307) and Framework 6 program under a contract for an Integrated Infrastructure Initiative. ST acknowledges the “Ramón y Cajal” MEC Program.
Smart Acquisition EELS

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In the STEM it is possible to image single atoms and simultaneously record electron energy loss spectra to give atomic resolution chemical information \cite{1}. However, this is only possible for radiation insensitive materials because of the large electron doses that are required: for radiation sensitive materials such as biological/inorganic interfaces, this goal is far off. Unstained biological macromolecules can only tolerate about $10^{-13}/\text{Å}^2$ with liquid nitrogen cooling, and will therefore require extensive averaging to obtain core-loss EELS with a good signal to noise ratio. Averaging of EEL spectra recorded with readout noise, as is the case with CCD detectors, enhances the noise. This prevents the binning or summarisation of individual spectra collected from each pixel of a spectrum image taken with low electron doses or at high edge energies.

Our solution is to scan a STEM probe over similar areas of interest, while collecting a single spectrum, thus averaging the signal into one spectrum and avoiding noise with a single read-out. This concept is not entirely new, with similar ideas proposed by Hunt et al. \cite{2}. However, with the successful implementation of aberration correction and improved stage stability, atomically resolved areas can now be defined and analysed making this concept worth revisiting. We have tested this technique by beam writing in radiation sensitive amorphous $\text{AlF}_3$ thin films as shown in Figure 1. This technique has direct application in the study of materials with a moderate radiation sensitivity such as iron oxide particles, core-shell nanoparticles, interfaces and grain boundaries.

The development of noise-less direct electron detectors, such as the Medipix detector \cite{3}, could also overcome this problem, but will require hardware modifications to spectrometers to make it possible, so is a long term goal.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Smart Acquisition: HAADF STEM imaging of beam writing in amorphous $\text{AlF}_3$ demonstrating STEM beam position control.}
\end{figure}

References

\begin{enumerate}
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Correction of Higher Order Geometrical Aberration Corrector by Triple Three-Fold Astigmatism Fields in Electron Microscopy

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We have developed a spherical aberration correction system with three dodecapoles (DELT: Dodecapole ELement Triple Aberration Corrector). In the system, the six-fold astigmatism is eliminated by the axially rotated arrangement of three hexapole fields from three dodecapoles with uniquely determined azimuth inter-angles, which are predicted by our calculation. The negative spherical aberration to compensate the positive one from the objective lens is generated in summation of three dodecapoles. Total amount of three three-fold astigmatisms is compensated by a sum of three vectors. This optical system was experimentally tested with an actual scanning transmission electron microscope at 60 kV acceleration. Figures 1 (a), (b) and (c) show experimental Ronchigrams. Figures 1 (c) indicates the successful compensation of a six-fold astigmatism as well as spherical aberration, resulting in the roughly double size of infinite magnification area compared to one for double hexapole system shown in Fig. 1 (b). This work is supported by the CREST project under Japan Science and Technology agency (JST).

Figure 1: Experimental Ronchigrams; (a) non-corrected. (b) corrected by double dodecapole system, (c) corrected by triple dodecapole system. Calculated trajectories of electron are shown in lower for Figs. (b) and (c). the electron trajectories in the dodecapoles are shown to show the cross section of the beam. Each of the contours corresponds to the convergent semi-angle on a specimen, which is listed in left of the figure.
EELS detection limits revisited: Ruby – a case study

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EELS in an (energy filtering or scanning) transmission electron microscope provides unprecedented sensitivity for elemental analysis; one that is said to approach single atom sensitivity [1,2]. However, several problems like low signal to noise ratios due to detector noise, small and uncertain inelastic ionization as well as problems with background extrapolation (extrapolation error / cross-sections), overlapping edges and multiple scattering in case of thicker specimens remain in the process of extracting reliable compositional answers. In a mineralogy related PhD thesis project, we studied Cr traces in natural ruby and carried out systematic theoretical simulations and experimental studies to optimize the detection sensitivity. First, the noise performance of the detection system was determined (MTF, DQE), turning out to be vastly underestimated in literature, as there was hardly any consideration of the dose dependence. The superiority of the multiple linear least squares fit technique over conventional background subtraction for quantitating low chromium concentrations has been proven, and could be further supported by numerical SNR analysis of simulated noise free and Poisson-noisy EEL spectra. MLS fitting of ruby spectra by using appropriate standard specimens was also investigated from an experimental point of view, by studying the influence of different instrumental configurations (monochromator / non-monochromator) on the quantification results. It is possible to detect atomic concentrations of chromium in alumina down to 0.03 % for a given optimal determined set of parameters at a particular microscope setting. The detection limits could be re-established within a novel mathematical framework based on MLS fit parameters, avoiding the need of using factors that are hard to estimate otherwise [3].

FIG. 1. SNR vs. chi² analysis for a best fitting window width (180eV) for an MLS-fitted ruby spectrum (energy range shown around oxygen).

References
Performance of the MANDOLINE filter in combination with a monochromator

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The MANDOLINE filter, proposed by Uhlemann and Rose [1] and developed by Zeiss, shows an extraordinary filter acceptance, isochromaticity, and energy resolution, even for large fields of view. This outstanding analytical performance is seen in the Zeiss SESAM microscope, which furthermore includes the CEOS electrostatic Omega-type monochromator [2,3], a highly stable 200 kV high voltage supply, and a highly stable current supply of the filter.

In Figure 1 the attainable energy resolution is shown to be 43 meV (FWHM) for a small filter entrance aperture. At short exposure times, this is mainly limited by the energy window width of the smallest monochromator slit, which is about 40 meV. Although long exposure times and large fields of view lead to some degradation in the energy resolution due to instabilities and the filter’s geometric aberrations respectively, the results are still excellent: For an exposure time of a 100 s, an energy resolution of only 87 meV (FWHM) is attainable, which demonstrates the stability of both the high voltage and the MANDOLINE filter current. Figure 2 shows a logarithmic plot of the EEL spectrum of the zero-loss peak for a large filter entrance aperture, which in the imaging mode would correspond to a field of view of 184 mm in the plane of the SSCCD camera. The energy resolution of only 52 meV (FWHM) proves the success in correcting the geometric aberrations of the MANDOLINE filter, while the steep drop of the zero-loss peak establishes ideal preconditions for band gap measurements and investigations in the very low-loss region.

References
EELS Mode AutoTuning for a Post-Column Energy Filter in TEM

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A fully automated software procedure is presented for correction of spectral aberrations for a post-column energy-filter in EELS mode. The software allows for more precise alignments than can be attained otherwise, and provides validation of alignment states prior to spectrum acquisition. This is achieved through external control of the multipole optics of the energy filter, which themselves are ideally suited to obtain a large range of high quality spectral dispersions [1]. Quadrupoles can control the spectrum magnifications in the dispersive and non-dispersive directions independently, thereby optimizing the available dynamic range of the detector for each dispersion (Figure 1). Furthermore, any remaining spectral distortions from the prism, such as spectrum linearity, rotations or barrel distortions can be corrected by higher order multipoles in the projection optics (Figure 2). These corrections are significant for the determination of the attainable energy resolution and also for the integrity of data acquired in techniques such as $\omega,q$ mapping [2].

Automated spectrum aberration correction using higher order multipoles particularly improves the quality of the spectrometer alignment for large energy ranges. Spectrum acquisitions with lower dispersion are useful for locating multiple edges in a single frame and allows for higher frame rates for a given signal to noise. High speed spectral acquisitions are of particular interest for spectrum imaging applications.

**Fig. 1. Dispersion Height and Focus tuning.** Fig. 1a] shows the initial, untuned state. The green annotation reflects the target height and dispersion for the 2 ZLP peaks. Fig. 1b] demonstrates the result after auto-tuning.

**Fig. 2. Correction of moon bend (Fig.2a] (initial state) and Fig.2b] (final state)).**

References
SMART Spectrum-Imaging: Customized acquisition schemes for improved STEM EELS SI data

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20 years after the concept of spectrum-imaging (SI) was first introduced to analytical TEM [1], it has now become a routinely applied technique capable of mapping specimen properties derived from electron energy-loss spectroscopy (EELS) data. Combined with c\textsubscript{c}-corrected microscopes in scanning (STEM) mode, maps with atomic resolution can be acquired [2]. Conventionally, one-dimensional line scans or two-dimensional area scans are performed, placing the electron probe on equidistantly spaced positions along a line or on an orthogonal grid, respectively. Under-sampling effects, which arise for probe diameters smaller than this spacing, can be dealt with by so called ‘sub-pixel scanning’. Here, the probe is rapidly scanned through a set of closely spaced points during spectral acquisition for each ‘pixel’ of the spectrum-image.

In addition to the now established routines, the ability to control the probe position independently of the EELS acquisition gives the flexibility to tailor routines for the special requirements of some specimens. In particular, issues of radiation damage and specimen contamination can be addressed by integrating the signal from many particles or from larger areas of any shape, which are rapidly scanned during one signal integration period of the EELS detector [3]. Other applications include irregular line scans following an arbitrarily shaped path and ‘compressed’ SIs containing several areas of interest but which omit uninteresting areas in between them (e.g. particles in a matrix or layer structures with small and larger layer thicknesses). Additionally, adjusting EELS exposure times and energy shifts of the spectrometer for each pixel of the dataset allows the acquisition of different energy ranges within one acquisition, giving better spatial correlation of data than a set of sequentially acquired spectrum-images; however, a fast beam shutter is needed to overcome the dynamic range limitations of the detector for combined zero-loss / core-loss measurements [4].

We have developed a set of acquisition scripts called ‘SMART SI’, which give a user friendly interface to quickly set up and perform such highly customized scans.

References
Fast EELS elemental mapping in the STEM

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Aberration correction combined with bright electron guns makes it possible to focus probe currents of 1 nA and higher into atom-sized electron probes [1]. Optimized coupling optics allows nearly 100% of the available Electron Energy Loss Spectroscopy (EELS) signal to be coupled into an EEL spectrometer, by accepting EELS scattering angles up to about 50 mr. In such systems, a probe current of 1 nA produces enough core-loss signal for EELS elemental mapping to proceed at rather high speeds, of the order of 1 ms/pixel. A 256x256 elemental map acquired and processed at 1 ms/pixel would take just 66 s, allowing many such maps to be acquired from different sample areas in a single experimental session. There is even more signal available for low-loss EELS mapping, which could be done with pixel dwell times of the order of 10 μs, i.e. just 2.5 s for a 512x512 map. This would allow low-loss imaging to serve as a STEM real-time survey tool for finding interesting sample areas by their distinct low loss features, such as plasmons characteristic of single-layer graphene.

Achieving per-pixel times of 10 μs should be possible with a CCD read-out rate of 10 MHz, provided that the spectrum is compressed into just 100 pixels, compression is done without incurring a substantial overhead, and pixel advance and spectrum read-out are synchronized with no substantial per-pixel delay. This is not readily achieved. For instance, the Gatan Enfina EELS – which uses a 1 MHz read-out of a 1340x100 pixel CCD and allows each spectrum to be compressed into 134 pixels before digitization – should be able to do EELS mapping much faster than 1 ms/pixel. In reality, however, compressing the spectrum gives an overhead of about 4 ms per read-out, and a maximum spectrum read-out rate of about 250 per second. Synchronizing the spectrum read-out with pixel advance (done in software) takes about another 5 ms per pixel, and gives a fastest mapping rate of about 100 pixels per second.

This presentation will focus on ways to overcome these limitations, by speeding up the spectrum read-out, improving the spectrum compression overhead, and improving synchronization between spectrum read-out and pixel advance.

Current successes and challenges in DFT-based EELS modeling


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DFT (Wien2k) modeling was used to study CrAlYN/CrN nanoscale multilayer coatings (with unknown stoichiometries) by finding theoretical N K edges for various alloys (FIG. 1) [1]. The CrAlN layer was thought to be Al rich compared to CrAlYN, and indeed the closest theoretical match to ELNES data for CrAlN was for NC\textsubscript{0.25}Al\textsubscript{0.75}. For the Fe(100)/MgO(100) interface (FIG. 2), simulated O K edges were found using CASTEP at points A and B. For interfacial oxygen (versus bulk) pre-edge intensity is observed. This edge intensity just above the Fermi level is likely to be as a result of additional states available due to p / transition metal d orbital interactions. A consistent result for a similar system has arguably been observed experimentally. Broadening of results is crucial in modeling [2,3]. In particular, the incorporation of the exact variation of instrumental broadening with edge onset energy is a challenge. A consistent approach to core-hole treatment in various materials classes is required, as is a rigorous approach to low-loss modeling and dual transition channels for L\textsubscript{2,3}, M\textsubscript{2,3} and M\textsubscript{4,5} edges. These key topics in \textit{ab initio} spectral modeling of EELS will be discussed in this contribution.

FIG. 1. Experimental N K edges for CrN, CrAlYN, CrAlN layers (thick lines) and theoretical data (dashed line numerical broadening, solid line energy dependent final state lifetime broadening). a) NCr b) NC\textsubscript{0.75}Al\textsubscript{0.25} c) NC\textsubscript{0.625}Al\textsubscript{0.375} d) NC\textsubscript{0.5}Al\textsubscript{0.5} e) NC\textsubscript{0.375}Al\textsubscript{0.625} f) NC\textsubscript{0.25}Al\textsubscript{0.75} g) NA1.

[4] CrAlYN/CrN experimental data from SuperSTEM, coordinated by Ian Ross (Sheffield University). MgO interface experimental discussions have been with Amit Kohn’s group at Oxford University.
Calculation of phase changes of electron waves near excited nanoparticles.

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The excited states of valence electrons in a nanoparticle generate electric and magnetic fields outside the particle. These fields can be probed by measuring the loss of energy of an electron wave passing near the particle or by determining the phase shift of the wave.

Expressions for the fields generated by the valence electrons of a sphere are given by Garcia de Abajo [1]. The phase change along the path defined by $r(t)$ in the induced field of angular frequency $\omega$ is given by $(c/2\pi\omega) \int dt \text{Im} \left( e^{-i\omega t} \mathbf{E}^{\text{ind}}[r(t),\omega] \right)$ in atomic and electromagnetic units. Fig. 1 shows how the phase changes as a function of the energy of excitation for gold and polystyrene spheres.

The valence electrons may be excited by electromagnetic radiation or by the probing electron wave itself. In the latter case many frequencies are excited simultaneously. An average change of phase can be measured using the transport of intensity equation [2] and is found to be close to the value predicted by weighting a curve such as those in fig. 1 with the corresponding energy loss spectrum.

![Graphs showing phase change as a function of energy for gold and polystyrene spheres.](image)

FIG. 1. Phase change of a 100-keV electron wave along a path passing 1 nm from gold and polystyrene spheres of radius 18 nm excited by radiation of energy $E = hf$.

[3] Discussions with Dr. T.C. Petersen and Dr. V.J. Keast are gratefully acknowledged.
Site-selective EELS analysis by utilizing electron channeling, multivariate curve resolution and first principles calculation

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Recent analytical techniques in STEM-EELS demonstrate elemental and valence-sensitive imaging at atomic resolution, using a finer and more intense electron probe achieved by improving the electron gun optics and electron source design. However, its focused beam sometimes causes serious radiation damage on the sample. One of the alternative atom-probe analyses can be accomplished by utilizing the electron channeling effects for EELS in a similar way to ALCHEMI. We have improved this site-selective EELS by applying the deconvolution, multivariate curve resolution and digital beam-control [1]. We have analyzed the site-specific electronic structure around the transition metal ions in several oxides with the aid of the ab-initio configuration interaction (CI) calculations [2].

Fig. 1 shows the 400 plane channeling results on two spinel oxides, in which a negative (positive) 400-excitation error S enhances the signals of the octahedral (tetrahedral) site. The results of Mn L\textsubscript{2,3} spectra indicated that the experimental distinct variation in the relative intensity of peaks a and b is due to the chemical shifts between the different Mn valence states, evidencing the Mn charge ordering. In the experimental Fe L\textsubscript{2,3} spectra, peak a is enhanced significantly at S<0. The theoretical octahedral spectrum consistently shows the corresponding sharp peak a. A further theoretical analysis confirmed that this spectral feature originates from the site-specific crystal field splitting, not from the different valence states.

FIG. 1. Atom positions in the spinel unit-cell, projected along [001] (a). The experimental spectra under electron channeling conditions and the site-specific theoretical spectra: Mn L\textsubscript{2,3} of Mn\textsubscript{3}O\textsubscript{4} (b) and Fe L\textsubscript{2,3} of CoFe\textsubscript{2}O\textsubscript{4} (c).

The charge-ordered spinel AlV$_2$O$_4$: EELS and DFT studies

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It has been suggested [1] that the cubic spinel AlV$_2$O$_4$ displays a charge-ordering transition at approximately 400°C, with the proposed low-temperature phase containing vanadium in two different valence states. Materials exhibiting strong electron–electron interaction have recently been the focus of several studies due to their often high thermoelectric power [2]. In particular, systems showing charge ordering and mixed valance are of interest [3].

We have performed low-loss and core-loss EELS studies of the AlV$_2$O$_4$ system both above and below the charge ordering transition in order to investigate the electronic structure. These experiments were performed with a 0.15 eV energy resolution using the Zeiss SESAM microscope and are compared to calculations of the dielectric function and density of states using density functional theory, see figure 1. At this stage the agreement between experiment and theory is considered to be very good, particularly for the O K edge where the calculations reproduce all the main features with only minor deviations from the experiments. [4].

FIG. 1. (a) Comparison of the experimental low loss spectrum with the theoretical loss function calculated from the dielectric function $\varepsilon$. Due to the trigonal symmetry of the crystal $\varepsilon_{xx} = \varepsilon_{yy}$. (b) The experimental oxygen K edge together with the calculated p-projected DOS.

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Electron energy loss magnetic chiral dichroism (EMCD) is a technique which has been discovered recently [1,2] and should give access to quantitative information on the magnetic moments in magnetic samples [3,4] with the spatial resolution of the transmission electron microscope. The fine structure of the EMCD spectra depends on the electronic structure of the sample, on its thickness and on dynamical diffraction effects.

Calculated spectra are necessary to interpret the fine structure of the magnetic dichroic signal and understand the influence of the different physical effects which affect the spectra. It has recently been shown that the EMCD spectra of metallic magnetic samples such as Fe, Co or Ni can be calculated with a good accuracy using density functional theory (DFT) based codes [5]. On the other hand, core-level X-ray absorption and electron energy loss spectra of transition metal oxides show pronounced multiplet effects, which are better described by atomic multiplet codes [6].

In the present communication, we make a comparison between the EMCD spectra of magnetite (Fe₃O₄), calculated either using the DFT-based code Wien2k or the atomic multiplet code TT-Multiplet.