Book of Tutorials and Abstracts

European Microbeam Analysis Society

EMAS 2024

14th

REGIONAL WORKSHOP

on

THE EDGE OF NEW EM AND MICROANALYSIS TECHNOLOGY

12 to 15 May 2024
at the
Brno University of Technology, Brno, Czech Republic

Organised in collaboration with:
Brno University of Technology (VUT)
Central European Institute of Technology (CEITEC)

EMAS
European Microbeam Analysis Society eV
www.microbeamanalysis.eu/

This volume is published by:
European Microbeam Analysis Society eV (EMAS)
EMAS Secretariat
c/o Eidgenössische Technische Hochschule, Institut für Geochemie und Petrologie
Clausiusstrasse 25
8092 Zürich
Switzerland

ISBN 978 90 8227 6978
NUR code: 971 – Materials Science

INTRODUCTION TO TRANSMISSION ELECTRON MICROSCOPY

Mariana Klementová

Czech Academy of Sciences, FZU - Institute of Physics
Na Slovance 2, 18221 Prague, Czech Republic
e-mail: klemari@fzu.cz

Mariana Klementová is a researcher and the Head of the Laboratory of Electron Microscopy at the Department of Material Analysis at the Institute of Physics of the Czech Academy of Sciences in Prague. Her work is focussed on characterisation of inorganic materials at the micro-/nanoscale using various methods of transmission electron microscopy. By combining electron diffraction for structure determination with spectroscopy methods (EDS/EELS) for elemental composition and high-resolution imaging it is possible to obtain complex information on materials down to atomic resolution. She is also interested in 3D electron diffraction for structure determination of new inorganic crystalline compounds. She has authored 146 scientific publications with over 2500 citations, and H-index of 30.

1. ABSTRACT

Basic principles of methods of transmission electron microscopy (TEM) – imaging, diffraction, and spectroscopy – are introduced complemented by examples. Moreover, current trends and several advanced applications are mentioned.

2. INTRODUCTION

Transmission electron microscopy (TEM, an abbreviation also stands for the instrument, a transmission electron microscope) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image/diffraction pattern. The specimen is most often an ultrathin foil less than 100 nm thick or a suspension of nanoparticles on a grid.

The power of TEM lies in the possibility of combining analyses of various signals arising from the electron beam hitting a thin specimen over an area as small as several nanometres. Thus, information acquired from imaging techniques such as bright-field (BF), dark-field (DF), high-resolution (HR) TEM can be combined with structural information obtained from diffraction techniques such as selected-area electron diffraction (SAED), convergent-beam electron diffraction (CBED), as well as with chemical information obtained by spectroscopic techniques such as energy-dispersive X-ray spectrometry (EDS) or electron energy-loss spectroscopy (EELS). All this information is retrieved from the same area of several nanometres in diameter, which makes TEM a complex characterisation tool for nanomaterials.

Since the first TEM was built by Ernst Ruska and Max Knoll in Berlin in 1930s, there have been written many textbooks covering the subject of transmission electron microscopy [e.g., 1-3].

3. MICROSCOPE DESCRIPTION

TEM is in its construction very similar to light microscope (LM). It is composed of several parts (Fig. 1):
(1) The source of electrons (gun);
(2) Electromagnetic lenses for focussing;
(3) Deflection coils for beam tilt/shift;
(4) Selecting apertures;
(5) Screen or CCD for observation;
(6) Specimen holder.
However, there are also significant differences that allow TEM to reach 100 times better resolution compared to LM. Foremost, in TEM electrons accelerated to certain high tension give "monochromated" electron beam with much shorter wavelength (0.0037 nm for 100 kV)

compared to polychromatic light used in LM (300 - 700 nm). However, this advantage is greatly hampered by the bad quality of electromagnetic lenses, and therefore the resolution of a conventional TEM reaches only about 0.2 nm.

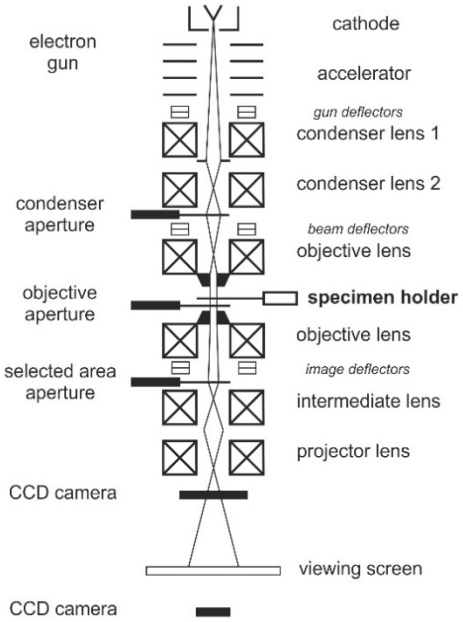

Figure 1. TEM description.

Various holders can be used in TEM. The basic holders are single-tilt and double-tilt holder. Double-tilt holder is essential for tilting the sample into special orientation for BF/DF imaging, ED or HRTEM observation. The tilt range is determined by the type of objective lens pole piece in the microscope. For analytical purposes, dedicated holder tips are made of beryllium. For tomography applications, very thin holders are on offer that allow the largest possible tilt range (up to +/-80°). For air sensitive samples, cryo or vacuum transfer holders are available. Last but not least, holders allowing wide range of in-situ measurements are on the market including holders for heating and cooling, straining, nanoindentation, electrical characterisation, gas and liquid cell for environmental studies.

4. ELECTRON OPTICS - IMAGE FORMATION

Electromagnetic lenses are the magnetic equivalent of the glass lenses in an optical microscope and to a large extent, we can draw comparisons between the two. The electromagnetic lens consists of copper coils with soft iron pole pieces. A strong magnetic field is generated by passing a current through the set of windings. This field acts as a convex lens, bringing off-axis rays back to focus. The image is rotated, to a degree that depends on the strength of the lens (beware in the older TEMs). Focus and focal length can be altered by changing the strength of the current.

The electrons passing through the lens follow a spiral path, however the direction of the rays behaves in the same way as it is known from light optics (Fig. 2a). When an object is illuminated by a parallel beam:

(1) The beam scattered along the optic axis is deflected through back focal point of the lens;

(2) The beam scattered through the centre of the lens is not deflected;

(3) The beam scattered through the front focal point of the lens is deflected parallel to the optical axis.

The beams intersect in the image plane, where they form an inverted image of the object. In an ideal (aberration free) lens, every point of the image contains information from exactly one corresponding point in the object. Moreover, if we consider beams that are scattered from the sample under the same angle, they all must end in their respective points in the image. These beams intersect in the back focal plane forming a diffraction pattern. Every point of the diffraction pattern contains information from the whole object, and therefore can be used to form an image. This will be exploited in the next chapter in which the principles of diffraction contrast will be explained.

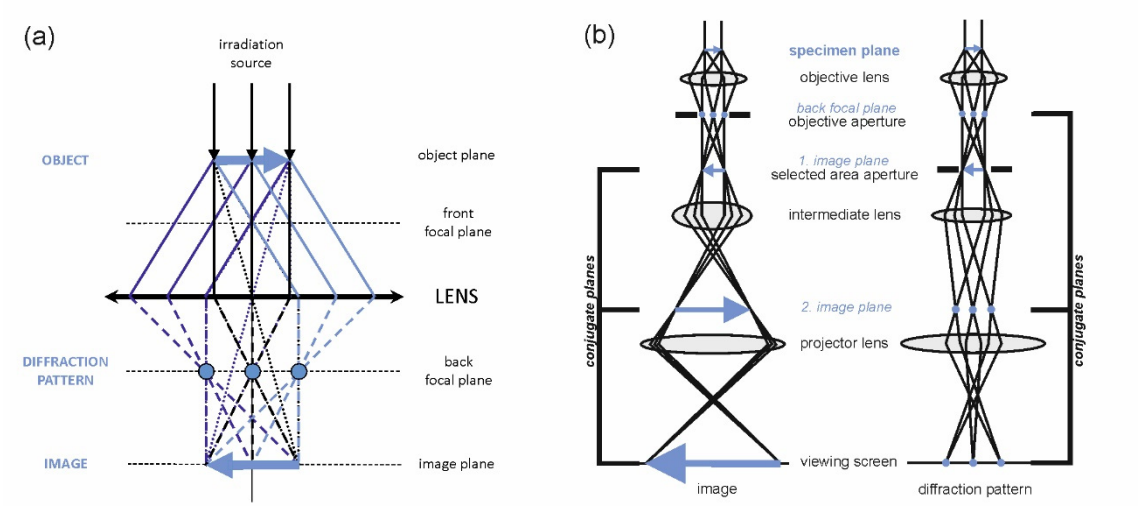

Figure 2. a) Image and diffraction pattern formation by a convex lens, and b) Ray paths for imaging and diffraction mode in TEM.

A TEM is constructed so that it is very easy to switch between a diffraction pattern formed in the back focal plane of the objective lens and an image formed in the image plane. The switching can be performed almost instantly just by pushing a button and thus changing the focus of the intermediate (diffraction) lens (Fig. 2b).

5. *CONTRAST - IMAGING TECHNIQUES*

Imaging techniques in TEM employ various types of contrast arising due to the scattering of electrons by a sample, during which the amplitude and/or the phase of the incoming electron waves are changed. Thus, the two major types of contrast are amplitude contrast and phase contrast. In most cases, both types of contrast contribute to the image; however, conditions can be selected so that only one is enhanced. The basic difference between the two types of contrast lies in the number of electron beams used for image formation. The beams are selected by the objective aperture located in the back focal plane of the objective lens (the plane of the diffraction pattern) to form the final image in the image plane (Fig. 2b). In case of amplitude contrast only one beam is used, whereas for phase-contrast imaging at least two beams are necessary to form an interference image.

5.1. Amplitude contrast

In crystalline samples, the most pronounced amplitude contrast is diffraction contrast, which appears if only some of the elastically scattered electrons are used, for the image formation. When a crystalline sample is illuminated by a parallel beam, the electrons scattered under the same angle from different parts of a single-crystal sample are focussed to a single point at the back focal plane of objective lens, forming a diffracted beam. A single beam (either the direct, undiffracted beam or any diffracted beam) contains information from the whole crystal and, therefore, can be used to image the crystal.

To enhance the amplitude contrast only one electron beam is selected by the objective aperture located in the back focal plane of the objective lens to form the final image. When the direct beam (undiffracted beam) is selected, the resulting image is called a bright-field image (BF). If there is a diffracting crystal on a non-diffracting background, the crystal will appear dark on the bright background (field). When any of the diffracted beams is selected, the resulting image is called a dark-field image (DF). In this case, the diffracting part corresponding to the diffracted beam will appear bright on a dark background (field). In Fig. 3, BF/DF imaging of a twinned crystal is demonstrated. Lamellas belonging to two different orientations are enhanced.

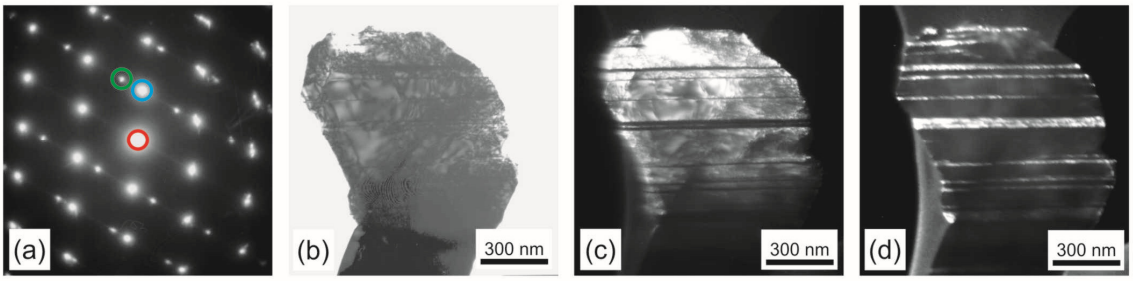

Figure 3. Diffraction contrast imaging. a) SAED with circles representing the position of objective aperture (OLA) used for imaging; b) BF image - red OLA; c) DF image - blue OLA; and d) DF image - green OLA.

Other types of diffraction contrast include thickness and bending contours. Thickness contours can be used for thickness determination of a known sample. However, when thickness contours are visible, it means the sample is not thin enough for high-resolution imaging.

The contrast in BF/DF imaging is very sensitive to any feature that affects the local crystal structure. Therefore, it is used widely to localise crystal defects such as dislocations and stacking faults and to characterise the strain fields induced by them. DF imaging becomes very effective in these applications if it is performed in weak beam mode. In this mode, the diffracted beam selected by the objective aperture is far from the exact Bragg condition (large excitation error). Most of the crystal then remains almost dark, while those defects, which bend the crystal planes corresponding to the selected reflection back to Bragg condition, yield a sharp, well localised bright feature in the image. The use of a beam with a large excitation error guarantees a much sharper contrast and a better localisation of the defect with respect to standard BF/DF imaging.

Mass-thickness contrast is another type of amplitude contrast, which dominates in non-crystalline samples such as polymers or biological samples. It results from incoherent elastic scattering of electrons (Rutherford scattering), which is heavily dependent on the atomic number Z and the thickness. The mass-thickness contrast can be enhanced by inserting an objective aperture in the back focal plane, staining different areas of specimens with heavy metals such as Os, Pb and U, or decreasing the energy of the incident beam (lowering the accelerating voltage of the TEM).

5.2. Phase contrast

The most commonly used phase contrast technique is high-resolution imaging (HRTEM), which is used for imaging details at the atomic level. The HRTEM images are in fact interference images formed by interaction of at least two beams in the image plane of the objective lens. Therefore, a larger objective aperture must be used to gather more than one beam (Fig. 4a). In HRTEM, we are observing a projection of the structure. We do not see individual atoms, but we observe interference fringes corresponding to the periodicity of atomic columns in a given direction. The contrast of the fringes depends on many parameters, among which the thickness and objective lens defocus are the most important (Fig. 4). To determine the exact positions of the atoms, simulations based on the structure model and the microscope parameters must be carried out. However, there are many applications of HRTEM where the exact positions of atoms are not necessary, such as studying dislocations or grain boundaries.

The resolution of a common HRTEM varies between 1.6 and 2.3 Å, which might seem quite poor considering the wavelength of 200 kV electrons (0.0251 Å). Such deterioration is due to the aberrations of electromagnetic lenses, mainly the spherical and chromatic aberration. The top-end microscopes nowadays include correctors of these aberrations and achieve resolution down to 0.5 Å.

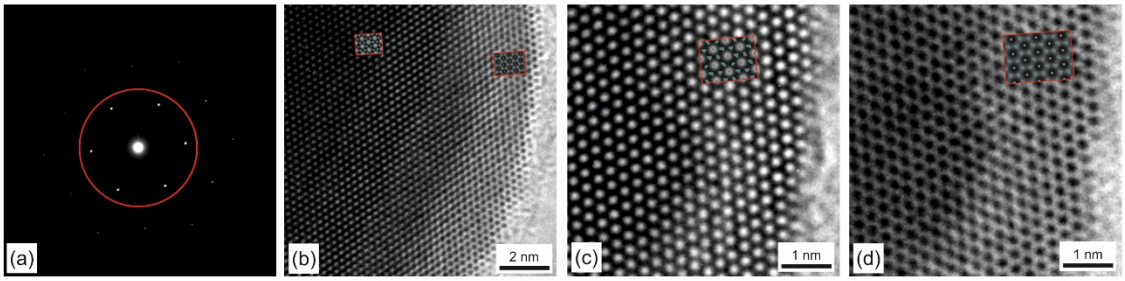

Figure 4. HRTEM images of hematite along [001] with corresponding simulations in the insets. a) SAED with a red circle representing position of objective aperture used for HRTEM imaging; b) Variation of phase contrast with thickness, and variation of phase contrast with defocus; c) Defocus 60.5 nm, thickness 5.5 nm; d) Defocus 80.5 nm, thickness 5.5 nm. Fe - grey, O - teal.

Other phase-contrast imaging techniques include Moiré fringes, Fresnel fringes, electron holography, and Lorentz microscopy. Fresnel fringes are caused by an abrupt change in electrostatic potential and can be visualised by taking images with a strong defocus. They are used to study gas or liquid bubbles, voids, and high-angle phase boundaries. Moiré fringes result from the overlap of two or more lattice periodicities and are often present in images of overlapping crystals (beware during interpretation). Both electron holography and Lorentz microscopy are very specialised techniques. In order to use these techniques, a TEM must be equipped with a biprism or Lorentz lens, respectively. Electron holography is used for imaging magnetic and electric fields. Lorentz microscopy is used for imaging magnetic domains.

6. DIFFRACTION TECHNIQUES

Electron diffraction (ED) follows the same geometrical laws as X-ray diffraction. However, the availability of electromagnetic lenses for electrons makes electron diffraction a very flexible diffraction technique. This flexibility gives rise to many different diffraction techniques embedded in the same instrument. Three methods will be introduced here – parallel beam selected area ED and microdiffraction, and convergent beam ED. In the past decade, electron diffraction has been experiencing rebirth with its application to structure solution of nanocrystals using 3D electron diffraction techniques (see chapter 10.2.).

6.1. Selected area electron diffraction (SAED)

Selected area electron diffraction is the standard electron diffraction technique. The sample is illuminated with a parallel beam and the area from which we want to collect the diffraction pattern is selected by inserting an aperture called selected area (SA) diaphragm in the 2nd image plane of the objective lens. Depending on the dimension of the SA diaphragm, the diffracting area can be varied from a few hundred nanometres to several microns in diameter.

Due to the small electron wavelength, the Ewald sphere has a very large radius, and it can be approximated by a plane in the vicinity of the origin of the reciprocal space. Because the crystal is thin, the nodes of reciprocal lattice in the Ewald construction are not points but are elongated in the direction perpendicular to the surface of the sample. As a result, if the crystal is oriented with the electron beam normal to a set of reciprocal lattice planes, all the reciprocal vectors of the plane passing through the origin are so close to the Ewald sphere that they are visible in the pattern. These SAED patterns are called zone-axis patterns and are used widely as they are very informative (Fig. 5a). They display undistorted representation of reciprocal lattice planes carrying information on the geometry and symmetry of the crystal lattice. SAED patterns have different forms depending on the crystallinity of material (Fig. 5):

(1) Spot patterns from individual single crystals;

(2) Ring patterns from polycrystalline samples;

(3) Diffuse ring patterns from amorphous material.

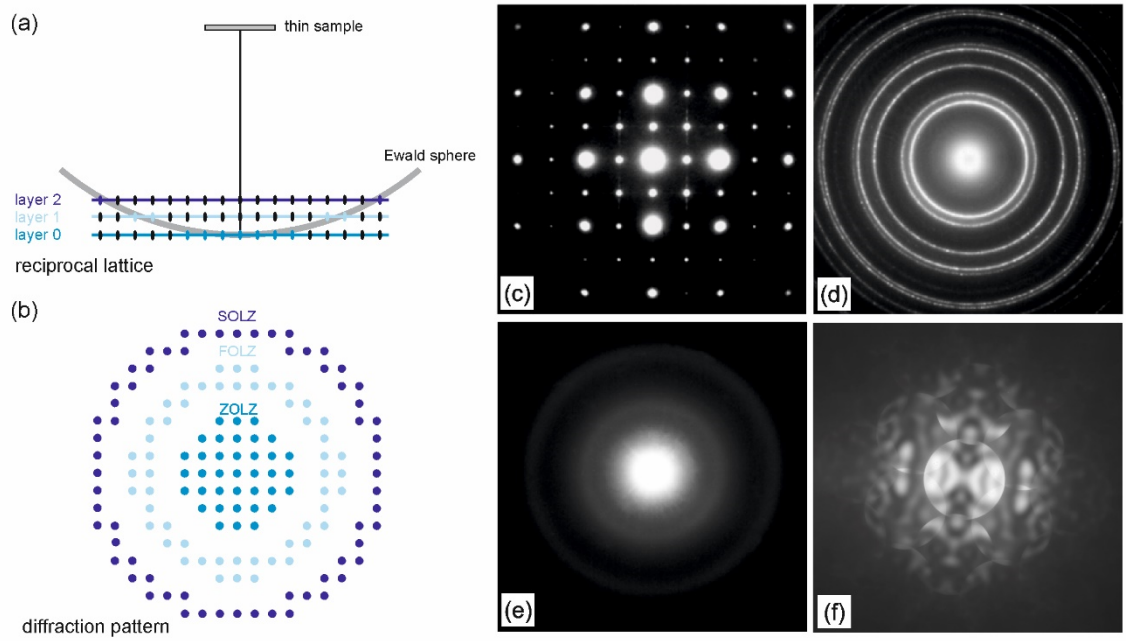

Figure 5. Electron diffraction. a) Ewald construction; b) Resulting diffraction pattern including zero-order (ZOLZ), first- (FOLZ) and second-order Laue zones (SOLZ); c) SAED pattern from an oriented single crystal; d) SAED pattern from a polycrystalline sample; e) SAED pattern from an amorphous sample; f) CBED pattern of oriented silicon single crystal.

SAED allows us to relate the images we obtain to the structure of the material. It is mostly used for phase identification, determining preferred orientation (e.g., growth direction of nanowires, epitaxial relationship in thin films), and define the orientation of the sample for imaging techniques.

6.2. Micro- and nanodiffraction

Micro- and nanodiffraction is an alternative way of collecting an electron diffraction pattern with parallel or slightly convergent illumination. In this case, the diffracting area is selected directly by forming a small parallel beam on the sample and not through an aperture. In this setting, the diffraction pattern is less affected by the aberrations caused by the objective lens compared to SAED. Moreover, the beam size can be smaller than the minimum area attainable with even the smallest SA diaphragm. With this diffraction mode, we can obtain diffraction patterns with very high spatial resolution keeping the simple spot-like appearance of a SAED pattern.

6.3. Convergent beam electron diffraction (CBED)

The beam used for CBED is not parallel but convergent, and as such it can be thought of as a collection of many narrow beams, each with a different propagation direction in the illumination cone. Because each direction of the incident beam generates its own set of diffracted beams, the resulting diffraction pattern contains discs rich in information from all the diffraction angles within the illumination cone (Fig. 5d).

Depending on the gun type of the TEM the minimum probe size for a CBED pattern can be reduced from 20 nm down to a few nm. Therefore, the crystal information recorded in CBED patterns comes from a homogeneous area in terms of chemical composition, unit-cell parameters, symmetry, and thickness.

The main applications of CBED are accurate determination of lattice parameters, full and (almost) unambiguous characterisation of the space-group symmetry, accurate refinement of structural parameters and direct determination of the amplitudes of structure factors. Moreover, accurate thickness determination is possible from the analysis of two-beam condition CBED patterns [4].

7. SPECTROSCOPY TECHNIQUES

The two spectroscopic techniques that will be described here are both result of inelastic interaction of incoming electron beam with atoms in the sample. When an electron beam hits a specimen, some of the incoming electrons can knock out an electron from inner atomic energy levels creating a hole. This hole can be filled with an electron from a higher level. As this electron fills the hole, it loses energy, which is emitted in the form of characteristic X-rays. The energy of the X-ray generated thus corresponds to the energy difference between the two atomic levels and, therefore, is characteristic for a given element. In energy-dispersive X-ray spectrometry (EDS), the energy of the emitted characteristic X-rays is detected and thus the elemental composition of the sample can be determined. During this process, the incident

electron loses some energy depending on the type of atom and interaction (core loss, valence loss). Such electrons can be detected by a spectrometer and the technique is called electron energy-loss spectroscopy (EELS).

7.1. Energy-dispersive X-ray spectrometry (EDS)

The basic principle and instrumentation of EDS are common to both TEM and scanning electron microscopy (SEM). However, there is one significant advantage of EDS in a TEM – the spatial resolution of the analysis. Due to the thin samples, the interaction volume of the electrons in TEM equals a cylinder defined by the diameter of the beam and the sample thickness; therefore, nanometre special resolution can be achieved (Fig. 6a). In a thin specimen in TEM, X-ray absorption and fluorescence can, to a first approximation, be ignored and the X-ray intensity ratios, I_A/I_B, observed can be converted into weight fraction ratios, C_A/C_B, by multiplying by a constant k_{AB}, which can be calculated or determined experimentally [5].

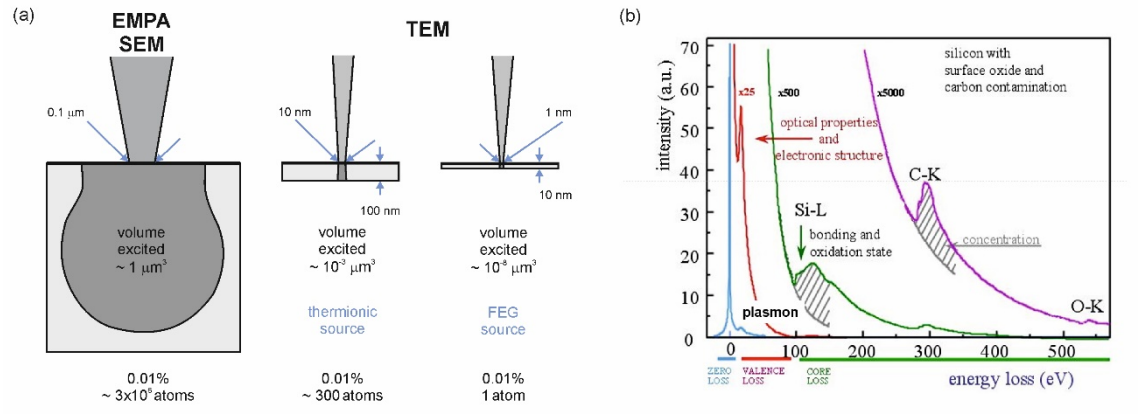

Figure 6. Spectroscopy. a) Comparison of interaction volume in a bulk sample used in SEM or EMPA with a thin sample used in TEM (after [3]); b) Parts of EEL spectrum.

7.2. Electron energy-loss spectroscopy (EELS)

EEL spectrum is composed of three parts depending on the energy loss (Fig. 6b). These regions also represent different applications of EELS.

(1) Zero-loss peak (ZLP) contains electrons without any loss. Its FWHM defines the energy resolution of EELS (~0.8 eV).

(2) Low-loss region contains electrons after interaction with valence-band electrons (VEELS) and plasmon interactions (1 - 100 eV). From the intensity ratio of plasmon/ZLP, thickness of the sample can be determined (including amorphous materials). VEELS gives information on optical properties (e.g., band gap, plasmonic excitations) and electronic structure (e.g., dielectric constant).

(3) High-loss region contains core-loss edges (100 - 3,000 eV). The area under the edge reflects concentration of the element, while the shape depends on oxidation state and bonding. In EELS compared to EDS, light elements such as He, B, N can be analysed. In addition, signal from elements overlaps in EDS is usually well separated in EELS (e.g., Ti and N).

8. SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM)

In the scanning transmission electron microscopy (STEM), the microscope lenses are adjusted to create a focussed convergent electron beam (probe) at the sample surface. This focussed probe is then scanned across the sample and various signals are collected point-by-point to form an image. The convergence of the beam destroys its coherency, so the dominant contrast comes from incoherent elastic scattering of electrons (Rutherford scattering) which is dependent on the atomic number Z squared. Therefore, the method is called Z-contrast imaging or very often also high-angle annular dark field (HAADF) imaging after the detector used for collecting the signal. Z-contrast images have double the resolution of coherent images, and do not reverse contrast with focus or specimen thickness. The images represent a direct map of the scattering power at atomic resolution. There is no phase problem in an incoherent image, so it can be directly inverted to the object, avoiding the need for numerous simulations of trial structures.

High-resolution compositional maps and line profiles may also be obtained in the STEM mode by collecting the EDS and EELS signals point-by-point as the electron probe is scanned across the sample. Using the Z-contrast image to locate the probe over specific atomic columns, EELS and EDS may be performed to give composition and electronic structure information at atomic resolution.

9. STATE-OF-THE-ART S/TEM

Spherical (Cs) and chromatic (Cc) aberrations of lenses limit the resolution of conventional electron microscopes to about $d = 100\ \lambda$. The wavelength of the electrons at an acceleration voltage of 200 kV is roughly 2.5 pm giving a resolution limit of about 0.25 nm, which does not suffice to resolve individual atoms of non-periodic objects. Both aberrations are unavoidable in the case of static rotationally symmetric electromagnetic fields (Scherzer's theorem). The breakthrough came with the use of non-round lenses, the principle of which were first outlined by Scherzer in 1947 [6]. These multipole lenses are capable of generating a negative value of spherical/chromatic aberration and thus can cancel the positive Cs of the round lens.

In the state-of-the-art instruments [7], two types of spherical aberration correctors are commercially available:
(1) Image corrector for TEM - cancelling Cs of objective lens;
(2) Probe corrector for STEM - cancelling Cs of condenser lens.

The resolution of aberration-corrected S/TEM is nowadays approx. 50 pm in both modes. Development of Cc corrector for imaging is important for low voltage S/TEM (20 - 80 kV) and is currently under development [8]. As the quality of the incident beam affects all the outcoming S/TEM signals, a great effort has been put into the development of beam monochromators, which are now also available commercially. They are mostly beneficial for the energy resolution of EELS, which has been reduced from 0.8 eV in non-monochromated sources to tens of meV in monochromated instruments. Such advancements in technology opened the doors for qualitatively new scientific results such as atomic resolution in EDS, EELS and even 3D tomography.

10. ADVANCED APPLICATIONS

10.1. 3D atomic resolution tomography

Over the last two decades, three-dimensional (3D) imaging by TEM or "electron tomography" has evolved into a powerful tool to investigate a variety of nanomaterials in different fields. Most of these results were obtained with nanometre-scale resolution, but different approaches have recently pushed the resolution to the atomic level [9]. Usually, only a few zone-axis STEM/HAADF images are used as the input. The investigations of shape of nanoparticles, interfaces, defects, and lattice deviations with the same resolution in noble materials with a typical fcc crystal structure (Au, Pt) were carried out. However, determining the positions of the atoms in an unknown crystal structure remains challenging.

10.2. Structure determination by 3D electron diffraction

Crystallography of nanocrystalline materials has witnessed a true revolution in the past 10 years, thanks to the introduction of protocols for 3D acquisition and analysis of electron diffraction data (3D ED). This method provides single-crystal data suitable for structure solution and refinement, allowing the atomic structure determination of those materials that remained hitherto unknown because of their limited crystal size. Several experimental protocols exist, which share the common idea of sampling a sequence of diffraction patterns while the crystal is tilted around a non-crystallographic axis, the goniometer axis of the TEM sample stage [10]. Structure refinement using dynamical diffraction theory has brought structure determination from 3D ED data to the level of single-crystal X-ray diffraction analysis [11, 12].

10.3. 4D STEM

Recent advances in detector technology and computational methods have enabled many experiments that record a full image of the STEM probe for many probe positions, either in diffraction space or real space. These four-dimensional STEM (4D STEM) experiments are the basis for number of techniques such as virtual diffraction imaging, phase, orientation and strain

mapping, measurements of medium-range order, thickness and tilt of samples, and phase contrast imaging methods, including differential phase contrast for measuring electric and magnetic fields, and ptychography [13].

10.4. Aloof EELS – vibrational spectroscopy

Electron energy loss spectroscopy (EELS) in the electron microscope has progressed remarkably in the last five years. Advances in monochromator and spectrometer design have improved the energy resolution attainable in a STEM to 4.2 meV, and new applications of ultrahigh-energy resolution EELS have not lagged behind. They include vibrational spectroscopy in the electron microscope, a field that did not exist 5 years ago but has now grown very substantially. Notable examples include vibrational mapping with about 1 nm spatial resolution, analysing the momentum dependence of vibrational states in very small volumes, determining the local temperature of the sample from the ratio of energy gains to energy losses, detecting hydrogen and analysing its bonding, probing radiation-sensitive materials with minimized damage by aloof spectroscopy and leap-frog scanning, and identifying biological molecules with different isotopic substitutions [14].

11. REFERENCES

[1] De Graef M 2003 *Introduction to conventional transmission electron microscopy*. [Cambridge, UK: Cambridge University Press]

[2] Fultz B and Howe J M 2008 *Transmission electron microscopy and diffractometry of materials* (First edition 2001, second edition 2002, third edition 2008) [Berlin, Germany: Springer]

[3] Williams D B and Carter C B 2009 *Transmission electron microscopy* (First edition 2004, second edition 2009). [New York, NY: Springer]

[4] Delille D, Pantel R, Vincent G and Van Cappellen E 2002 *Ultramicroscopy* **93** 1-9

[5] Lorimer G W 1987 *Mineralogical Mag.* **51** 49-60

[6] Scherzer O 1947 *Optik* **2** 114-132

[7] Erni R 2015 Aberration-corrected Imaging. in: *Transmission electron Microscopy: An Introduction* (2nd Edition). [London, UK: Imperial College Press].

[8] Linck M, Hartel P, Uhlemann S, Kahl F, Muller H, Zach J, Haider M, Niestadt M, Bischoff M, Biskupek J, Lee Z, Lehnert T, Borrnert F, Rose H and Kaiser U 2016 *Phys. Rev. Lett.* **117** 076101

[9] Bals S, Goris B, De Backer A, Van Aert S and Van Tendeloo G 2016 *MRS Bull.* **41** 525-530

[10] Gemmi M, Mugnaioli E, Gorelik T E, Kolb U, Palatinus L, Boullay P, Hovmoller S and Abrahams J P 2019 *ASC Central Sci.* **5** 1315-1329

[11] Palatinus L, Petříček V and Correa C A 2015 *Acta Crystallographica A* **71** 235-244

[12] Palatinus L, Correa C A, Steciuk G, Jacob D, Roussel P, Boullay P, Klementová M, Gemmi M, Kopeček J, Domeneghetti M C, Camara F and Petříček V 2015b *Acta Crystallographica B* **71** 740-751
[13] Ophus C 2019 *Microsc. Microanal.* **25** 563-582
[14] Krivanek O L, Dellby N, Hachtel J A, Idrobo J-C, Hotz M T, Plotkin-Swing B, Bacon N J, Bleloch A L, Corbin G J, Hoffman M V, Meyera C E and Lovejoy T C 2019 *Ultramicroscopy* **203** 60-67