

Introduction to Inelastic Scattering Interaction (EELS) or Relaxation (EDX)

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With material shamelessly stolen from Gerald Kothleitner (FELMI) Graz University of Technology, Austria







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- Specialised high-resolution electron microscopy and spectroscopy laboratory, based on the STFC SciTech Campus in Daresbury.
- Operates the U.K. National Research Facility for Advanced EM, a free-at-thepoint-of-use open access scheme funded by EPSRC and regulated on scientific merit via a proposal system.
- Strong community and academic links through the 'SuperSTEM Consortium', currently including the universities of Leeds, Liverpool, Manchester, Oxford, Glasgow and York.







https://www.superstem.org/access





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- User PublicationsComplaints



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SuperSTEM capabilities





- Dedicated STEM instruments 1V-100kV for atomic resolution at 'gentle' conditions
 - Nion UltraSTEM Cs-corrected STEM, EELS (DED), EDX
 - Nion UltraSTEM Cs-corrected MC, EELS (DED) 6meV ZLP FHWM
 - Hitachi SU9000 T(SEM), EDX, EELS
 - New spectroscopies: vibrational, momentum-resolved spectroscopy
- Sample interactions: electrothermal, cryo-stage
- Multi-modal microscopy: 4D STEM, imaging etc..

Nanofabrication – Sample prep SuperFIB - Hitachi Ethos NX5000



- Triple beam system with electron, 30 kV Ga ion and low-kV Ar ion 'polisher' beam
- 7-axis substage, cryo-capable side entry holder





Fischione Model 1040 NanoMill for polishing of FIB specimens

Fischione Model 1051 ion beam polisher

We are hiring!!!

Postdoctoral Research Associate/Fellow

Photocatalysts Mapping using Super-resolution Electron Microscopy







Contact us:

www.lanternaresearchgroup.com anabel.lanterna@nottingham.ac.uk dmkepap@superstem.org vlado.lazarov@york.ac.uk



UNIVERSITY



Electron microscopy beyond imaging & diffraction







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Electron microscopy beyond imaging & diffraction







- Microanalysis
- Phase & bonding
- Optical excitations
- Plasmonics, Phonons etc
- Microanalysis



J. Hachtel et al Scientific Reports (2018)

https://www.gatan.com/resources/media-library/fast-joint-eels-eds-colormap-across-32-nm-transistor-device?modal=1

A simple particle picture of scattering





Electrons can undergo both elastic and inelastic scattering events (often multiple)

E > 50eV elemental analysis E ~ 1eV – 50 eV various uses

A simple particle picture of scattering







*see Sean's talk tomorrow

R. Egerton, Electron Energy Loss spectroscopy in the Electron Microscope, 3rd edition

Inner-shell inelastic scattering & relaxation



Interaction

- If $E_0 > E_c$ then an inner shell electron may be *ionized*
- An inner-shell electron is ejected from the core level
- The ejected core electron can only scatter into unoccupied states above E_F
- The incident electron has lost kinetic energy

Relaxation

The excited atom will return to its ground state

- The core hole will be filled an electron from an outer shell (single or cascade of events)
- During this secondary process an X-ray <u>may</u> be emitted



Interact : Electron Energy Loss Spectroscopy

- Instrumentation for EELS
- Background theory
 - Basic edge Shapes
 - Near Edge Fine structure
- Qualitative / Quantitative analysis
- Some additional considerations
- Examples





Very long story...

- **1929:** First report on Electron Loss (Rudberg, Nobel Inst.)
- **1941:** First EEL spectrum from transmitted electrons (Ruthemann, Gdansk)
- 1968 : First EDS detector (Fitzgerald, UCL)
- Plenty of things happening
- 1993: First atomic resolution spectrum plane-by- plane (Browning, ORNL)
- 2004: First single atom EELS (Varela, ORNL)
- 2006: First 2D EELS map (Bosman, SuperSTEM & Kimoto, NIMS)
- 2012: First single atom EDXS (Suenaga, AIST & Lovejoy, SuperSTEM)
- **2012:** Bonding changes in single graphene dopants (Zhou, ORNL & Ramasse, SuperSTEM)
- 2013: Atomically resolved EFTEM (Urban, Juelich)
- 2014: Vibrational spectroscopy (Krivanek, Nion & Mizoguchi, U Tokyo)
- 2016: Spatially resolved phonon spectroscopy (Dwyer, ASU)
- 2018: Atomic resolution phonon spectroscopy (Hage, SuperSTEM)

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Characteristic Energy Lasses of Electrons Scattered from Incandescent Solids.

By KRIN RUDBERR, Nobel Institute, Stockholm, Sweden.

(Communicated by O. W. Richardson, F.B.S .-- Received January 15, 1950.)

Introduction. The electron emission produced when solid conductors are bombarded with electrons of controlled speed has formed the subject of a great number of investigations. It is now generally recognized that this emission consists of these different parts: (1) Primary electrons, truly reflected without loss of Microanalysis by Means of Electrons

JAMES HULLER AND R. F. BAKER RCA Laboratories, Princeton, New Jersey (Received June 26, 1944)

E. Rudberg, Proc. R. Soc. Lond. A 127 (1930) p 111 Ruthemann, Naturwissenschaften 29 (1941) p 648



On a Search for Radiation accompanying the Scattering of Comparatively Slow Electrons at the Surface of Incandescent Solids.

By ERIK RUDBERG, Nobel Institute, Stockholm, Sweden.

Diskrete Energieverluste schneller Elektronen in Festkörpern.

Energieveçluste schnellerer Elektronen beim Durchgang durch Festkörper sind bisher meist nur an Folien von mehreren 1000 AE. Dicke beobachtet worden¹). Dabei tritt als Folge von Vielfachprozessen ein kontinuterliches Geschwindigkeitspektrum auf, dessen Intensitätsmaximum von dem bekannten WHIDDINGTONSchen Gesetz ($v_0^* - v_2^* = a \cdot d$ angegeben wird²).







820 850 88 E loss (eV)





Electron Energy loss spectrum















Post column filter













CEOS - CEFID

- The magnetic field of the prism bends the electron trajectory and causes energy-dependent dispersion
- Focusing effect –electrons of a given energy will be returned to a single image point in the dispersion plane

Simple older generation PEELS

- Q0 focusing electrons at spectrometer entrance
- Q1 focusing electrons along the nondispersive direction (squashing q)
- Q2,3 magnifying parts of the dispersion

Gatan Continuum

Nion (Bruker) IRIS

SuperSTEM





Also Thermo ILIAD, Hitachi spectrometer



Scattering vectors and angles





Know your optical conditions in numbers (mrad)!!

Inelastic processes are strongly forward scattered small angle scattering (< 10 mrad)

Spectroscopy in STEM vs TEM





STEM EELS (or EDX) mapping





- STEM EELS geometry allows for simultaneous imaging and 2D spectroscopy
- 1-to-1 correlation of structural and chemical information!!



The double differential cross-section

- Proportional to the number of incident probe particles scattered within an energy range ΔE and momentum variation into a solid angle $\Delta \Omega$ $\frac{d^2\sigma}{d\omega dE} \propto S(k,\omega)$
- The dynamic Structure Factor is a mathematical representation of the space and time-dependent structure within the system
- It describes inter-particle correlations and their time evolution ; contains the transition probability amplitudes from an initial **|i>** to a final state **|f>**
- *Depends on the transition and energy* & can be expressed by different theoretical approaches



Dynamic Structure Factor: An Introduction*

K. Sturm

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-W-5170 Jülich

Z. Naturforsch. 48a, 233-242 (1993); received December 10, 1991

The doubly differential cross-section for weak inelastic scattering of waves or particles by manybody systems is derived in Born approximation and expressed in terms of the dynamic structure factor according to van Hove. The application of this very general scheme to scattering of neutrons,



Inelastic Scattering – Basic edge shapes

The double differential scattering cross-section is calculated assuming:

(i) First order perturbation theory (first Born approximation for scattering) > Single scattering event

(ii) A plane-wave description of the fast electron > Neglects propagation/channelling in the crystal
(iii) An electrostatic interaction (instantaneous) between the fast electron and the solid

$$I(E, \Theta) \propto \frac{d^2\sigma}{dEd\Omega} = \frac{4\gamma^2}{a_0q^4} \times \frac{1}{(\Theta^2 + \Theta_E^2)} \times \sum_f |\langle fexp(iqr)i\rangle|^2$$

$$Amplitude factor^{**}$$
Depends on the incident e-
Depends on the excited atom

The Inelastic form factor contains a Transition Matrix Element determines the basic edge shape and the cross-section, which can be calculated using free atom models.

- Represents probability for an atom to transition from one energy state to another due to the interaction with the incoming particle
- Depends on the wave functions of the initial ψ_0 and final states ψ_n
- The overlap will be similar for each set of initial and final states e.g.: $s \rightarrow p$: sawtooth-like as for K & L1
- To a first approximation the TME varies slowly with energy



**Rutherford scattering formula describes the final direction ϑ that a particle will scatter

Core loss EELS - ionization edges:

- The ionization edges are classified according to standard spectroscopic notation
 - K:1s \rightarrow
 - − $L_1: 2s \rightarrow$
 - $L_2: 2p_{1/2} \rightarrow$
 - − $L_3: 2p_{3/2} \rightarrow$
 - The subscript refers to the total angular momentum (sum of orbital angular momentum, plus spin)
- K edges: rationalise with the density of unoccupied states.
- L, M, ... edges: solid state effects dominate, use multiplet theory for calculations.



G. Radtke and G.A. Botton, chapter 5 in STEM, P.D. Nellist and S.J. Pennycook (Eds.) D.B. Williams and C.B. Carter, Transmission Electron Microscopy, Springer (2009)



Qualitative analysis – Basic edge shapes





- The energy position of the ionisation edge is element dependent – monotonic with Z
- Shape of the ionisation edge is specific for type of transition

arrier ᅙ	6:03	РМ
〈 Match	ies Thuli	um (
69		Weight: 168.9 Density: 9.32 g/cr
Τ	m	Principle Edges:
m		180 6
Major E	dges	
O	32 eV	
N _{4,5}	180 eV	
$M_{_{5}}$	1468 eV	
M₄	1515 eV	L
Minor E	dges	
0,	53 eV	
N _{2,3}	337 eV	1

Gatan EELS Atlas App

Core edge background





a) bkgd 30 Counts x 10^4 20 10 176 eV 104 eV -280 eV 160 180 200 220 240 260 280 300 320 340 360 eV b) 40 bkgd 30 Counts x 10^4 20 10 249 eV--31 eV--280 eV 160 180 200 220 260 280 300 320 340 360 240 eV

40

In the simplest case the ionization edges ride the tail of the plasmon peak

Can be modeled by a power law decay •

J(E)=AE^{-r}

A = Scaling constant r = Slope exponent

Elemental mapping at different length scales





Chemical mapping of light elements (source JEOL)





Core/shell $Fe_3O_4/Mn_xFe_{3-x}O_4$ nanoparticles Sci Rep (2018) 8 , 3425



Atomically resolved mapping in nickelates Nature Comms (2024) 15, 378

Which edges can be used for identification?



- Convenient edges are typically between the 100 2500 eV
- EELS is not really suitable for **black box** microanalysis prior information is needed

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Inelastic Scattering – ELNES



Bonding imposes an additional term:
$$I(E, \Theta) \propto \frac{d^2\sigma}{dEd\Omega} = \frac{4\gamma^2}{a_0q^4} \times \frac{1}{(\Theta^2 + \Theta_E^2)} \times \sum_f |\langle fexp(iqr)i \rangle|^2 \times N_f(E)$$

- The density of final states (DOS) considers overlap of outer electrons w/ those on neighbouring atoms
- Each individual cross section from the initial state to all possible final states requires to be weighted by the number of final states available at a particular energy



Inelastic Scattering – ELNES



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Dipole approximation

Assuming small q allows for some additional mathematical simplifications

$$I(E, \Theta) \propto \frac{d^2\sigma}{dEd\Omega} = \frac{4\gamma^2}{a_0q^4} \times \frac{1}{(\Theta^2 + \Theta_E^2)} \times \sum_f |\langle qr \rangle i|^2 \times N_f(E)$$

- For a transition to occur the final state needs to be unoccupied
- **TME** only has significant magnitude when final state has a component localized at the same atomic site sufficient to overlap with the initial state at the core
- TME ≠ 0 when △ℓ= ±1 (dipole selection rule), wave-function symmetry has to change during transition
- Because the TME hardly varies w/ energy, DOS term determines ELNES and reflects atomic environment and bonding
- Therefore, ELNES probes the local (site), symmetry-projected, unoccupied, partial DOS

In practice –finite aperture size non diple effects are included – however due to the $1/q^4$ pre factor the dipole term dominates.

R. Egerton, Electron Energy Loss spectroscopy in the Electron Microscope, 3rd edition *G.* Radtke and G.A. Botton, chapter 5 in STEM, P.D. Nellist and S.J. Pennycook (Eds.)



Taylor series expansion

$$\exp(iqr) = 1 + qr - \frac{1}{2!}(qr)^2 + \cdots$$

For orthogonal wavefunctions

for small q (and q*r) higher order terms can be neglected -

Core state	Spectroscopic name	Symmetry of the probed LDOS
1 <i>s</i>	К	р
2 <i>s</i>	L ₁	р
$2p_{1/2}$ and $2p_{3/2}$	L ₂₃	s + d
3s	M ₁	р
$3p_{1/2}$ and $3p_{3/2}$	M ₂₃	s + d
$3d_{3/2}$ and $3d_{5/2}$	M_{45}	p + f
4s	N ₁	p
$4p_{1/2}$ and $4p_{3/2}$	N ₂₃	s + d
$4d_{3/2}$ and $4d_{5/2}$	N45	p + f
$4f_{5/2}$ and $4f_{7/2}$	N ₆₇	d + g

ELNES fingerprinting







Initial approach: compare ELNES with literature data & XANES









Small practical break?!





Made of stardust



Figure adapted, with permission from https://doi.org/10.1111/maps.13389 Terrestrial Weathering Parent body alteration by fluid reactions 500 nm 20 pc **Fischer-Tropsch reactions** on catalytic mineral surfaces (clays, metal) Chondrite Maribo ¹⁵N/14N RENAZZO 2 µm Emilia, Italien gefailen 15.1.1824



From the solar nebula to the laboratory: organic matter from the parent molecular cloud of our solar system can be found on Earth in primitive extra-terrestrial samples like meteorites. The unique instrumentation at SuperSTEM is exceptionally well-suited to study these materials at the highest energy and spatial resolution. *Image credits: NASA/JPL*



Chemical state mapping of organic inclusions in meteorites

NWA 852





SuperSTEM





PNAS 111(43) 2014

energy (eV)

energy (eV)

Scientific Reports 10 (20251) 2020

Chemical shifts



Core level screening : electrons in a material respond to and reduce the electrostatic influence of a core hole created during an excitation or ionization event.

- The change in the onset energy of a core-loss spectrum influenced by the chemical environment of an atom
- Redistribution of valence charge will alter core level screening and thus change the potential energy of initial core states.
- The final energy states will change depending on the band structure of the material (e.g., Fermi level shift or opening of a band gap in the material).
- General rule higher oxidation \rightarrow higher edge onset



Hybridisation of states



- Mixing of atomic orbitals to form new molecular orbitals influencing the electronic structure of a material.
- Affects the density of states (DOS) and is reflected in the ELNES









- In graphite, 2 2p and 1 2s orbitals hybridize to form sp² orbitals;
 1 2p orbital remains unhybridized, forming π and π* molecular orbitals
- In diamond 2s and all 3 2p orbitals hybridize to form sp³ orbitals, resulting in a tetrahedral bonding structure with no unhybridized p orbitals remaining.
- Sp² solids have both σ/σ* and π/π* states; sp³ solids only have σ/σ* states
- Electron transitions to unoccupied states create characteristic features in EEL spectra:
 - In diamond, excitation of 1s electrons to σ* states produces the carbon K-edge peak.
 - In graphite, inner shell electrons transition into π^* states, generating a peak before the edge; valence electrons also transition into π^* states around 6 eV.

https://www.jeol.com/

Modelling ELNES: find yourself a theory friend!



Band structure Infinite number of atoms	Multiple Scatterin ~ few hundreds ator cluster	n 1 atom
Monoelectronic		Multielectronic
Density of States		Multiplets (overlap of initial and final state WF)
Wien2k (LAPW) http://www.wien2k.at/ Castep (Pseudopotentials) http://www.castep.org/ ELK (FP-LAPW) http://elk.sourceforge.net/ Quantum espresso (coming soon) http://www.quantum-espresso.org/	FEFF http://leonardo.phys.washingt on.edu/feff/welcome.html 	TT-Multiplets http://www.anorg.chem.uu.nl/CTM4XAS/ MultiX http://people.web.psi.ch/uldry/multiplets/ Quanty http://www.quanty.org

Ion-implanted graphene









Nano Letters 13, 4902-4907 (2013), ACS Nano 11, 11398-11407 (2015)
Spectroscopic signature: *p*-type doping





 Band structure calculations : missing charge density on the B dopant causes the Fermi energy to sink into the π band. Low lying π state occupies the charge carrier hole: shows up as shoulder on the low energy side of the B K edge.

Anisotropy and Experimental Conditions



- The selection of a particular direction of the scattering vector to probe a particular symmetry of the unoccupied electronic states
- Caused by the angular dependence of the electronic structure and the choice of experimental conditions.
- **Magic angle** a value of the collection at which energy-loss spectrum becomes independent of the tilt angle of the sample with respect to the beam direction.





I (E)

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ELNES of 3d and 4d Transition metals

- The unoccupied d band is energetically narrow and partially filled, leading to strong L edge features (p→d transitions).
- Spin—orbit splitting shifts the binding energy **2p** levels (2p_{1/2}, 2p3/2): two sharp peaks with separation increasing as the atomic number increases.
- Under purely statistical considerations, the L3 / L2 intensity ratio of white lines should be 2:1.
 The degeneracy (number of initial states) is L3 (j=3/2): 4, L2 (j=1/2): 2
- Observed deviations arise from strong correlation between the initial core-hole states and the final electronic states.
- This complexity signifies a breakdown of the simple, single-electron excitation picture, requiring a more detailed many-electron, correlated approach to understand the spectral features.
- Systematic variation in intensity as a function of the number of **d** electrons
 - \rightarrow oxidation state determination \rightarrow other effects

Similar effect for $M_{4,5}$ edges, (3d \rightarrow 4f, degeneracy 3:2)



ntensity

а

CoSi,

5

Valence from TM white line ratios



- Works reasonably well for simple TM oxides
- **BUT** very sensitive to background subtraction & additional initial state background
- Single scattering data only (very thin samples)
- Only compare to data under the same optical conditions



Co₃O₄

3

Estimating valence





Core shell Fe-Mn-oxide nanocubes

Fe shows a higher oxidation state in the shell compared to the core

Mn 2⁺ state in both shell & core ; higher oxidation state only at a very thin (<1 nm) surface layer.

Core : FeO/MnO with Fe and Mn in the 2⁺ state

Shell : spinel like MnFe₂O₄ structure.

Atonic Valence State mapping



Mapping of $Fe^{2+/}Fe^{3+}$ charge ordering in the ferromagnetic hematite-ilmenite $Fe_{1.35}Ti_{0.65}O_{3-\delta}$ thin films

A sites: $Fe2^+$ / $Fe3^+$ ordering (ratio 2:1) B sites: Ti^{4+} - Fe^{2+} / Fe^{3+} ordering (ratio 1.2)



PRL 111 (2013) 167202

Hybridisation of states



- Mixing of atomic orbitals to form new molecular orbitals influencing the electronic structure of a material.
- Affects the density of states (DOS) and is reflected in the ELNES



Changes in ELNES of Ni and Al hybridization between the narrow **d**-like states at the Ni sites and the more free-electron like states on surrounding Al atoms.

Valence from TM white line ratios







Not as straight forward as we would like

- Works well enough for simple TM oxides and trends with in the same system
- Across (complex) oxide systems:
 - Valence, charge transfer, coordination, spin state, etc..
- **NEVER EVER EVER EVER EVER** compare L₃/L₂ ratios with values from dissimilar systems (e.g intermetallic, carbide vs oxide)

Chem. Minerals (2002) 29, 188 Ultramicroscopy 106 (2006) 561–573 Journal of Solid State Chemistry 178(2005) 1008-1016



[Bi_{0.87}SrO₂]₂[CoO₂]_{1.82} – high performance p-type TE





- Bi deficiencies in the BiO layers induce charge redistribution in the COL: EELS reveals 4⁺ Co valence localised to the COL.
- Extra Co⁴⁺ states just above the Fermi level fingerprinted through O K ELNES (and Co L_{2,3} branching ratio).



Population analysis (pDos overlap) **COL A1** : O-2p with Co₄₊ states **A** : Co-3d and O-2p hybridized states

- **SRO B** : Sr-4d and O-2p state overlap
- **BiO** A : Bi-6p states hybridized with O-2p states.

Crystal field splitting

- Crystal field splitting is the process where degenerate energy levels of d-orbitals (e_g and t_{2g}) due to the electric field created by nearby ions or surrounding molecules.
- The e_g orbitals (higher energy) point directly at ligands, while the t_{2g} orbitals (lower energy) are oriented between ligands.
- This energy difference causes splitting of the extra peaks
- Local distortion of the ligand field fill alter energy levels











Crystal field splitting





Interface: reduction in the hybridization of Ti 3d and Pb 6sp states with O 2p, and thus tetragonal distortion of the TiO_6 octahedron. Gradual change _gradual over ~2-3 nm

Energy resolution

(Spectrometer aside) The energy resolution of the EEL spectrum is governed by the energy spread of the electron source



Low Loss Spectroscopy & thickness









Bulk plasmons : $E_p \propto N$ N the valence electron density

With increasing specimen thickness the probability of (single) plasmon excitation increases and so does the probability of multiple inelastic scattering events i.e multiple plasmons!

The specimen thickness: $t = \lambda \cdot \ln(I_T/I_{ZL})$

 I_{ZL} is the intensity of the ZLP I_{T} is the total energy of the spectrum (area)

 $\lambda~$ electron free mean path for ${\rm E_0}$

For any sensible EELS at least: $t/\lambda < 1$ but ideally $t/\lambda \le 0.5$

Scales with E₀ Si λ_{200kV} = 93.74nm, Si λ_{60kV} =46.48nm

Effect of specimen thickness on edge visibility:





• Plasmon scattering contributes to the core-loss integral in the same proportion as it contributes to intensity in the low-loss region

$$I_m/I_{k1} = I_p/I_0$$

- Increasingly thick specimens cause a redistribution of intensities in the EELS spectrum-The background increases and makes the extraction of edge signals more difficult
- Specimens suitable for EELS analysis should always be thinner than t/ $\lambda <<\!\! 1$, hence less than 100nm

- It is possible to deconvolute (Fourier ratio deconvolution) up to a point
- Should you? If you have no other option
- Start with think samples!!!

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Absolute: $N_A = [I_A(\beta, \Delta) / I_I(\beta, \Delta)] / \sigma_A(\beta, \Delta)$

Relative: $N_A/N_B = [I_A(\beta, \Delta)/I_B(\beta, \Delta)] [\sigma_B(\beta, \Delta)/\sigma_A(\beta, \Delta)]$

- Thin specimens only (thin!!). Typical error still ~10%
- Cross-sections for certain types of edges not tabulated, or not easily calculable.
- Atomic resolution? Don't even think about it other effects are in play (....)
- Talk to Jo Verbeck about model based approaches but rule of thumb: quantification is not straightforward (not in EDXS either: lots of hard work beforehand is needed).



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EELS resolution/localisation

Spatial resolution of EELS depends on:

- **1. Electron optics** (probe size, aberrations, diffraction...) optimized by STEM probe, image coupling to spectrometer
- 2. Beam spreading (geometrical, elastic scattering) $d_s \sim \beta t$ for $\beta < 10$ mrad, more complicated for a crystal Thin samples!!!!
- 3. **Delocalization*** of inelastic scattering $d_d \sim 0.5 \lambda/\theta_E^{3/4} \sim (15 nm) / E^{0.75}$ if E in eV Use the higher energy edges (e.g Si, Al K instead of L_{2,3})

4. **Electron statistics** (limited by radiation damage), i.e. dose-limited resolution

*The signal used EELS arises from the inelastic scattering by atomic electrons, which can be excited by a primary electron passing some distance away.



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Interpretation of EELS intensities





- EELS map intensity \rightarrow integrated signal above a selected background
- *'representative' of local chemistry*
- tread carefully → nice to have some sort of agreement with zcontrast images
- How far can these intensities be trusted?
- What about quantification of atomically resolved maps?

Contributions to EELS intensities

EDX O maps



It is difficult to interpret the intensities of EELS (EDX) maps directly & quantitatively

EELS signal is convolved with

- Elastic scattering, Thermal scattering
- Delocalization of inelastic scattering



When travelling down a strong column potential, the probe gets 'captured' 1s Bloch states and slowly leaks to other columns along z.

Wave optics of the probe

PRB 86 (2012) 024108

Thickness (Å)

-- 0

Fractional intensity

Micron 39 (2008) 653-657



Is my interface sharp?











- *BaTiO₃/SrTiO₃ interface*
- Is the interface sharp?!
- for quantitative interpretation of EELS maps, inelastic image simulations are necessary

µSTEM

(SIM as been user when when every gravity (SM) are determined up of the line come in phone as when an addet in microscopy (STD) is regarding to various developed mainly at the University of Ms bears. The come ting user is even of an interment the restor. Here shall and a loss if in mean way and the following as and the paper.

Hode ing the industrial according of fair electrons, U.I. Allery, A.I. DW forms and S.D. finding, Ultranizoroopy, Vol. 151, pp. 11-52, (2013).



Prerequisites

GPU version

have preserved events betw

64 bit windows 70

https://github.com/HamishGBrown/MuSTEM





https://abtem.readthedocs.io/en/latest/intro.html#

Ultramicroscopy 110 (2010) 926–934

Potential inversion





- Remove elastic and thermal scattering contributions from experimental EELS maps.
- True also for EELS fine structure



Neish MJ et al, Physical Review B 88 (2013) 115120 N. Lugg, et al., APL 101 (2012) 183112

Relax : X-ray energy dispersive spectrometry (XEDS)





Instrument set-up

• Detector collection angle (W): is the solid angle subtended at the analysis point on the specimen by the active area of the front face of the detector

$$\Omega = \frac{A\cos\delta}{S^2}$$

- Large W: collect max counts
- ideally : $\delta = 0$
- take-off angle α : is the angle between the specimen surface (at 0 tilt) and a line to the center of the detector
 - ideally large a to minimize X-ray absorption





Semiconductor detectors: Si(Li)

- Incoming X-rays generate e-h pairs ∝ E_{Xray}
- The energy required in Si is 3.8 eV @ liquid-N₂ so thousands of e-h pairs can be generated by a single X-ray
- Dead layers are regions within the detector that are unresponsive to incoming X-rays and therefore do not contribute to the detection signal.
- Low energy efficiency further limited by the type of window





SuperSTEN

Si-drift detectors (SDD)

- Concentric rings of p-doped Si implanted on a single crystal of n-Si - Voltage is applied from the inside to the outside the detector permitting the collection generated electrons at lower voltage.
- Thinner dead layers better energy resolution
- Due to low capacitance very high throughput of counts is possible
- Larger sizes & collection angles (better overall efficiency)
- High purity materials, no LN₂ cooling required





X-ray energy dispersive spectrometry (XEDS)





X-ray count rate and dead time



The XEDS system detects X-rays and disperses them into an energy spectrum

- In principle XEDS system can process only one photon at a time
- X-rays entering too close in time are discarded to prevent recording photons at incorrect energies

Dead time is the time frame when the detector is not counting X-rays but processing the previous photon

The Dead time increases with X-ray count rate

- Specimen thickness, tilt angle
- Voltage, beam current

Energy resolution





Process Time, Resolution and Dead Time

- EDS resolution is determined by the detector current best performance 120eV ۲
- Can be affected by Process / Dead time ٠

Manufacturers have a good idea of 'ideal' performance with Dead/ Process Time

Relax : X-ray energy dispersive spectrometry (XEDS)





Characteristic X-rays

- Elemental identification
- Quantitative analysis

Continuum X-rays - Bremsstrahlung

- Background radiation
- must be subtracted for quantitative analysis

Instrumentation

Continuum X-rays - Bremsstrahlung

- Interaction of incident e⁻ with the nuclei of the specimen • atoms
 - Change in momentum \rightarrow X-ray •
- The shape of the continuum spectrum is approximately ۲ described by Kramers' cross section

$$N(E) = \frac{K \cdot Z \cdot (E_0 - E)}{E}$$

- N(E) number of bremsstrahlung X-rays of energy E produced by electrons of energy $E_0 \& K$ constant
- At low energies, bremsstrahlung is absorbed by the specimen ulletand the detector



Continuum X-rays - Bremsstrahlung

- Arises from the interaction of incident beam electrons with the nuclei of the specimen atoms
 - The electron can suffer change in momentum
 - During this process it may emit an X-ray
- The shape of the continuum spectrum is approximately described by Kramers' cross section

$$N(E) = \frac{K \cdot Z \cdot (E_0 - E)}{E}$$

- N(E) number of bremsstrahlung X-rays of energy E produced by electrons of energy E₀ & K constant
- At low energies, **bremsstrahlung** is absorbed by the specimen and the detector
 - Needs to be subtracted for quantitative analysis



Wavelength (Å)

Characteristic X-ray generation

Total cross section for ionisation of a closed subshell $n\ell j$ with $2j + 1 e^{-1}$

$$\sigma_i = (2j+1) \frac{2\pi e^4}{m_e u^2} \frac{1}{E_i} \left(1 - \frac{1}{U}\right)$$

 E_i is the binding energy of an electron in the subshell & $U\equiv E/Ei$ overvoltage

Return to ground state (almost!!) by filling in the hole with an electron from an outer shell

• X-ray may be emitted with $E_{x-ray} = E_{initial} - E_{final}$

Not all of the possible X-ray lines will be found in a spectrum

 Selection rules for emission and absorption of electromagnetic radiation △n≠0, △l = ±1, △j= 0, ±1. (tot. ang.momentum).



The ionized atom returns to ground state not via a single event but by a cascade of transitions, depending on the complexity of the electronic structure of the atom.

In practice overvoltage rule $E_0 \sim 3 \times E_{x-rav}$

Characteristic X-ray energies

- Generation of X-rays are characteristic to each element
- E_{X-ray} depends monotonically on Z
- Empirically described by Moseley's law

$$E_{x-ray}(eV) = K(Z-1)^2$$

where K an empirically derived constant.







Henry Moseley

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Nomenclature

Siegbahn $\rightarrow X_{y_n}$

- X : K, L and M (family)→ shell from which the core electron was knocked out
- y: a, b, g → the number of shells that the orbital electron dropped to fill the corehole
- \circ *n*: **1**,**2**,**3** \rightarrow the subshell that the donating electron came from

$IUPAC \rightarrow X_n - Y_n$

- $\circ X_n \rightarrow$ shell from which the electron was knocked out
- \circ Y_n \rightarrow shell from corehole was filled



TABLE 1. Radiative transitions for the relevant groups in the K, L, and M series. Transitions for the indicated lines are represented using the IUPAC notation (S0-S1) and the corresponding Siegbahn notation is indicated in parentheses

Group	Lines	Group	Lines
Κα	K-L ₂ (Kα ₂)		L2-N6 (Lv)
	K-L ₃ (Ka ₁)		L_2-N_7 (Lv)
Κβ	K-M ₂ (K β_3)		L_2-O_1 (L γ_8)
	K-M ₃ (K β_1)		L_2-O_4 ($L\gamma_6$)
	K-M ₄ (K β_5^{II})	$L_3\ell$	L_3 - M_1 ($L\ell$)
	K-M ₅ $(K\beta_5^I)$	L ₃ t	L_3-M_2 (Lt)
	K-N ₂ (K β_2^{II})	$L_{3}s$	L3-M3 (Ls)
	K-N ₃ $(K\beta_2^I)$	$L_3 a$	L_3-M_4 (La ₂)
	K-N ₄ (K β_4^{II})		L_3-M_5 (La_1)
	K-N ₅ (K β_4^{I})	$L_3\beta$	L ₃ -N ₁ (L β_6)
L ₁ β	L_1-M_2 $(L\beta_4)$		L_3-N_4 ($L\beta_{15}$)
	L_1-M_3 ($L\beta_3$)		L_3-N_5 ($L\beta_2$)
	L_1-M_4 ($L\beta_{10}$)	L ₃ u	L3-N6 (Lu)
	L_1-M_5 (L β_9)		L_3-N_7 (Lu)
L ₁ γ	L_1-N_2 ($L\gamma_2$)	Mγ	M_2-N_5 (My)
	L_1-N_3 ($L\gamma_3$)	$M\beta$	$M_4-N_6 (M\beta)$
	L_1-N_4 (Ly_1)	Μζ	M_5-N_2 ($M\zeta_2$)
$L_2\eta$	L_2-M_1 (L η)		M_5-N_3 ($M\zeta_1$)
$L_2\beta$	L_2-M_3 ($L\beta_{17}$)	Mα	M_5-N_6 (M α_2)
	L_2-M_4 ($L\beta_1$)		$M_{5}-N_{7}$ ($M\alpha_{1}$)
L ₂ y	L_2-N_1 ($L\gamma_5$)		
	L_2-N_4 ($L\gamma_1$)		

Fluorescent (Auger) yield



- An ionized atom can also lose energy by ejecting Auger e⁻
- Fluorescent yield: $\omega = \frac{Z^4}{a+Z^4}$

with a~10⁶ for K shells

- $\circ w_c \sim 10^{-3} \rightarrow 1000$ ionization events to produce 1 C K_a
- $\circ \omega_{Ge} \sim 0.5 \rightarrow 2$ ionization events to produce 1 Ge K_a
- the rest of the ionization events will produce Auger e⁻
- Light element atoms return to ground state mainly by Auger emission. For that reason, their K-lines are weak.
- Fluorescent yield needs to be accounted for in quantification



Absorption & fluorescence



- X-rays generated by electrons can be **absorbed** by the specimen
- If E_{Xray} ≈ E_{C_ionization} then it is possible that the X-ray will be absorbed, and a **photo-electron** produced.
- Fluorescence → X-rays generated by atoms can generate
 X-rays from other atoms
- Absorption and fluorescence need to be taken into account in X-ray quantification

$$I_i^i = \int_0^t I_i'(t) \exp\left(-(\mu/\rho)_s^i \rho t'\right) dt$$

ρ density mass attenuation coefficient for the element i in
 the specimen s :a measure of how strongly the element i
 absorbs X-rays

• t' absorption path length: $t'=t \operatorname{socsec} \alpha$





X-rays family lines

- X-rays come in families
- Not all excitations are equally probable
- The ratios between family lines of each element are known and don't change
- Peak overlaps are possible



EDX K line simulation using DTSA-II -assuming 100% wt of elements @60kV http://www.cstl.nist.gov/div837/837.02/epq/dtsa2/index.html





Qualitative x-ray analysis

- The relative positions and weights of the E_{x-ray} lines in each family are consistent
- Allows peaks in the X-ray spectrum to be recognized.
- By measuring the energies of the major X-ray peaks in each family, the corresponding element can be identified
- Most EDXs manufactures provide software which is pretty good at peak identification
- Open source software is available
- Tables for manual peak identification

Results from automatic software identification need to be verified!!



Nanomaterials 2021, 11(8), 2073
EDX of light elements (Z<11)

- Cannot be <u>routinely</u> analysed
- H_{z=1} and He_{z=2} do not have characteristic X-rays
- $Li_{Z=3}$ K_a are of too low energy to be detected
- $Be_{Z=4}$ to $Ne_{Z=10}$ K_a can be detected

<u>BUT</u>

- $\circ~$ low fluorescent yield
- o subject to strong specimen & detector absorption

• EDX is best suited for heavy elements while EELS for light elements (with the added benefit of electronic structure information)





Scanning 38, 571–578 (2016)

Elemental mapping







Don't forget beam propagation

EDX O maps



PRB 86 (2012) 024108

Scientific Reports 7, 45970 (2017)

Scientific Reports 11, 18022 (2021)

Single atoms









Appl. Phys. Lett. 100, 154101 (2012)

Useful spectroscopy?



SuperSTEN

- Very large probe currents needed for useful signal collection!
- Poor energy resolution.

Quantitative x-ray analysis: Cliff-Lorimmer Technique



- Castaing (1951) : The concentration Ci of an element i in the specimen will generate a certain intensity of characteristic X-rays.
- The wt% CA and CB of two elements A and B can be determined by the ration of their simultaneously acquired characteristic intensities, IA and IB respectively:

$$\frac{C_A}{C_B} = XRCF\frac{I_A}{I_B}$$

XRCF is the x-ray correction (sensitivity factor)

 Cliff Lorimmer technique - k_{AB} is a sensitivity factor and is related only to the atomicnumber correction factor (Z)
 It varies according to the instrumentation and the acceleration voltage
 The k factors are independent of thickness variations if the specimen is thin, i.e no absortion

• ζ (zeta) factor extension – ζ_i of element i is defined ionization cross section Qi, fluorescence yield ω_i , electron illumination dose D_e

mass thickness
$$\varrho t = \zeta \frac{I_A}{C_A D_e}$$
 where $\zeta_i = \frac{M_i}{N_0 Q_i \omega_i \alpha_i D_e \varepsilon_A \left[\frac{\Omega}{4\pi}\right]}$

- Standarelss techniques
- 'remote standards', or 'remote standard method',



Journal of Microscopy, Vol. 221, Pt 2 February 2006, pp. 89–109

Quantitative x-ray analysis : Stop and think





Out of the box automatic quantitative analysis can be qualitative at best Error often in >>1% (worse for light elements)

Know your system, compare with standards if you have to (under similar conditions) EDX O maps



Avoid strong channelling conditions if you can

EDX

III. Battle EDX vs EELS





PdAu Catalyst : Acknowledgments to: P. Longo, Gatan Ind

EELS vs EDX : Ease of use

EDX







EELS a bit more involved



EELS vs EDX : Sample Restrictions



EELS – Fewer elements are easy to detect

K edges $L_{2,3}$ edges $M_{2,3}$ edges $M_{4,5}$ edges $N_{4,5}$ edges $O_{2,3}$ edges



EELS – is more sensitive to thickness & specimen quality



EELS vs EDX : Spatial Resolution





It's a draw: EELS is more efficient overall, EDX has access to more elements

EELS vs EDX : Spectral Resolution



EDX ~100 *eV* – *limited by detector*



EELS vs EDX : Which one to detect light elements





EELS vs EDX : Quantification



EDX + Machine Learning



Kim, H.-Ket al, *Scientific Reports* **2020**, *10* (1), 13699.



J. Gázquez et al, Materials Science in Semi. Proc., 65, 2017,







EELS and EDX together : Correlative Study





Florence Pettinari-Sturmel et al Mat. Sc. and Eng.: A, Elsevier, 2019

EELS and EDX together : Coincidence Detection







D. Jannis et al, Appl. Sci. 2021, 11(19), 9058



EELS vs EDXS





EELS

- \odot better spectral resolution
- \odot superior for lighter elements
- more powerful experiment more than elemental analysis
- \bigcirc more difficult experiment
- ⊖ requires prior knowledge
- ⊖ limited spectral range (high energies)
- $\ensuremath{\mathfrak{S}}$ 'quantification' possible but more difficult
- $\ensuremath{\mathfrak{S}}$ far more sensitive to sample quality



EDXS

- © wide spectral energy range for efficient data collection
- ③ easier experiment
- \odot easier quantification (with caveats)
- $\ensuremath{\mathfrak{S}}$ lower Z element detection limit
- $\ensuremath{\mathfrak{S}}$ limited to elemental analysis



Thank you for your attention





Further reading



David B. Williams • C. Barry Carter Transmission Electron Microscopy A Textbook for Materials Science



Second Edition

Electron Energy Loss Spectroscopy



Rik Brydson



Scanning Transmission Electron Microscopy

Imaging and Analysis

R.F. Egerton Electron Energy-Loss Spectroscopy in the Electron Microscope

Third Edition

Deringer

D Springer