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Transmission Electron Microscopy
III - Spectroscopy

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Electron Energy Loss Spectrometry

Electrons that are inelastically (forward) scattered in the TEM are used for chemical analysis of the specimen. Electron energy loss spectrometry (EELS)

The inelastic scattering process can promote:

1) The transition of an electron from an inner-shell (K,L,M) to an unoccupied energy level (i.e. above the Fermi level) or to the vacuum (ionization).

2) Transition of a valence electron across the energy gap (insulators and semiconductors) or excitation of a plasmon resonance (collective oscillation of free electrons)

The energy loss by the incident electrons is characteristic of the chemical properties of the specimen

In EELS we are interested in measuring the "number of electrons" that have lost a given amount of energy. -> this traduces the relative probability that a particular transition occurs

When a core electron is promoted to an unoccupied state, the density of these final states determines the relative probability of the transition

By EELS one can study the electronic structure (Density of states above the Fermi level) of a material with resolution at the nanometer scale !

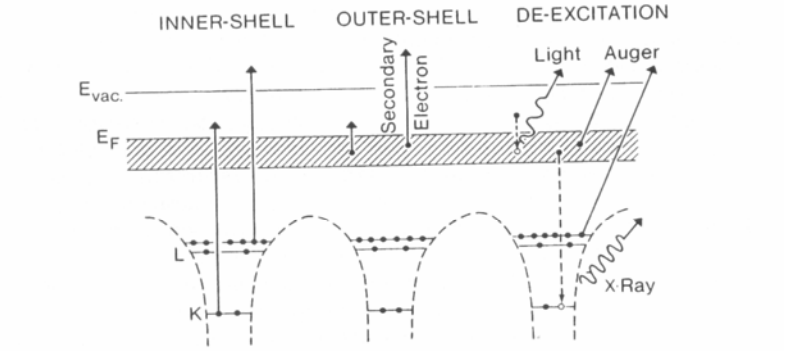

Figure 1.2. Energy-level diagram of a solid, including K- and L-shell core levels and a valence band of delocalized states (shaded); E_F is the Fermi level and E_{vac} the vacuum level. The primary processes of inner- and outer-shell excitation are shown on the left, secondary processes of photon and electron emission on the right.

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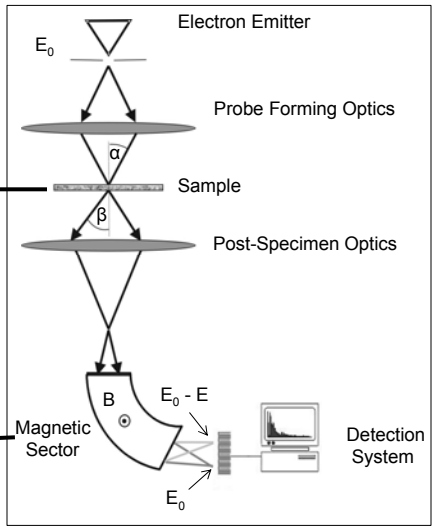
Principle of EELS

TEM with a post-column EELS Spectrometer

Philips CM200 FEG



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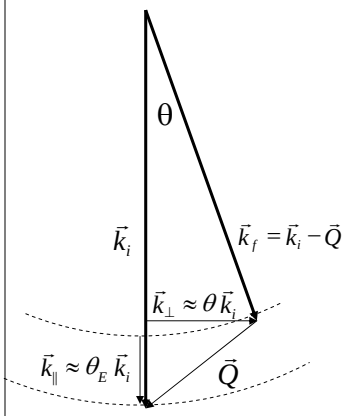
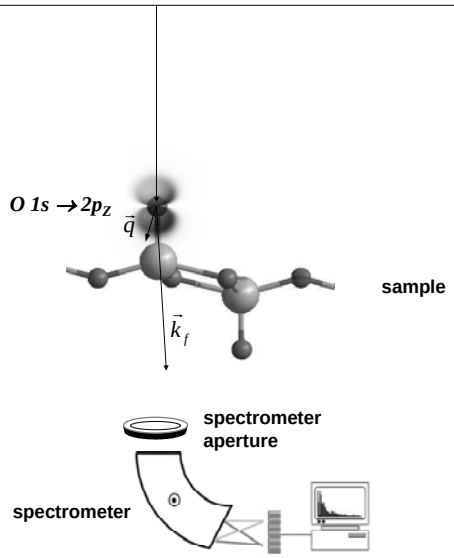
Principle of EELS

Momentum transfer





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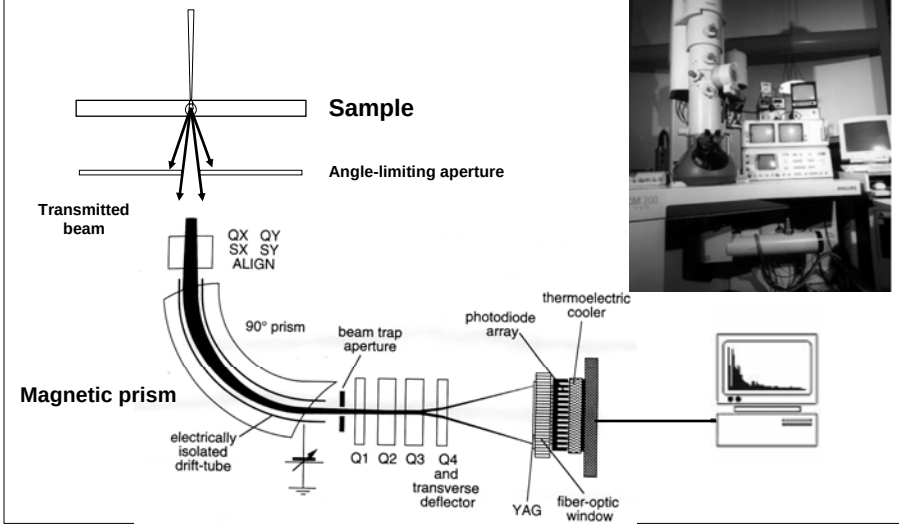
Energy Filter



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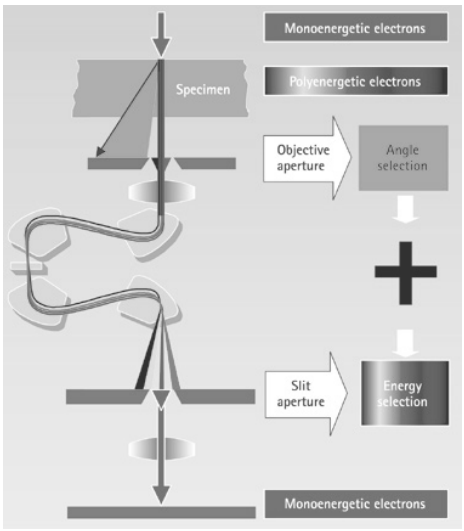

JEOL JEM2200FS

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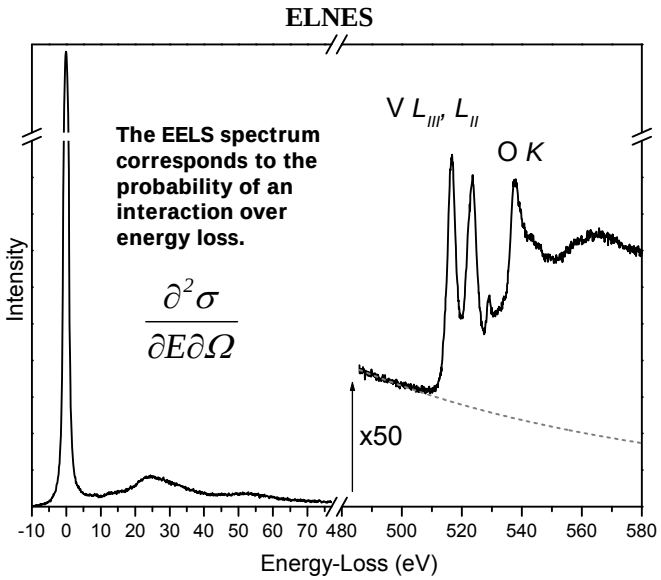
ELNES



The EELS spectrum corresponds to the probability of an interaction over energy loss.

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega}$$

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What kind of information do you get?

1 – Elemental composition

2 – Chemical information

3 – "Structural" information

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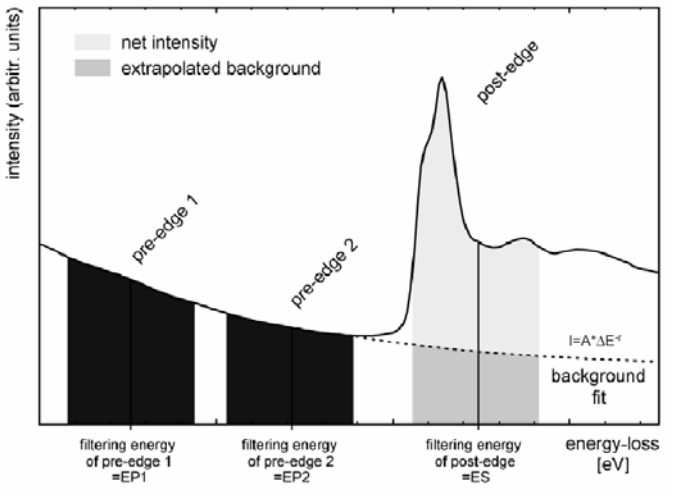
Using energy loss electrons for imaging



G. Kothleitner, Felmi, Graz, Austria

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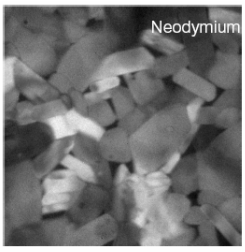
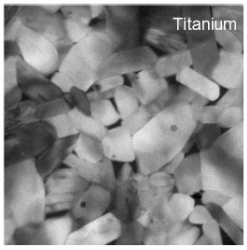
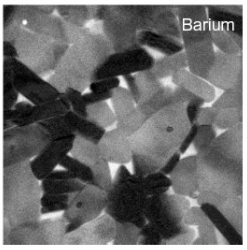
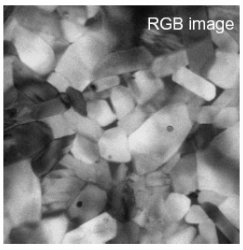
Elemental Composition: EFTEM









3 images/element using:

Nd M_{45} edge: @ 978 eV
Ti L_{23} edge: @ 455 eV
Ba M_{45} edge: @ 781 eV

Color overlays,RGB images:

- assign a color to each elemental map: Ti green, Nd blue and Ba red
- superimpose three color layers to form RGB composite

shows chemical phase distribution qualitatively only

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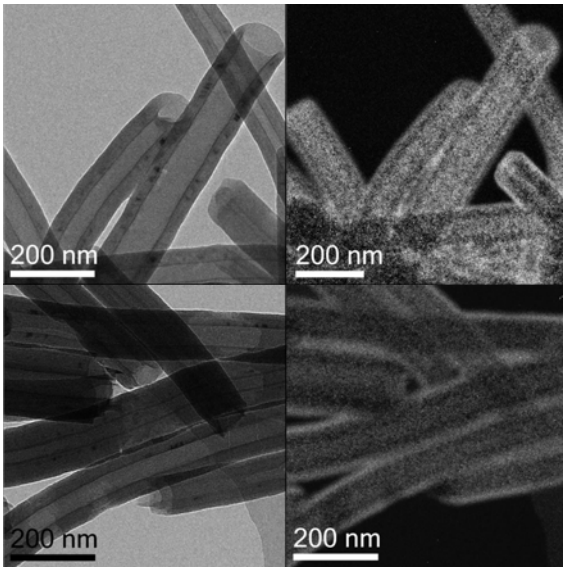
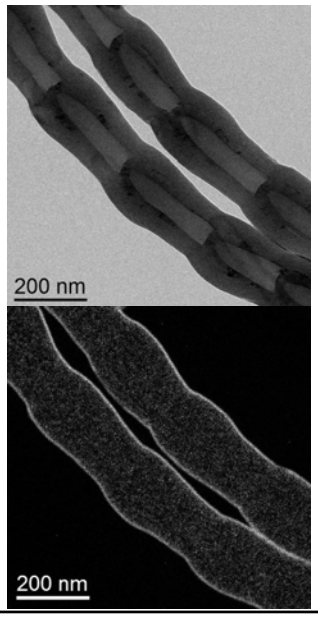
Energy filtering in images





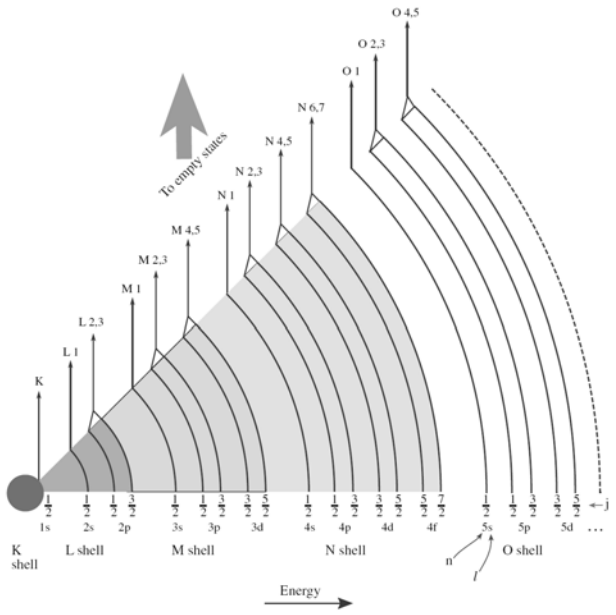


FIGURE 39.1. The full range of possible edges in the energy-loss spectrum due to core-shell ionization and the associated nomenclature.

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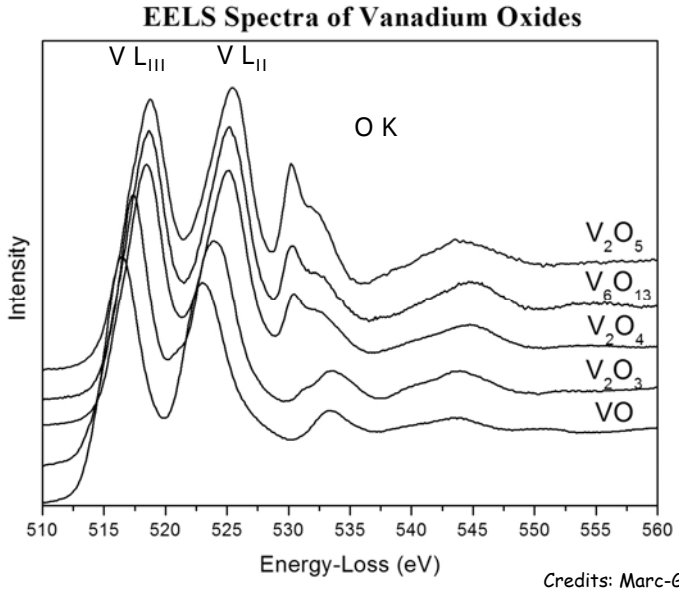
Chemical Information



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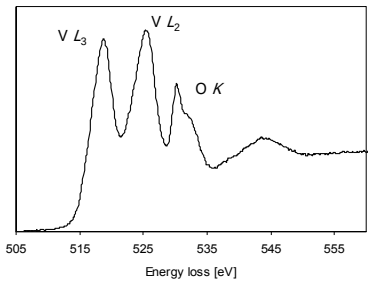
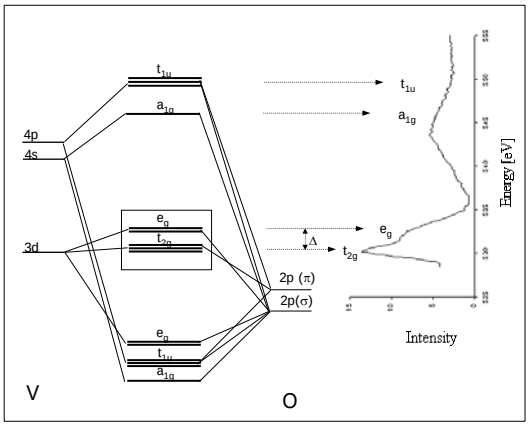
Chemical Information

V L-edge and O K-edge of V_2O_5:



Molecular orbital energy-level diagram and an O-K ELNES of V_2O_5:



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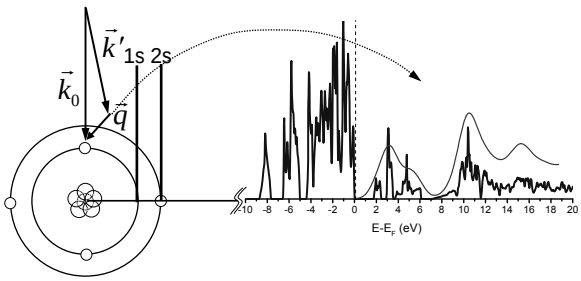
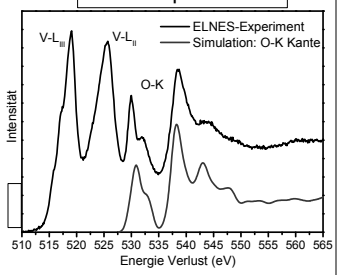
The near edge fine structure (ELNES)

Excitation of an electron from a core shell...

... into an unoccupied state above the Fermi-level



EELS Spectra



O Atom $\frac{\partial^2\sigma}{\partial\Omega\,\partial E} \propto \frac{1}{\vec{q}^4}\sum_F\sum_I \left|\langle I|e^{i\vec{q}\vec{R}_j}|F\rangle\right|^2 \delta\left(E-(E_F-E_I)\right)$ { Matrix element term & density of states term (DOS)

Dipole Approximation & Orthogonality of $|i\rangle, |f\rangle$: $\langle f|e^{i\vec{q}\vec{R}}|i\rangle \Rightarrow \langle f|i\vec{q}\vec{R}|i\rangle$ { **Matrix element equal to XAS**

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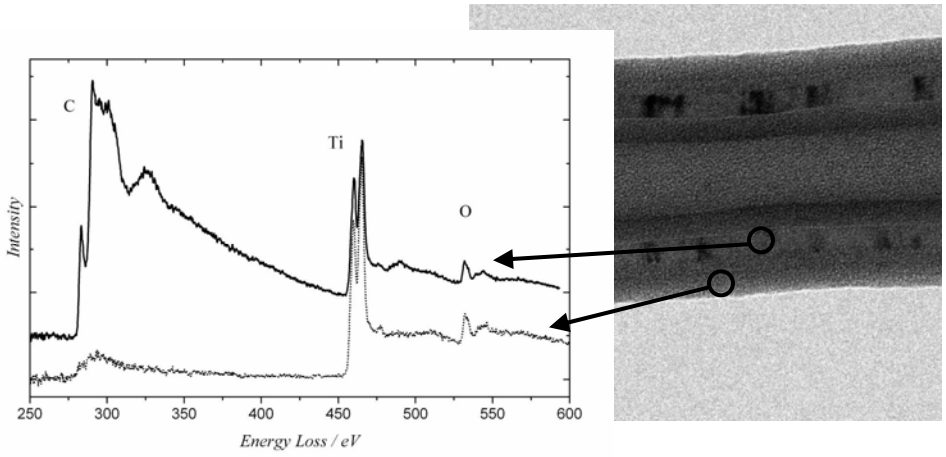
Chemical Information with High Spatial Resolution



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Comparison to X-Ray absorption spectroscopy (XAS)

The fundamental phenomenon underlying is the absorption of an X-ray photon by a core level of an atom in a solid and consequent emission of a photoelectron (EXAFS) or promotion of an electron to an unoccupied orbital.

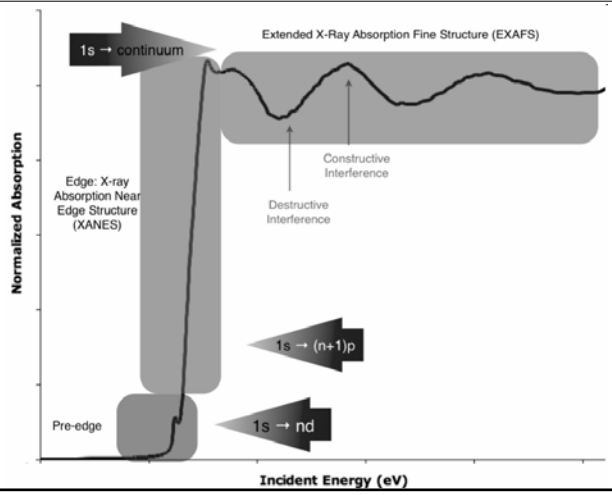
Here we are not interested in studying the photoelectron (XPS) or the deexitation of the ionized atom (Auger – X-ray emission)

In XAS we measure the absorption as a function of the incident energy

Similar information can also be acquired by collecting the fluorescence intensity as a function of the incident energy of the X-rays

Finally, the information acquired is similar to EELS (information on the unoccupied states)

The absorption edge structure often consists of discrete absorption bands superimposed on the steeply rising continuum absorption edge. These discrete absorption bands are caused by transitions of core electrons to discrete bound valence levels. The absorption edges that are of most interest are the K-edge (e.g. 1s – 3p), followed by the three L-edges. These edges are element specific and shifts to higher energies when the atomic number increases. Since the core levels depend on the element and its chemical environment, they also show chemical specificity. X-ray absorption spectroscopy is therefore not only an element specific technique, but it is also sensitive to the immediate environment of the absorbing atom.



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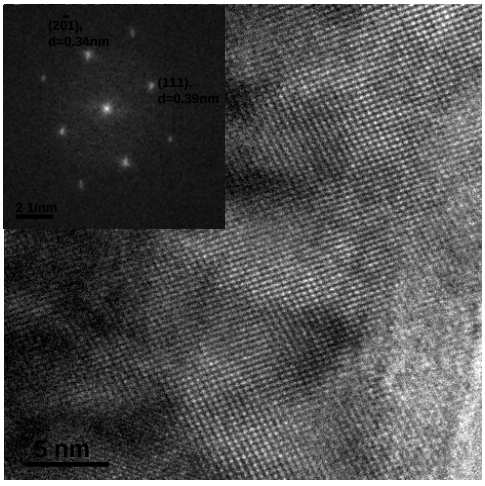
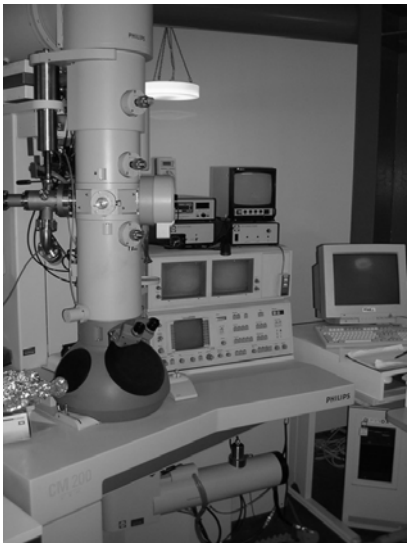
Synchrotron-TEM: NEXAFS-EELS





TEM offers very high spatial resolution!

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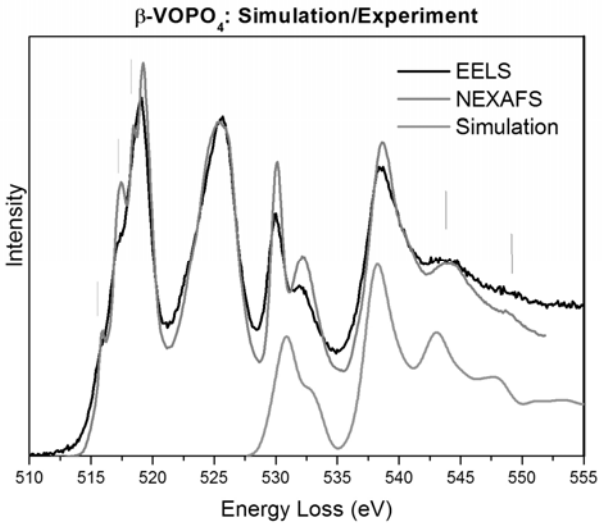
Synchrotron-TEM: NEXAFS-EELS



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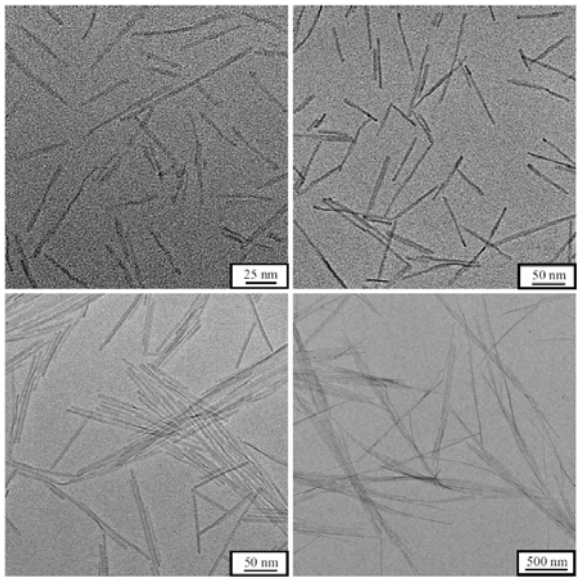
Size Control of V_2O_5 nanorods and nanowires



N. Pinna, U. Wild, J. Urban, R. Schlögl. Adv. Mat. 15, 329, 2003

Vanadium Pentoxide Structures

α-V_2O_5 γ-V_2O_5

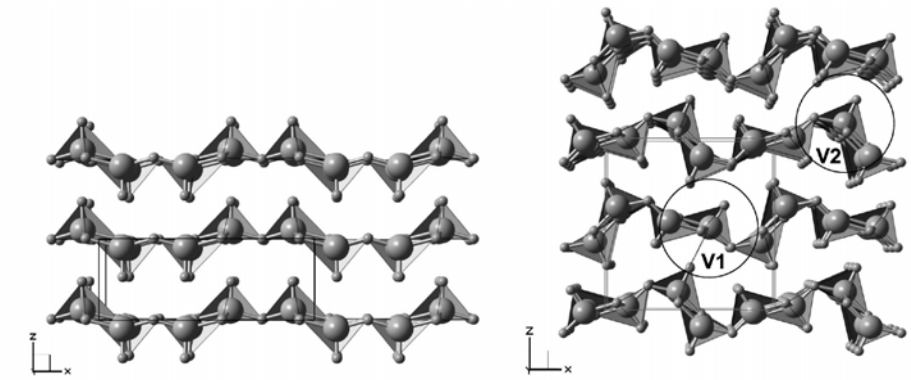


FIG. 1. Crystal structure of α-V_2O_5 and γ-V_2O_5. The orthorhombic unit cells are indicated; a, b, and c are parallel to x, y, and z, respectively. Circles labeled V1 and V2 highlight the two differently surrounded vanadium sites existing in γ-V_2O_5.

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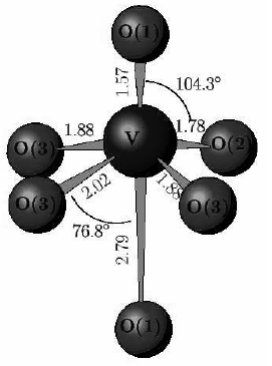
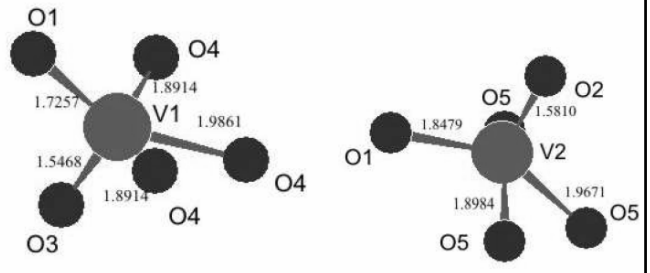
α-V_2O_5 γ-V_2O_5

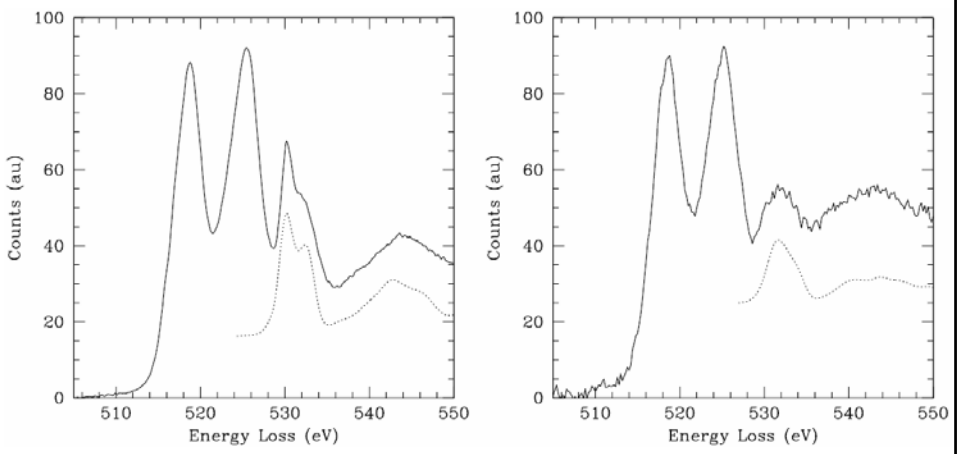




Atom1	Atom2	Distance (Å)
V	O1	1.5759
V	O2	1.7783
V	O3	2.0176
V	O3	1.8776

Atom1	Atom2	Distance (Å)
V1	O1	1.7257
V1	O3	1.5468
V1	O4	1.8914
V1	O4	1.9861
V2	O1	1.8479
V2	O2	1.5810
V2	O5	1.8984
V2	O5	1.9671

Electron Energy Loss Spectroscopy



N. Pinna, M. Willinger, K. Weiss, J. Urban, R. Schlögl, Nano Lett, 3, 1131, 2003

M. Willinger, N. Pinna, D.S. Su, R. Schlögl, Phys. Rev. B, **2004**, 69, 155114

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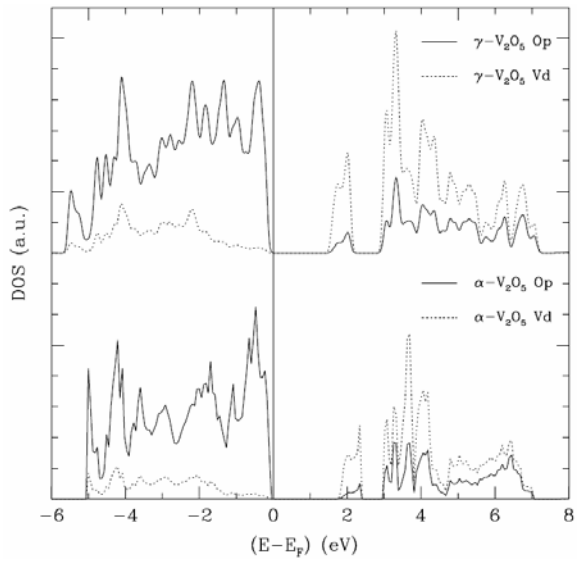
Density of States



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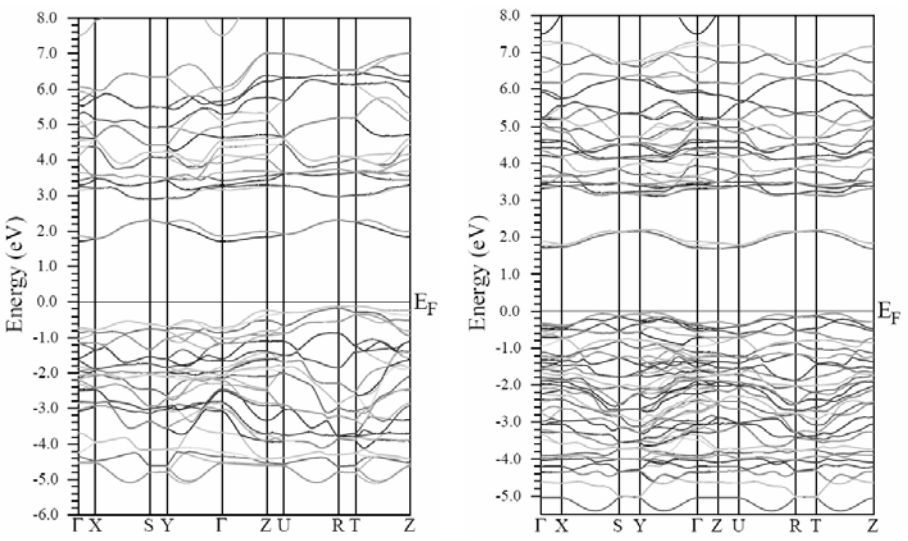
Band Structure

α-V_2O_5 γ-V_2O_5



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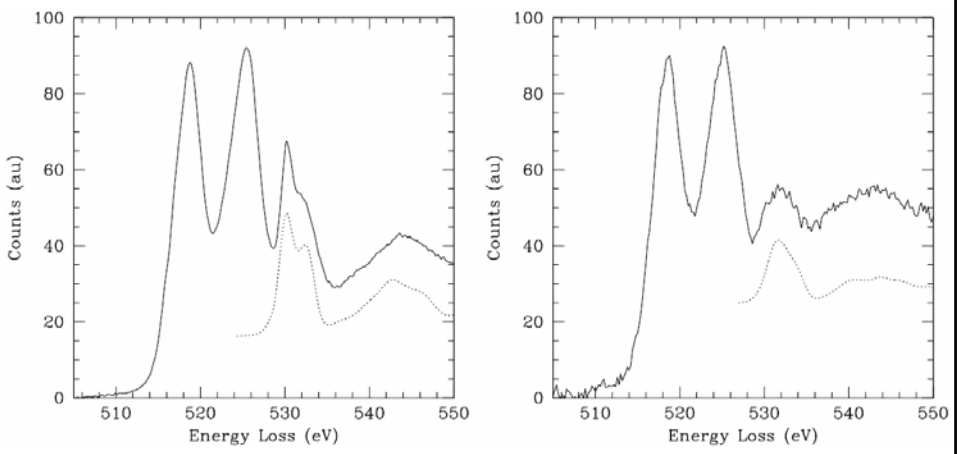
Electron Energy Loss Spectroscopy



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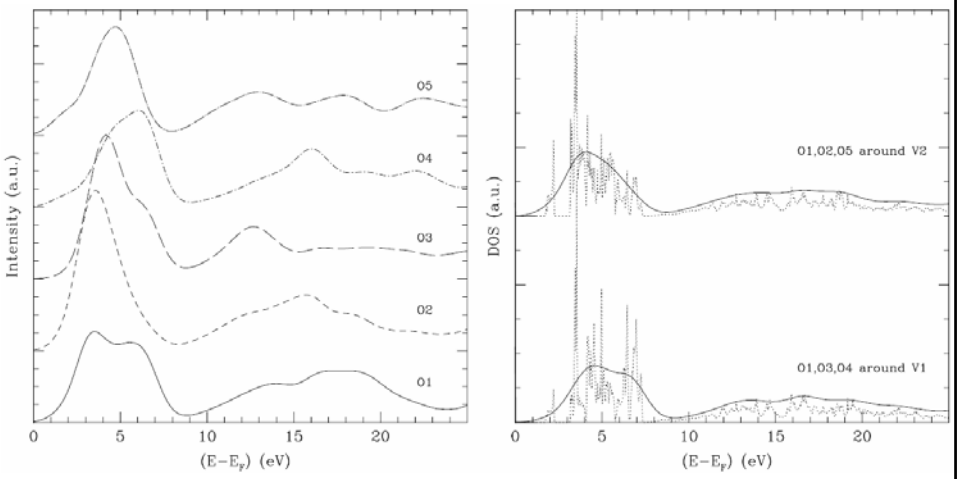
Electron Energy Loss Spectroscopy



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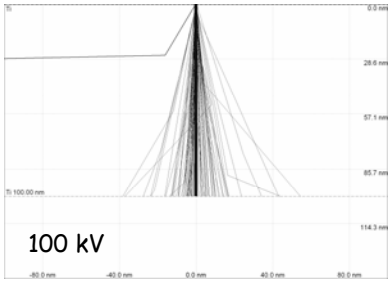
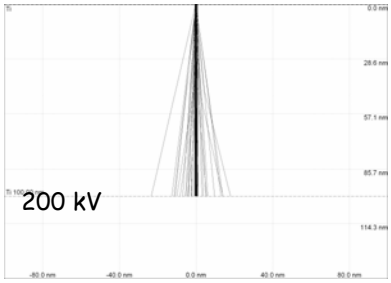
EDX – TEM vs. SEM

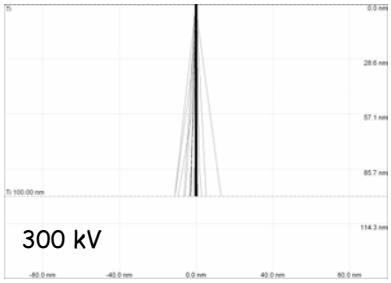
Simulation of the electron trajectories in a solid constituted of 100 nm thick Ti film

- 1000 electron trajectories are displayed
- Incident energy varies from 100 to 300 keV (step 100 keV)

EDX in the TEM: resolution just slightly lower than the probe size! Resolution increases with incident energy!







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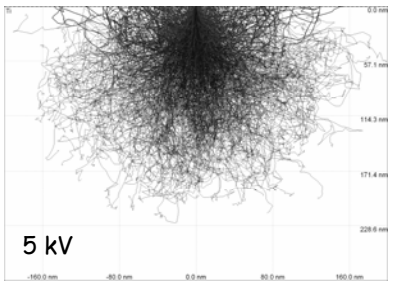
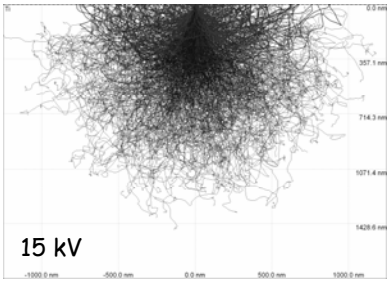
EDX – TEM vs. SEM

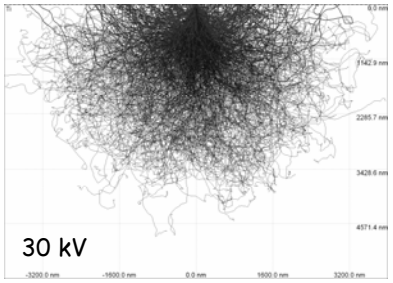
Simulation of the electron trajectories in a bulk solid constituted Ti

- 1000 electron trajectories are displayed
- Incident energy varies from 5 to 30 keV

EDX in the SEM: resolution much lower than the probe size! Resolution decreases with incident energy!







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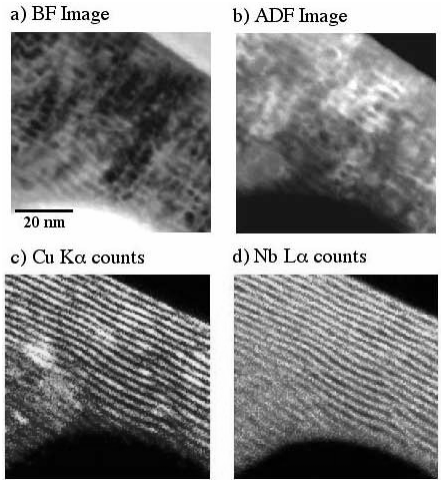
EDX map from a Cu/Nb multilayer

Electron Microscopy Group in the Department of Materials Science and Metallurgy, University of Cambridge



http://www-hrem.msm.cam.ac.uk/hrem/index.shtml