Electron Beam Induced Excitation Methods

A. Reflection Scanning Electron Microscopy
B. Auger Electron Microscopy/Spectroscopy
C. Electron Beam Induced X-Ray Analysis
D. Electron Energy Loss Spectroscopy
E. Transmission Electron Microscopy
   a. Scanning Transmission Electron Microscopy (STEM)
   b. Conventional Transmission Electron Microscopy (TEM)
   c. Energy Filtered Electron Microscopy
X-Ray Analysis (unit)

detectors:

- basically 4 types (3 used most widely)

1. X-ray spectrometers, wavelength dispersive (WDX)
2. Lithium drifted silicon, energy dispersive (EDX)
3. micro calorimeters (heat to energy) — not widely used
4. silicon drift detector (SSD), energy dispersive (newest)

- advantages of WDX is very high energy resolution but essentially a serial detector — i.e. 1 mg at a time

- advantages of EDX is collection in parallel but resolution poorer than WDX

1. X-ray spectrometers

\[
\text{incident beam} \quad \text{d} \quad \text{CRISTAL} \quad \text{diffracted beam}
\]

\[
n\lambda = \overline{ABC} = 2d \sin \theta
\]

\[\text{diff} \lambda \text{ hence, energy } \rightarrow E \propto \frac{12395}{\lambda} \text{ eV/Å}^2\]

dioc camera / Rowland Circle / fully focusing spectrometer

unit
How to Detect X-Rays?

1. by wavelength (WDS)

\[ \bar{AB} + \bar{BC} = 2d \sin \theta \]

Constructive interference between the two beams diffracted (reflected) off the 2 layers is:

\[ \text{Path diff} = n \lambda, \quad n = 0, 1, 2. \]

\[ \lambda = \text{X-ray wavelength} \]

\[ n \lambda = 2d \sin \theta \]

Bragg's law

\[ E = h \nu = \frac{hc}{\lambda} \]
crystal spectrometer geometry

\[ \overline{OP} = R = \overline{PC} \]

Rowland Circle (radius = 12)
focussing circle
(radius $R$)

S

D

crystal

crystal lattice plane
(radius $2R$)

— Johansson mounting.
Since many crystals are difficult to grind properly, a simpler crystal mounting is one on which the crystal is just bent to a radius of 2R (Johann mounting). The focusing is no longer perfect and gets worse the further the x-rays are from the crystal center. Thus, for a given collimation, the wavelength resolution is less than for the Johannsson mounting.
XRAYS

vacuum "window"

Li drifted region (intrinsic)

\( \bar{e} \)

h

p type

dead layer

n type

to low noise pre-amp (floating)

Au layer

metal layer

\(-kV\)
X-Ray Analysis

2. Li Drifted Si, energy dispersive

Li acts as donor to compensate for impurity acceptor levels (B)
- results in intrinsic region in which e^-h^+ can only be created by external ionizing radiation
- bias the detector to drag e^- to one side.

x-ray absorbed in intrinsic layers, $E_x$
#e^-h^+ pairs produced = $\frac{E_x}{e} - 3.7$eV in Si

$Q = \frac{(E_x)}{e}$ charge collected

detector has capacitance, so we actually get a voltage pulse $V = \frac{Q}{C} = \frac{e}{C} \frac{(E_x)}{e}$

pulse height $\propto$ x-ray energy $\rightarrow$ energy dispersion

we count pulses (one at a time)

assuming Poisson statistics for Q then

stand. dev. of voltage pulse is

$\Delta V = \frac{e}{C} \sqrt{\frac{E_x}{e}}$

$\Delta V \frac{E}{V} = \frac{e}{C} \frac{\sqrt{E_x}}{e} = \frac{\sqrt{E_x}}{E}$

$\frac{\Delta E_x}{E_x} = \sqrt{\frac{V}{N}}$

not Poisson exactly
$\Delta N < \sqrt{N}$

FWHM = 2.36 $\Delta E_x$
X-ray Anal (mit)

call \( \text{St.
\text{dev}} = F \Rightarrow \text{for Poisson, } F = 1 \)

\( F = \text{Fano factor -- for } Si(Li) = .12 \)

\( \Delta E_{X}^{Si(Li)} = 1.61\sqrt{E_{x}} \text{ meV} \)

\( \text{intrinsic energy resolution} \)

but pulses are small, need amplification

\( \Delta E_{FWHM} = \sqrt{(1.61\sqrt{E_{x}})^{2} + E_{noise}^{2}} \)

(\( E_{noise} \approx 50-100\text{eV} \))

need to cool to cry N\(_{2}\)

to reduce thermal noise

\text{efficiency of detector:}

1) Solid X

2) window, metalization, layer, dead layer etc...

\all of these depend upon the X-ray energy

\text{Z effects:}

1) X-ray absorption in these layers resulting in fewer e-+h+ produced

2) X-rays of high energy energy and get absorbed in intrinsic layer

this is similar for all EDX type detectors
X-Ray Analysis (Int)

Consider the effluence resulting from three various layers:

\[ f_{\text{DET}} = \left[ \prod_{i} e^{-\frac{\lambda_i}{\lambda}} \right] \left[ 1 - e^{-\frac{\lambda_i}{\lambda}} \right] \]

The product of probability that a X-ray must be absorbed in each layer in intrinsic region.

NOTE: If we call for a layer of given thickness \( t \), we can do any thickness \( t' \) as
\[ t' = Nt \quad \Rightarrow e^{-Nt} = (e^{-t})^N \]

It is clear that to minimize absorption in front layers, want to make them as thin as possible. Best is "window-less" detector — no vacuum window frame. || Probs.

pt. to note: Light element detection is poor since X-ray energies are so low — any kind of physical window cuts down on transmission.
Energy Dispersive XRay Analysis
(real detector/sample)


EDS spectrum of the mineral crust of R. exoculata. [1]
Comparison between EOS and WDS X-ray Spectra from the same material (from NBS.)

Fig. 6.24. Comparison of spectra of a glass (NBS K252) with a Si(Li) detector (above) and with a 10-cm radius LiF curved-crystal spectrometer (below). Both performed at 20-kV excitation potential. The composition of the glass is as follows: \( \text{SiO}_2: 0.40, \text{BaO}: 0.35, \text{MnO}: 0.10, \text{MnO}_2: 0.05, \text{CuO}: 0.05, \text{CoO}: 0.05 \), all mass fractions.

NOTE: energy resolution, range and peak to background differences.
Silicon Drift Detector for X-ray spectroscopy.

[up]
3. silicon drift detector (SDD).

Same Si PN junction concept. (1983)
- Recently used in EM's for X-ray detection (last few yrs)
  - Differences with Si(Li).
    - Electric field parallel to the surface (rather than)
    - Drives electrons towards small central anode
    - Thus, lower capacitance
        \[ L \approx + \text{capac. indep. of active area} \]
    - Whereas in Si(Li) depends on active area.
        - Small capacitance means shorter shaping time \( \Rightarrow \) fast dead time
    - Geometry minimizes pickup (elec or mesh)
    - Virtually no det. dead time
    - Leakage currents extremely low so no liq N\(_2\) cooling
      - Uses Peltier cooling \((-20^\circ \text{C} \text{ vs } -170^\circ \text{C Si(Li)})\)
    - Resolution comparable to Si(Li)
Function of Silicon Drift Detector
X-ray analysis (untitled)

Spatial resolution of X-ray signal for thin films: beam spreading

\[ \text{inc. beam spread} \]

Rough calculation:

Consider Ruth. Scott

\[ \text{Crossing } \theta: \quad \sigma_R(>\theta) = \int_{\theta}^{\infty} d\theta \quad \text{d} \theta \]

\[ = \int_{\theta}^{\infty} \pi \rho \sin \theta \left[ \frac{\pi^2}{\sin^2 \theta} \right] \left[ \frac{\lambda}{\sin \theta} \right]^4 \text{eV} \]

\[ \rho = \lambda = \sqrt{\frac{\pi^2}{E_0^*}} \quad E_0^* = E_0 \left( 1 + \frac{1}{2} \frac{E_0}{mc^2} \right) \]

Relative corr. wavelength

\[ \Rightarrow \sigma(>\theta) \approx \frac{16\pi^2}{E_0^*} \frac{\pi^2}{\sin^2 \theta} \frac{\sin^2 \theta}{\cosh^2 \theta} \quad \text{in } \text{A}^2 \quad \text{and } \text{mE} \]

Assuming single scatter, then prob. of scatter thus \( \theta \) independent:

\[ P(>\theta) = N \sigma(>\theta) t \]

\[ \Rightarrow P(>\theta) \propto \frac{nt \pi^2}{E_0^*} \frac{\sin \theta}{\cosh^2 \theta} \]
X-ray and (not)

What is scatter X

whereby 90% events inside?

1e only 10% scattered outside.

Call this \( P(\theta) = 10^{-1} \)

Assume (wrong) scatter occurs from middle

of film, \( \theta = \theta' \)

Then \( \frac{b}{t} = \tan(\theta_1) \) which for small \( \theta \) gives:

\[
\frac{b}{t} \propto \frac{1}{E_0} \sqrt{\frac{P}{A}} \sqrt{t}
\]

That is

beam spreading \( \propto t^{3/2} \)

\[
\frac{b}{t} \propto \sqrt{t}
\]

Valid in limit \( \tan \frac{\theta}{2} \approx \frac{\theta}{2} \)

Can find and what that is.

\[
t \approx \frac{3.12 \times A}{E_0^2} \text{ in cm, if } 1 \text{ Pm/} \text{cm}^2
\]

unverified by MC results

\[
E_0 \text{ in meV}
\]

Note: For high Z - long tails outside 10% can be significant
Fig. 3. Au X-ray counts at accelerating voltages of 40 and 100 kV as a function of probe position (a) and (b) from an area approximately 2400 Å thick and (c) from an area ~1.2 Å thick.

from Hutchings et al.

Hutchings, et al. (1978)

Ultramicroscopy. 3, 49.

single scattering model
1. **UNSCATTERED**
   \[ \Delta E = 0, \Delta P = 0 \]
   \[ I_{UN} \]
   \[ a_0 \quad \theta \]

2. **ELastically SCATTERED**
   \[ \Delta E \neq 0 \]
   \[ \sigma_{EL} \sim Z^{3/2} \]
   \[ \theta_0 \sim \lambda / 2 \pi a \approx \theta_B \]
   \[ I_{EL} \quad \left[ \theta^2 + \theta_0^2 \right]^{-2} \]
   \[ a_0 \quad \theta_B \quad \theta \]

3. **INelastically SCATTERED**
   \[ \theta_E \approx \frac{\Delta E}{P_0 \nu_0} \]
   \[ \sigma_{IN} \sim Z^{1/2} \]
   \[ \frac{d\sigma_{IN}}{dE} \text{ material specific} \]
   \[ I_{IN}(E) \]
   \[ a_0 \quad \theta \]
   \[ \Delta E \quad \Delta E \text{ large} \quad \Delta E \text{ small} \]
   \[ \times 1 \quad \times 10^3 \]

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**EE 213, Nanocharacterization/M.Isaacson**
EELS of Nucleic Acid Bases obtained Using 25keV Incident Electrons


Energy Loss Spectra of Metal Fluorides

Single Atom Identification in STEM