

4.5 Reflection High Energy Electron Diffraction (RHEED)

In LEED, low energy electrons were used to

- provide large elastic scattering cross-section for *back*-scattered electrons
- keep the penetration depth of the electrons short

In RHEED, another solution is used

- provide large elastic scattering cross-section for *forward*-scattered electrons
- keep penetration depth small by using grazing incidence

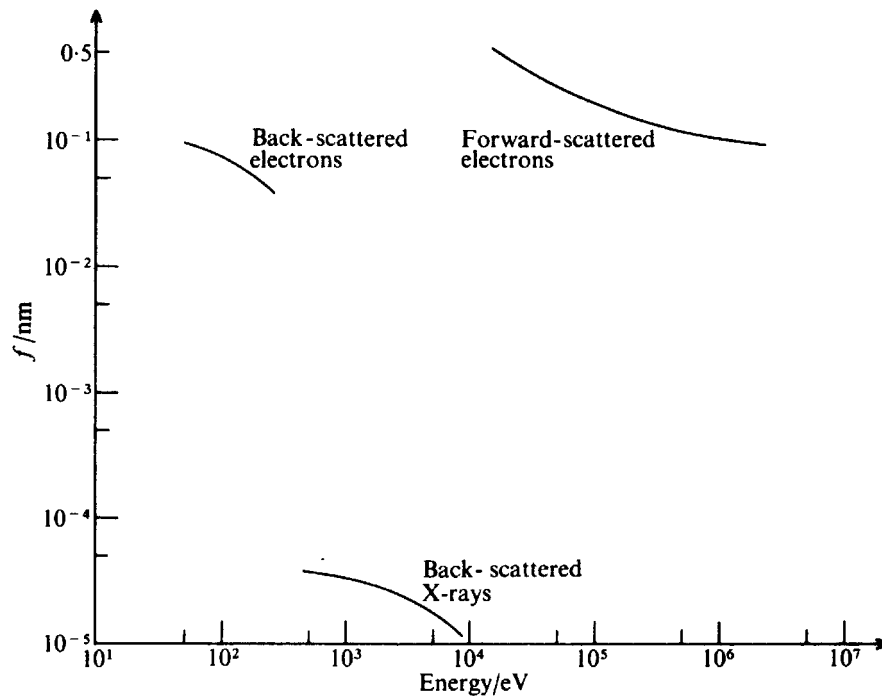


FIG. 3.4. Approximate atomic scattering amplitudes for aluminium as a function of energy of electrons and X-rays,

4.5.1 Instrumentation

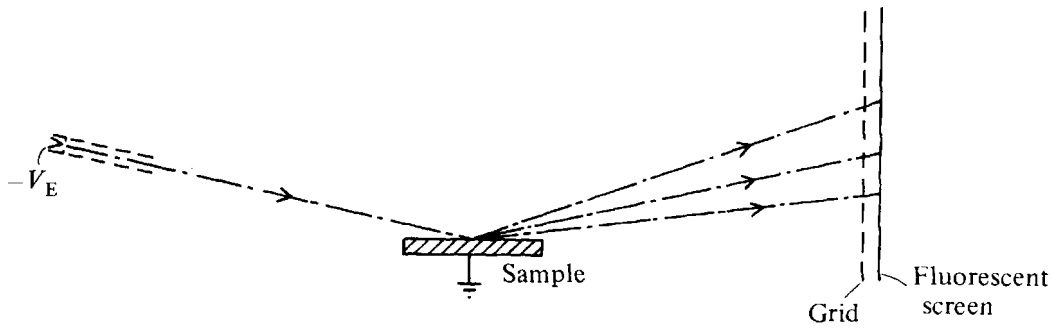


Fig. 2.30 Schematic diagram of the experimental arrangement for RHEED.

Electrons 5-100 keV directed towards sample at very near $\theta_i \approx 90^\circ$ - keeps even long-pathlength (high-energy) electrons in near-surface region

Forward-diffracted electrons strike phosphor screen

Grid used to repel secondary and inelastically scattered electrons

4.5.2 Basic Theory of RHEED

Theory very similar to LEED (Ewald sphere) but incident wavevector $|\vec{k}|$ now very large:

Example: 50 keV electron incident in $[110]$ direction of Cu ($a_0=3.56 \text{ \AA}$)

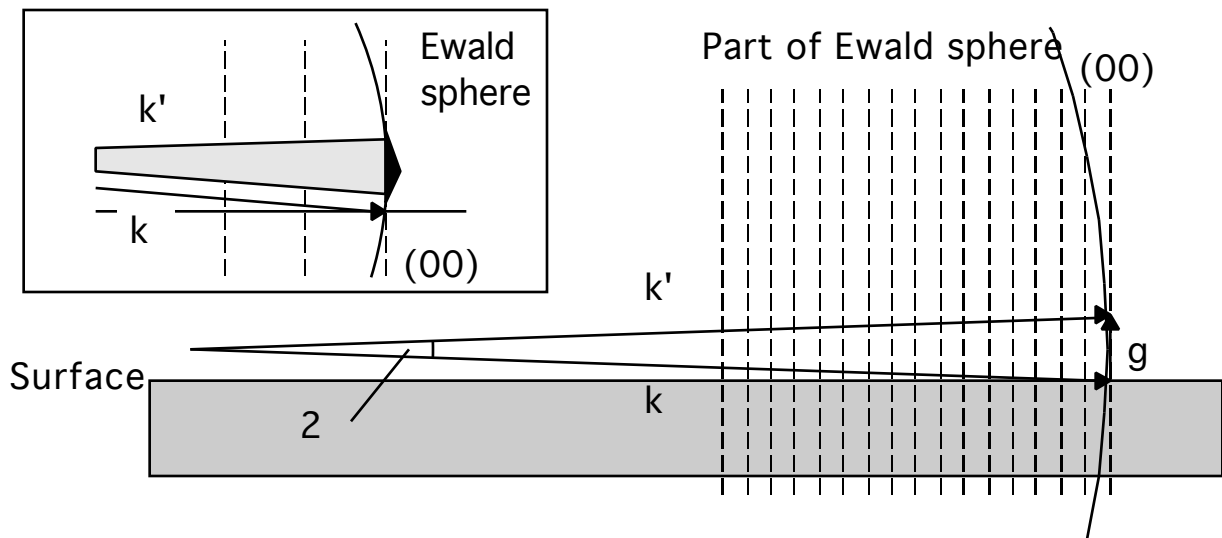
$$\begin{aligned} &= \sqrt{2m(eV)} \\ &= 5.5 \times 10^{-12} \text{ m} \\ &= 0.055 \text{ \AA} \end{aligned}$$

$$\begin{aligned} |\vec{k}| &= \frac{2\pi}{\lambda} \\ &= 114 \text{ \AA}^{-1} \end{aligned}$$

and reciprocal lattice spacing is

$$\begin{aligned}
 a &= \frac{2}{d} \\
 &= \frac{2}{3.56 \text{ \AA} / \sqrt{2}} \\
 &= 2.49 \text{ \AA}^{-1}
 \end{aligned}$$

Draw Ewald sphere for an incidence angle of 88° :



Consequences?

- (1) Ewald sphere crosses many lattice rods - many spots separated by small diffraction angle differences
but few near grazing exit angles - usually only see (00) beam and perhaps $(\bar{1}0)$ beam
- (2) Crossing of Ewald sphere with lattice (condition for diffraction) rod very poorly defined - RHEED spots are broadened into "vertical" streaks

Now diffraction out of incidence plane (determined by periodicity orthogonal to incidence plane) becomes important

The RHEED pattern can be used to measure surface periodicity orthogonal to incidence plane by measuring the separation between the streaks:

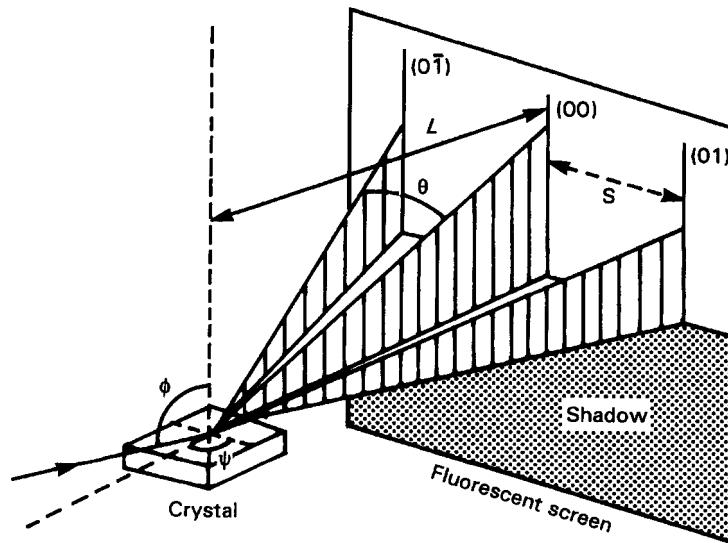
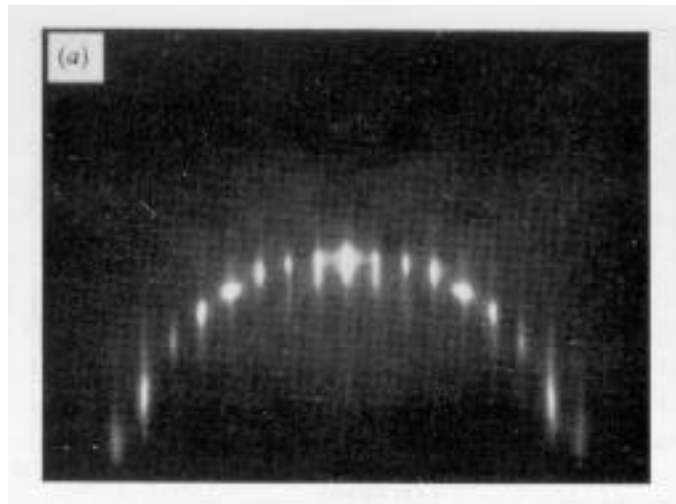


Figure 8.17. A schematic diagram of the experimental geometry of a LEED experiment, ϕ is the angle of incidence (which is close to 90°), ψ is the azimuthal angle, and θ is the diffraction angle. Reproduced by kind permission from ref. [1]

$$\tan \theta = \frac{S}{L} \sin \psi \quad \text{since } \psi \text{ is small}$$

$$d = \frac{S}{L} \sqrt{h^2 + l^2}$$

If information about periodicity in plane of incidence is required, ψ must be increased so that the Ewald sphere cuts several reciprocal lattice rods

- streaks then become rows of (blurred) spots

Intensity versus ψ - $I(\psi)$ "rocking curves" - can be used with dynamical theory to extract detailed atomic spacing

- theory less well developed than LEED
- includes many more multiple scattering events
- includes many more inelastic events
- quantitative RHEED usually not performed

4.5.3 Applications of RHEED

RHEED is very sensitive to surface roughness on 100-1000 Å scale

Since pathlength of RHEED electron is high, electron may pass through a small surface feature and cause true bulk-like diffraction

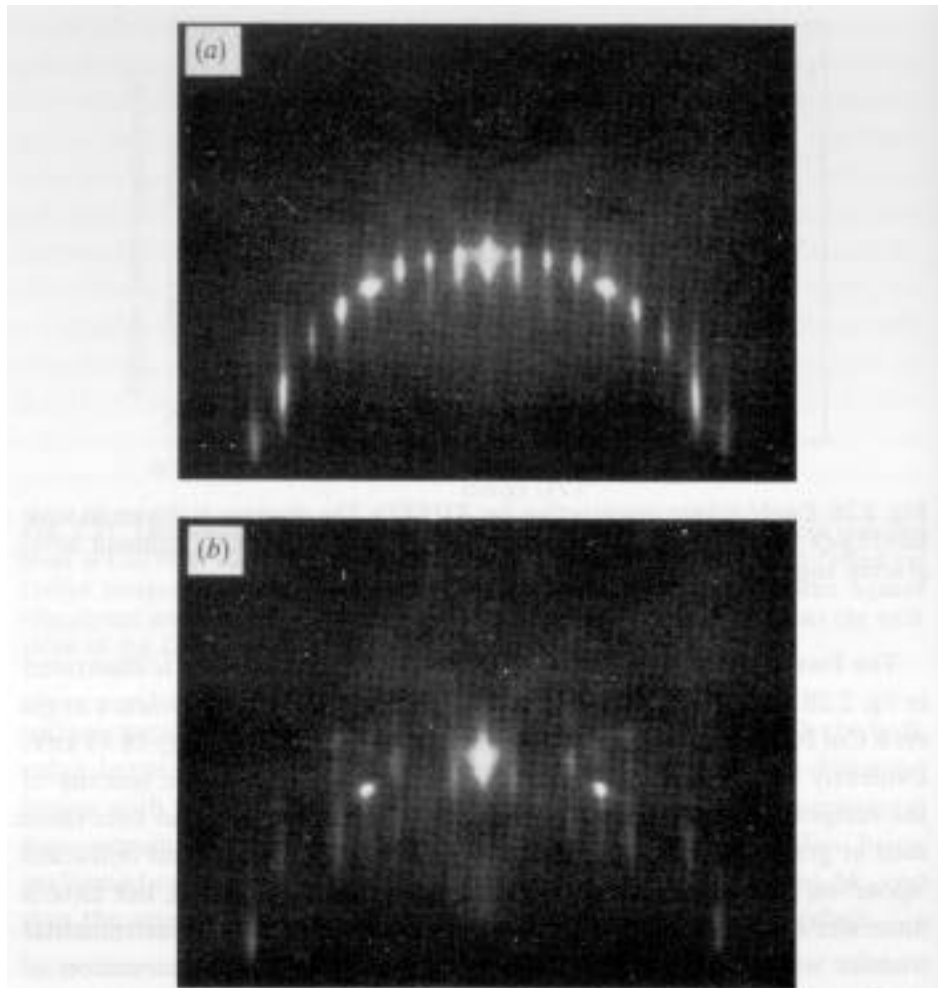


Fig. 2.29 RHEED patterns recorded from a GaAs(001)(2 × 4) surface in the [110] azimuth at an electron energy of 12.5 keV and an incident angle of 2.85°: (a) corresponds to a static annealed surface, and (b) to the situation during steady state growth by molecular beam epitaxy (after Larsen & Meyer-Ehmsen, 1990).

Such bulk diffraction

- reduces intensity in RHEED streaks
- causes sharp spots in RHEED pattern

Can use RHEED to follow growth of one material on another (epitaxy) - As, Ga molecular beams on GaAs(001) surface

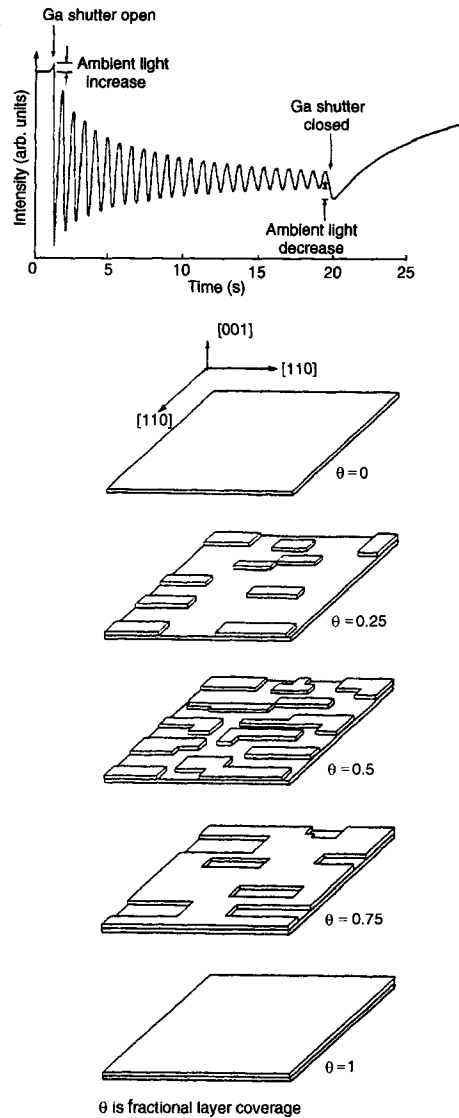


Figure 8.19. Intensity oscillations of the specular beam in the RHEED pattern from a GaAs(001) (2×4) reconstructed surface, during semiconductor growth by MBE. Intensity maxima correspond to atomically smooth surfaces ($\theta \approx 0$ and $\theta \approx 1$), while minima correspond to completely disordered surfaces ($\theta \approx 0.5$). The period of the oscillations then exactly corresponds to the growth rate of a single Ga + As layer. Inflections at the beginning and end of growth result from ambient light change as the effusion cell shutters are opened and closed. Reproduced by kind permission of Elsevier Science – NL from ref. [18]

In this case, growth proceeds by Franck-Van der Merwe growth mode (layer-by-layer)

Experimental arrangement of RHEED (compared with LEED) makes it especially suited to *molecular beam epitaxy* (MBE) and *metal-organic chemical vapor deposition* (MOCVD) studies

RHEED used widely in semiconductor growth industry

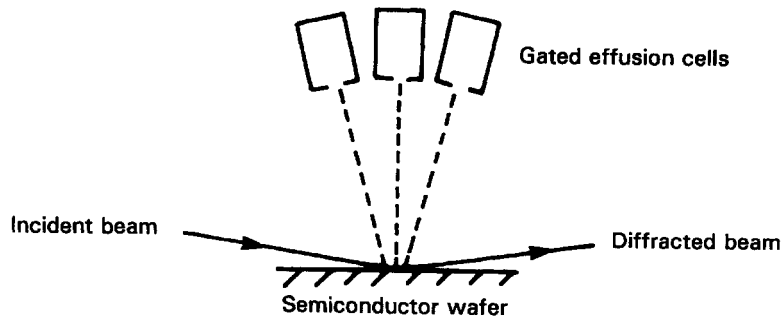


Figure 8.20. Schematic diagram illustrating the advantages of the RHEED geometry over LEED during semiconductor growth by MBE. Effusion cells are usually mounted directly in front of the sample, so that LEED cannot in general be accommodated. The grazing incidence geometry of RHEED means that it can be used to probe surface order during growth

4.6 X-ray Techniques for Surface Structure Determination

X-ray absorption process very similar to optical absorption - obeys Beers Law

x-rays are energetic enough to ionize both *valence electrons* and some *core electrons*

Absorption characterized by series of "absorption edges" corresponding to ionization of each core level

Each edge denoted by *x-ray notation* and is made up of several closely-spaced edges

"Atomic notation": $n l_j \quad j = l \pm s$

Atomic Notation	X-ray Notation
1s	K ₁
2s	L ₁
2p _{1/2}	L ₂
2p _{3/2}	L ₃
3s	M ₁
3p _{1/2}	M ₂
3p _{3/2}	M ₃
3d _{3/2}	M ₄
3d _{5/2}	M ₅

Position of edge slightly sensitive to "chemical environment" of atom - oxidation state, bonding environment - producing a *chemical shift*

Absorption is same as optical absorption

$$I = I_0 \exp(-(\mu) l)$$

$$A = \left| \langle i | \mu | f \rangle \right|^2$$

Absorption (μ) generally strongest at absorption edge then decreases

Fine structure (small intensity modulation) appears in x-ray absorption spectrum above edge

- (1) Extended X-ray Absorption Fine Structure (EXAFS)
- (2) Near-Edge X-ray Absorption Fine Structure (NEXAFS) or X-ray Absorption Near-Edge Structure (XANES)

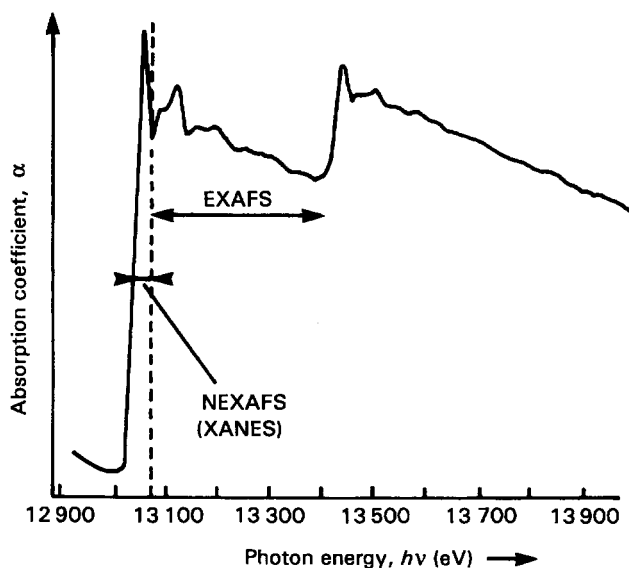


Figure 8.24. A typical X-ray absorption spectrum of a condensed medium. The sample is $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, and the figure shows the L_{III} absorption edge of Pb, with the NEXAFS and EXAFS regions indicated. Absorption above around 13400 eV is due to the L_{III} edge of Bi, which is close in energy to the Pb edge

4.6.1 Extended X-ray Absorption Fine Structure (EXAFS)

Effect is due to *interference* between outgoing electron wave (photoelectron) and part of outgoing electron wave scattered by neighboring atoms

- oscillations in x-ray intensity 50~200 eV from absorption edge

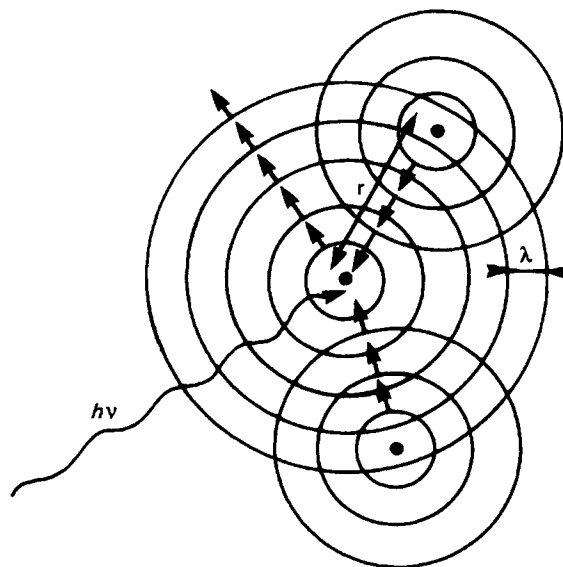


Figure 8.25. In the EXAFS process, the excited electron wavefunction (wavelength λ) propagates away from the atom at which photon absorption occurs, and is backscattered from surrounding atoms. The interatomic distance is r

- does not occur for isolated atoms
- outgoing photoelectron (KE > 50 eV) behaves like free electron
- most interference from nearest neighbors
- sensitive to *short-range* order (unlike diffraction) - works for amorphous, polycrystalline, glassy materials, liquids
- can select absorption edge for one particular species (C, O, N...)

If we assume that outgoing and back-scattered electrons can be treated as plane waves, constructive interference occurs when

$$n \lambda = 2 r$$

Destructive interference will occur when

$$\frac{n \lambda}{2} = 2 r$$

At intermediate values of λ , intermediate interference results that affects the intensity of the outgoing wave.

Energy of outgoing photoelectron (at absorption edge threshold photoelectron has zero KE)

$$E = h \nu_{\text{photon}} - h \nu_{\text{threshold}}$$

Since

$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m}$$

$$\text{and } p = \frac{h}{\lambda}$$

we can write

$$E = h_{\text{photon}} - h_{\text{threshold}}$$

$$= \frac{h}{\left(2m[h_{\text{photon}} - h_{\text{threshold}}]\right)^{1/2}}$$

Constructive interference occurs whenever,

$$n = 2r$$

$$n = \frac{h}{2r \left(2m[h_{\text{photon}} - h_{\text{threshold}}]\right)^{1/2}}$$

where n is really a measure of the "degree of interference"

Interference modulates amplitude of μ_f and hence modulates x-ray absorbance

$$A = \left| \left\langle i \left| \mu_f \right. \right\rangle \right|^2$$

- when n is an integer, constructive interference between outgoing and scattered photoelectron wave causes strong x-ray absorption
- when n is integer + half, destructive interference between outgoing and scattered photoelectron causing reduced x-ray absorption

Other features to note:

- (1) period of oscillations increase as h increases above $h_{\text{threshold}}$
- (2) period of oscillations becomes longer if r is decreased
- (3) intensity of oscillations increases with more scatterers at distance r

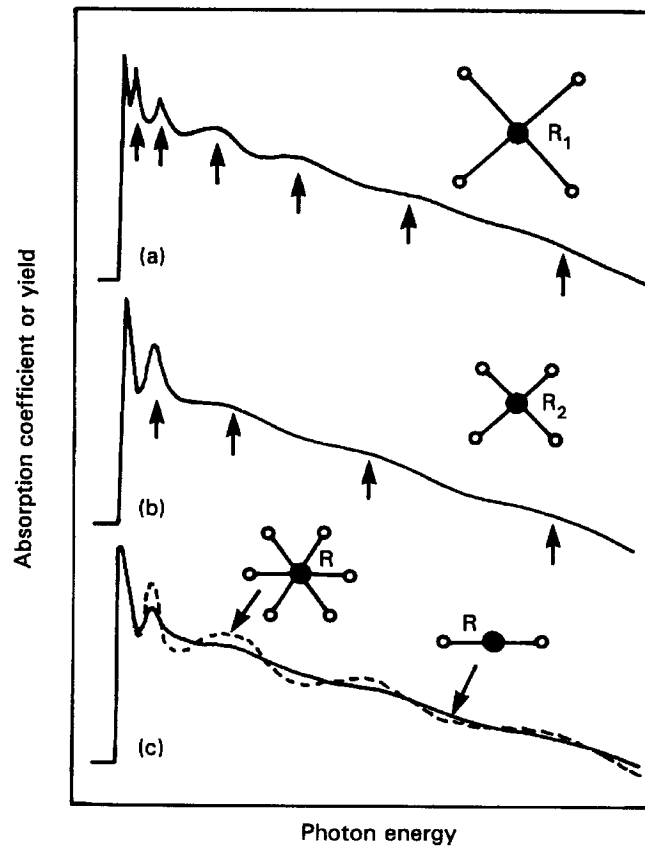


Figure 8.27. The effect of coordination number and nearest-neighbour distance on the form of the EXAFS spectrum. Shorter bonds give rise to larger spaced oscillations (compare R_1 (a) and R_2 (b)), whilst an increase in coordination number gives a larger amplitude (compare the traces for a two-coordinate and a six-coordinate species in (c)) [22]. Shorter bonds are characterised by larger-spaced EXAFS oscillations, and the EXAFS amplitude increases with the number of nearest-neighbour atoms

Most often raw $\chi(k)$ versus k data is re-plotted versus wavevector k ($= 2\pi/\lambda$)

$$n = \frac{h}{2r \left(2m \left[h_{\text{photon}} - h_{\text{threshold}} \right] \right)^{1/2}} = \frac{2}{2rk}$$

$$k = \frac{\left(2m \left[h_{\text{photon}} - h_{\text{threshold}} \right] \right)^{1/2}}{2h}$$

$$= 0.5123 \left(h_{\text{photon}} - h_{\text{threshold}} \right)^{1/2}$$

where k is in \AA^{-1} and h in eV. Fourier-transform of $\chi(k)$ versus k gives nearest-neighbor distances (and intensity gives number of atoms)

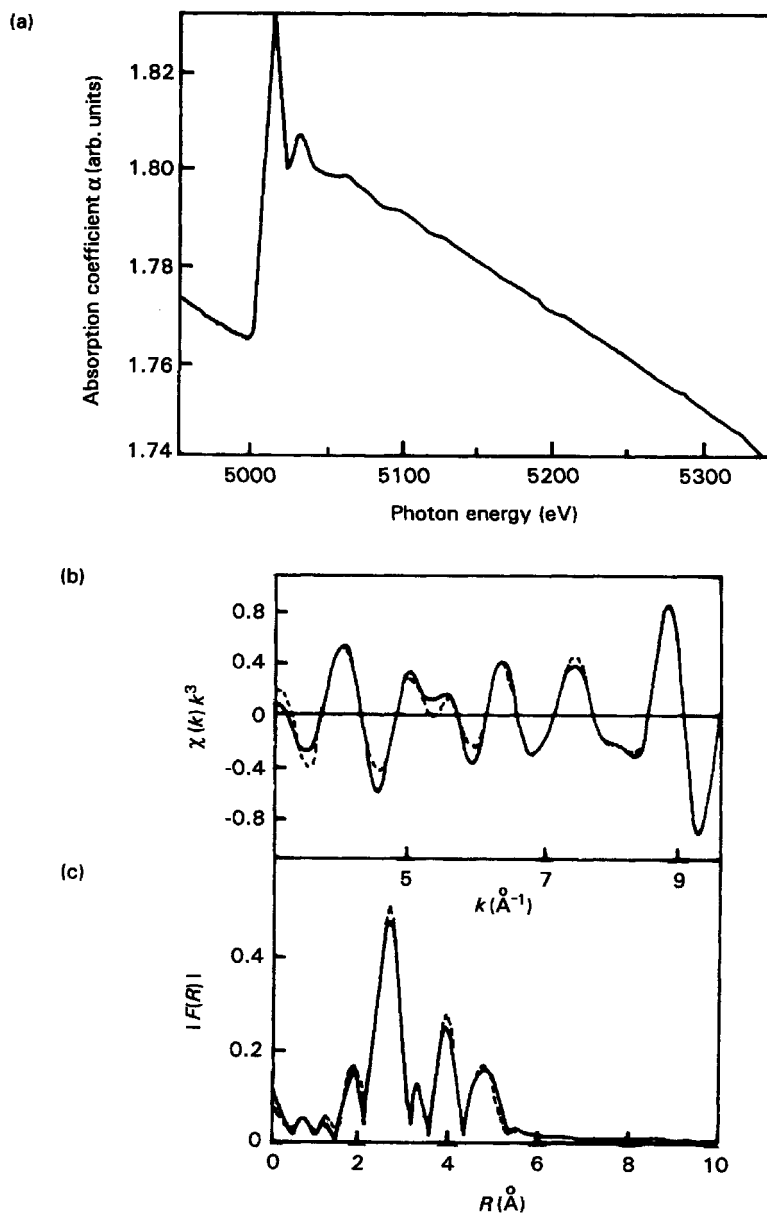


Figure 8.32. Stages in the manipulation of EXAFS data. The spectra shown are from surface EXAFS (SEXAFS) experiments using various adsorbates on Ag(111) [25]. (a) Raw EXAFS data as a function of photon energy, at the Cs L_{III} -edge for Cs on Ag(111). (b) $k^3 \chi(k)$ plot for Cl on Ag(111). The data has been Fourier filtered to include real space components up to 5 \AA from the absorbing atom, then back-transformed into k space (as described in the text). The data is compared with a theoretical calculation (broken line). (c) The experimental and theoretical Fourier transforms of $k^3 \chi(k)$. The major peak gives a nearest neighbour Ag–Cl distance of $2.70 \pm 0.01 \text{\AA}$. Reproduced by kind permission from ref. [25]

4.6.2 Instrumentation for EXAFS

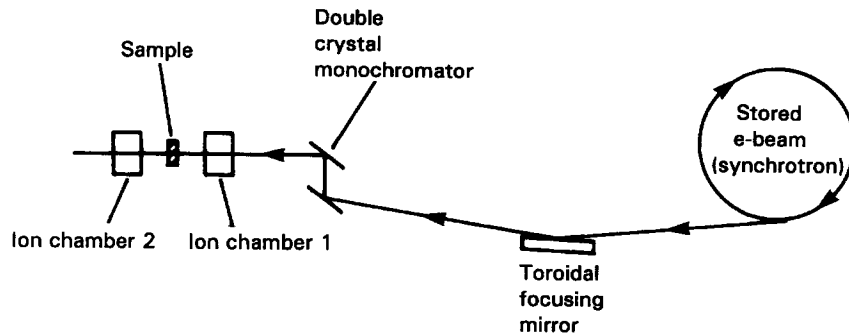


Figure 8.30. Schematic experimental arrangement for transmission EXAFS

Tunable x-ray source (electron storage ring - synchrotron)

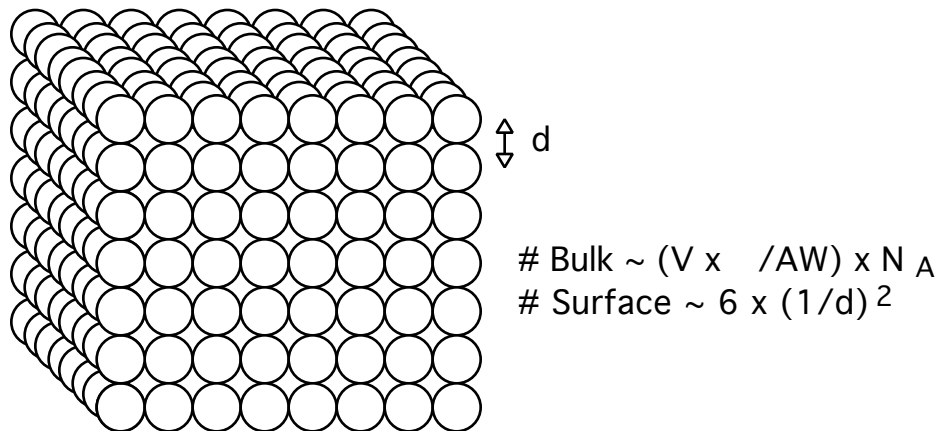
- pulsed, plane polarized output

X-ray monochromator (< few eV resolution)

Detector for I and I_0 - ion chamber (total ion current intensity)

4.6.3 Surface EXAFS (SEXAFS)

Basic problem in making EXAFS surface sensitive is removing contribution from bulk absorption



For $1 \times 1 \times 1 \text{ cm}^3$ Au: (NN distance = 2.89 \AA , $AW = 197 \text{ g}\cdot\text{mol}^{-1}$, $\rho = 19.3 \text{ g}\cdot\text{cm}^{-3}$) # bulk atoms = 6×10^{22} , number surface atoms = 6×10^{15} (0.1 ppm)

The conventional EXAFS technique can be made more surface sensitive by grazing incidence

- by varying incidence angle, surface sensitivity can be altered from nm to mm
- can detect reflected beam directly or x-ray fluorescence (absorption)
- photons have long pathlength in solids (1-100 μm)

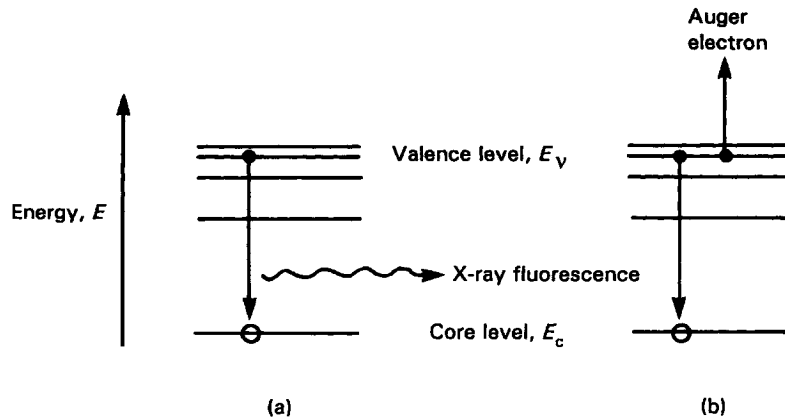


Figure 8.31. (a) The core hole created in XAS may be filled by an electron from a higher level, with the excess energy emitted as X-ray photons. (b) Alternatively, the excess energy may be dissipated by the emission of a second, Auger electron

One way is to measure x-ray fluorescence from atom known to be present on surface only

- fluorescence from O or C atoms for $c(2 \times 2)\text{CO-Ni}(100)$

Another way is to measure low energy photoelectrons coming from surface

Low energy electrons have short inelastic mean free path (IMFP), λ , in solids (used in LEED to give surface sensitivity, remember?)

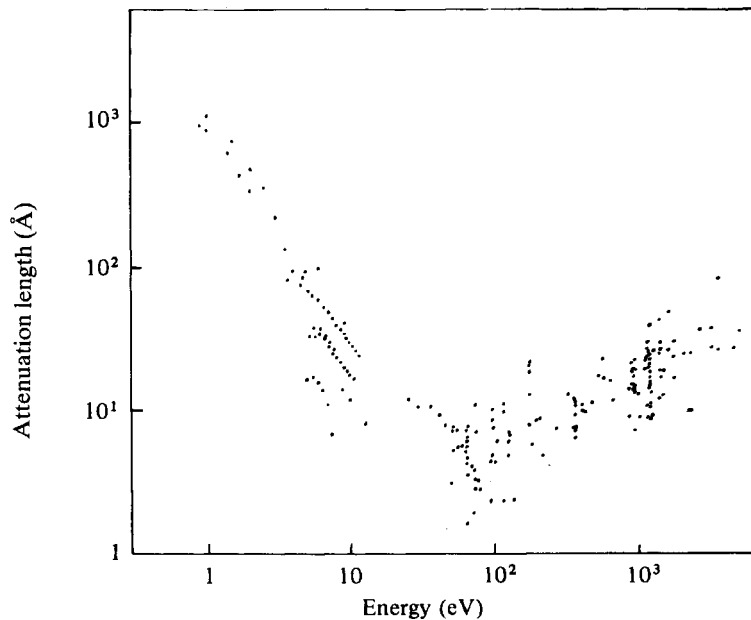


Fig. 3.2 Collection of experimental determinations of attenuation length as a function of energy above the Fermi level for many different materials (after Seah & Dench, 1979).

Electrons of KE ~ 100 eV have shortest IMFP so are most surface sensitive

May collect

- total electron yield
- Auger electron yield

Low signal intensities

Long data collection time - require UHV to minimize surface contamination during data acquisition

4.7 Near-Edge X-ray Absorption Fine Structure (NEXAFS or XANES)

Fine structure less than ~ 50 eV from absorption edge

In EXAFS, interaction between outgoing wave and scatterer strong - single scattering events dominate

In NEXAFS, interaction between outgoing wave and scatterer weak - multiple scattering events dominate

Need *dynamical calculations* to determine origin of fine structure peaks

For molecules adsorbed on surfaces, often see additional absorption features (resonances) due to intramolecular excitation (π^* , σ^*)

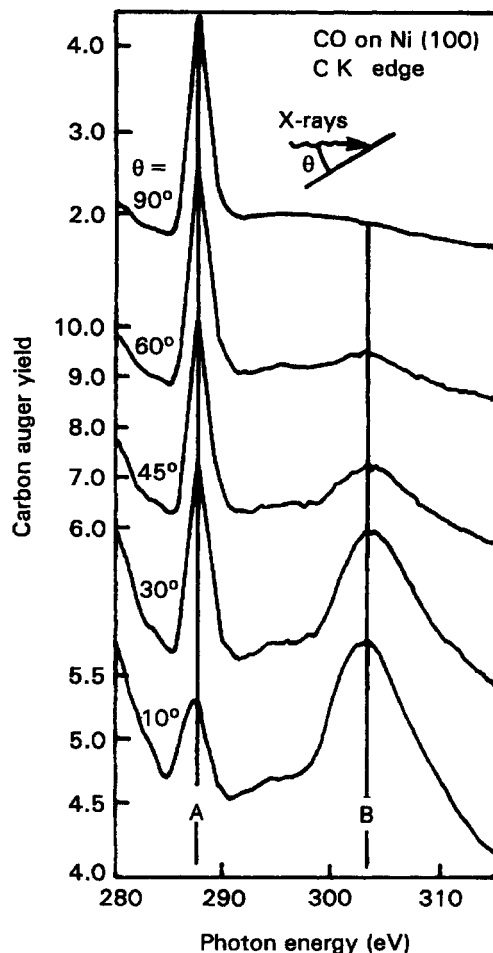


Figure 8.38. NEXAFS data above the C K-edge for CO on Ni(100) at 180 K, as a function of incidence angle. Reproduced by kind permission of the American Institute of Physics from ref. [33]

For CO on Ni(100)

A - π^* (allowed when E vector perpendicular to -C O bond)

B - σ^* (allowed when E vector parallel to -C O bond)

Alteration of incidence angle can be used to determine alignment of adsorbate bonds

4.8 Summary

RHEED provides similar information to LEED

Surface sensitivity can be varied somewhat by changing incidence angle (20- $>500 \text{ \AA}$)

Very simple, inexpensive instrumentation amenable to MBE, MOCVD and film growth situations

Rapid for simple analysis

Rocking curves can be used with theory to measure atomic positions but difficult

BUT

RHEED theory not fully developed (many body multiple scattering theory)

Only information in 1-D without azimuthal crystal rotation

Sensitive to surface roughness - not intrinsically surface sensitive

X-ray scattering techniques sensitive to short range order - accurate nearest neighbor distances

Works for disordered materials unlike diffraction

Information about chemical environment

Intrinsically bulk sensitive - can be made surface sensitive by

- grazing incidence
- using core edge of adsorbate
- collecting low energy electrons

Simple instrumentation (in principle)

NEXAFS resonances useful for determining orientation of adsorbate

BUT

Requires synchrotron for tunable x-rays - very expensive

Complex theory needed to fully interpret data

- single scattering (EXAFS)
- multiple scattering (NEXAFS/XANES)