Experimental methods in nanotechnology II

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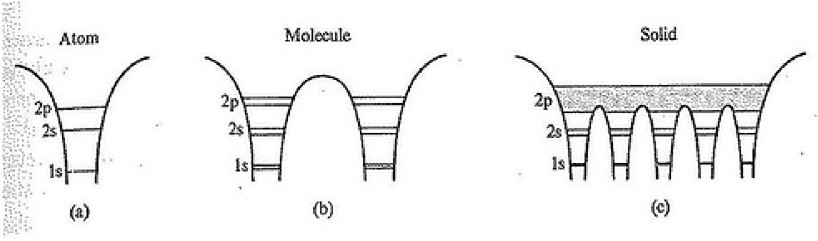
Outline

Intro

- electronics structure of solids.
- electron-photon transitions in solids.
- description of experimental techniques, related with the electronic structure.

Motivation



- In single atom, electron's state provides sharp energy levels, $E_n \sim \frac{1}{n^2}$. Electrons are localized in the vicinity of the nucleus.
- In molecules, electrons can be shared by the atoms of the molecules. I.e., the electron's states hybridize, resulting in an energy splitting.
- In solids, electrons can be shared by all atoms in the solid. The continuous electrons bands are formed.

Outline

1. Introduction
2. Electron in periodic potential
   - Free electron
   - Bloch theorem
   - Brillouin zone
   - Reciprocal space
   - Number of k-states in the First Brillouin zone
   - Free electron states
   - Density of states
   - Fermi surface
   - Understanding of Brillouin zone
3. Diffraction
   - X-ray diffraction

   - Inverse photoelectron spectroscopy (IPES)
   - Auger and characteristic X-ray
   - Synchrotron

5. Magneto-optical effect
   - Examples of magneto-optical effects
   - Origin of magneto-optical effects
   - Use of magneto-optical effects
6. Time resolved investigations
   - Relation between energy

Free electron

Free electron's state is described by Schrödinger equation:

$$H\psi = E\psi$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\psi = E\psi, \quad \text{where } U(\vec{r}) = 0$$

In case of free electron, the solution of the electron's wavefunction is plane wave $\psi = \exp(i\vec{k}\cdot\vec{r})$ and the corresponding electron's energy is:

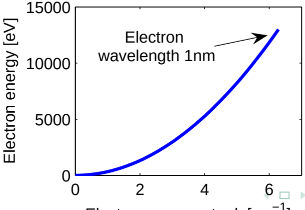
$$E = \frac{\hbar^2|\vec{k}|^2}{2m}.$$

Free electron energy: $E = \dfrac{\hbar^2|\vec{k}|^2}{2m}$

- Relation between wavelength λ and wavevector $\vec{k}$ is $\lambda = \dfrac{2\pi}{|\vec{k}|}$.
- When compared with the classical relation $E = \frac{p^2}{2m}$, we obtain relation between the linear momentum $\vec{p}$ and the wavevector $\vec{k}$ (de Broglie relation):

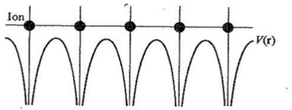
$$\vec{p} = \hbar\vec{k}.$$

- Example: for free electron with wavelength 1 nm, electron energy is 13 keV (quite a high energy).



Electron in periodic potential – Bloch theorem

- Let us assume electron's potential to be periodical: $U_0(\vec{r}) = U_0(\vec{r} + \vec{T})$, where $\vec{T}$ is the lattice vector.



- We assume *one-electron approximation*, i.e. interaction with other electrons (exchange, correlation, Coulomb force) are included as the additional effective potential acting on electron, $U_{\text{eff}}(\vec{r})$, with the same periodicity as $U_0(\vec{r})$: $U(\vec{r}) = U_0(\vec{r}) + U_{\text{eff}}(\vec{r})$.
- Then, the electron's state is described by a wavefunction ψ fulfilling the Schrödinger equation:

$$H\psi = E\psi$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\psi = E\psi.$$

http://electrons.wikidot.com/energy-bands-in-solids-and-their-calculations

Bloch theorem: proof I

- All observables must have the same periodicity as the lattice. Hence, the electron probability $|\psi|^2$ must fulfill: $|\psi(\vec{r})|^2 = |\psi(\vec{r}+\vec{T})|^2$. Therefore, we can express $\psi(\vec{r})$ as:

$$\psi(\vec{r}+\vec{T}) = e^{i\theta(\vec{T})}\psi(\vec{r}),$$

  where $\theta(\vec{T})$ is (at this stage arbitrary) phase, as $|e^{i\theta(\vec{T})}|^2 = 1$
- For two translations $\vec{T}_1$ and $\vec{T}_2$ we have

$$\psi(\vec{r}+\vec{T}_1+\vec{T}_2) = e^{i\theta(\vec{T}_1+\vec{T}_2)}\psi(\vec{r}) = e^{i\theta(\vec{T}_1)}e^{i\theta(\vec{T}_2)}\psi(\vec{r})$$

  Hence, $\theta(\vec{T}_1+\vec{T}_2) = \theta(\vec{T}_1)+\theta(\vec{T}_2)$. Hence, the phase $\theta(\vec{T})$ has form $\theta(\vec{T}) = \vec{k}\cdot\vec{T}$, as the only this function fulfills the requirement.

Bloch theorem: proof I

- In final, the electron wavefunction of the periodical potential writes: $\psi(\vec{r}+\vec{T}) = e^{i\vec{k}\cdot\vec{T}}\psi(\vec{r})$. In another words, the translation by a lattice vector $\vec{T}$ is equivalent to multiplaying the wavefunction $\psi(\vec{r})$ by a phase factor $e^{i\vec{k}\cdot\vec{T}}$.

Bloch theorem: proof II

- Let us assume, that the solution of $\psi(\vec{r})$ is in form:
  $$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}).$$
  Then, we show that $u_{\vec{k}}(\vec{r})$ has the same periodicity as the lattice.
- In point $\vec{r} + \vec{T}$ the wavefunction has value:
  $$\psi(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot(\vec{r}+\vec{T})} u_{\vec{k}}(\vec{r} + \vec{T}),$$
  whereas the previous proof provides:
  $$\psi(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}} \psi(\vec{r}) = e^{i\vec{k}\cdot\vec{T}} e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}).$$
- By comparing both equations, we see:
  $$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{T}),$$
  i.e. $u_{\vec{k}}(\vec{r})$ has the same periodicity as the lattice.

The resulting wavefunction of the periodic potential is (Bloch theorem):

$$\psi_{\vec{k}}(\vec{r}) = \exp(i\vec{k}\cdot\vec{r})u_{\vec{k}}(\vec{r}),$$

- $u_{\vec{k}}(\vec{r})$ has equal periodicity as the lattice, $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{T})$.
- $\exp(i\vec{k}\cdot\vec{r})$ corresponds to free-electron wave (free-electron propagation). It implies that the electron propagates through the crystal like a free (pseudo-free) particle.
- Function $u_{\vec{k}}(\vec{r})$ modulates this free-electron-like wave so that the amplitude oscillates periodically form one cell to the next. It does not affect the basic character of ψ, which is that of a traveling wave. In reality the electron is not free, (it interacts with the lattice, electrons etc), but its propagation has features of a free electron propagation.

- As the electron behaves like a wave with wavevector $\vec{k}$, it has a deBroglie wavelength and thus a corresponding momentum $\vec{p} = \hbar\vec{k}$.

Reduction to Brillouin zone

The periodicity of the lattice is described by the lattice vector $\vec{T}$. Let us assume electron's wavevector $\vec{k} = \vec{G}$, such that $e^{i\vec{G}\cdot\vec{T}} = 1$. (In case of 1D system with periodicity $T = a$, G-vector has value $G = 2\pi/a$). Then:

- For $\vec{k} = \vec{G}$: $\psi_{\vec{G}}(\vec{r} + \vec{T}) = e^{i\vec{G}\cdot\vec{T}}\psi_{\vec{G}}(\vec{r}) = \psi_{\vec{G}}(\vec{r})$. I.e. for $\vec{k} = \vec{G}$, $\psi_{\vec{G}}$ is periodical. It means, that $\psi_{\vec{G}}$ does not change for lattice translation $\vec{T}$. In another words, $\psi_{\vec{G}}$ satisfies Bloch theorem in the same way as for $\vec{k} = 0$.

⇒ For both cases, $\vec{k} = 0$ and $\vec{k} = \vec{G}$, the wavefunction does not propagate, and its propagation can be described by $\vec{k} = 0$.

- For a general wavevector $\vec{k}' = \vec{k} + \vec{G}$, the wavefunction is:

$$\psi_{\vec{k}'}(\vec{r} + \vec{T}) = e^{i(\vec{k}+\vec{G})\cdot\vec{T}}\psi_{\vec{k}'}(\vec{r}) = e^{i\vec{k}\cdot\vec{T}}\psi_{\vec{k}'}(\vec{r}).$$

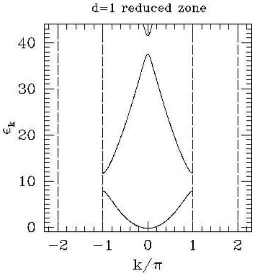
It means, waves both with $\vec{k}' = \vec{k} + \vec{G}$ and with $\vec{k}$ propagate as having the same phase speed.

Reduction to Brillouin zone

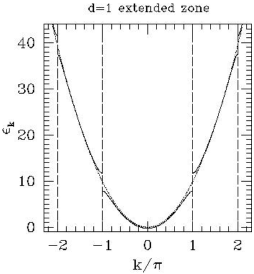
Hence, wavevector value $\vec{k}$ can be chosen from many possibilities, as any wavevector $\vec{G}$ can be added to it. Hence,

- in 1D with periodicity a, wavevector is chosen to be $-\pi/a < k \leq \pi/a$, i.e. inside 1D Brillouin zone (Wigner-Seitz cell in the reciprocal space)

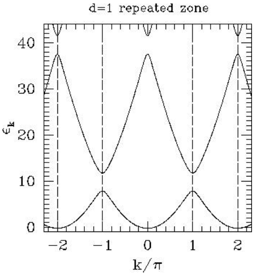
reduced zone



extended zone



repeated zone



- in 3D, Brillouin zone and reciprocal space will be derived later

...

1D Fourier transform

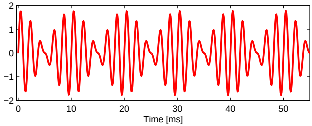
Fourier transform:

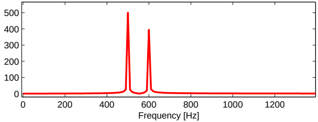
$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)\exp(-ikx)\mathrm{d}x$$

Inverse Fourier transform:

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k)\exp(ikx)\mathrm{d}k$$

Example: sound in real (time) and reciprocal (frequency) space:





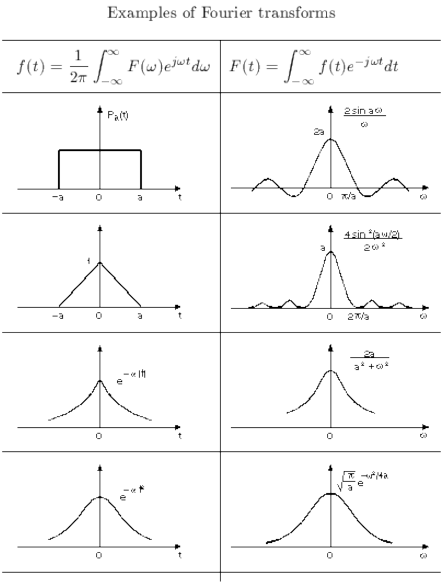
Example: Fourier transform of the rectangular function $f(x)$

$$f(x) = \begin{cases} x < -a: & f(x) = 0 \\ -a < x < a: & f(x) = 1 \\ x > a: & f(x) = 0 \end{cases}$$

Then its Fourier transform is:

$$\begin{aligned} F(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \exp(-ikx) \mathrm{d}x = \frac{1}{\sqrt{2\pi}} \int_{-a}^{a} 1 \exp(-ikx) \mathrm{d}x \\ &= \frac{1}{\sqrt{2\pi}} \left(\frac{1}{ik}\right) \left[\exp(-ikx)\right]_{-a}^{a} = \frac{2}{\sqrt{2\pi}} \frac{\sin(ka)}{k} \end{aligned} \tag{1}$$

Note: output of Fourier transform is in general complex function.
Discussion about shape when a varies.
calculation of FT for Gauss function $FT(e^{x^2/a^2}) = \frac{a}{\sqrt{2\pi}} e^{-a^2 k^2/4}$
`http://www4.ncsu.edu/~franzen/public_html/CH795Z/math/ft/gaussian.html`



Examples of Fourier transforms

$$f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(\omega)e^{j\omega t}d\omega \qquad F(t) = \int_{-\infty}^{\infty} f(t)e^{-j\omega t}dt$$

http://www.etc.tuiasi.ro/cin/Downloads/Fourier/Fourier.html

Basic properties of 1D Fourier transformations

$f(t) = \frac{1}{\sqrt{2\pi}} \int_{\infty}^{\infty} F(\omega) e^{i\omega t} \mathrm{d}\omega$	$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{\infty}^{\infty} f(t) e^{-i\omega t} \mathrm{d}t$
$f(at)$	$\frac{1}{\lvert a \rvert} F\left(\frac{\omega}{a}\right)$
$f^{\star}(t)$	$F^{\star}(-\omega)$ (conjugation)
$f(t - t_0)$	$F(\omega) e^{-it_0\omega}$
$f(t) e^{i\omega_0 t}$	$F(\omega - \omega_0)$
$f(t) \cos(\omega t)$	$\frac{1}{2} \left[F(\omega + \omega_0) + F(\omega - \omega_0) \right]$
$\frac{\mathrm{d}^n f(t)}{\mathrm{d}t^n}$	$(i\omega)^n F(\omega)$
$(-it)^n f(t)$	$\frac{\mathrm{d}^n F(\omega)}{\mathrm{d}\omega^n}$

http://www.etc.tuiasi.ro/cin/Downloads/Fourier/Fourier.html

Dirac δ-function

How to describe periodical function in a reciprocal space?
Example:

$$f(x) = \cos(k_0 x) = \frac{1}{2}\left(e^{ik_0 x} + e^{-ik_0 x}\right).$$

Its Fourier transformation (expression in reciprocal space) is:

$$F(k) = \frac{1}{2\sqrt{2\pi}} \int_{-\infty}^{\infty} \left(e^{i(k_0-k)x} + e^{-i(k_0+k)x}\right) \mathrm{d}x$$
$$= \begin{cases} k = k_0: & \infty \\ k = -k_0: & \infty \\ \text{otherwise}: & 0 \end{cases}$$

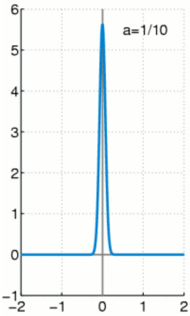
This very inconvenient: (i) handling infinity (ii) not expressed how 'strong' is here the infinity.
Therefore, Dirac δ-function is introduced.

Dirac δ-function

Definition:

$$\delta(x) = \begin{cases} +\infty, & x = 0 \\ 0, & x \neq 0 \end{cases}$$

$$\text{so that} \quad \int_{-\infty}^{\infty} \delta(x)\, dx = 1$$



Properties:

$$\int_{-\infty}^{\infty} f(x)\, \delta(x-a) \mathrm{d}x = f(a)$$

$$\delta(ax) = \frac{\delta(x)}{|a|}$$

Derivation of δ-function (per partes):

$$\int_{-\infty}^{\infty} \frac{\partial}{\partial x} \delta(x-a) f(x) = -\int_{-\infty}^{\infty} \delta(x-a) \frac{\partial}{\partial x} f(x)$$

δ-function and Fourier transform

$$\int_{-\infty}^{\infty} e^{i2\pi\xi x}\mathrm{d}\xi = \delta(x)$$

Hence,

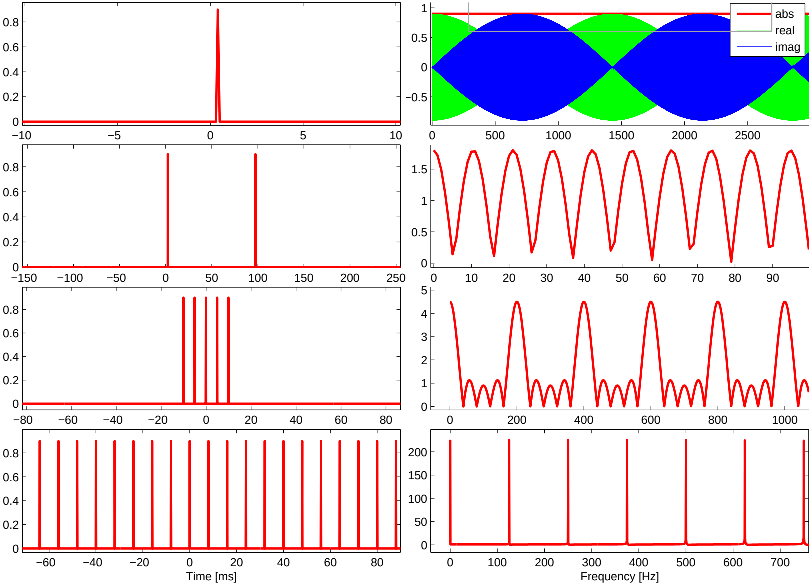
$$\int_{-\infty}^{\infty} e^{ikx}\mathrm{d}k = 2\pi\delta(x)$$

Basic properties:

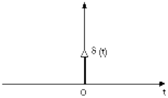
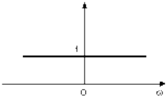
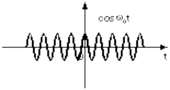
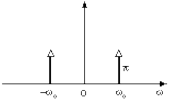
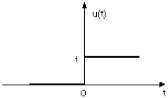
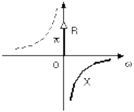
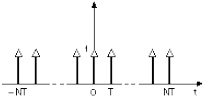
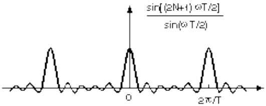
$$\int_{-\infty}^{\infty} e^{i(k_1-k_2)x}\mathrm{d}x = 2\pi\delta(k_1-k_2)$$

Calculate Fourier transform of: 1, $\delta(x-x_0)$, $\cos(k_0 x)$, $\sin(k_0 x)$.

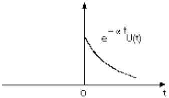
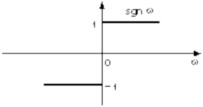
Examples of F.T. of δ-functions



Transforms of singularity functions

$f(t) \longleftrightarrow F(\omega)$	
	
	
	
	

Examples of Fourier transforms (continued)

$f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(\omega)e^{j\omega t}d\omega$	$F(t) = \int_{-\infty}^{\infty} f(t)e^{-j\omega t}dt$
	$\frac{1}{\alpha + j\omega}$
$\frac{j}{\pi t}$	

http://www.etc.tuiasi.ro/cin/Downloads/Fourier/Fourier.html

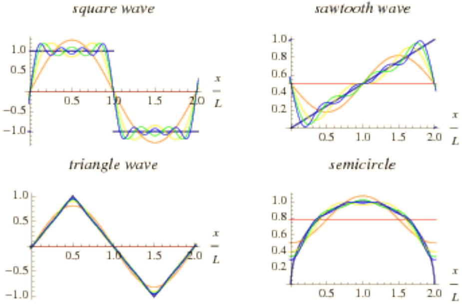
Fourier series

Let us have periodic function $f(x)$ with period T, $f(x) = f(x+L)$. Then,

$$f(x) = \sum_{n=-\infty}^{\infty} c_n \exp(in\frac{2\pi x}{L}).$$

where

$$c_n = \frac{1}{L}\int_{-L/2}^{L/2} f(x)\exp(-in\frac{2\pi}{L}x)\mathrm{d}x$$



Fourier series and Fourier transformation

Periodic function writes as: $f(x) = \sum_{n=-\infty}^{\infty} c_n \exp(in\frac{2\pi x}{L})$.

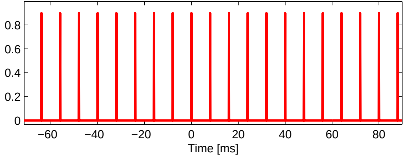
Then, its Fourier transform of periodic function $f(x)$ writes:

$$\begin{aligned} F(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \exp(-ikx) \mathrm{d}x \\ &= \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} c_n \int_{-\infty}^{\infty} \exp\left[ix(-n\frac{2\pi}{L} + k)\right] \mathrm{d}x \\ &= \sum_{n=-\infty}^{\infty} \sqrt{2\pi} c_n \delta(k - n\frac{2\pi}{L}). \end{aligned}$$

Hence, Fourier series and Fourier transforms can be expressed equivalently by an infinite set of δ-functions.

Dirac comb

Dirac comb is a periodic set of δ-functions.



- Dirac comb in real space, with spacing A:

$$D(x) = \sum_{n=-\infty}^{\infty} \delta(x - nA) = \frac{1}{A} \sum_{n=-\infty}^{\infty} e^{inx2\pi/A} = \frac{K_0}{2\pi} \sum_{n=-\infty}^{\infty} e^{inK_0x}$$

- Dirac comb in reciprocal (frequency) space, with spacing $K_0 = 2\pi/A$:

$$D(k) = \sum_{n=-\infty}^{\infty} \delta(k - nK_0) = \frac{1}{K_0} \sum_{n=-\infty}^{\infty} e^{ink2\pi/K_0} = \frac{A}{2\pi} \sum_{n=-\infty}^{\infty} e^{inAk}$$

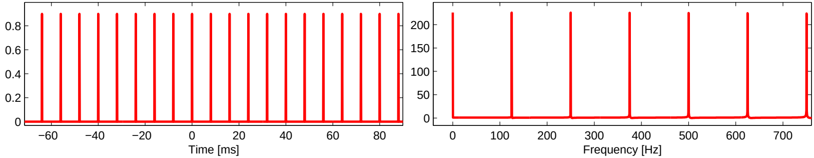
Fourier transform of the Dirac comb

Fourier transform of the Dirac comb is again a Dirac comb.

$$\mathrm{F.T.}\left(\sum_{n=-\infty}^{\infty}\delta(x-nA)\right)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\sum_{n=-\infty}^{\infty}\delta(x-nA)e^{-ikx}\mathrm{d}x$$

$$=\frac{1}{\sqrt{2\pi}}\sum_{n=-\infty}^{\infty}e^{-iknA}=\frac{\sqrt{2\pi}}{A}\sum_{n=-\infty}^{\infty}\delta(k-n\frac{2\pi}{A})$$

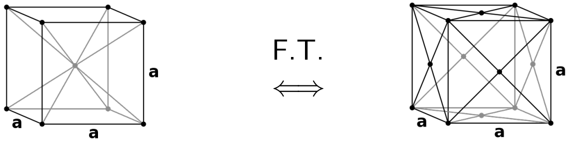
where $2\pi/A=K_0$.



Dirac comb in 3D

Dirac comb in 3D - transform from real 3D space of atoms (defined by δ-functions) to reciprocal space, consisting also of δ-functions.

body centered cubic (bcc) face centered cubic (fcc)



bcc in real space: $\mathrm{bcc}(\vec{r}) =$

$$\sum_{u,v,w=-\infty}^{\infty}\left[\delta(\vec{x}-u\hat{a}_x-v\hat{a}_y-w\hat{a}_z)+\delta(\vec{x}-(u+\frac{1}{2})\hat{a}_x-(v+\frac{1}{2})\hat{a}_y-(w+\frac{1}{2})\hat{a}_z)\right]$$

bcc in reciprocal space: $\mathrm{bcc}(\vec{k}) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{-i\vec{k}\cdot\vec{r}}\mathrm{bcc}(\vec{r})\mathrm{d}\vec{r}$

bcc in reciprocal space

bcc in real space: $\mathrm{bcc}(\vec{r}) =$

$$\sum_{u,v,w=-\infty}^{\infty}\left[\delta(\vec{x}-u\hat{a}_x-v\hat{a}_y-w\hat{a}_z)+\delta(\vec{x}-(u+\frac{1}{2})\hat{a}_x-(v+\frac{1}{2})\hat{a}_y-(w+\frac{1}{2})\hat{a}_z)\right]$$

bcc in reciprocal space: $\mathrm{bcc}(\vec{k}) = \dfrac{1}{(2\pi)^{3/2}}\displaystyle\int_{-\infty}^{\infty} e^{-i\vec{k}\cdot\vec{r}}\mathrm{bcc}(\vec{r})\mathrm{d}\vec{r}$

$$= \frac{1}{(2\pi)^{3/2}}\sum_{u,v,w=-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-(ik_x u a_x+ik_y v a_y+ik_z w a_z)}\left[1+e^{-i\frac{1}{2}(k_x a_x+k_y a_y+k_z a_z)}\right]\mathrm{d}x\mathrm{d}y\mathrm{d}z$$

$$= \frac{(2\pi)^{3/2}}{a_x a_y a_z}\sum_{u,v,w=-\infty}^{\infty}\delta(\vec{k}-u\hat{k}_x-v\hat{k}_y-w\hat{k}_z)\left[1+e^{-i\frac{1}{2}(k_x a_x+k_y a_y+k_z a_z)}\right].$$

The 3D Dirac comb multiplied by '1' forms basis of an ordinary cubic lattice. Second part is real only when $k_x = 0$ OR $k_y = 0$, OR $k_z = 0$. Hence, it forms remaining points in fcc lattice.

Reciprocal space

- In the real space, the quantities are expressed as function of positions, e.g. $V(\vec{r})$, $\Psi_{\vec{k}}(\vec{r})$.
- In the reciprocal space, the quantities are expressed as function of wave-vector $\vec{k}$ or momentum $\vec{p} = \hbar\vec{k}$.
- Conversion between real and reciprocal space is Fourier transform, e.g. $V(\vec{k}) = \mathrm{F.T.}(V(\vec{r}))$, and $V(\vec{r}) = \mathrm{inv.F.T.}(V(\vec{k}))$.
  - $V(\vec{r})$ Potential $V(\vec{r})$ is periodical in the crystal. Hence, in reciprocal space, $V(\vec{k})$ consists of lattice of δ-functions.
  - $\Psi(\vec{r})$ is not in general periodical, but the potential $V(\vec{r})$ is periodical. Hence, $\Psi(\vec{r})$ can be written $\Psi(\vec{r}) \Rightarrow \Psi(\vec{k}) = \Psi(\vec{k}_{\mathrm{inside\_1st_Brillouin\_zone}} + \vec{K}) = \Psi(\vec{k}_{\mathrm{inside\_1st_Brillouin\_zone}})$.

(First) Brillouin zone

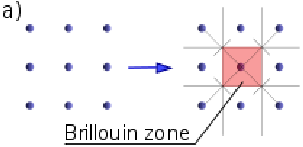
Definitions:

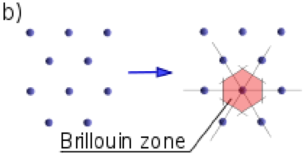
Def1: First Brillouin zone is a smallest possible cell in reciprocal space, which by translation can form whole reciprocal space.

Def2: Any point of the reciprocal space $\vec{k}$ can be reached from the first Brillouin zone $\vec{k}_{\mathrm{inside\_1st_Brillouin\_zone}}$ added to a translation vector of the reciprocal lattice $\vec{K}$:

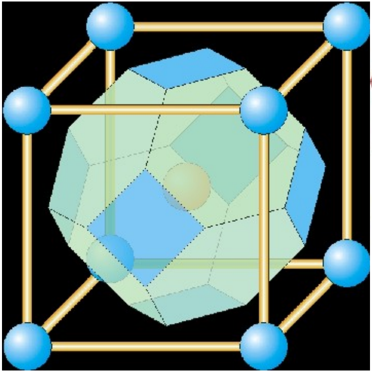
$$\vec{k} = \vec{k}_{\mathrm{inside\_Brillouin\_zone}} + \vec{K}.$$

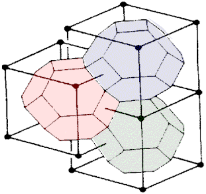
$\vec{K}$: translation (or primitive) vector of the reciprocal space



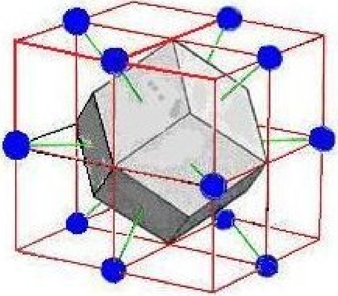


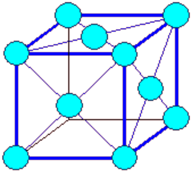
(First) Brillouin zone of fcc real space (bcc reciprocal)





(First) Brillouin zone of bcc real space (fcc reciprocal)

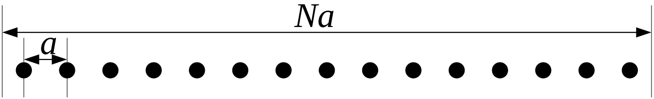




Properties of Brillouin zone:

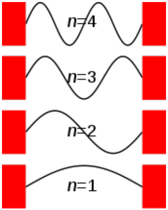
- For any real translation vector $\vec{T}$ and reciprocal translation vector $\vec{K}$ is valid:
$$e^{i\vec{T}\cdot\vec{K}} = 1,$$
i.e. $\vec{T}\cdot\vec{K} = 2\pi n$, n is integer.
- Volume of the (First) Brillouin zone $V_{\vec{k}}$ is inversely proportional to volume of unit cell of the real (direct) lattice $V_{\vec{r}}$:
$$V_{\vec{k}} = \frac{(2\pi)^3}{V_{\vec{r}}}$$

Boundary conditions on surface of the crystal:



We need to know, how many *k*-states are available inside a given crystal. Hence, boundary conditions on crystal's interfaces must be handled.

1st opt: Describe standing waves inside the box, having boundary conditions $\psi(x<0)=\psi(x>N_x a_x)=0$, where a_x is inter-atomic distance and N_x is number of atoms in x-direction. However, difficult to handle numerically.



2nd opt: Cyclic (Born – von Kármán) boundary conditions $\psi(x)=\psi(x+N_x a_x)$. Not a real (physical) boundary conditions, but accounts correct number of allowed *k*-states.

Cyclic boundary conditions:

Let us demonstrate cyclic boundary conditions in x-direction:

$$\psi(x) = \psi(x + N_x a_x)$$

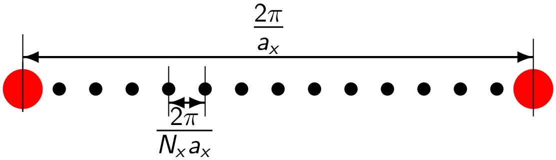
For free electron in x-direction:

$$\psi(x) = e^{ik_x x}$$
$$\psi(x + N_x a_x) = e^{ik_x N_x a_x} e^{ik_x x} = e^{ik_x N_x a_x} \psi(x)$$

And hence: $e^{ik_x N_x a_x} = 1$, providing $k_x N_x a_x = 2\pi m_x$, m_x being integer. Hence, allowed values of k_x are:

$$k_x = \frac{2\pi m_x}{N_x a_x}$$

Cyclic boundary conditions:



Due to the boundary conditions, not all values of k-vector are allowed. Only allowed values of k_x are (m_x is an integer):

$$k_x = \frac{2\pi m_x}{N_x a_x},$$

i.e. the reciprocal translation vector $2\pi/a_x$ is divided to N_x parts.

To generalize to 3D and general unit cell (general Brillouin zone): *There are exactly as many allowed k-vector states in the Brillouin zone as there are unit cells in the crystal.*

Free electron in 2D cubic crystal

Let us assume an electron inside 2D periodic lattice. However, we assume wavefunction $\psi = e^{i\vec{k}\cdot\vec{r}}$ (which is solution for $U(\vec{r}) = 0$), with energy $E = \frac{\hbar^2 k^2}{2m}$.

- Assume we have N unit cells per 2D crystal, and Z electrons per unit cell. Then, whole crystal provides NZ electrons.
- Pauli principle states that on each quantum state (i.e. for each value of k-vector), one can fill only two electrons (with spin-up and spin-down).
- We fill electrons to the electronic structure starting from smallest energy. So we first fill electrons with smallest energy, i.e. with small k-vectors.

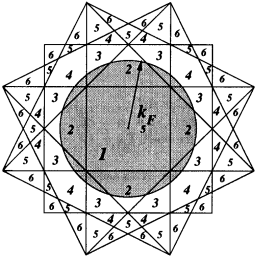
- In volume of 2D Brillouin zone $V_k = 4\pi^2/V_r$ there is 2N electrons' k-states (times 2 because of two spins).
- As here, the electron energy depends solely on $|k|$, the area of constant energy is a sphere in the reciprocal space.

- When we fill all electrons available, we form a circle up to the highest occupied wavevector (*Fermi level*), with k-vector k_F.
- This 2D circle occupies reciprocal space $V_k = \pi k_F^2$, providing $\pi k_F^2/(NZ) = (4\pi^2/V_r)/(2N)$. Hence, the Fermi level of this circle has radius:

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

$$k_F = \sqrt{\frac{2\pi}{V_r} Z} \equiv \sqrt{\frac{2\pi}{V} NZ}.$$

Free electron in 2D cubic crystal



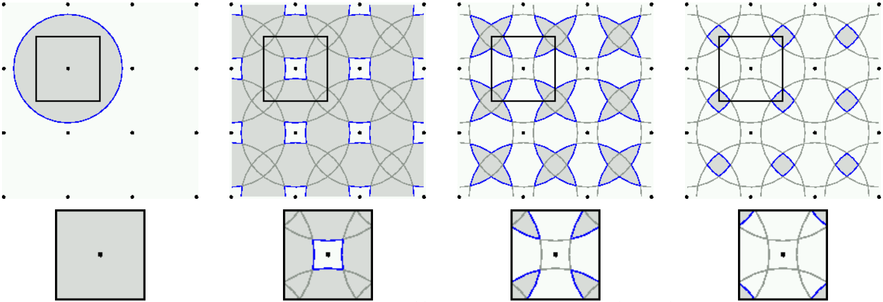
$Z = 4$

What states are occupied and what are filled?

square length: $k_a = 2\pi/a = 6.28/a$

$k_F = \sqrt{2\pi Z/(a^2)} = 5.01/a$

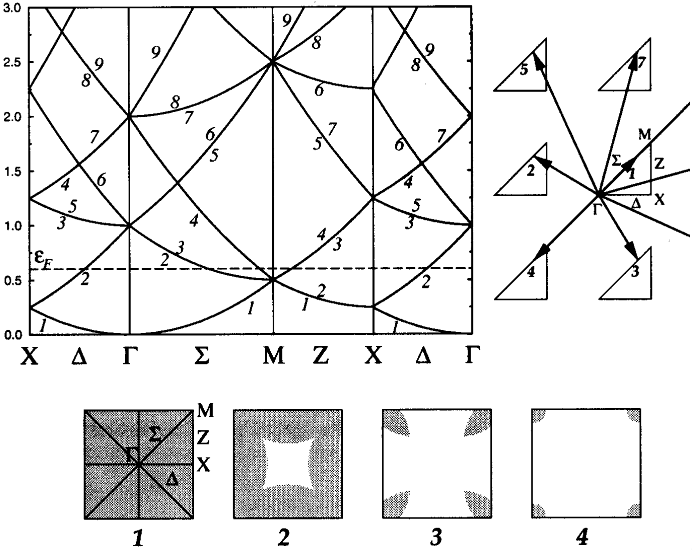
$k_F/(k_a/2) = 1.60 > \sqrt{2}$



1st Brill. zone 2nd Brill. zone 3rd Brill. zone 4th Brill. zone

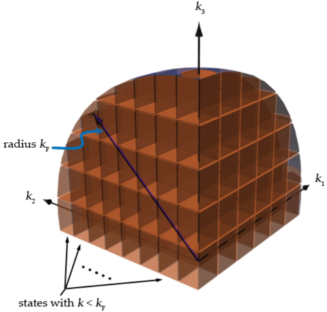
http://phycomp.technion.ac.il/~nika/fermi_surfaces.html

Band structure of 2D electrons in cubic crystal



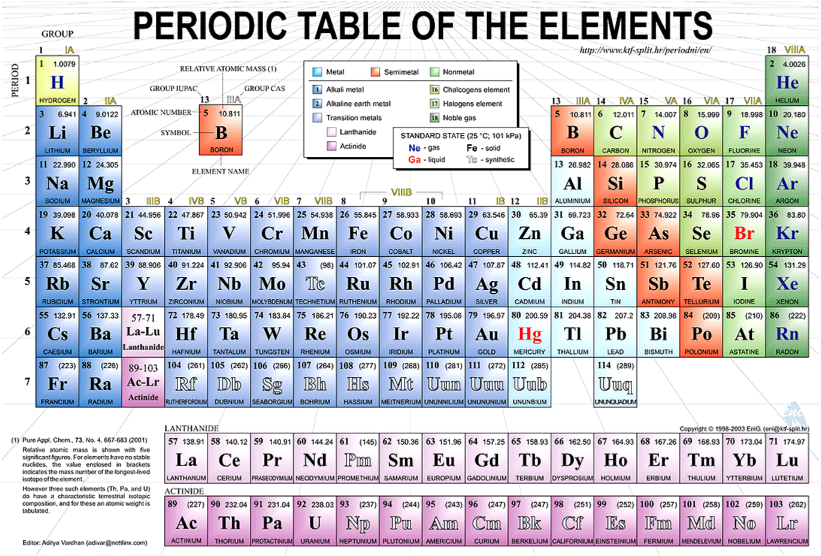
Free electron in 3D

- In the volume of the Brillouin zone $V_k = 8\pi^3/V_r$ there is 2N electrons' k-states.
- As here, the electron energy depends solely on $|k|$, the area of constant energy is a sphere in the reciprocal space.
- When we fill all electrons available, we form a sphere called Fermi sphere (terminated by *Fermi surface*), with maximal k-vector k_F.
- This sphere occupies reciprocal space $V_k = \frac{4}{3}\pi k_F^3$, providing $\frac{4}{3}\pi k_F^3/(NZ) = (8\pi^3/V_r)/(2N)$. Hence, the Fermi sphere has radius:



$$k_F = \sqrt[3]{\frac{3\pi^2}{V_r}Z} \equiv \sqrt[3]{\frac{3\pi^2}{V}NZ}.$$

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$



PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

PERIOD \ GROUP	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

RELATIVE ATOMIC MASS (1)
GROUP IUPAC — 13 — GROUP CAS — IIIA
ATOMIC NUMBER — 5 10.811
SYMBOL — B
ELEMENT NAME — BORON

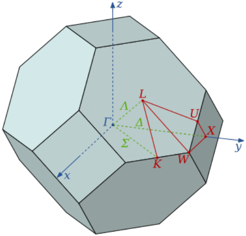
- 🟦 Metal
- 🟥 Semimetal
- 🟩 Nonmetal
- 1 Alkali metal
- 2 Alkaline earth metal
- Transition metals
- Lanthanide
- Actinide
- 16 Chalcogens element
- 17 Halogens element
- 18 Noble gas

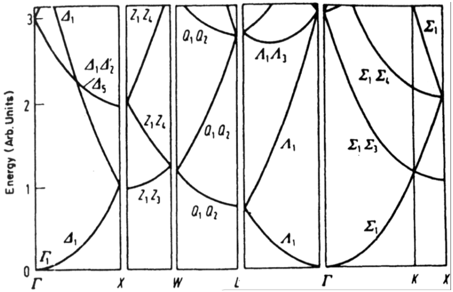
STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Fe - solid
Ga - liquid
Tc - synthetic

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netlinx.com)

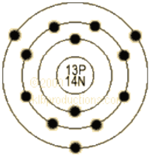
Free electron in fcc:

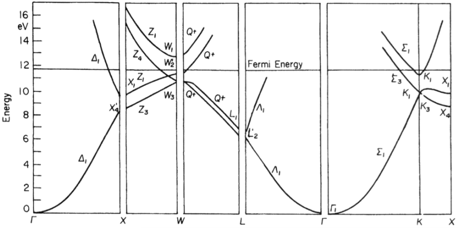




Aluminium (fcc):

- $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
- three unbounded electrons





Aluminium (fcc):

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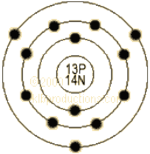
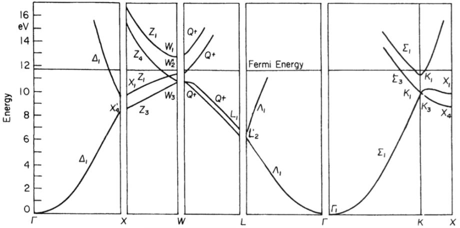
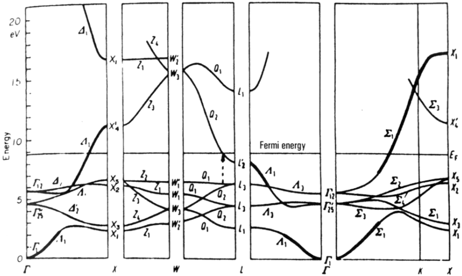




Cuprum (fcc):

- [Ar] $3d^{10}\ 4s^1$
- eleven unbounded electrons



Density of states (DOS):

Density of states (DOS): number of electron's states per energy interval:

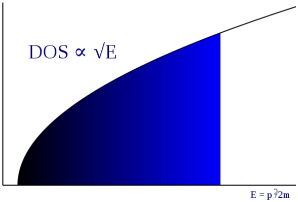
$$g = \frac{\mathrm{d}N}{\mathrm{d}E}.$$

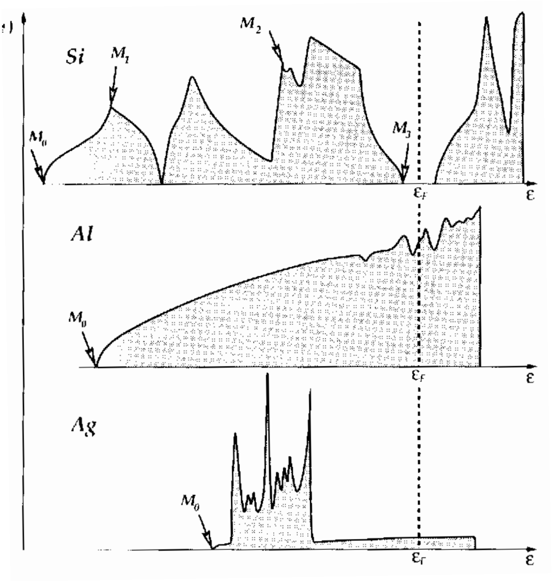
For free elecctron, $E_F = \frac{\hbar^2 k_F^2}{2m}$, where $k_F = \sqrt[3]{\frac{3\pi^2}{V} NZ}$.
Hence:

$$N = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

Therefore, Density of states $g(E)$ of free electron is:

$$g(E) = \frac{\mathrm{d}N}{\mathrm{d}E} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$





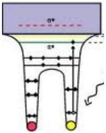
Si: complicated DOS, contains gap at Fermi level.

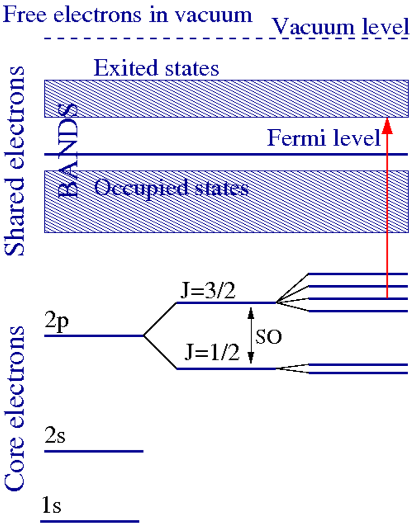
Al: nearly free electrons DOS $\sim \sqrt{E}$.

Ag: *d* electrons are burried and the only electrons on the Fermi level are *s*-electrons.

Complete energy levels in solids:

Core states: Electrons in the energy well of the nucleus (bounded, not shared, electrons). Approximately, they correspond to electrons in filled electronic shells. They provide sharp energies.



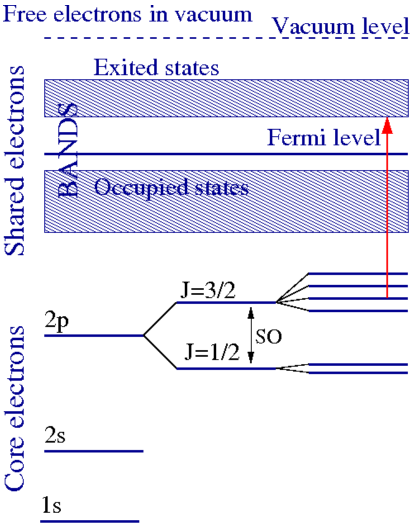


Complete energy levels in solids:

Occupied states: Electrons which are shared through the crystal. They are approximately valence electrons of the atoms. They form energy bands.

Fermi level: Energy level separating occupied and unoccupied states.

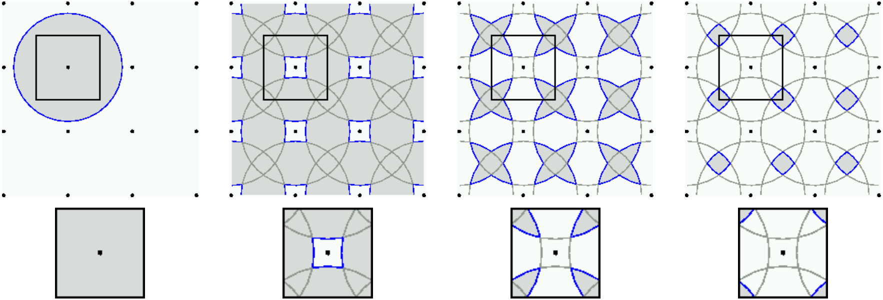
Excited states: Empty energy levels above Fermi level. Electrons can be excited to those states and then they relax back



Fermi surface

As electrons fill the reciprocal space up to E_F, they create a boundary in the reciprocal space between filled and empty k-spaces. This boundary is called Fermi surface.

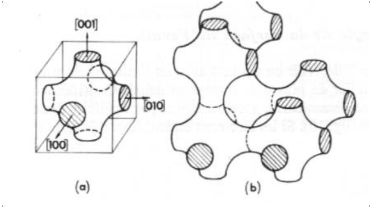
Fermi surface in 2D, cubic (blue line):



1st Brill. zone
2nd Brill. zone
3rd Brill. zone
4th Brill. zone

Fermi surface in 3D

cubic:

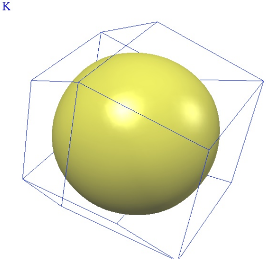


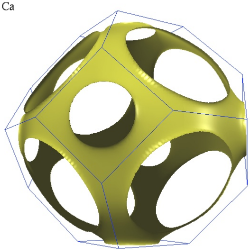
Real atoms:

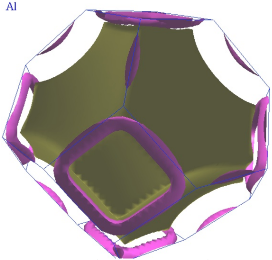
K(bcc) [Ar] $4s^1$

Ca(fcc) [Ar] $4s^2$

Al (fcc) [Ne] $3s^2$ $3p^1$

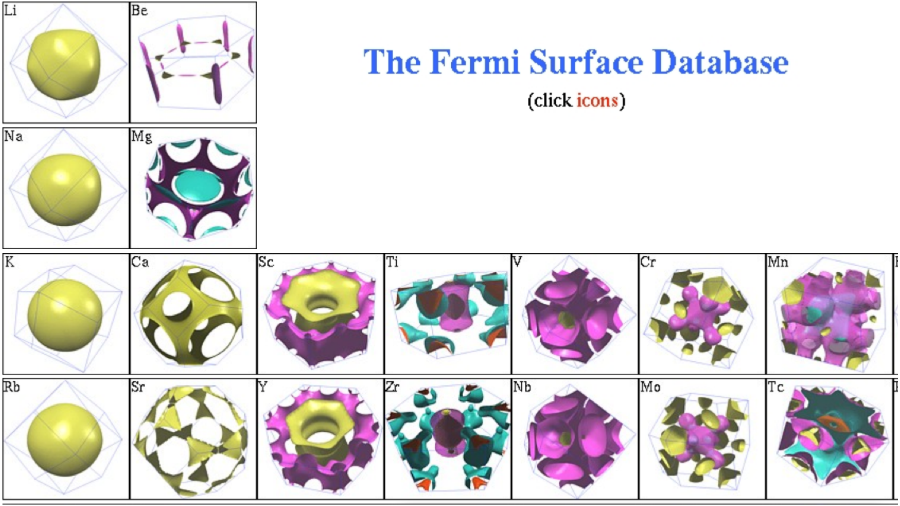






http://www.phys.ufl.edu/fermisurface/

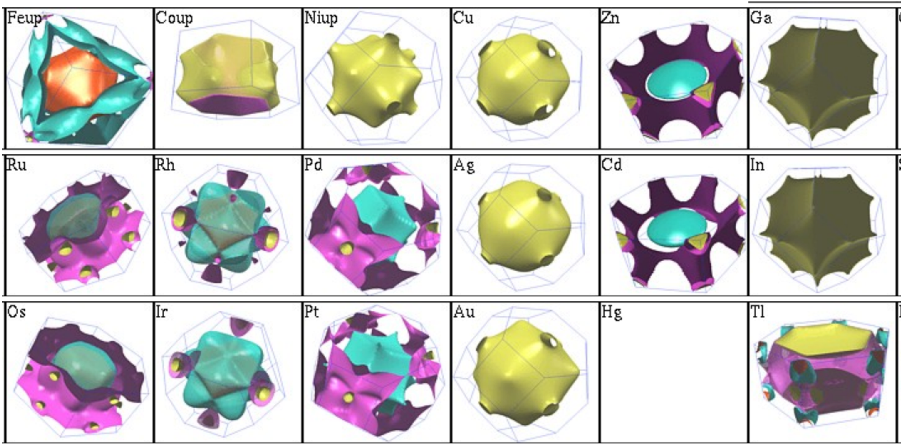
Example of some elements' Fermi surfaces.



The Fermi Surface Database

(click icons)

Example of some elements' Fermi surfaces.



Comments on Fermi surface

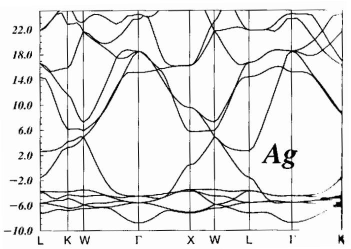
- Fermi surface means, that there are free (unbounded or easily excited) electrons. Such electrons are providing e.g. electrical or thermal conductivity.
- Hence, the metal can be defined as 'material having Fermi surface'.
- Semiconductors and insulators do not have Fermi surfaces, because they do not have free electrons on Fermi level. In this case, one Brillouin zone is completely full and next Brillouin zone is completely empty.

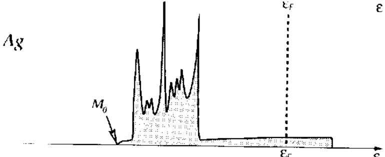
Basic classification of materials (according to DOS):

metal

no gap on Fermi

Fermi surface

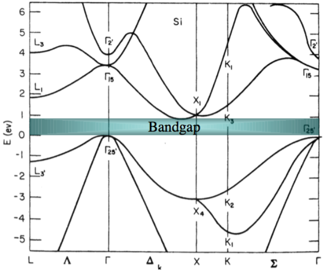


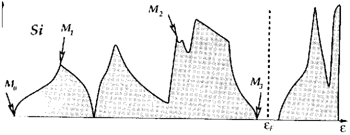


semiconductor/isolator

gap on Fermi

no Fermi surface (filled BZ)





Basic classification of materials (according to DOS):

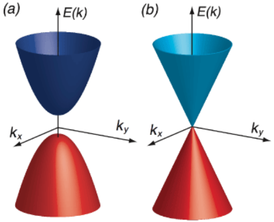
ferromagnet

different DOS for up and down electrons

Fe(bcc): [Ar]$4s^2 3d^6$

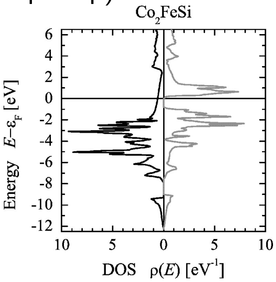
topological isolator

cone on Fermi (graphene, Nobel price 2010)



half-metal

gap only for spin down (or only for spin up)



Duality of the electron I:

Electron is described using both:

Probability wave function $\psi(\vec{r})$:

- probability desnity $|\psi(\vec{r})|^2$, with $\int |\psi(\vec{r})|^2 \mathrm{d}\vec{r} \equiv \langle\psi|\psi\rangle = 1$.
- wavevector $\vec{k}$.
- has wave properties, such as diffraction, interference, beam splitting etc. However, the only observable quantity is probability density $|\psi(\vec{r})|^2$ during the measurements.

Particle properties:

- energy E (mass m).
- momentum $\vec{p}$.

Duality of the electron II:

Both wave and particle descriptions are related by quantum mechanics (should be called 'wave mechanics') through Planck constant $\hbar$:

$$E = \frac{\hbar^2 |\vec{k}|^2}{2m} \qquad \vec{p} = \hbar \vec{k}$$

Difference between the classical wave and the quantum particle wave is, that quantum wave collapses in event of measurement. In the moment the electron is measured (detected) all wavefunction immediately collapses (vanishes).

Conservation laws

Energy conservation E: due to time-invariant space.

Momentum conservation $\vec{p}$: due to translation-invariant space.

Angular momentum conservation $\vec{L}$: due to rotation-invariant space.

But in a periodical crystal, there is no invariance in space in both translation and rotation. Hence, momentum $\vec{p}$ of the electron in crystal is not well-defined, and it can provide any value $\vec{p} = \hbar(\vec{k} + \vec{K})$, $\vec{K}$ being any reciprocal vector in the lattice.

Outline

1 Introduction

2 Electron in periodic potential
- Free electron
- Bloch theorem
- Brillouin zone
- Reciprocal space
- Number of *k*-states in the First Brillouin zone
- Free electron states
- Density of states
- Fermi surface
- Understanding of Brillouin zone

3 Diffraction
- X-ray diffraction

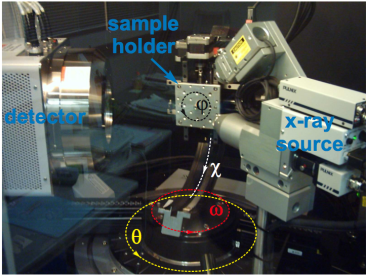
- Inverse photoelectron spectroscopy (IPES)
- Auger and characteristic X-ray
- Synchrotron

5 Magneto-optical effect
- Examples of magneto-optical effects
- Origin of magneto-optical effects
- Use of magneto-optical effects

6 Time resolved investigations
- Relation between energy

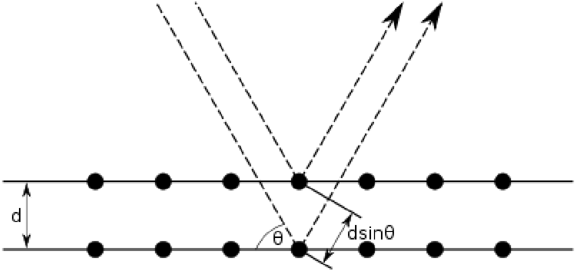
Experimental techniques based on diffraction:

- Usually, diffraction techniques are based on elastic scattering, i.e. the particle or photon is only scattered (it changes only its flight direction, i.e. its $\vec{k}$-vector), but the energy is kept.
- Diffraction probes reciprocal space of the crystal.
- To study atomic positions, wavelength of the probing beam must be of similar length as the atomic distance. Hence, following diffraction techniques are mostly used:
    - X-ray diffraction.
    - neutron diffraction.
    - electron diffraction.



X-ray diffraction: Bragg condition:

Real space:



$$2d \sin\theta = n\lambda$$

X-ray diffraction: Laue condition I:

- $f(\vec{r})$: density of scatters (e.g. for X-ray scattering, $f(\vec{r}) \sim$ is approximately density of electrons).
- Incident wave: $E_{\mathrm{in}} = e^{i\vec{k}_i\cdot\vec{r}}$.
- We assume, each illuminated point of crystal having volume $\mathrm{d}V$ radiates a spherical wave of intensity

$$\mathrm{d}E = e^{i\vec{k}_i\cdot\vec{r}} f(\vec{r})\mathrm{d}V.$$

- Sum of all scattered light to detector at $\vec{r}_d$ in direction $\vec{k}_d$

$$\begin{aligned} E_{\mathrm{det}} &= \int_V e^{i\vec{k}_d\cdot(\vec{r}_d-\vec{r})}\mathrm{d}E = e^{i\vec{k}_d\cdot\vec{r}_d}\int_V e^{-i\vec{r}\cdot(\vec{k}_d-\vec{k}_i)} f(\vec{r})\mathrm{d}V \\ &= (2\pi)^{3/2} e^{i\vec{k}_d\cdot\vec{r}_d} F(\vec{k}_d-\vec{k}_i). \end{aligned}$$

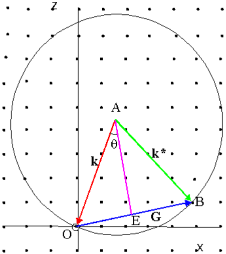
- Hence, detected scattered intensity $I_{\mathrm{det}} \sim |E_d|^2 \sim |F(\vec{q})|^2$ is proportional to the strength of the reciprocal space of $f(\vec{r})$, $F(\vec{q})$, in position $\vec{q} = (\vec{k}_d - \vec{k}_i)$.

X-ray diffraction: Laue condition I

- Detected scattered intensity $I_d \sim |E_d|^2 \sim |F(\vec{q})|^2$ is proportional to the absolute value of the reciprocal space of $f(\vec{r})$, $|F(\vec{q})|$, in position $\vec{q} = (\vec{k}_d - \vec{k}_i)$.
- Hence, if $\vec{q} = (\vec{k}_d - \vec{k}_i)$ equals to any reciprocal vector $\vec{G}$, one obtain large scattered intensity. Otherwise, the observed intensity is (for infinite periodical crystal) zero.
- Condition to observe large scattered intensity $(\vec{k}_d - \vec{k}_i) = \vec{G}$ can be visualized in the reciprocal space by two similar approaches: (i) Ewald sphere and (ii) stepping inside the reciprocal space.
- Scattered intensity is sensitive only to norm of the reciprocal space value, $|F(\vec{k})|$, insensitive to the phase of $F(\vec{k})$. So, some information is missing to reconstruct real space structure – so called phase problem.

X-ray diffraction: Laue condition II

Interpretation 1: Ewald sphere (in the reciprocal space):

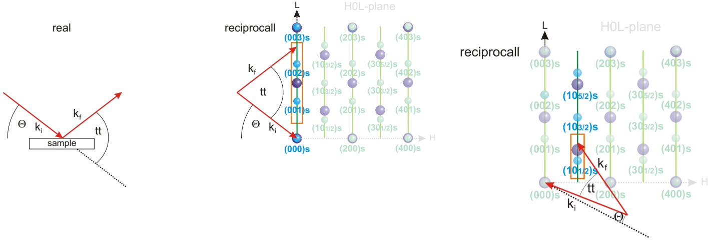


- Incident $\vec{k}_i$ points to any reciprocal point, e.g. to $\vec{k} = (0, 0, 0)$.
- For fixed position of light source and fixed sample position (i.e. fixed $\vec{k}_i$ with respect to the reciprocal space), the detector probes only intersection of the reciprocal space with reach of $\vec{k}_d$ Ewald sphere. I.e. non-zero intensity is detected only when reciprocal vector $\vec{G}$ is the same as difference $\vec{G} = \vec{q} = (\vec{k}_d - \vec{k}_i)$.

X-ray diffraction: Laue condition III

Interpretation two: stepping inside the reciprocal space.

- tt : angle between the incident and the detection beam.
- θ: incidence angle of the incident beam.
- Lengths $|\vec{k}_i|$, $|\vec{k}_d|$ are fixed by X-ray wavelength. Hence, degrees of freedom to probe the reciprocal space are variations of tt, θ and sample orientations.
    - Not all reciprocal points accessible.
    - 3D intensity distribution of reciprocal points can be obtained.



Figures courteously Timo Kuschel, Uni Osnabrueck.

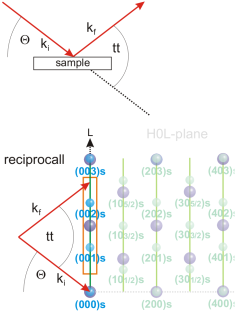
What can be obtained from X-ray diffraction:

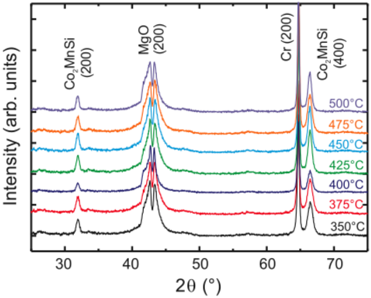
- Position of peaks in the reciprocal space → crystal symmetry, lattice distance, lattice orientation, etc.
- Ratios of peak intensities → ordering factors for alloys.
- Peak widths → amount of mosaicity of the crystal, change in lattice distance, grain size etc.
- Using small (grazing) incidence angles: thin layer properties (thickness, roughness, structure, etc.).

Typical XRD investigations: $\theta - 2\theta$ scan

$\theta - 2\theta$ scan: $tt = 2\theta$: probing specular (like reflected) beam:

- vertical lattice distance determination.
- probes reciprocal space in vertical direction.

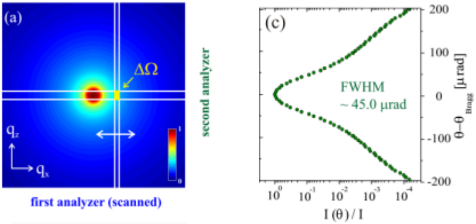




Typical XRD investigations: Rocking curve

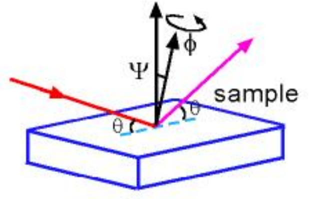
Rocking curve: *tt* fixed, slightly varied θ:

- so called rocking the sample.
- peak width determination $\Rightarrow$ amount of mosaicity of structure, i.e. crystallographic misalignment of different grains.

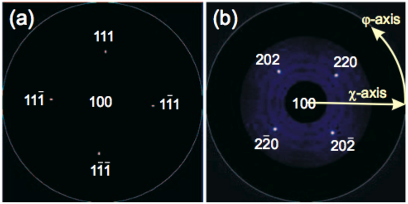


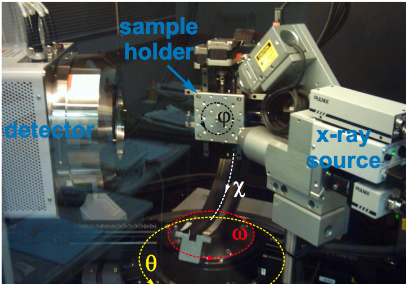
Typical XRD investigations: Pole figure

- Pole figure: *tt* constant, sample rotated ⇒ texture analyses.



Pole Figure Measurement

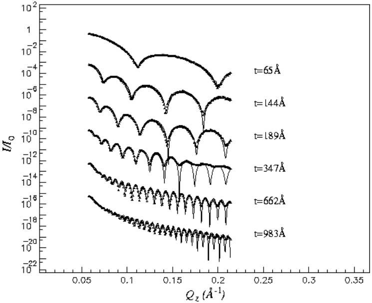




Figs courteously Oksana Gajer, PhD thesis

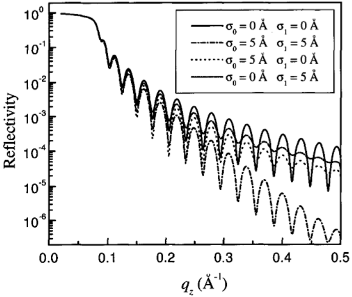
XRD investigations: X-ray reflectivity

X-ray reflectivity (XRR): $tt = 2\theta$, being very small. No diffraction, interference between surface and interface. Roughness and thickness determination.



different thicknesses

XRR on Mo film

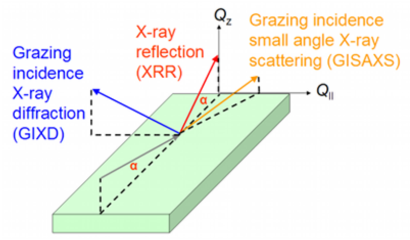


different roughness

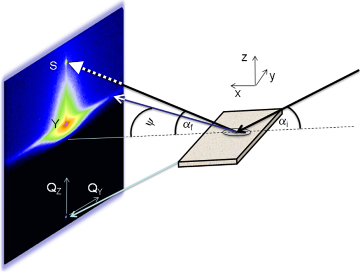
XRR on Au/Si, Cur. Sci. **78**, 25 (2000)

XRD investigations: Grazing incidence X-ray diffraction

Grazing incidence X-ray diffraction
(GIXRD, GID, GIXD): *tt* very small, and for example θ and χ varies.



`http://www.diamond.ac.uk/Home/Beamlines`



R. Gebhardt, Dairy Sci. Technol. 90 (2010) 75

For GIXRD, $\vec{q} = \vec{k}_d - \vec{k}_i$ is small. Hence, GIXRD probes the reciprocal space nearby reciprocal point $\vec{k} = (0, 0, 0)$.

$\Rightarrow$ sensitivity to surface (reduced sensitivity to susbstrate).

$\Rightarrow$ sensitivity to effects with larger lateral dimensions, such as surface roughness, thickness.

Neutron:

- rest mass: $m_0 = 1.67 \times 10^{-27}\,\mathrm{kg}$
- rest energy: $E_0 = m_0 c^2 = 940\,\mathrm{MeV}$
- DeBroglie wavelength λ: $p = \hbar k = \frac{2\pi\hbar}{\lambda}$
- relation between total particle energy E_{tot} and momentum p: $E_{tot} = \sqrt{E_0^2 + p^2 c^2}$, which for $pc \ll E_0$: $E_{tot} \approx E_0 + \frac{p^2}{2m_0}$

(Kinetic) energy $E = E_{tot} - E_0$ of neutrons (examples):

fast neutrons: $E > 1\,\mathrm{MeV}$, $\Rightarrow \lambda < 0.3 \times 10^{-6}\,\mathrm{nm}$ This energy is generated by atomic fission. But λ too small for diffraction $\Rightarrow$ neutrons must be slowed down (moderated).

thermal neutrons: $E = kT = 0.03\,\mathrm{eV}$ ($T = 300\,\mathrm{K}$) $\Rightarrow$ $\lambda = 0.18\,\mathrm{nm}$. Energy useful for diffraction on atoms.

Neutron diffraction:

Very similar to X-ray diffraction. Differences from X-ray:

- Requires large samples (usually powder technique).
- Neutrons scattered mainly on nucleus
  - ⇒ isotope sensitive.
  - ⇒ precise nucleus position determination (stress determination).
- Neutron has magnetic moment ⇒ Neutron diffraction can probe magnetic properties (interaction with electron's cloud).
- Sensitive to Hydrogen, Deuterium. (X-ray is nearly insensitive to them).

Neutron sources:

- nuclear reactor
- spallation (typically high energy proton hits metal target (e.g. mercury); it generates high-energy neutrons, which are slowed down by moderators).

Electron:

- rest mass: $m_e = 9.109382 \times 10^{-31}\,\mathrm{kg}$
- rest energy $E_0 = m_e c^2 = 510.998\,\mathrm{keV}$

Electron energy [keV]	wavelength [nm]	
0.001	1.23	
0.01	0.388	typical low energy electron
0.1	0.123	
1	0.0388	
30	0.00708	typical electron energy in microscopes
100	0.00370	

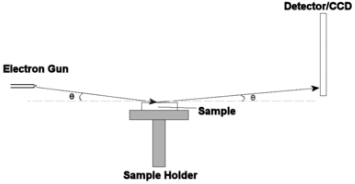
Electron diffraction:

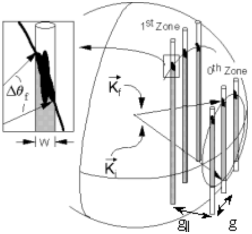
- For common electron energies, the wavelength of electron is very small.

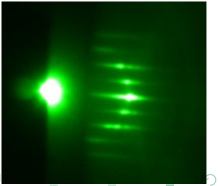
⇒ Ewald spere diameter is very large in the reciprocal space.

⇒ Together with the fact, that electrons are basically surface sensitive, reciprocal space provides in the vertical direction rods, not points.

⇒ Hence, many diffraction points are visible in the diffracted beams.

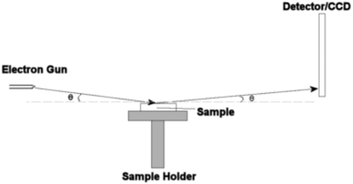


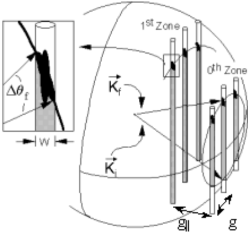


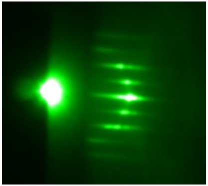


Reflection high energy electron diffraction (RHEED)

- Electron energy typically 10-30 keV (λ =0.012–0.007 nm).
- Bragg diffraction for small angles, used grazing incidence 1–3 deg.
- Used to observe growth of thin films.
- Also, RHEED does not obstruct during the deposition in the vacuum chamber.
- Surface sensitive technique due to grazing incidence angle.



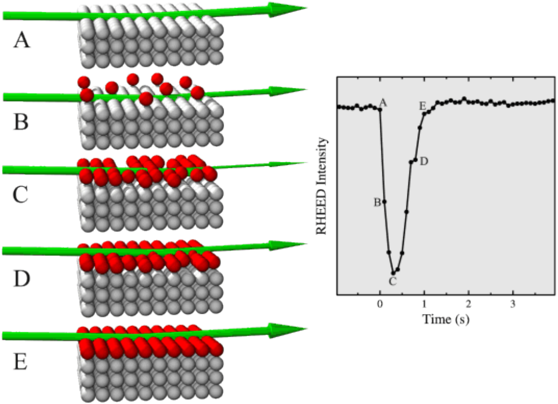




Electron diffraction: RHEED

- RHEED intensity is proportional to the surface roughness. Smooth surfaces give a high reflected intensity, rough surfaces reflects lower intensity.

- Hence, e.g. number of deposited atomic layers can be counted.



`http://lippmaa.issp.u-tokyo.ac.jp/rheed/`

RHEED

RHEED permet ensuite de déterminer:

- la structure cristalline de la surface.
- les paramètres de maille.
- les réorganisations de surface.
- par suivi temporelle de l'intensité diffracté, la vitesse, l'épaisseur et la composition du film déposé.

Les paramètres importants sont:

- l'énergie des électrons.
- l'angle d'incidence du faisceau électronique.

`http://www.gemac.uvsq.fr/Equipement/rheed_theorie.html`

RHEED

RHEED allows to determine:

- The crystal structure of the surface.
- The lattice parameters.
- The reorganization of surface.
- Temporal dependence of the diffracted intensity, speed, thickness and composition of the deposited film.

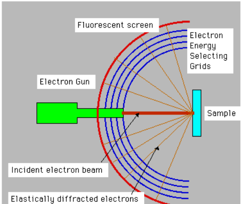
Important parameters are:

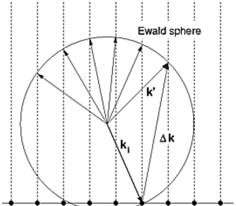
- Energy of the electrons
- Incidence angle of the electron's beam.

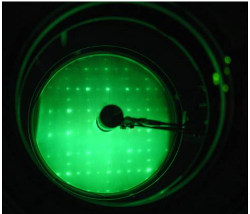
`http://www.gemac.uvsq.fr/Equipement/rheed_theorie.html`

Low-energy electron diffraction (LEED):

- Low energy electrons (20-200eV) $\Rightarrow \lambda = 0.27–0.087\,\mathrm{nm}$.
- Compared to RHEED, Ewald sphere smaller, diffraction angles larger (backscattering geometry).
- Spot positions provides information on the symmetry, size, roughness and rotational alignment of the adsorbate unit cell.
- Intensities of the various diffracted beams are recorded as a function of the incident electron beam energy. The obtained I-V curves provide information about atomic positions (Spot-profile analyzing LEED – SPA-LEED).

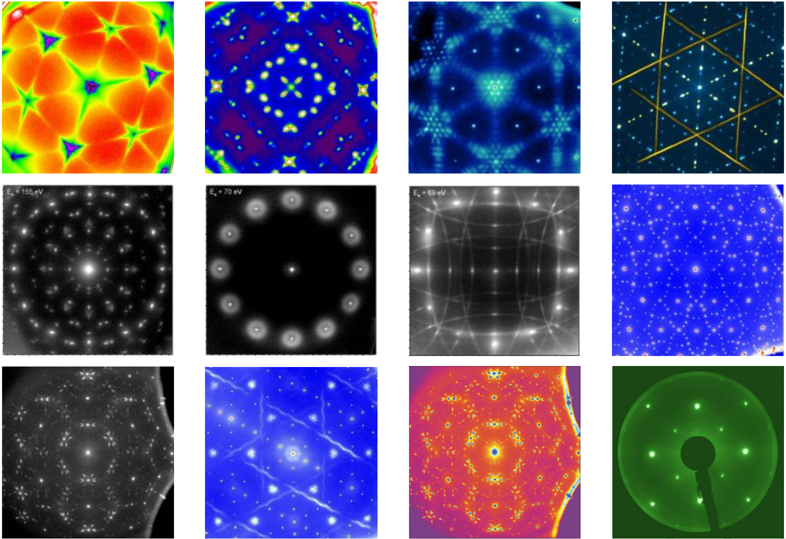






SPA-LEED pattern examples:

`http://www.spaleed.de/`, `http://www.omicron.de`



Electron diffraction:

Basically surface sensitive technique.
Overview of used names:

- RHEED (Reflection high energy electron diffraction).
- LEED (Low energy electron diffraction) 20-200 eV.
- SEM (Scanning electron microscopy).
- SEMPA (Scanning electron microscopy with polarization analysis).
- SPA-LEED (Spot-profile analyzing LEED).

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   - X-ray diffraction

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   - Relation between energy

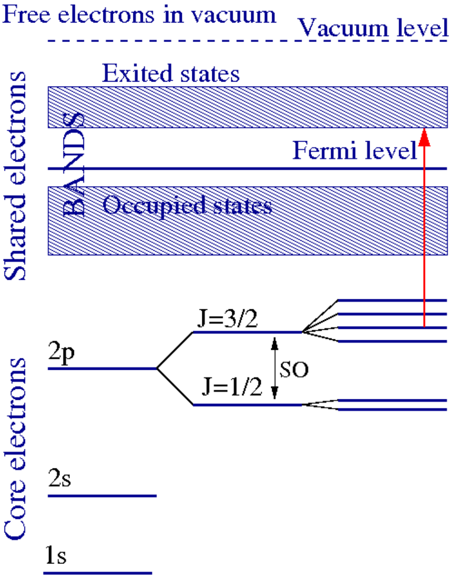
Spectroscopy

Spectroscopy is a study interaction between energy or particle with a matter.

- incoming particles (energy) can be photons, electrons, neutrons etc with different energies.
- the outgoing particles
  - can change the particle (e.g. photon-in–electron-out, electron-in–electron-out etc.)
  - can change momentum (scattering)
  - can change energy (inelastic scattering)

Sketch of the electronic structure in solids:

Core electrons: localized electrons on each atoms.
Shared electrons: form occupied band structure.
Excited electrons: excited to excited states of the crystal, still interacting wit (bonded to) the crystal.
Ionized electrons: excited above vacuum level and hence they are free (no interaction with the crystal).



Photon-photon spectroscopies (absorption) I:

Type of investigations (polarized light x non-polarized light, reflection x transmission, different properties for different polarizations):

- ellipsometry, reflectometry, transmittivity, magneto-optical Kerr effect spectroscopy, magnetic linear/circular dichroism/birefringence, etc.

Photon-photon spectroscopies (absorption) II:

Different energy ranges probes different part of the electronic structure of the matter.

dc conductivity, THz=far-infrared: energy about $kT \approx 30\,\mathrm{meV}$. Excites vicinity of the Fermi surface (all dc conductivities, VA characteristics,).

extended visible light (mid-infrared – far-UV): $\sim 30\,\mathrm{meV}$ - $100\,\mathrm{eV}$. Excites band structure of the matter. (reflectometry, ellipsometry, etc). Both starting and final states are in the band structure (both unknown).

X-ray: $\sim 120\,\mathrm{eV}$ – $120\,\mathrm{keV}$. Excites deep core levels of the atoms. XAS (X-ray absorption spectroscopy). Starting levels are from core levels and hence they are well known.

Photon-photon spectroscopies (absorption) III:

The underlying physics is based on absorption (the same as emission) of the photons.

1. material's absorption of photons i.e. imaginary part of permittivity $\Im(\varepsilon)$ [determined usually by electric-dipole approximations].
2. real part of permittivity $\Re(\varepsilon)$ by Kramers-Kronig relations Then, complex optical properties of matter are known (complex permittivity ε or complex refraction index N or complex conductivity σ, $\varepsilon = N^2 = 1 + i\sigma/\omega$)
3. optical response of the multilayer structure (including interface roughness etc.)

Photon-photon spectroscopies: electric-dipole approximation:

- The largest contribution to the absorption is given by so-called electric-dipole approximation (valid for $\lambda \gg a$), providing so-called electric-dipole transitions.
- Hence, whole vast energy range can be described by so-called Kubo formula, determining conductivity (absorption) for a given photon energy (shown later).

Selection rules of electric-dipole transitions:

Electric dipole transition is allowed when following conditions are fulfilled:

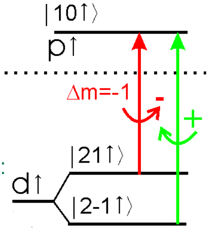
Energy: $E_f - E_i = \hbar\omega$ (absorbed photon energy is difference between energies of the final and initial electron states)

Momentum: $\hbar\omega/c \approx 0$ (photon has negligible momentum compared to one of the electron. I.e. the momentum of the electron is kept between initial and final state (vertical transitions)).

Electron spin : $\Delta s = 0$ (probability photon's spin=1 is transferred to electron's spin is tiny $\Rightarrow$ electron's spin is preserved for electric dipole transitions)

Orbital momentum: $\Delta l = \pm 1$ (photon has angular momentum $1\hbar$). Therefore only $s \leftrightarrow p$, $p \leftrightarrow d$ etc. transitions are allowed.

Orbital momentum along z-axis (magnetic number): $\Delta m = \pm 1$ (determines if photon is circularly right or left polarized).



Conductivity (and hence absorption of the photon)

Kubo formula: conductivity determination.

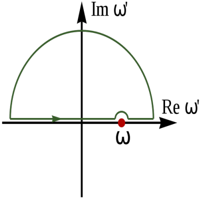
$$\Im(\varepsilon_{xx}) \sim \Re(\sigma_{xx}) \sim$$

$$\sum_{i,f} [f(E_i) - f(E_f)] \times [|\langle i|p_+|f\rangle|^2 + |\langle i|p_-|f\rangle|^2] \times \delta(E_f - E_i - \hbar\omega)$$

where

- $\langle i|$, $|f\rangle$: initial and final states, respectively.
- $p_\pm = p_x \pm ip_y$, $p_x = i\hbar\partial/\partial x$, momentum operator
- terms in the Kubo formula means:
  - summation over all initial and final states, $\langle i|$ and $|f\rangle$
  - $f(E_f)$, $f(E_i)$: electron occupancy of initial and final states.
  - $|\langle i|p_\pm|f\rangle|^2$: probability of the photon to be absorbed between $\langle i|$ and $|f\rangle$ states for circularly left/right polarized light (non-zero only when electric-dipole selection rules are fulfilled).
  - $\delta(E_f - E_i - \hbar\omega)$ assures energy conservation.

Kramers-Kroning relations I



Purely based on mathematical relation between real and imaginary part of 'polite' functions (Cauchy integral).
1) mathematics: Cauchy residual theorem states (for any function without poles in integration area):

$$\oint \frac{\chi(\omega')}{\omega' - \omega}\, d\omega' = 0$$

2) for function $\chi(\omega')/(\omega' - \omega)$, we create pole in point $\omega' = \omega$. Hence Cauchy integral becomes (assuming the integral over 'arc' is zero, i.e. function χ is enough small at infinity):

$$\oint \frac{\chi(\omega')}{\omega' - \omega}\, d\omega' = \mathcal{P}\int_{-\infty}^{\infty} \frac{\chi(\omega')}{\omega' - \omega}\, d\omega' - i\pi\chi(\omega) = 0.$$

I.e. function in point $\chi(\omega)$ equals to the integral over whole ω'!

Kramers-Kroning relations II

Rearranging:

$$\chi(\omega) = \frac{1}{i\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\chi(\omega')}{\omega' - \omega}\, d\omega'.$$

3) Thermodynamics shows $\chi(-\omega) = \chi^*(\omega)$ (because time flows only in one direction). Hence, relation between $\Re(\chi)$ and $\Im(\chi)$ is

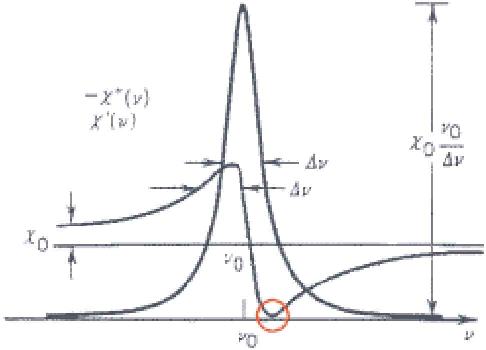
$$\Re(\chi(\omega)) = \frac{2}{\pi}\mathcal{P}\int_{0}^{\infty} \frac{\omega'\Im(\chi(\omega'))}{\omega'^2 - \omega^2}\, d\omega'$$

$$\Im(\chi(\omega)) = -\frac{2\omega}{\pi}\mathcal{P}\int_{0}^{\infty} \frac{\Re(\chi(\omega'))}{\omega'^2 - \omega^2}\, d\omega'$$

Which are famous Kramers-Kronig relations.

Kramers-Kroning relations III

Example: Lorenzian function

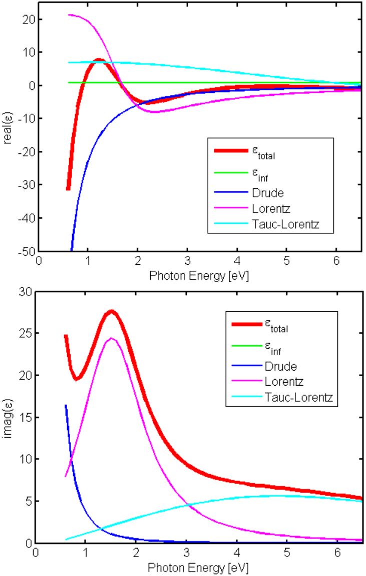


Absorption line (i.e. $\Im(\varepsilon)$) is described by Lorenzian function. Kramers-Kronig then determines its real part.

Description of optical properties of materials I:

Optical permittivity ε: $\varepsilon = \Re(\varepsilon) + i\Im(\varepsilon)$

- $\Im(\varepsilon)$ means light absorption.
- $\Re(\varepsilon)$ and $\Im(\varepsilon)$ are related by Kramers-Kronig (KK) relations.
- in order to assure KK-relations when determining ε, it is advantageous to describe ε by set of optical functions, each one fulfilling KK-relations. For example:
    1. Drude term (free electron contribution).
    2. Lorentz term (resonance line).
    3. Tauc-Lorentz (semiconductor gap).
    4. etc.



Description of optical properties of materials II:

Lorentz term - description of absorption between two energy levels

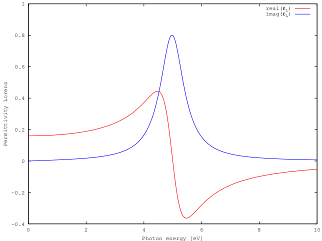
$$\varepsilon = \frac{A}{\omega^2 - \omega_0^2 + i\Gamma\omega}$$

ω: Photon energy

ω_0: Energy distance between the lines (i.e. resonance energy)

A: Amplitude (probability of the absorption)

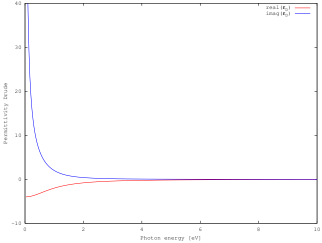
Γ: Width of the line (sharpness of the absorption) (i.e. full-width-at-half-maxima: FWHM)



Description of optical properties of materials III:

Drude term - description of absorption due to free electrons (i.e. due to conductivity)

Like Lorenz, for $\omega_0 = 0$



Description of optical properties of materials IV:

Optical permittivity ε: $\varepsilon = \Re(\varepsilon) + i\Im(\varepsilon)$
Another way how to describe spectra:

1. imaginary part $\Im(\varepsilon)$ given as arbitrary spectra for energies E_i, $\Im(\varepsilon_i)$
2. real part $\Re(\varepsilon)$ then calculated from Kramers-Kronig relation

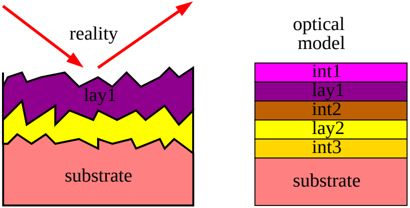
Optics of multilayers I

Total optical response of multilayer described by reflection matrix:

$$R = \begin{bmatrix} r_{ss} & r_{sp} \\ r_{ps} & r_{pp} \end{bmatrix}$$

Reflection matrix is the only quantity accessible for sample investigations by optical means. Roughness of the interfaces is included by:

1. usually described by effective sub-layers.
2. their optical properties described by e.g. effective-medium-approximation (EMA).



Optics of multilayers II

Total optical response of multilayer described by reflection matrix:

$$R = \begin{bmatrix} r_{ss} & r_{ps} \\ r_{sp} & r_{pp} \end{bmatrix}$$

Different quantities can be investigated on reflection:

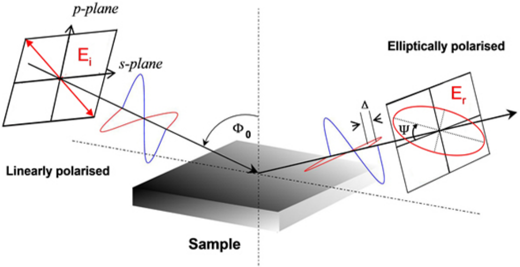
- reflectivity (unpolarized light): $I = 1/2(|r_{ss}|^2 + |r_{pp}|^2)$
- reflectivity of *s*-polarized light: $I_s = |r_{ss}|^2$
- magneto-optical Kerr *s*-effect: $\Phi_s = \theta_s + i\epsilon_s = \frac{r_{sp}}{r_{ss}}$
- ellipsometry: $\rho = \tan\Psi \exp(-i\Delta) = \frac{r_{pp}}{r_{ss}}$
- magnetic linear dichroism for *s*-wave ($\vec{M}$ in-plane): $MLD = |r_{ss}(M \parallel s)|^2 - |r_{ss}(M \parallel p)|^2$

Ellipsometry I

Ellipsometry measures complex ratio of diagonal reflection coefficients:

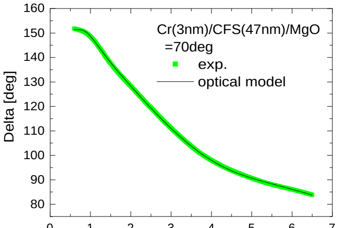
$$\rho = \tan\Psi \exp(-i\Delta) = \frac{r_{pp}}{r_{ss}}$$

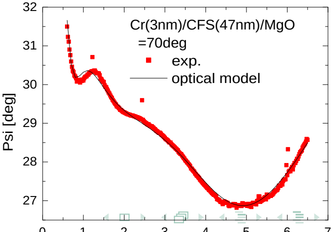
- Ψ, Δ: so-called ellipsometric angles Ψ, Δ
- Ψ expresses ratio of reflected s- and p-waves
- Δ expresses phase difference of reflected s- and p- waves.



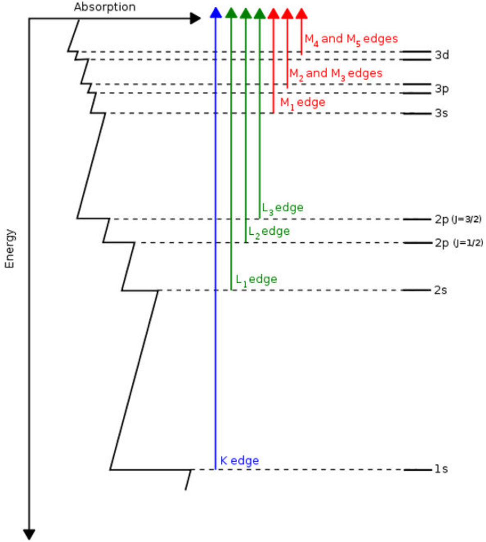
Ellipsometry II

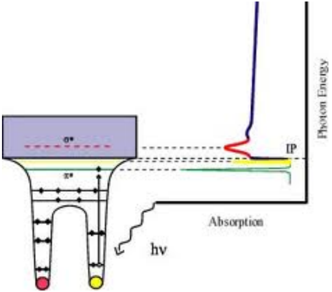
- experimental setup provides spectra of Ψ, Δ
- those spectra are fitted into optical model, where various parameters can be free parameters in the fit (but not all at the same fit):
    - optical constants of a given layer (can be further described by a various functions)
    - layer thicknesses
    - interface roughnesses
- Example of fit to spectra of Ψ, Δ





X-ray absorption spectroscopy (XAS):

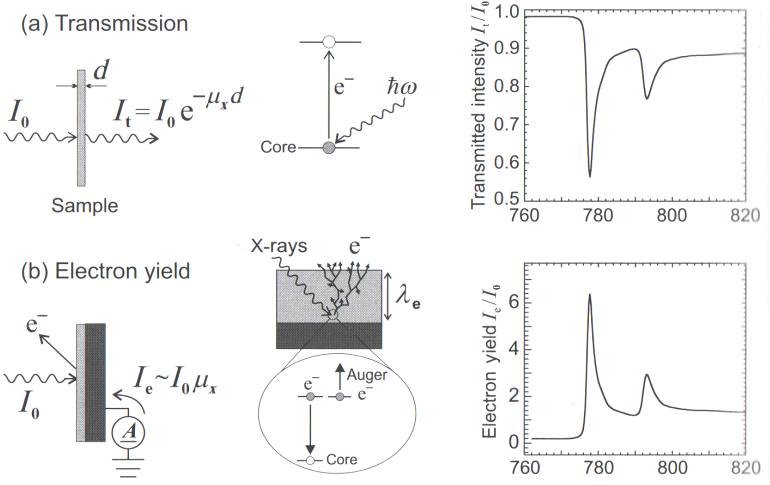




http://news.softpedia.com

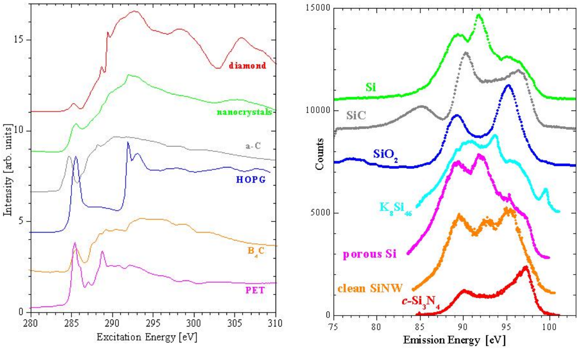
Experimental setup of XAS

X-ray absorption spectroscopy techniques



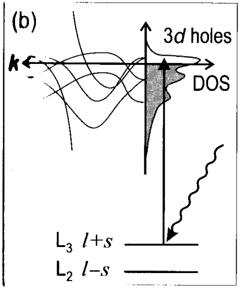
X-ray absorption spectroscopy (XAS):

XAS is extremely sensitive to the chemical state each element, as each element have its own characteristic binding energies. XAS measurements can distinguish the form in which the element crystallizes (for example one can distinguish diamond and graphite, which both entirely consist of C), and can also distinguish between different sites of the same element.

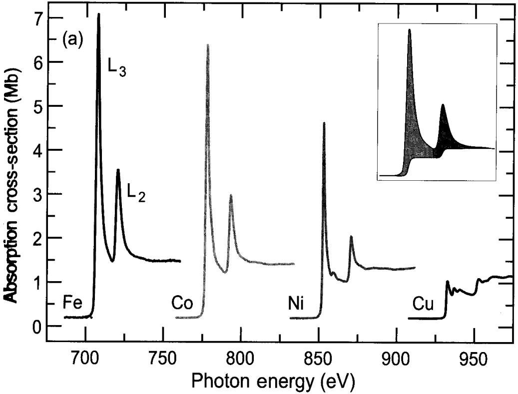


http://beamteam.usask.ca/

XAS on Fe:



Stöhr, Siegmann, Magnetism: From fundamentals to nanoscale dynamics



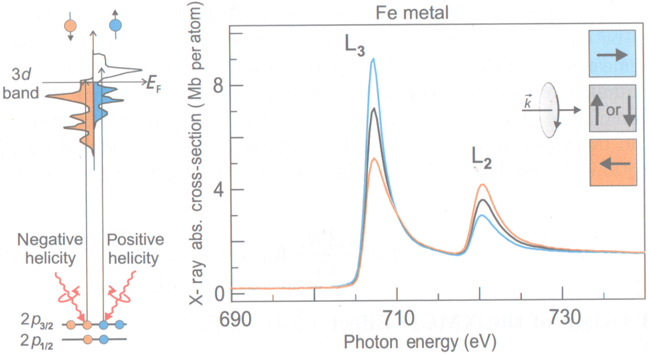
Starting L2, L3 edge (i.e. 2p$^{1/2}$, 2p$^{3/2}$, respectively):

$$I_{XAS,\ p\rightarrow d} \sim N_h$$

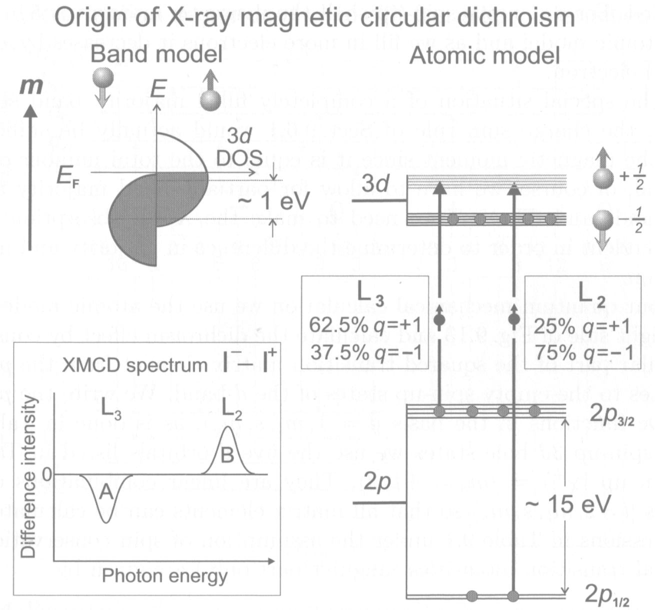
N_h: number of free d-states. $p \rightarrow s$ has small contribution.

XMCD: X-ray Magnetic circular dichroism:

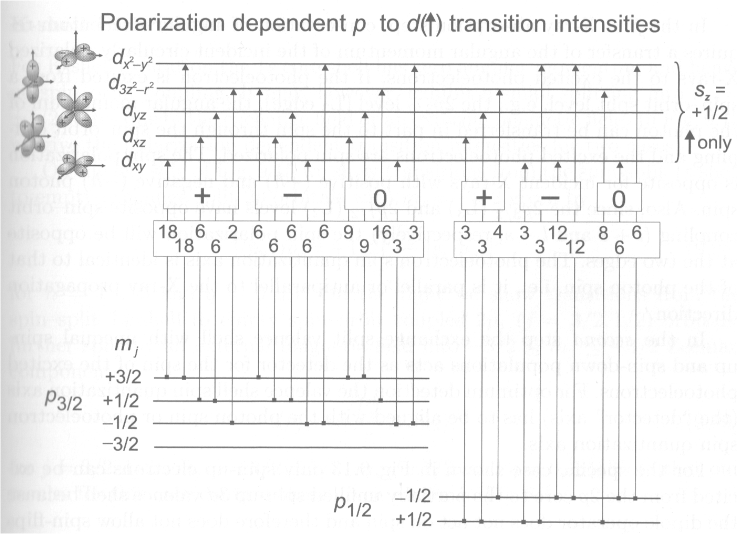
Circular Dichroism: different absorption for circularly left and right light polarization.



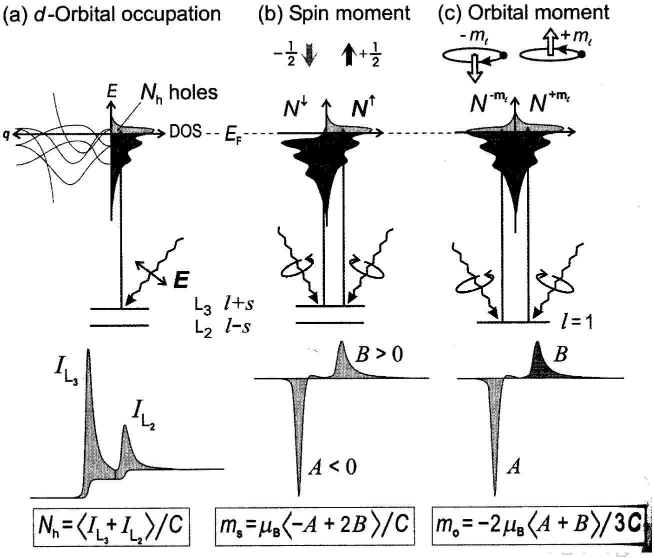
Different absorbed intensity for opposite magnetization orientations.


Origin of X-ray magnetic circular dichroism
Band model
Atomic model
m
E
3d
DOS
E_F
~ 1 eV
3d
+1/2
−1/2
L 3
62.5% q=+1
37.5% q=−1
L 2
25% q=+1
75% q=−1
XMCD spectrum I⁻ − I⁺
Difference intensity
0
L3
L2
A
B
Photon energy
2p
2p3/2
~ 15 eV
2p1/2

XMCD: Detailes p → d transition



XMCD: sum rules:



http://ssrl.slac.stanford.edu/stohr/xmcd.htm

Advantages of X-ray spectroscopies:

- element selective.
- quantitative determination of material characterization (e.g. magnetic moment, orbital moment).
- can be both interface or bulk sensitive.
- can provide excellent lateral resolution ($\sim 15\,\mathrm{nm}$).
- can provide excellent time resolution ($\sim 100\,\mathrm{fs}$).

Disadvantages:

- due to width of the initial (core) line, the energy resolution is limited to $\sim 1\,\mathrm{eV}$.
- synchrotron needed.

Photon-photon spectroscopies (absorption):

Different energies probe different part of the electronic structure

dc conductivity, far-infrared: energy about $kT \approx 30\,\mathrm{meV}$. Excites vicinity of the Fermi surface (dc conductivities, VA characteristics).
[Probing Fermi level, interband transitions, atom and molecule vibrations.]

extended visible light (mid-infrared – far-UV): $\sim 30\,\mathrm{meV}$ - $100\,\mathrm{eV}$. Excites band structure of the matter. (reflectometry, ellipsometry, etc). Both starting and final states are in the band structure (both unknown).
[Interband transitions, gaps, types of bonds in molecules.]

X-ray: $\sim 120\,\mathrm{eV}$ – $120\,\mathrm{keV}$. Excites deep core levels of the atoms. XAS (X-ray absorption spectroscopy). Starting levels are core levels and hence they are sharp (well known).
[Probing core or excited levels, constituting element determination.]

Optical and magneto-optical spectroscopy

Basically the same as X-ray spectroscopy, but:

- photon energy cca 0.1 – 100 eV.
- both initial and final states are within band structure (for solids).
- different quantities are often measured (usually ellipsometry, reflectometry for optics and Kerr rotation/ellipticity (MOKE) for magneto-optics).
- microscopic picture determines only absorption or difference of absorption for different light polarizations. This corresponds to imaginary part of the optical constant.

$\Rightarrow$ real part of the optical constants must be determined from Kramers-Kronig relations.

DC conductivity:

DC conductivity can be understand as a limit of absorption spectroscopy for $\omega \to 0$.
Due to different history and different available experimental techniques, different names are used in each area:

Transport (dc)	Optics	X-ray
conductivity	absorption	$\sim$ X-ray absorption (XAS)
Hall effect	MOKE effect	XMCD
quadratic-Hall effect	quadratic MOKE (QMOKE)	$\sim$ X-ray linear magnetic dichroism
Anisotropy magneto-resistance (AMR)	Cotton-Mouton, Voigt effect	X-ray linear magnetic dichroism

Spectroscopies according involved particles

Photon-photon spectroscopy: conductivity, optical and magento-optical properties (from GHz to hard X-ray), X-ray absorption and reflectivity etc. Raman, Brillouin light scattering spectroscopy.

Photoemission spectroscopy: (X-ray in, electron out). Photoemission (or photoelectron) spectroscopy (PES), X-ray PES (XPES, XPS), hard energy PES (HAXPES), Ultraviolet Photoelectron Spectroscopy (UPS)

Electron-photon spectroscopy: (electron in, photon out) Energy-dispersive X-ray spectroscopy (EDS, EDX, XEDS, EDXA)

Electron-electron spectroscopy: Auger spectroscopy.

Spectroscopies according involved particles (continuing)

Time-resolved spectroscopy : FMR, two-photon-photon spectroscopy.

Nuclear spectroscopies: Mössbauer spectroscopy, NMR, neutron spin echo, inelastic neutron scattering.

Conductivity spectroscopies (V-A characteristics): Andreev reflections, STM spectroscopy, TMR, GMR V-A characterization.

Spectroscopies according nature of interaction

Absorption: reflectivity, absorption.

Emission: fluorescence, Raman.

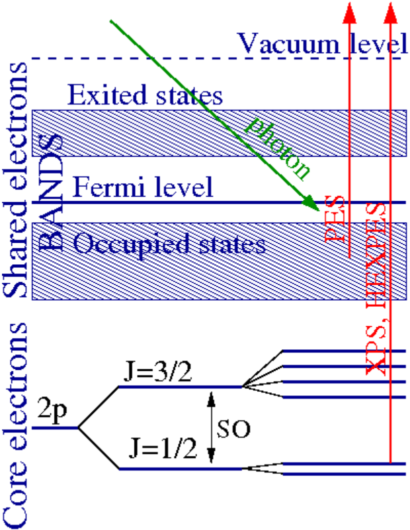
Coherent (resonance): FMR, BLS, NMR.

Elastic scattering: diffractions (XRD, RHEED, LEED).

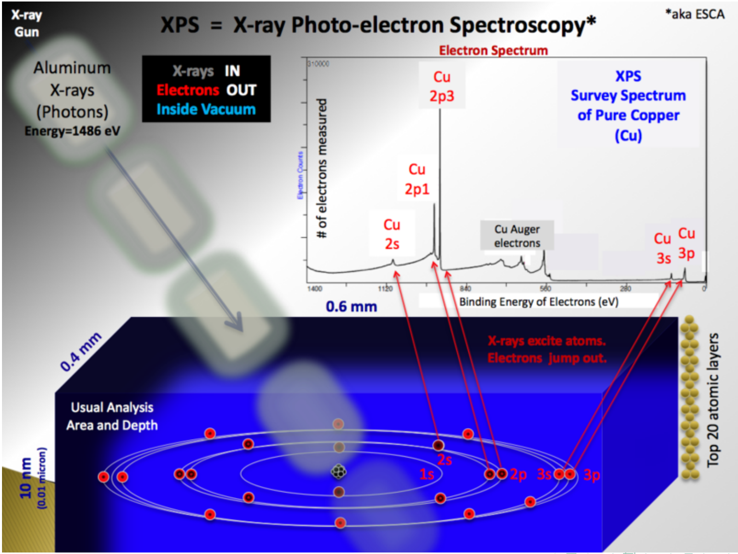
Inelestic scattering: Raman, BLS, Compton scattering.

Photoemission spectroscopy (PES)

- Photon in, electron out.
- Based on the photoelectric effect (electrons kick out by incoming photon).
- Also called Photoelectron spectroscopy.
- Probes density of states below Fermi level.

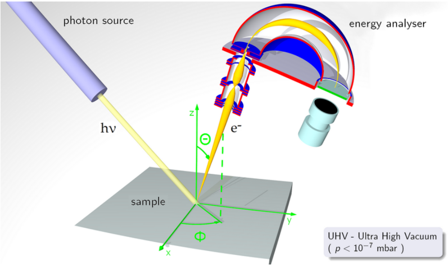


Photoemission spectroscopy (PES or XPS)



Photoemission spectroscopy (PES)

- photon in (known energy), electron out (energy measured)
- elemental composition of the surface (top 1–10 nm usually).
- detect all elements except H and He.
- chemical or electronic state of each element in the surface.
- mapping of elemental composition across the surface.



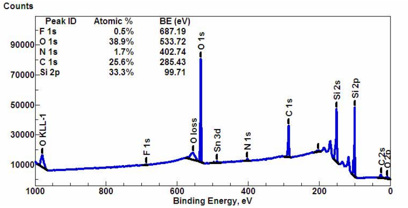
Photoemission spectroscopy principle

$$E_{\mathrm{photon}} = E_{\mathrm{ionized\ electron}} + E_{\mathrm{binding}}$$

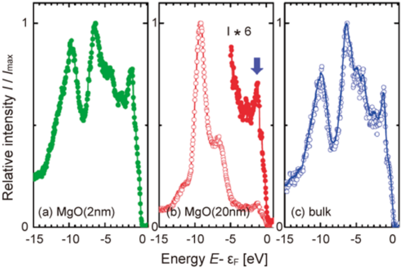
⇒ when ionizing core-levels, outgoing dependence electron yield on detected electron kinetic energy E_{electron} provides sharp peaks.

⇒ when exciting valence band, valence band occupancy can be found.

probing core levels



probing valence bands by HAXPES



Photoemission spectroscopy (PES)

- Ultraviolet photoemission spectroscopy (UPS)
  - vacuum UV radiation (photon energy of $E = 10$–45 eV) to examine valence levels.
  - when varied detection angles, one can map out energy in the reciprocal space.
- X-ray photoemission spectroscopy (XPS)
  - soft x-rays ($E = 200$–2000 eV) to examine down to core-levels.
  also known as Electron Spectroscopy for Chemical Analysis (ESCA).
- Hard X-ray photoemission spectroscopy (HAXPES, HX-PES):
  - using hard X-ray to excite down to deep core levels.
  - bulk sensitive

Angle resolved photoemission spectroscopy (ARPES):

Both energy and direction of the ionized electrons are measured.

Momentum conservation:

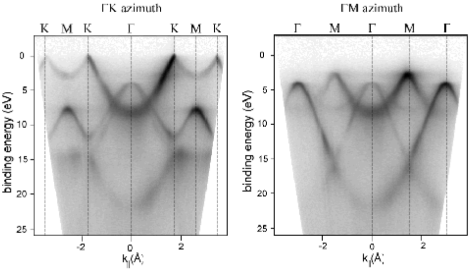
$$\vec{p}_{\text{ionized electron}} = \vec{p}_{\text{photon}} + \vec{p}_{\text{bound electron}} + \hbar\vec{K}$$

as $\vec{p}_{\text{photon}} \approx 0$, hence $\vec{p}_{\text{ionized electron}} = \vec{p}_{\text{bound electron}} + \hbar\vec{K}$.

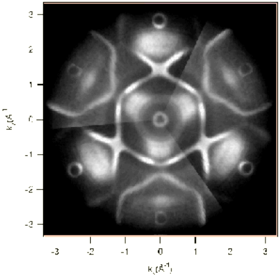
- hence, the ionized electron has the same momentum as the original bound electron (plus $\hbar\vec{K}$ due to lattice periodicity).
- hence, by measuring the excitation angle with respect to crystallographic direction, one can determine the dispersion relation $E(\vec{k})$ of the electrons inside the matter.

Angle resolved photoemission spectroscopy (ARPES)

Electronic structure of graphite



Fermi surface of $Cu_3Au(111)$

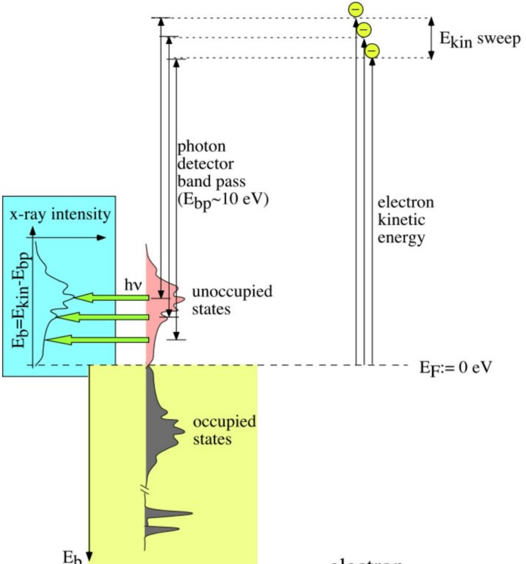


http://www.tp2.uni-erlangen.de

Inverse photoelectron spectroscopy (IPES)

Electron in, photon out.

- low incidence electron energy E_{kin} ($\sim 20\,\mathrm{eV}$).
→ those electrons couple to unoccupied states E_{kin} above Fermi level
→ when electrons decays to lower states, radiates photon.
- when photons pass narrow-band filter (i.e. only one energy passes), unoccupied DOS measured.

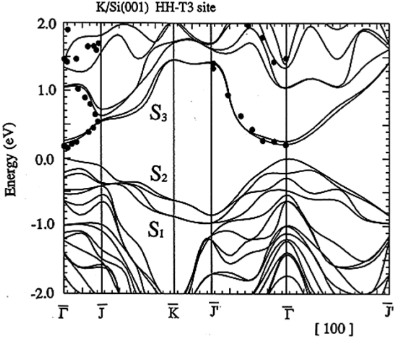


http://rsl.eng.usf.edu

Inverse photoelectron spectroscopy (IPES): properties

- as small electron energy, only surface is tested.
- can provide *k*-resolution, as ARPES.
- can provide spin-resolution.

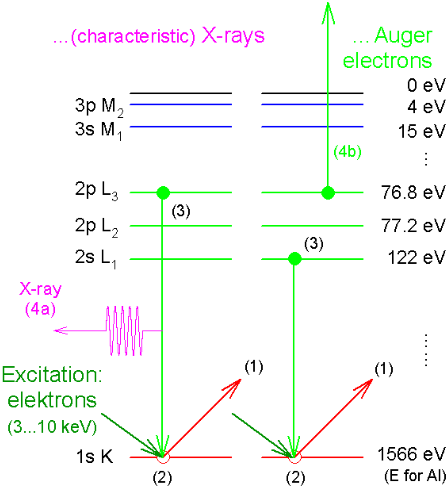
Example of IPES on Si(100) surface



http://e1.physik.uni-dortmund.de

Auger electron spectroscopy (AES) and characteristic X-ray

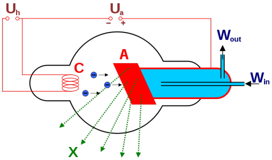
- electron in (~ 3 –10 keV).
- inner shell of an atom is ionized.
- the vacancy is filled by an electron from an outer shell.
- the released energy is emitted as (characteristic) X-ray or is transferred by electromagnetic interaction to a 3rd electron. If it gets sufficient energy it can leave the atom as Auger electron.
- energy of both radiations is determined by the energy levels of the atom and makes analysis of the composition possible.

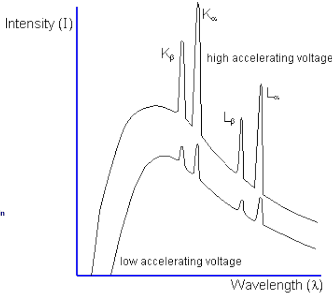


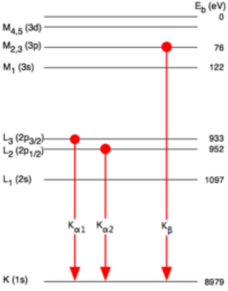
http://www.ifw-dresden.de/institutes/ikm/organisation/dep-31/methods/auger-electron-spectroscopy-aes

Characteristic X-ray radiation

Characteristic X-ray radiation is used to generate X-ray radiation in X-ray tubes. (most common X-ray source used e.g. in medical X-rays or X-ray diffractometers).







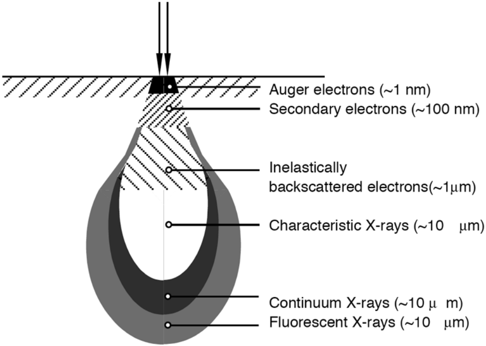
Radiation consists of characteristic single-energy radiation (denoted K_α, K_β etc) and continuous Bremsstrahlung. For example, Cu K_α has energy 8.06 keV (0.15418 nm). Also called X-ray fluorescence or X-ray emission spectroscopy (XES).

Auger electron spectroscopy:

- Only H and He do not emit Auger electrons (The Auger process).
- measured Auger electron spectra.

⇒ element and chemical states identification.

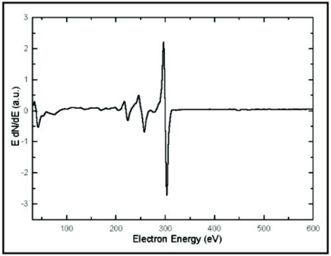
- element detect limit about $\leq 1\%$.
- depth information 0.5–5 nm (surface technique).
- in combination with electron microscopy, local analysis (points, areas, lines) are possible.
- Disadvantage: high energy and current density of the primary electron beam, producing many defects.



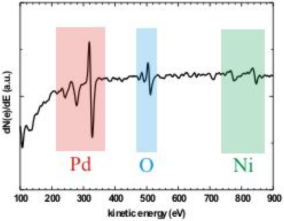
http://www.ifw-dresden.de/institutes/ikm/organisation/dep-31/methods/auger-electron-spectroscopy-aes

Examples of Auger spectra

Rh(111)

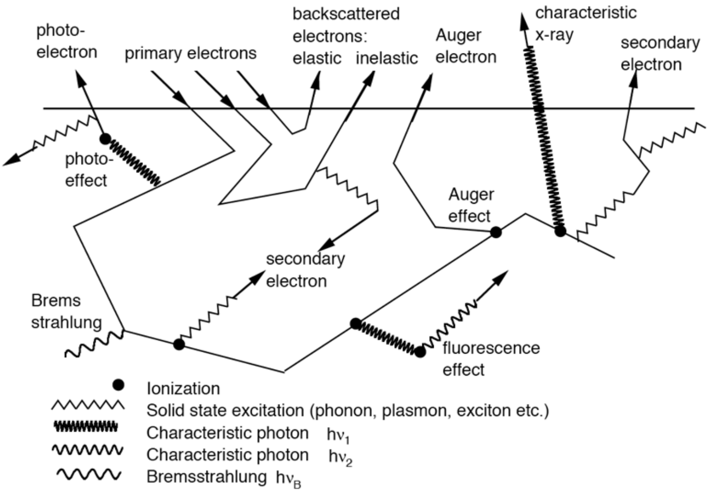


monolayer of NiO on Pd

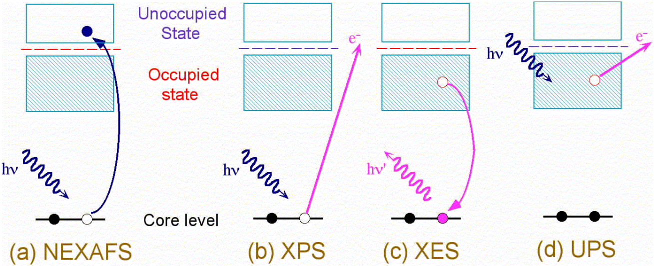


http://surface-science.uni-graz.at/main_frame/techniques/aes.htm

Processes related with electron-in



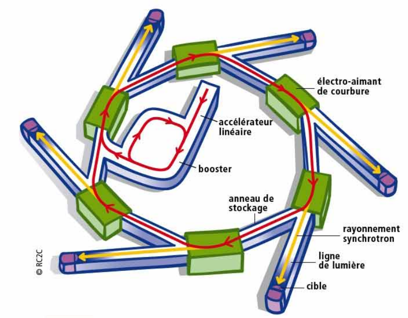
Processes related with photon-in

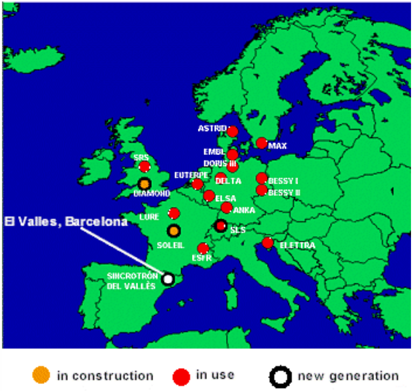


XAS	X-ray absorption spectroscopy
XMCD	X-ray magnetic circular dichroism
NEXAFS	near edge absorption fine structure
PES, XPS	photoemission spectroscopy, photoelectron spectroscopy
UPS	ultraviolet absorption spectroscopy
XES, XFS	X-ray emission spectroscopy, X-ray fluorescence spectroscopy
HAXPES	hard X-ray absorption photoemission spectroscopy

http://www.theochem.kth.se/research/xspectra/index.html

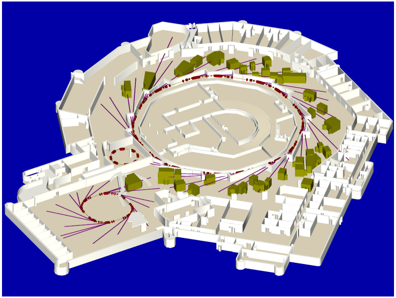
Synchrotron radiation source:





Synchrotron radiation source:

National Synchrotron Light source, USA

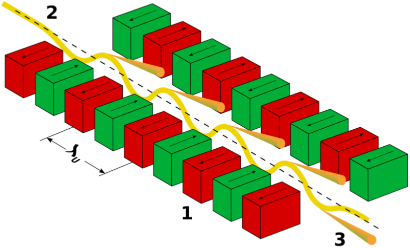


Grenoble

Light generation

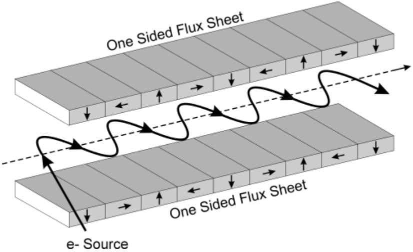
Undulator:

small electron oscillation amplitude, narrow energy band emission, smaller light intensity.



Wiggler:

large electron oscillation amplitude, wide energy band emission, higher light intensity



- Electron trajectory determines light polarization.
- Photon energy can be from IR to hard X-ray. Mostly used is X-ray.
- Quick X-ray pulses (up to 100 fs) are possible.

Outline

Magneto-optical Kerr effect:

- Change of optical properties (polarization state, reflectivity) by presence/change of magnetization of the sample.

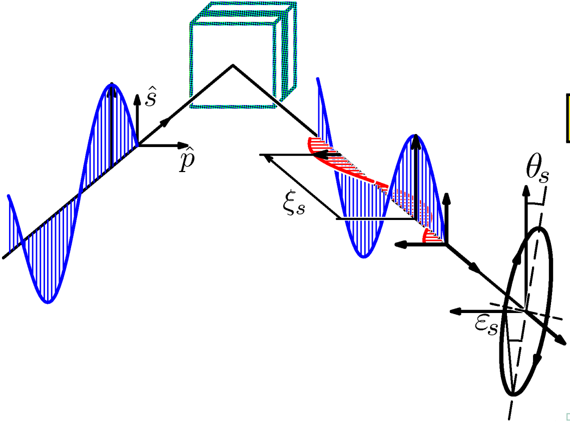
One can separate usage of magneto-optical (MO) effects to:

- MO as a metrology tool to study magnetism:
  - MO magnetometry (study of magnetization reversal).
  - MO microscopy (study of domain wall and its propagation).
  - Magnetization dynamic studies (precession etc.)
  - MO as a tool for ultrafast magnetization processes.

- MO spectroscopy to study optical properties of the MO effect:
  - Magnetism is understand as a perturbation, reducing symmetry of the solids and hence introducing new optical features.
  - Study of spin-orbit interaction.
  - Interaction between light and magnetism – a very fundamental interaction.

MO effect I: Magneto-optical Kerr effect (MOKE):

- For example: incident s-polarized wave.
- Magnetized sample
  $\Rightarrow$ hence: also p-polarized wave appears on the reflection.



MOKE linear in $\vec{M}$

- θ_s: Kerr rotation.
- ϵ_s: Kerr ellipticity.

Kerr and Faraday magneto-optical effect:

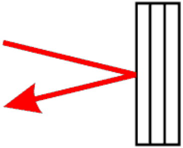
Due to historical reasons, there are different names for MO effects measured in reflection and transmission.

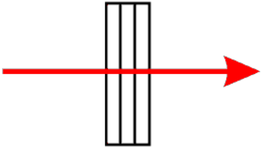
Kerr effect:

- measured in reflection.
- discovered 1876.

Faraday effect:

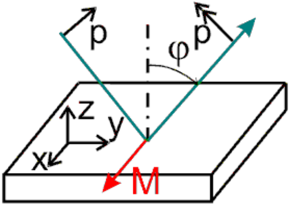
- measured in transmission.
- discovered 1845.





MO effect II: transversal MOKE:

- Incident p-polarized wave.
- Magnetization in-plane and perpendicular to the incident plane (so-called transversal magnetization direction).
- Change of the reflected p-polarized intensity due to magnetization in the sample (in this particular case, on change in polarization of the reflected light appears).



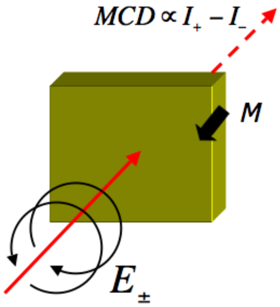
MO effect III: Magnetic dichroism and birefringence:

Dichroism: different damping of both light's eigen-modes.

Birefringence: different propagation speed of both light's eigen-modes.

Magnetic circular dichroism (MCD):

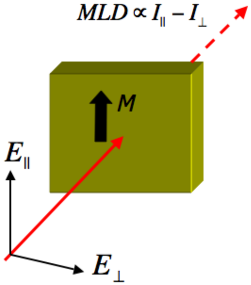
- Different absorption for circularly left and right polarized light.
- MCD linear in $\vec{M}$.
- MOKE and MCD has the same microscopic origin, they just manifest in different ways.



$$MCD \propto \mathrm{Im}[\varepsilon_+ - \varepsilon_-] \propto \mathrm{Im}[\sigma_{xy}(\omega)]$$

MO effect IV: Voigt effect:

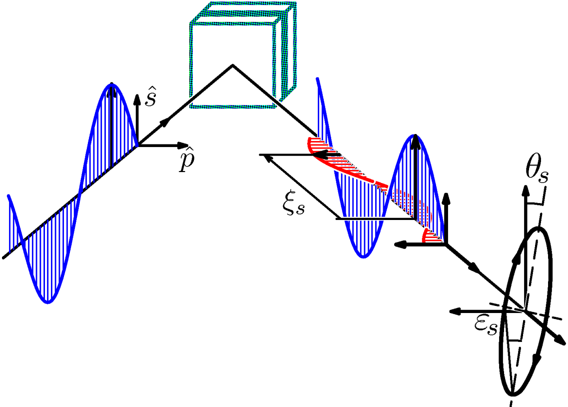
- Discovered 1899.
- Different absorption or phase shift for linear polarization parallel and perpendicular with the magnetization.
- Quadratic in $\vec{M}$ ($\sim M^2$).
- Also called Cotton-Mouton effect or linear magnetic dichroism/birefringence (LMD/LMB)
- The same microscopic origin as quadratic MOKE (QMOKE) (more precisely, Voigt effect is simplest case of QMOKE).



$$MLD \propto \mathrm{Im}[\varepsilon_{\parallel} - \varepsilon_{\perp}] \propto \mathrm{Re}[\sigma_{\parallel} - \sigma_{\perp}]$$

Classification of the MO effects:

- Even / odd effect in magnetization.
- Measured in transmission / reflection.
- Detected change of intensity / polarization.
- Probing light is linearly / circularly polarized.



Family of magneto-optical effects:

Linear pol.	Detected: Polariz.	Detected: Intensity
Linear in M	MOKE, (Kerr and Faraday effect) [Hall effect]	Transversal-MOKE
Quadratic in M	QMOKE, Voigt effect, Linear Magnetic Birefringence (LMB)	Linear Magnetic Dichroism (LMD) [AMR]
Circular pol.	Detected: Polariz.	Detected: Intensity
Linear in M	Mag. Circular Birefringence (MCB)	Magnetic Circular Dichroism (MCD)
Quadratic in M	?	quadratic-MCD (?)

[...] denotes nomenclature in research of conductivity.

Origin of MO effect (microscopical):

Electronic structure of the FM material

[microscopic description]

$$\Downarrow$$

Permittivity tensor of each layer

[phenomenological description]

$$\varepsilon = \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{bmatrix}$$

$$\Downarrow$$

Reflectivity matrix of whole sample

[maximal accessible optical information]

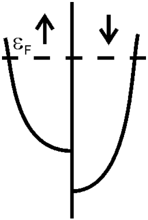
$$R = \begin{bmatrix} r_{ss} & r_{sp} \\ r_{ps} & r_{pp} \end{bmatrix}$$

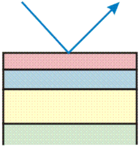
$$\Downarrow$$

Measured Kerr effect: $\Phi_s = \frac{r_{ps}}{r_{ss}}$

$$\Downarrow$$

Signal measured by MO setup



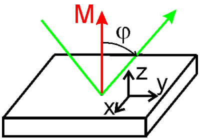


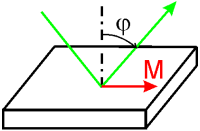
MOKE configurations and permittivity tensor:

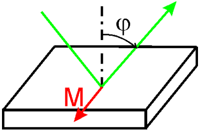
Polar MOKE
$M \perp$ sample surface

Longitudinal MOKE
$M \parallel$ plane of incidence

Transversal MOKE
$M \perp$ plane of incidence







Polarization induced by magnetization: $\Delta \vec{P}_M = \varepsilon_1 (\vec{M} \times \vec{E})$

$$\begin{bmatrix} \varepsilon_0 & -\varepsilon_1 m_z & 0 \\ \varepsilon_1 m_z & \varepsilon_0 & 0 \\ 0 & 0 & \varepsilon_0 \end{bmatrix} \qquad \begin{bmatrix} \varepsilon_0 & 0 & \varepsilon_1 m_y \\ 0 & \varepsilon_0 & 0 \\ -\varepsilon_1 m_y & 0 & \varepsilon_0 \end{bmatrix} \qquad \begin{bmatrix} \varepsilon_0 & 0 & 0 \\ 0 & \varepsilon_0 & -\varepsilon_1 m_x \\ 0 & \varepsilon_1 m_x & \varepsilon_0 \end{bmatrix}$$

$$\Phi_{s/p}(m_z) \qquad \Phi_{s/p}(m_y) \qquad \Delta r_{pp}(m_x)$$

MO effects and permittivity tensors

[Note: tensors on this slide are only illustrative.]

⇒ Linear MOKE: PMOKE, LMOKE, TMOKE, MCD, MCB, [Hall]

$$\begin{bmatrix} \varepsilon_0 & -\varepsilon_1 m_z & \varepsilon_1 m_y \\ \varepsilon_1 m_z & \varepsilon_0 & -\varepsilon_1 m_x \\ -\varepsilon_1 m_y & \varepsilon_1 m_x & \varepsilon_0 \end{bmatrix} \qquad \text{MO signal} \sim \varepsilon_1(m_i)$$

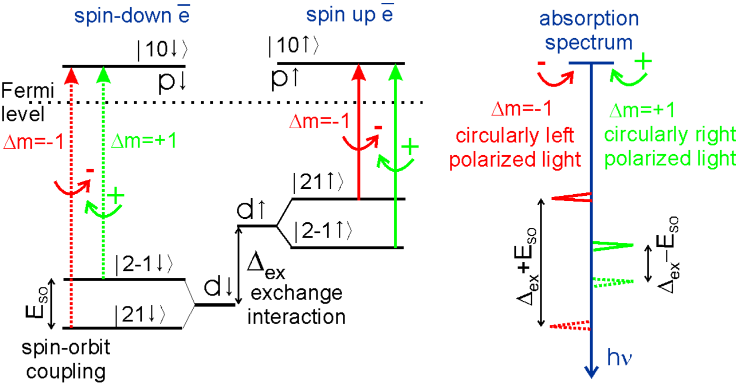
⇒ Quadratic MOKE:

$$\begin{bmatrix} \varepsilon_0 & \varepsilon_1(m_i m_j) & 0 \\ \varepsilon_1(m_i m_j) & \varepsilon_0 & 0 \\ 0 & 0 & \varepsilon_0 \end{bmatrix} \qquad \text{MO signal} \sim \varepsilon_1(m_i m_j)$$

⇒ Voigt effect: MLD, MLD, [AMR]

$$\begin{bmatrix} \varepsilon_{xx}(m_i m_j) & 0 & 0 \\ 0 & \varepsilon_{yy}(m_i m_j) & 0 \\ 0 & 0 & \varepsilon_{zz}(m_i m_j) \end{bmatrix} \qquad \text{MO signal} \sim \sqrt{\varepsilon_{zz}(m_i m_j) - \varepsilon_{yy}(m_i m_j)}$$

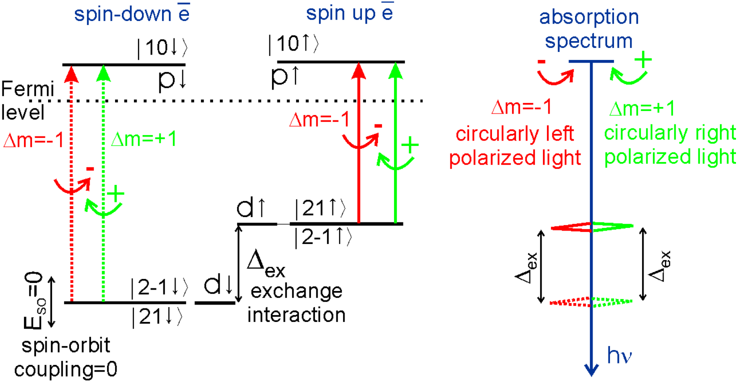
Magneto-optical spectroscopy microscopic picture



Simplified electronic structure for one point of the *k*-space.

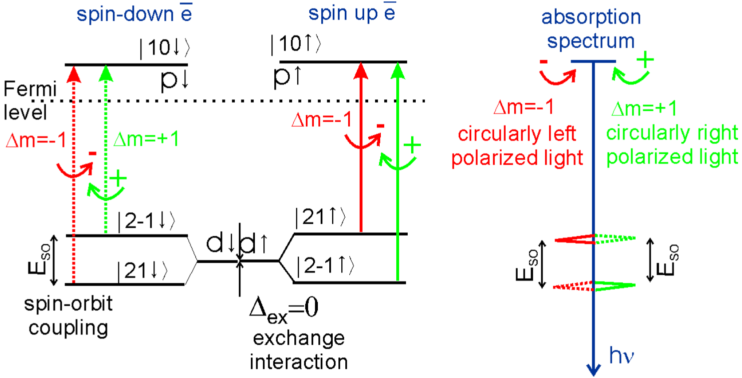
No spin-orbit coupling assumed:

⇒ no MOKE effect

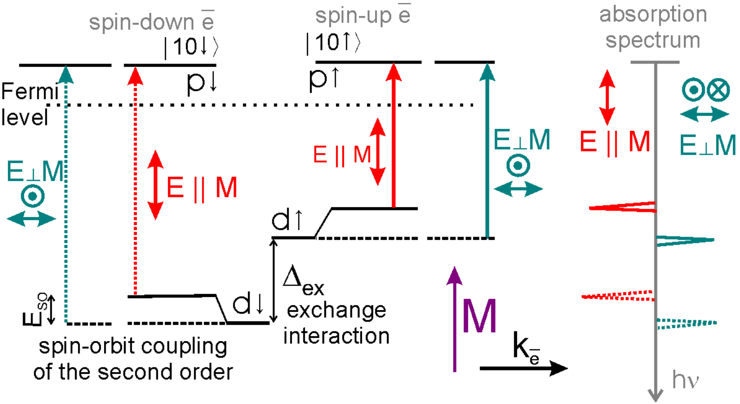


No exchange assumed:

- ⇒ no MOKE effect
- ⇒ both SO coupling and exchange must be present to have MOKE.

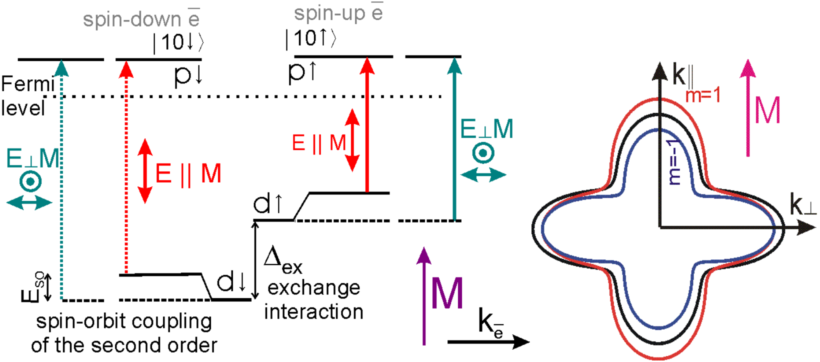


Quadratic Magneto-optical Kerr effect (QMOKE):



QMOKE arises from different absorptions for $\vec{E} \perp \vec{M}$ and $\vec{E} || \vec{M}$.

Quadratic Magneto-optical Kerr effect (QMOKE):



QMOKE arises from different absorptions for $\vec{E} \perp \vec{M}$ and $\vec{E}||\vec{M}$.
⇒ arrises from different electronic structure in $\vec{k}_e \perp \vec{M}$ and $\vec{k}_e||\vec{M}$.

Condutivity (and hence absorption of the photon)

Kubo formula: conductivity determination.

$$\Re[\sigma_{xx}] \sim \sum_{i,f}[f(E_i)-f(E_f)]\times[|\langle i|p_+|f\rangle|^2+|\langle i|p_-|f\rangle|^2]\times\delta(E_f-E_i-\hbar\omega)$$

$$\Im[\sigma_{xy}] \sim \sum_{i,f}[f(E_i)-f(E_f)]\times[|\langle i|p_+|f\rangle|^2-|\langle i|p_-|f\rangle|^2]\times\delta(E_f-E_i-\hbar\omega)$$

where

- $\langle i|$, $|f\rangle$: initial and final states, respectively.
- $p_\pm = p_x \pm ip_y$, $p_x = i\hbar\partial/\partial x$, momentum operator
- terms in the Kubo formula means:
    - summation over all initial and final states, $\langle i|$ and $|f\rangle$.
    - $f(E_f)$, $f(E_i)$: electron occupancy of initial and final states.
    - $|\langle i|p_\pm|f\rangle|^2$: probability of the photon to be absorbed between $\langle i|$ and $|f\rangle$ states for circularly left/right polarized light (non-zero only when electric-dipole selection rules are fulfilled).
    - $\delta(E_f - E_i - \hbar\omega)$ assures energy conservation.

MOKE advantages and disadvantages:

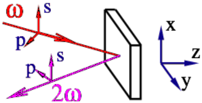
- spatial resolution limited by wavelength limit ($\sim$300nm for visible light) → but sub-wavelength resolution demonstrated.
- investigation on distance, light can be transported nearby sample by a fibre.
- no need of vacuum or special sample preparation.
- depth resolution about 30nm.
- measurements do not influence sample magnetization.
- high time resolution.
- depth selectivity.
- vectorial resolution (possible to determine all magnetization components).
- robust, cheap technique.

BUT:

- spatial resolution limited by wavelength limit.
- easy to overcome Kerr signal by spurious noise (S/N ratio problem).
- not direct information about the electronic structure or magnetic moments etc.

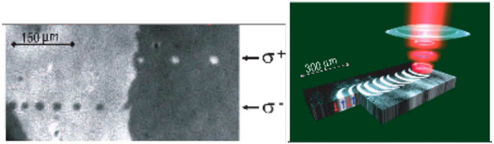
Extensions of MOKE:

- XMCD, XMLD for high photon energy.
- Non-linear magneto-optics
  ⇒ MO second harmonic generation.



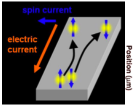
- Inverse Faraday effect (ultrafast optical switching).

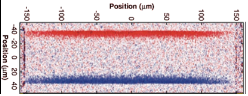
(Stanciu et al, PRL 99, 047601 (2007))



- Observation of spin accumulation in GaAs (spin Hall effect).

(Kato et al, Science, 2004)





Outline

1. Introduction
2. Electron in periodic potential
   - Free electron
   - Bloch theorem
   - Brillouin zone
   - Reciprocal space
   - Number of *k*-states in the First Brillouin zone
   - Free electron states
   - Density of states
   - Fermi surface
   - Understanding of Brillouin zone
3. Diffraction
   - X-ray diffraction
   - Inverse photoelectron spectroscopy (IPES)
   - Auger and characteristic X-ray
   - Synchrotron
5. Magneto-optical effect
   - Examples of magneto-optical effects
   - Origin of magneto-optical effects
   - Use of magneto-optical effects
6. Time resolved investigations
   - Relation between energy

Time resolved investigations:

Measure time response of selected sample property on excitation after frequency or pulse excitation.

Systematization by:

underlaying physics: thermally activated processed / decay / demagnetization / precession / etc.

way of measurements:

- in time t domain: $I(t)$
  - direct time dependence.
  - pump-probe.
- in frequency f (or in energy $E = hf = \hbar\omega$) domain: $I(E) \equiv I(hf) \equiv I(\hbar\omega)$.

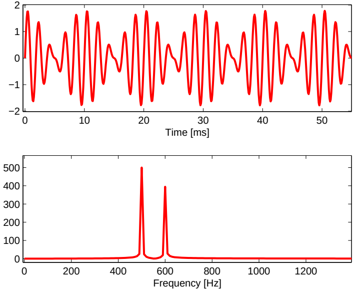
Reciprocal relation between time and frequency (energy)

As there is a reciprocal relation between position $\vec{r}$ and momentum $\vec{p} = \hbar\vec{k}$, there is an analogous relation between time t and energy $E = \hbar\omega$.

Fourier transform: $F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) \exp(-i\omega t)\mathrm{d}t$

Inverse Fourier transform: $f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) \exp(i\omega t)\mathrm{d}\omega$

Example: sound wave is in time domain and its reciprocal (frequency) expression as notes:



Frequecnies, energies and timescales

Many ways how to express energy. Therefore, if you can, use eV.

Energy	freq.	period	λ	cm^{-1}	temp.	comment
4.1 μeV	1 GHz	1 ns	300 mm	0.033	47 mK	1 GHz; radio freq.
4.1 meV	1 THz	1 ps	300 μm	33	47 K	1 THz; far-IR
25 meV	6.25 THz	160 fs	48 μm	209	300 K	300 K: room temp.
83 meV	20 THz	50 fs	15 μm	667	960 K	50 fs: min. pulse width
1 eV	242 THz	4.13 fs	1.24 μm	8065	11 kK	1 eV; near IR
1.91 eV	461 THz	2.2 fs	650 nm	15400	22 kK	red light
2.43 eV	588 THz	1.7 fs	510 nm	19600	28 kK	green light

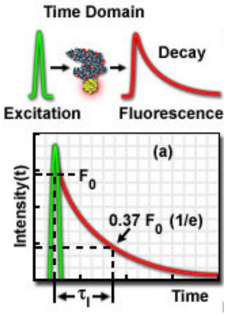
Note: relation between temperature and energy is $E = kT$, where k is Boltzmann constant.

Time resolved investigations:

Anything that allows you to measure the temporal dynamics and the kinetics of physical processes. In another words, what is the response of the system after an excitation?

- General response after excitation (dynamics).
- Eigenfrequencies (resonance frequencies) determination.
- Life-time determination.

Life-time

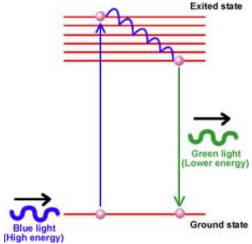


Eigenfrequency

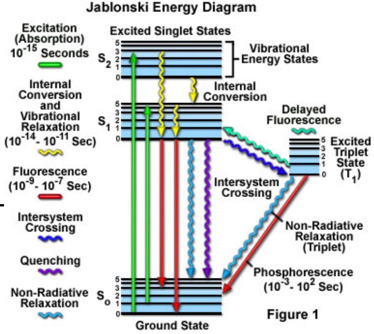
Time-resolved fluorescence

- excitation of electron by UV radiation.
- quick relaxation to excited state with longer lifetime.
- relaxation to original state and emission of photon (of smaller energy than the exciting one).
- fluorescence (quicker relaxation) / phosphorescence (slower relaxation).
- Key characteristics of fluorescence:
  - life-time.
  - frequency.
  - intensity (efficiency).

Simple sketch



More complicated sketch



Life-time determination

Life-time can be determined by both pulse and sinusoidal excitation.

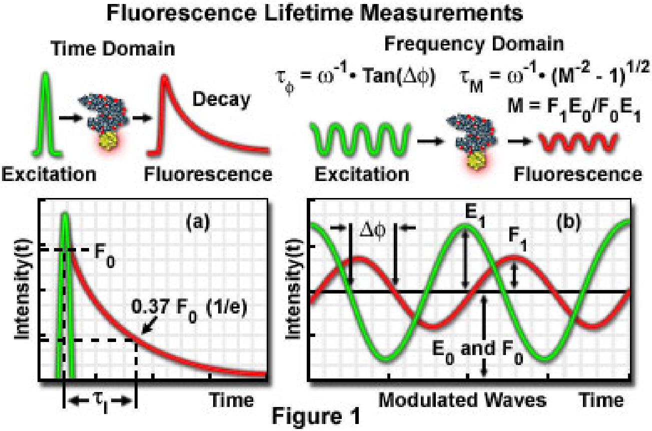


Figure 1

http://www.olympusfluoview.com/applications/flimintro.html

Relation between pulse and sinusoidal excitation

Assuming linear system, one can find solution using Green's function:

- Incoming excitation: $x_0(t) = \delta(t)$
- Outcoming excitation:
  $$y_0(t) = \begin{cases} t < 0: & y(t) = 0 \\ t > 0: & y(t) = A_0 \exp(-t/T_0) \end{cases}$$
  where T_0 is decay time (half-life time is $T_{1/2} = T_0 \ln 2$).

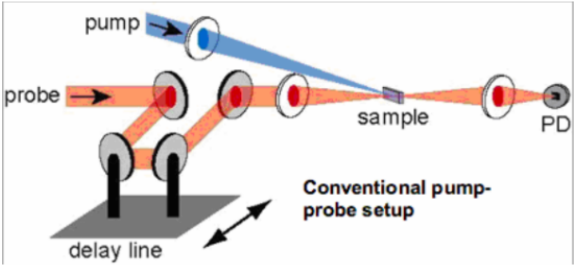
When excitation light is sinusoidally modulated:

- Incoming excitation: $x(t) = \cos(\omega t)$
- Outcoming excitation is summation over responses from δ-function: $y(t) = \int_{-\infty}^{t} x(\tau) y_0(t-\tau) = \cdots = A\cos(\omega t + \phi)$

$\Rightarrow$ Both sinusoidal and pulse excitations provides analogous information.

Pump-probe technique (stroboscopic technique):

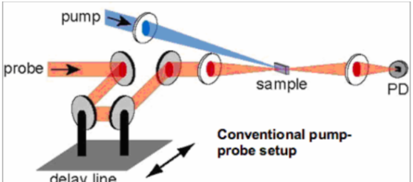
- For slow decay (up to MHz frequencies), one can just pump and then directly observe the decay by quick detector (e.g. by photodiode or quick CCD camera).
- For quicker processes, pump-probe technique must be used. Basically, it's time resolution is limited by pulse width of current lasers, being about 10-50 fs (3–15 μm long light pulse).

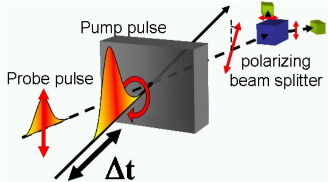


http://nelson.mit.edu

Pump-probe technique (here all optical):

- Strong pump pulse excites the system. Usually, the pump just heats the sample and excites the electrons.
- Second pulse arriving Δt later, probes the sample. Usually reflectivity (for matter/phonon investigation) or MOKE (for magnetization investigation) is detected.
- Different delay between both pulses is usually obtained by prolongation of optical path of one beam (so called delay line).
- Some or all of this sequence (pump-delay-probe) can also be done electrically for slower processes (e.g. fast electrical oscilloscopes $\sim$50 GHz are all electrical pump-probe).





Experimental techniques related with pulse lasers

- pulse laser itself (also called oscillator). Typical example Ti-Sapphire mode-locked laser, pulse width down to 10 fs (3 μm width in air), repetition rate about 80 MHz (i.e. distance 3.7 m in air), central wavelength about 800 nm (red). Averadge output $\sim$1 W.
- pulse picker: selects only few light pulses in the beam (i.e. reduces repetition rate).
- amplifiers: amplifies light intensity in the pulse.
- frequency doubler: generates second harmonic of the pulse (i.e. 400 nm from 800 nm).
- down-conversion: generates entangled pairs of photons with half-energy each.

Types of magnetization dynamics (example of complex dynamics)

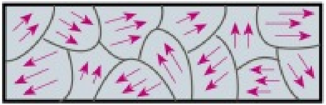
thermally activated	thermally activated domain wall motion, magnetization reversal [s-μs range].
field driven	field driven domain wall motion [s-μs range].
precession	precession of magnetic spins; [GHz=ns range].
spin demagnetization	spin demagnetization and relaxation; [ps-fs range].

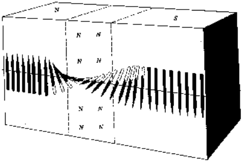
Magnetic domain wall propagation

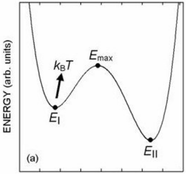
- Domain walls separates areas of magnetic materials with different magnetization directions.
- Slow magnetization reversal/dynamics is provided by domain wall movement.
- Domain wall movement is often thermally activated, i.e. probability per time $p(t)$ to overcome energetic barrier of height ΔE is

$$p(t) = 1 - \exp(-t/\tau_{2\to 1}), \quad \text{where} \quad \tau_{2\to 1} = \tau_0 \exp(\frac{\Delta E}{kT})$$

where $\tau_{2\to 1}$ is averadge time to overcome a barrier ΔE.





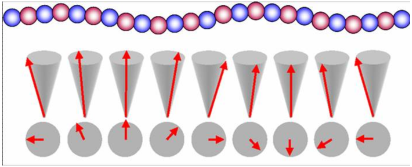


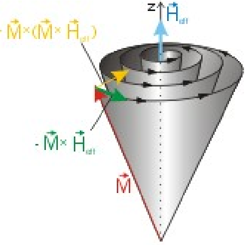
Magnetization precession (fast magnetization)

Magnetic spin precesses in external (effective) magnetic field (Landau-Lifshitz-Gilbert equation)

$$\frac{\partial \vec{M}}{\partial t} = -\gamma(\vec{M} \times \vec{H}_{eff}) + \frac{G}{\gamma M_s^2}\left[\vec{M} \times \frac{\partial \vec{M}}{\partial t}\right]$$

The magnetization precession is damped and relax to its equilibrium position.





Ultrafast demagnetization

- excitation of a ferromagnet by an ultrashort laser pulse leads to demagnetization on a time scale of a $\sim 100\,\mathrm{fs}$ (three temperature model):
  - light pulse excites the electrons.
  - those electrons quickly equilibrates (thermalized) (hot electrons).
  - hot electrons then relax to its original equilibrium state, creating e.g. lattice vibrations (phonons).
  - all those processes also modifies population of up and down electrons and hence influence sample magnetization.

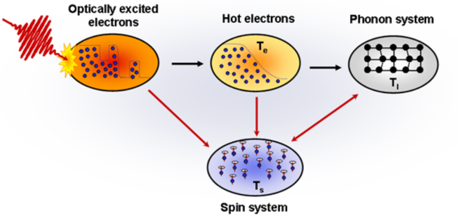
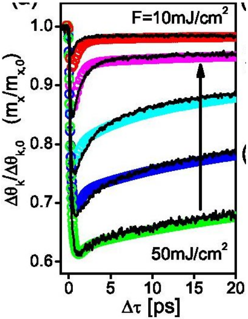
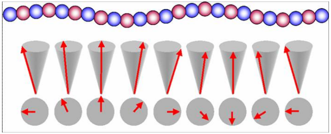


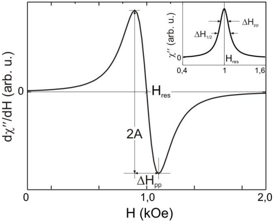
Figure 2: Three temperature model used to describe the interaction of an ultrashort laser pulse with the electron, phonon and spin subsystem of a ferromagnet. The microscopic mechanisms leading to an ultrafast demagnetization are still not clear.

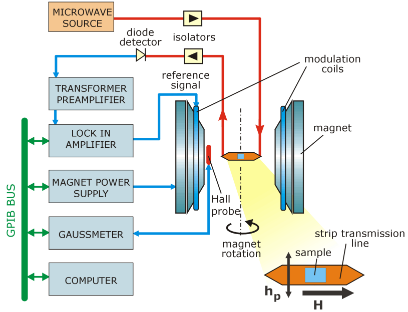


Ferromagnetic resonance (FMR)

Under certain conditions, all spins in feromagnetic material precesses in the same frequency ω. It is an eigenfrequency of a given system. The detection is based on pumping the system by various frequencies and detecting the absorptions for each frequency. For simplicity, often the frequency is kept fixed and the external magnetic field is varied.



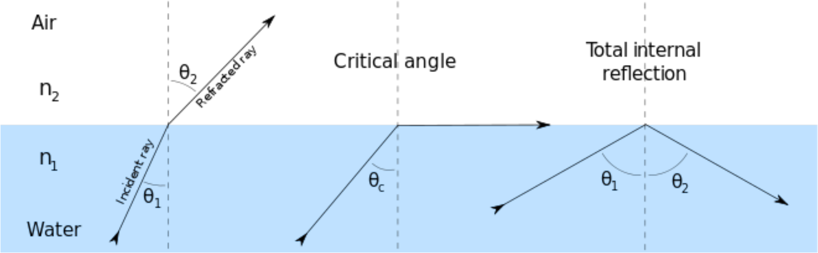




http://www.physics.colostate.edu/groups/PattonGroup

Outline

Reflection and total reflection



Snell law:

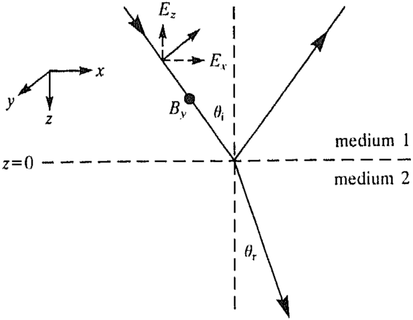
$$\sqrt{\varepsilon_1}\sin\varphi_1 = \sqrt{\varepsilon_2}\sin\varphi_2$$

Critical angle:

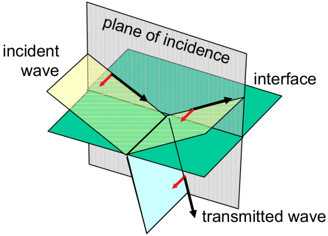
$$\sin\varphi_c = \sqrt{\frac{\varepsilon_2}{\varepsilon_1}}$$

Light reflection on the interface

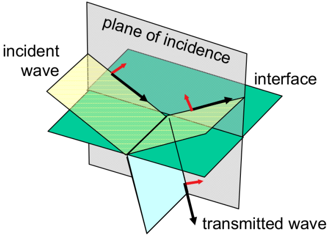
1. Maxwell equations
2. solution as plane wave
   $E = E_0 \exp(i(\vec{k} \cdot \vec{r} - \omega t))$
3. boundary conditions at the interface:
   $\vec{E}, \vec{H}$ fields: continuous transverse (x, y) components
   $\vec{D}, \vec{B}$ fields: continuous normal (z) components
4. for total reflection, solution of transverse wave is in form so called evanescent wave, non-propagating in z-direction
   $E = E \exp(-k_z z)$



Light reflection on the interface



s-polarized light:



p-polarized light:

$$r_\perp = \frac{n_i \cos(\theta_i) - n_t \cos(\theta_t)}{n_i \cos(\theta_i) + n_t \cos(\theta_t)}$$

$$t_\perp = \frac{2n_i \cos(\theta_i)}{n_i \cos(\theta_i) + n_t \cos(\theta_t)}$$

$$r_\parallel = \frac{n_i \cos(\theta_t) - n_t \cos(\theta_i)}{n_i \cos(\theta_t) + n_t \cos(\theta_i)}$$

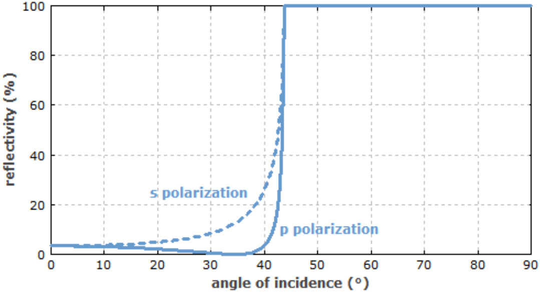
$$t_\parallel = \frac{2n_i \cos(\theta_i)}{n_i \cos(\theta_t) + n_t \cos(\theta_i)}$$

And, for both polarizations: $n_i \sin(\theta_i) = n_t \sin(\theta_t)$

http://www.ece.rice.edu/~daniel/262/pdf/lecture14.pdf

Light reflection on the interface

Reflection on glass/air



Total reflection

Critical angle:

$$\sin\varphi_c = \sqrt{\frac{\varepsilon_2}{\varepsilon_1}} = \frac{n_2}{n_1}$$

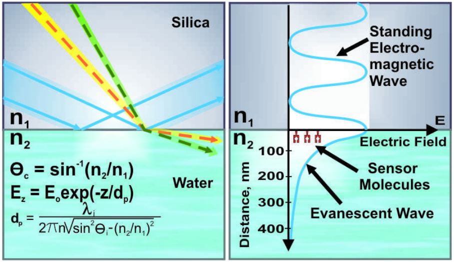
Evanescent wave:

$$E = E_t \exp(-z/\delta - i\omega t)$$

Penetration depth:

$$\delta = \frac{1}{k_0\sqrt{(n_1 \sin\varphi_1)^2 - (n_2^2)}}$$

Example: glass(n_1)/water(n_2) inteerface; $n_1 > n_2$

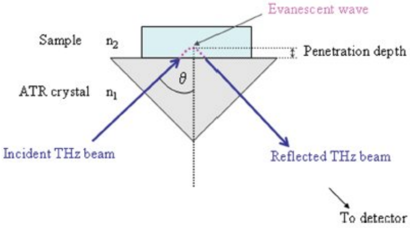


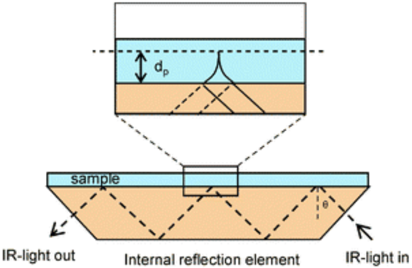
http://www.tirftechnologies.com/principles.php

Attenuated total reflectance (ATR)

(Zeslabený úplný odraz)

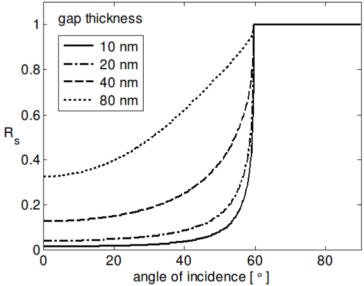
- probes sample by evanescent wave
- ⇒ sensitive to surface of the sample
- sample modifies evanescent wave → partial absorption or transmission of light in sample → total reflection is decreased (attenuated).



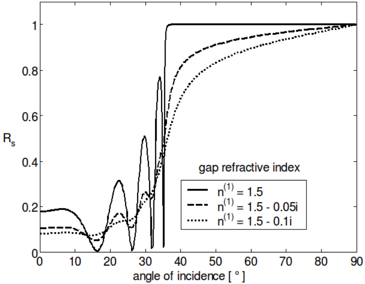


Attenuated total reflectance (ATR): gap effect

Gap thickness (refractivity of gap=1):



Absorption in gap (gap thickness 960 nm):



Surface plasmon (electrical excitation providing two adjacent evanescent waves in the vicinity of the interface)

Electric field in the vicinity of the interface:

$$E = E_O \exp[i(k_x x + k_z z - \omega t)]$$

where

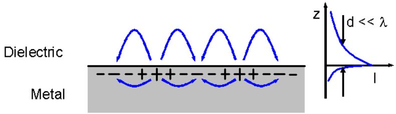
$$k^2 = k_x^2 + k_z^2 = \epsilon \left(\omega/c\right)^2 = \epsilon k_0^2 \qquad (2)$$

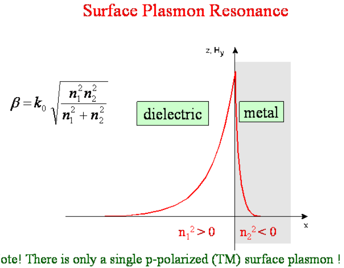
At the interface of two materials ϵ_1 and ϵ_2:
(a) k_x continuous over the interface;

$$k_{x1} = k_{x2} \qquad (3)$$

(b) D_z and E_x continuous over the interface

$$k_{z1}/\epsilon_1 = k_{z2}/\epsilon_2 \qquad (4)$$




Surface Plasmon Resonance

Note! There is only a single p-polarized (TM) surface plasmon !

`http://www.physics.uwo.ca/~smittler/`

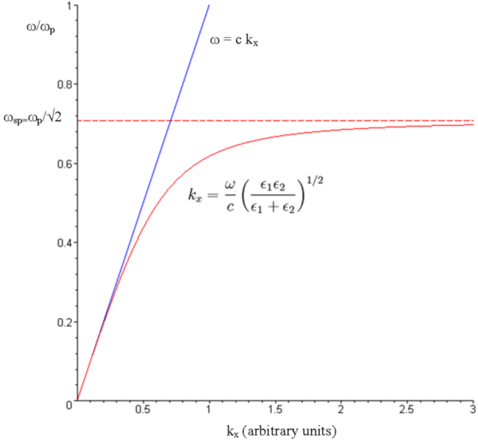
Surface plasmon II: dispersion relation

- From Eqs.(2–4) follows dispersion relation for surface plasmon:

$$k_x = k_0 \sqrt{\left(\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}\right)}, \qquad (5)$$

where $k_0 = \omega / c$.

- Surface plasmon appears only for p-polarized (TM) wave, as this mode has normal (z) component of $D = \epsilon \epsilon_0 E$ field.

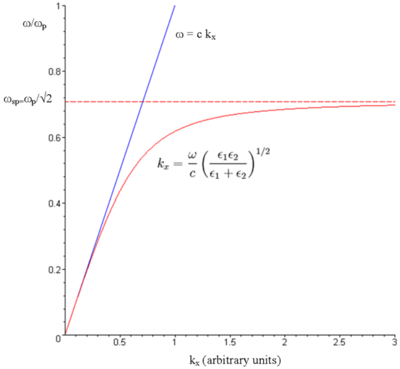


Surface plasmon III: example

Example: assuming $\epsilon_1 = 1$ (air) and $\epsilon_2 = 1 - \frac{\omega_p^2}{\omega^2}$ (metal as free electron model of an electron gas). Then

$$k_x = \frac{\omega}{c}\sqrt{\left(\frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2}\right)} \qquad (6)$$

Hybridization between photon ($\omega = ck_0$) and plasmon $\omega_{SP} = \omega_p/\sqrt{2}$.



Surface plasmon resonance (SPR) I

- Resonance between incident wave photon and surface plasmon.

Resonance means that both (pseudo)-particles have equal ω and $k_x = k_{x,inc} = \Re(k_{x,sp})$.

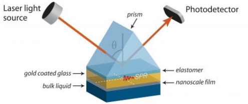
- Description of incident wave from material ϵ_1 under angle φ:

$$k_{x,inc} = \frac{\omega}{c}\sqrt{\epsilon_1}\sin\varphi \tag{7}$$

- Description of surface plasmon:

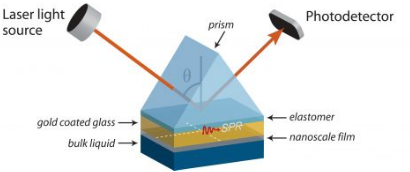
$$k_{x,sp} = \left(\frac{\omega}{c}\right)\sqrt{\left(\frac{\epsilon_1\epsilon_2}{\epsilon_1+\epsilon_2}\right)}, \tag{8}$$

Condition for existence of the resonance: $\Re(\epsilon_2) < -\epsilon_1$ (i.e. $\Re(\epsilon_2)$ must be negative; fulfilled by coinage metals, Au, Ag, Cu). Here, ϵ_1 is assumed to be non-absorbing material (i.e. $\Im(\epsilon_1) = 0$).



Surface plasmon resonance (SPR) II

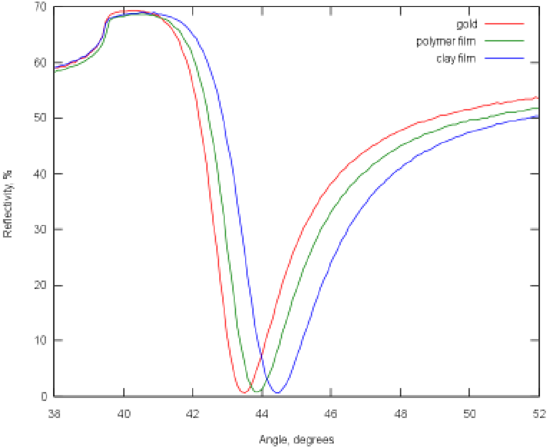
Surface plasmons are very sensitive to slight perturbations within the skin depth ⇒ surface plasmons are often used to probe tiny changes of refraction index near the interface (extreme sensitive detector of small changes of the refraction index). ⇒ Readout of many bio-sensors based on this detection technique.



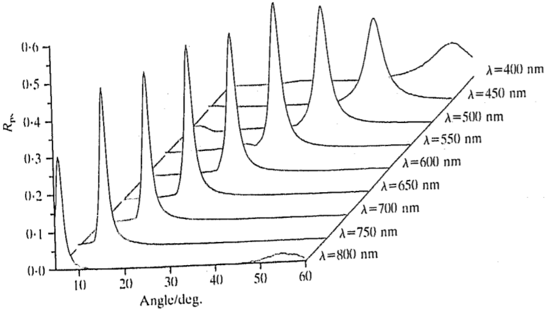
http://www.bionavis.com/technology/spr/

SPR: detection I

- presence of resonance increases absorption and reduces reflectivity.
- position of reflection minima very sensitive to refractivity index in position of the evanescent wave.



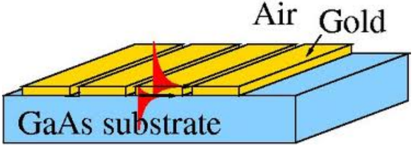
SPR: detection II



- presence of resonance increases absorption and reduces reflectivity.
- position of reflection minima very sensitive to refractivity index in position of the evanescent wave

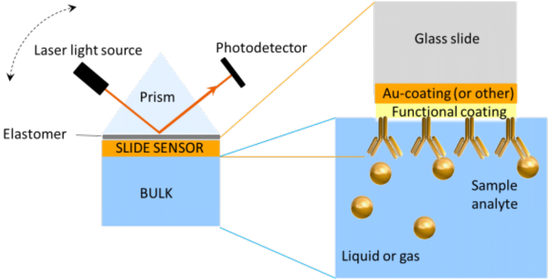
SPR: how to couple surface plasmon and photon?

- couple light by high-refraction index prism
- lateral modulation of the interface (roughness or structuring)



$$\omega/c \sin\varphi + 2\pi/b = \omega/c\sqrt{\frac{\varepsilon_2}{\varepsilon_2+1}} \tag{9}$$

SPR: bio sensors



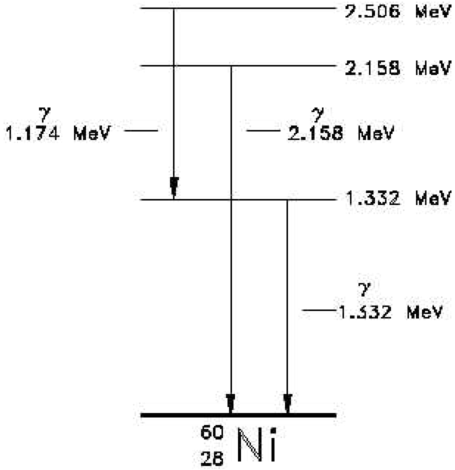
http://www.bionavis.com/technology/spr/

Outline

Energy Levels of the Nucleus

- The nucleons (protons and neutrons) in the nucleus of an atom, exist in shells. (like the electrons that circle the nucleus), having corresponding energy states.
- Ground state and excited state
- Usually, energies are much higher than for electrons
- Lifetime of the excited states may be much longer than of electrons.

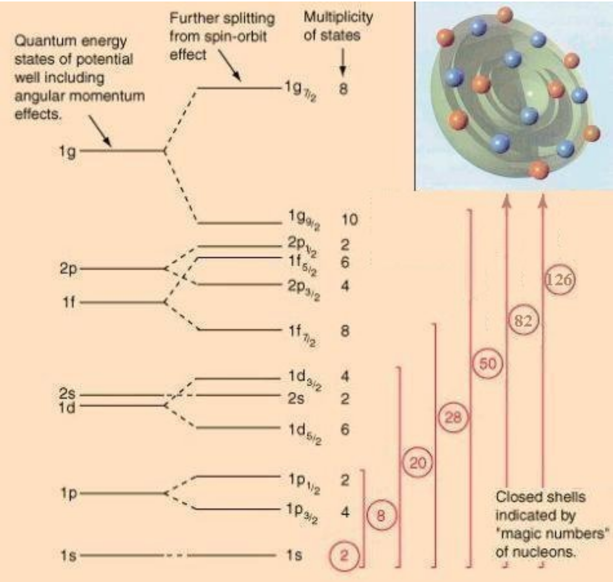
⇒ Hence, energy transitions may be very sharp.



http://www.tpub.com/content/doe/h1019v1/css/h1019v1_44.htr

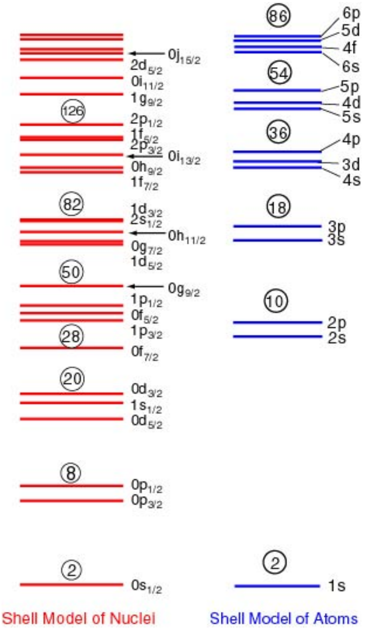
Nucleus shell model

- like electrons, nucleons in nucleus form a shells.
- (more) stable nucleus are for Z (atomic/proton number) or N (neutron number) = 2, 8, 20, 28, 50, 82, 126.
- compare with stable shells for electrons: $Q = 2, 10, 18, 36, 54, 86$.



http://universe-review.ca/F14-nucleus.htm

Comparison of electron and nuclues shell model



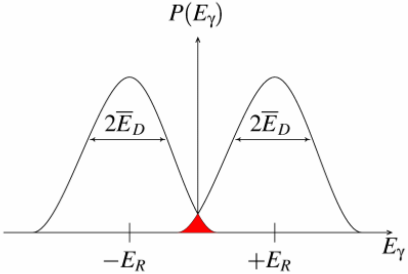
http://www.kutl.kyushu-u.ac.jp

Mössbauer effect

- When free nuclei absorbs or emits photon (energy), it recoils (kicks back), due to finite mass of the nuclei.

- Hence, the emitting energy (photon) is a bit different from spacing of the energy levels (in nucleus).

⇒ Absorption of the emitted photon by another nucleus is of low probability.

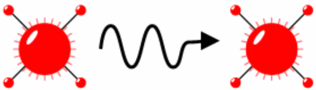


- E_D is linewidth due to Doppler effect caused by thermal motion.
- E_R is resonance (transition) energy.
- overlap the in picture strongly exaggerated.

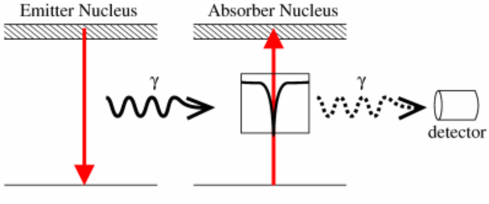
http://www.rsc.org/membership/networking/interestgroups/mossbauerspect

Mössbauer effect

- However, when nuclei is inside the lattice, the whole lattice can absorb the recoil. Then, the nuclei stays fixed and hence the photon energy is not blurred (i.e. remains sharp). It is so called recoil-free event.



- Then, if emitting and absorbing nuclei are in identical, cubic environments then the transition energies are identical.



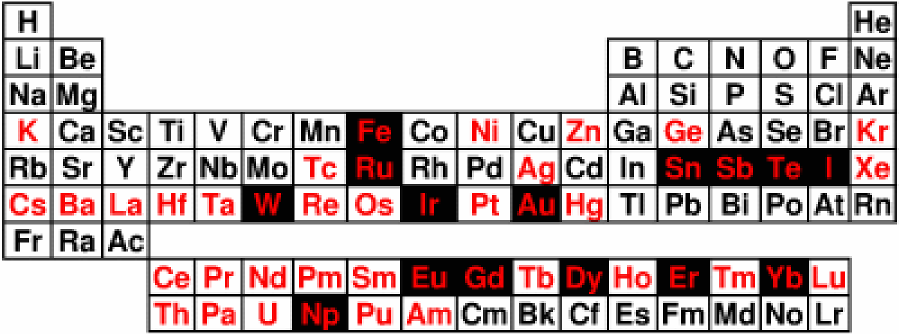
- Hence, the photon can be absorbed by other nucleus.

Mössbauer effect

- Isotope sensitive technique (response only from a particular isotope in the sample).
- Number of recoil-free events (and hence the strength of the signal) is strongly dependent upon the gamma-ray energy. Hence, the Mössbauer effect is only detected in isotopes with very low lying excited states.
- Hence, to have sharp transition and high probability absorption, the conditions are:
  - low energy of transitions (order of tens of keV).
  - long lifetime of the excited state (provides sharp lines).
- It limits the number of isotopes that can be used for Mössbauer spectroscopy.

Mössbauer effect

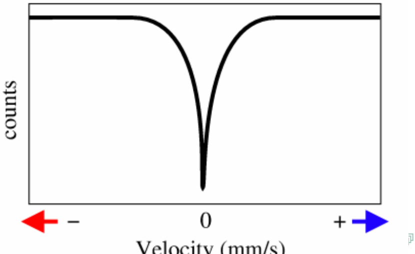
- The most common Mössbauer isotope is ^{57}Fe; linewidth is 5×10^{-9} eV, with Mössbauer gamma-ray energy of 14.4 keV. Corresponding energy resolution 10^{12}.
- Elements known to have Mössbauer isotopes (in red), and most often used (in black).



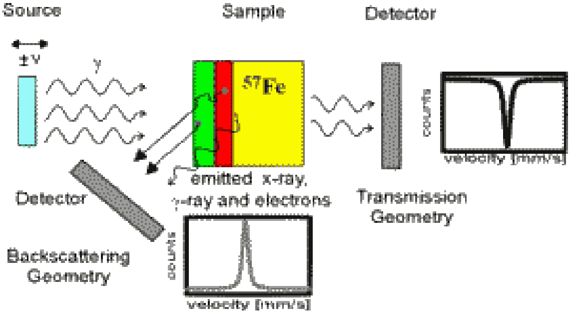
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

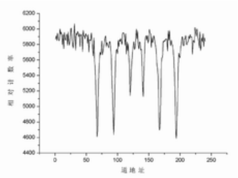
Mössbauer spectroscopy

- We want to measure changes in energy in order of $10^{-6} - 10^{-9}\,\text{eV}$.
- Energy can be slightly varied by Doppler effect by moving detector or source.
- Doppler effect $\Delta E = \frac{v}{c} E_0$
- ^{57}Fe provides $E_0 = 14.4\,\text{keV}$ with natural linewidth $\Delta E = 50\,\text{neV}$. Hence, corresponding speed of this Doppler shift is $v = 1\,\text{mm/s}$.



Measuring of Mössbauer spectra





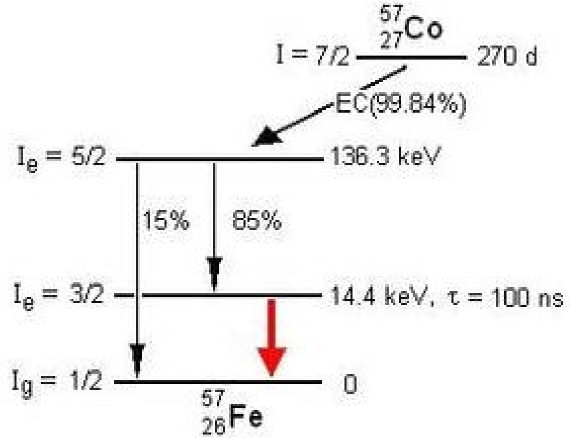
http://iacgu32.chemie.uni-mainz.de/moessbauer.php

transmission: Measures amount of absorbed photons; Bulk sensitive.

backscattering: Measures backscattered photons or emitted electrons; Surface sensitive. (Electrons are more sensitive to the surface).

Sources of X-rays for Mössbauer spectroscopy

Example: source ^{57}Fe.
β^+ decay of ^{57}Co: $^{57}_{27}\mathrm{Co} \rightarrow {}^{57}_{26}\mathrm{Fe} + e^+ + \nu_e$

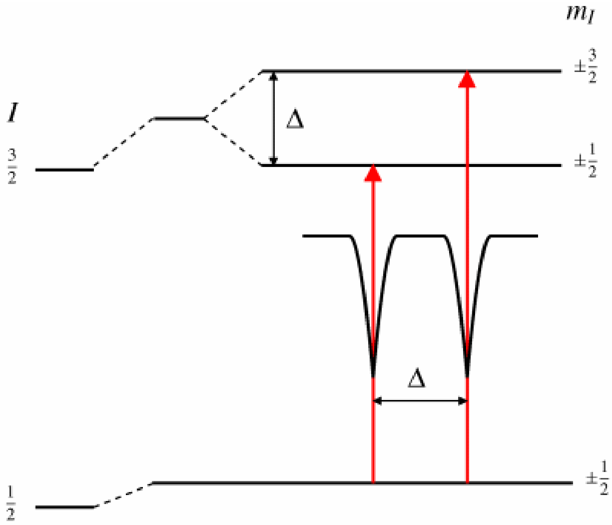


What Mössbauer spectra tell about the sample?

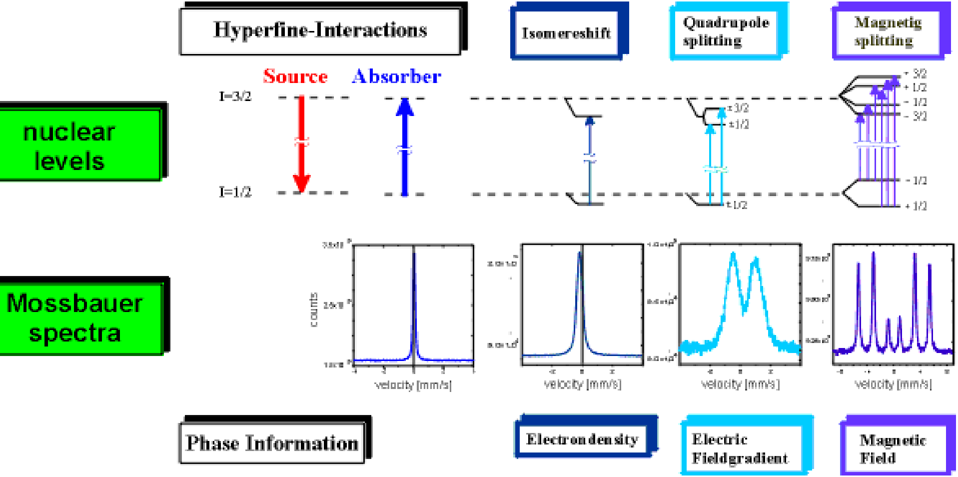
- Energy states of nucleus are sensitive to the electric and magnetic fields created either by external fields, or by surrounding electrons.
- In another words, nucleus serves as a very local detector of the electric and magnetic fields.
- There are three basics hyperfine energy splitting of the nuclear energy levels
  - isomer shift (chemical shift) ⇔ electric field.
  - quadrupole splitting ⇔ gradient of the electric field.
  - magnetic splitting (Zeeman Effect) ⇔ magnetic field.

Example of nucleus energy levels in ^{57}Fe

(here quadrupole splitting demonstrated)



Hyperfine splitting in Mössbauer spectra of ^{57}Fe



Hyperfine-Interactions

Isomereshift

Quadrupole splitting

Magnetig splitting

nuclear levels

Source **Absorber**

Mossbauer spectra

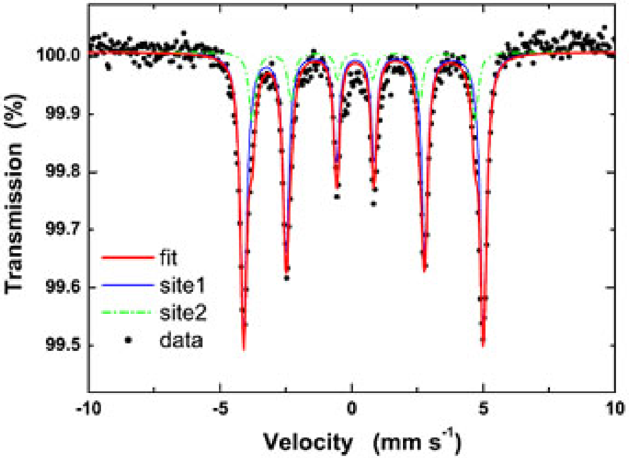
Phase Information

Electron density

Electric Fieldgradient

Magnetic Field

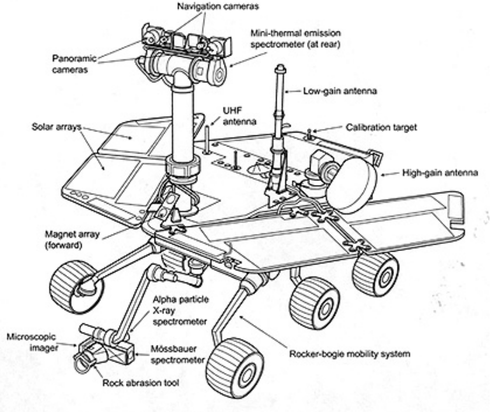
Examples of Mössbauer spectra in FePt nanopraticles



FePt alloy in two phases, L1_0-FePt and fcc-FePt.

http://ssc1.kuicr.kyoto-u.ac.jp/english/research/nanoparticle2.html

NASA's Mars Exploration Rover Spirit



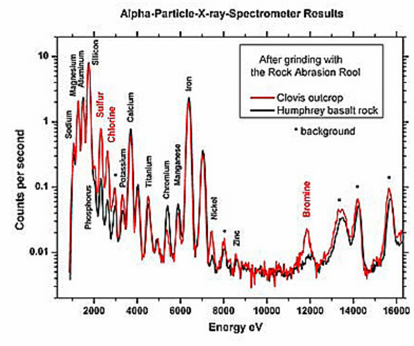
Mars Exploration Rover

Rock named Clovis:

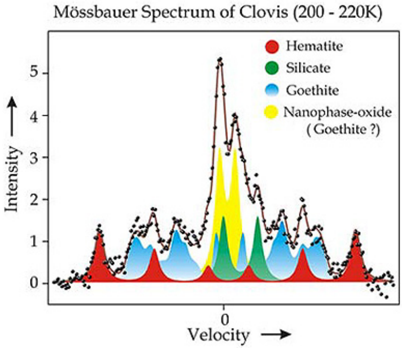
The Rovers are both designed to search for water using a variety of instruments, including a mini-Thermal Emission Spectrometer, a Mossbauer Spectrometer, and Alpha Particle X-ray Spectrometer.

http://rst.gsfc.nasa.gov/Sect19/Sect19_13a.html

NASA's Mars Exploration Rover Spirit



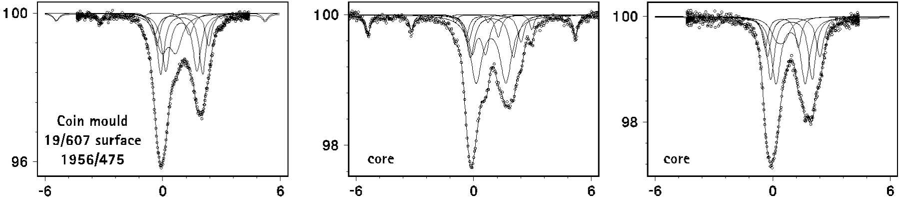
Alpha-Particle-X-ray-Spectrometer Results



Mössbauer Spectrum of Clovis (200 - 220K)

"On Earth, Goethite - a very common mineral associate with Limonite - is found as an alteration product or as a direct precipitate in the so-called "bog iron" deposits, which result from a reducing, water-rich swampy environment. That form of Goethite is usually produced with the aid of bacteria but can also form inorganically. The mode of origin of the Clovis Goethite is still "up for grabs" but the presence of this mineral suggests a significant role for water in Mars' past."

Coin Metal Working in Celtic Times



- Determination of Fe concentrations in states: magnetic, nonmagnetic Fe^{3+}, nonmagnetic Fe^{2+}, garnets (almandine), in both bulk and surface.
- The results compared with results coming from known fabrication.
- "In Celtic coin moulds iron-bearing components differ from the top to the bottom, showing that the top has been heated in a strongly reducing atmosphere to about 1200 C, while the bottom was mainly oxidized below 700 C. From this information the procedure for making coin blanks in Celtic times can be reconstructed."

http://einrichtungen.ph.tum.de/E15b/research/arch/coins.htm

(Nuclear) Magnetic Resonance (NMR)

- Based on precession of spin of the nucleus in magnetic field.

⇒ Can be used only for nuclei having magentic moment (i.e. spin).

⇒ The isotope must have odd number of protons and/or of neutrons. I.e. zero spin have only nuclides with even numbers of protons and neutrons.

  - magnetic moment of neutron: $-1.9130427(5)\mu_N$
  - magnetic moment of proton: $2.792847351(28)\mu_N$
  - magnetic moment of electron: $-1.00115965218111\mu_B$

where

  - Bohr magneton: $\mu_B = \frac{e\hbar}{2m_\mathrm{e}}$, m_e rest mass of electron.
  - Nuclear magneton: $\mu_N = \frac{e\hbar}{2m_\mathrm{p}}$, m_p rest mass of proton.

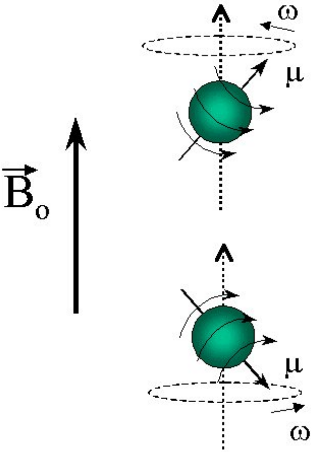
- Isotopes of particular interest and use to organic chemists are ^{1}H, ^{13}C, ^{19}F and ^{31}P, all of which have $I = 1/2$.

Larmor frequency

- Precession of magnetic moment inside magnetic filed.
- Larmor frequency of nucleus

$$\omega = \frac{2\mu_N}{\hbar} B$$

- Corresponding frequencies are:
  - $f_{\mathrm{proton}} = 42.578\,\mathrm{MHz/T}$
  - $f_{\mathrm{electron}} = 28.025\,\mathrm{GHz/T}$
- The spin of nucleus can be driven by an external electro-magnetic (EM) wave. When its frequency is in resonance (i.e. is equal) with Larmor frequency of the spin, the spin precesses more and the EM wave gets damped.



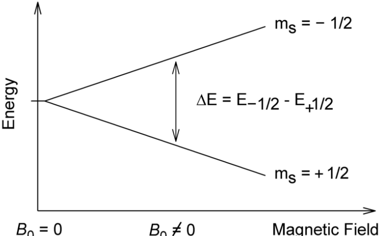
Larmor frequency - quantum picture

Alternatively, driving precession can be understand as absorption of photon

- Energy levels of nucleus spin direction are split by an external magnetic field (spin-up and spin-down)

$$\Delta E = \gamma \hbar B \equiv 2\mu_N B$$

- As electric-dipolar transition is not allowed, the transition is magnetic-dipolar transition.
- Note, magnetic dipole transitions are typically about 10^5 times more unlikely than similar electric dipole transitions.



Example of NMR typical frequencies

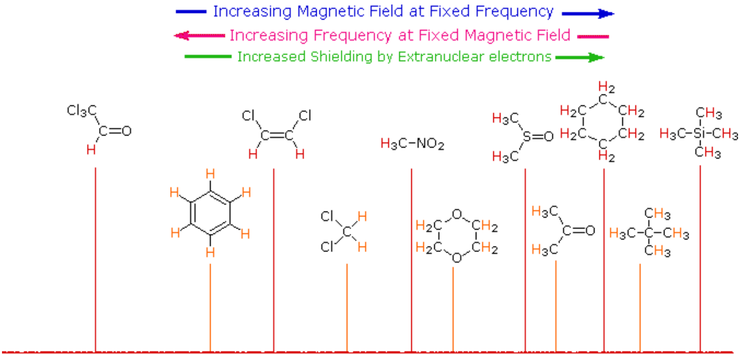
isotope	magnetic moment
^{1}H	$\mu = 2.7927\mu_N$
^{19}F	$\mu = 2.6273\mu_N$
^{31}P	$\mu = 1.1305\mu_N$
^{13}C	$\mu = 0.7022\mu_N$

Nuclear magneton: $\mu_N = \frac{e\hbar}{2m_\mathrm{p}}$, m_p rest mass of proton.

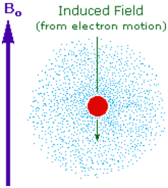
http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm

NMR spectroscopy

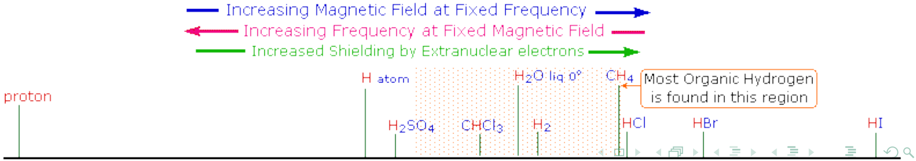
- Nucleus serves as a sensitive probe of local magnetic field.
- Local magnetic field in nucleus position slightly varies due to screening of surrounding electrons (chemical shift). Typical change in ppm - part per million.
- Sensitive only to one isotope (typically ^{1}H, i.e. proton).



NMR: Why different nuclei have different resonance frequency?

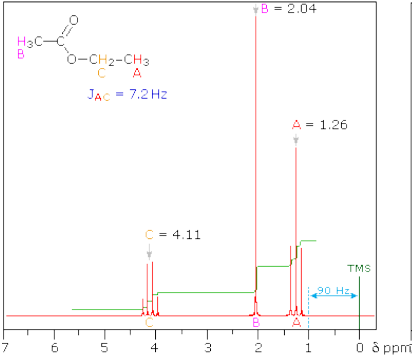


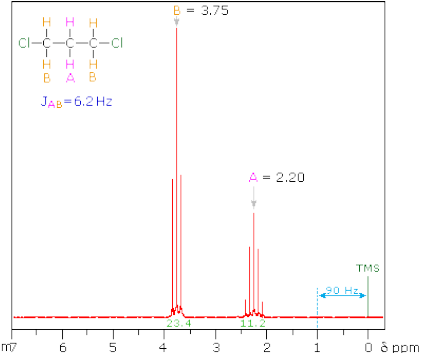
- Electrons are charged particles ⇒ they move in response to the external magnetic field ⇒ secondary field opposed to the applied field is created.
- The external magnetic field acting on nuclei are screened by surrounding electrons ⇒ the field acting on nuclei is smaller (i.e. resonance frequency get smaller)
- typical change due to electron screening is 0.005% (5 ppm).



NMR spectroscopy

- Signal strength → concentration of a given nucleus in a given enviroment.
- Exchange (spin-spin) interaction provides splitting of energy levels (so called J-coupling).





http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm

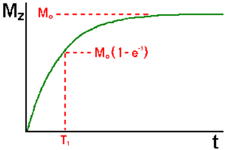
NMR relaxation

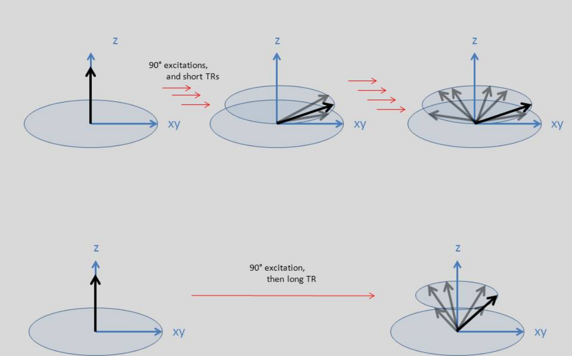
Measuring relaxation time of magnetization upon its excitation to its thermodynamically stable state.

- Spin excitation be external rf pulse → relaxation of spins back to thermodynamic state (i.e. aligned along applied field). At this stage, relaxation time is measured.
- two different relaxation times are measured, longitudinal T_1 and transversal T_2.
- those time constants says about surrounding electronic structure and inhomogeneity of magnetic field.

NMR relaxation: longitudinal

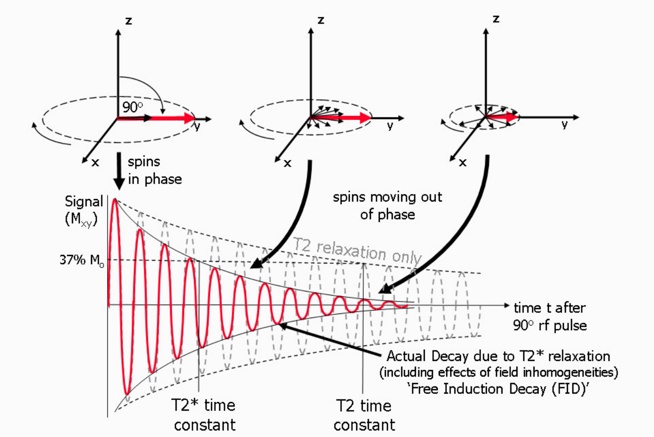
- longitudinal (or spin-lattice) relaxation time T_1: the decay constant for the recovery of the $\hat{z}$ component of the nuclear spin magnetization M_z, towards its thermal equilibrium value $M_{z,eq}$.
- $\vec{B} \parallel \hat{z}$. If M has been tilted into the xy plane, then and the recovery is simply $M_z(t) = M_{z,eq}(1 - \exp(-t/T_1))$





NMR relaxation: transversal

- transversal (or spin-spin) relaxation time T_2: the net magnetization starts to dephase as the spins feel a slightly different magnetic field and hence rotates at its own Larmor frequency.



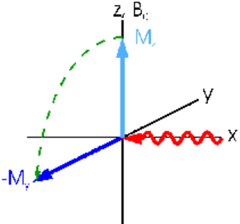
NMR — $\pi/2$-pulse and π-pulse

- $\vec{B} \parallel \hat{z} \Rightarrow$ Larmor frequency of magnetization at frequency ω.
- pulse of oscillating magnetic field in xy-plane $\vec{B} = B_1(\hat{x}\cos\omega t + \hat{y}\sin\omega t)$ applied in y direction.

$\Rightarrow$ than the magnetization precess with increasing amplitude.

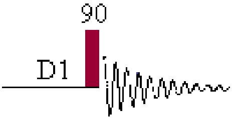
$\Rightarrow$ when duration of pulse has correct length, the magnetization precession angle reaches 90°, i.e. it rotates in xy-plane (so called $\pi/2$-pulse).

$\rightarrow$ similarly, one can create π-pulse, which reverses magnetization direction.



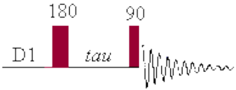
Determination of relaxation by pulse trains: T_1 determination

Progressive Saturation

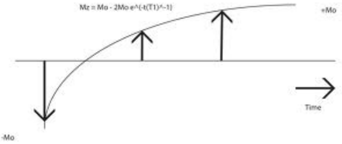


$$M(\tau)/M_0 = 1 - \exp(-\tau/T_1)$$

Inversion Recovery



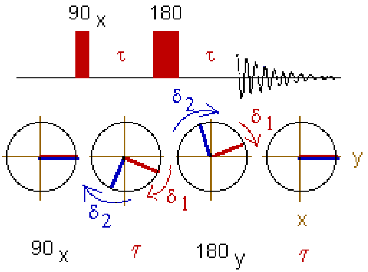
$$M(\tau)/M_0 = 1 - 2\exp(-\tau/T_1)$$



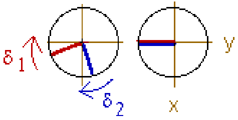
http://www.chem.queensu.ca/facilities/nmr/nmr/webcourse/

Determination of relaxation by pulse trains: T_2 determination

- first $\pi/2$ pulse move spins to *xy* plane.
- then, spins starts to become out-of-phase, due to slightly different precession frequencies.
- after time τ, π-pulse is applied. Spins are still in *xy*-plane, but their position is mirrored by *yz*-plane.
- spins goes the same way, and go to coherence back (so called spin echo).



or:



NMR imaging: encoding I

T_1 and T_2 relaxation times measured for selected points in the body.
Field gradient selects spin under resonance frequency.

Frequency encoding

- field B_0 with added gradient of field G_z: $B(z) = B_0 + G_z z$
- then, resonance frequency is $f(z) = \gamma B_0 + \gamma G_z z$

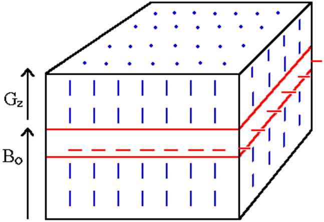
$\Rightarrow$ different resonance frequencies at different positions

- base of all NMR imaging.

NMR imaging: encoding II

Slice selection

- switch on gradient of the field
- apply 90° excitation pulse at a given frequency ⇒ spins starts to precess only in one plane, where resonance condition is fulfilled
- gradient of field turns off ⇒ *spin precesses only in a slice selected by applied field gradient*



NMR imaging: encoding III

Phase Encoding Gradient

1. spins are excited (precessing)
2. gradient of field along x is applied
3. then, spins starts to precess at different frequencies
4. gradient is off, spin precess again at equal frequency, but with different phases ⇒ *spin precession modulated in phase*

NMR imaging: example of imaging sequence I

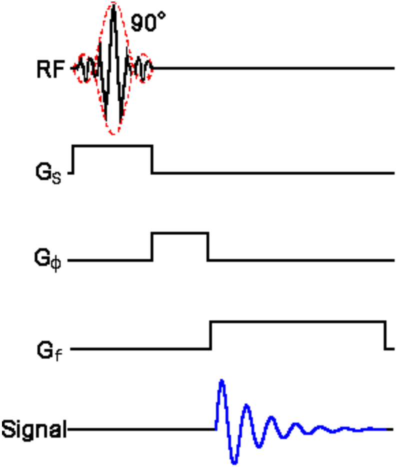
RF : 90° rf pulse

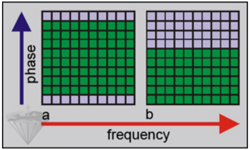
G_s : slice selection pulse (e.g. along z)

G_φ : phase encoding gradient pulse (e.g. along y)

G_f : frequency encoding gradient pulse (e.g. along x)

⇒ : spins at different locations precess by a unique phase angle φ and precessional frequency f!

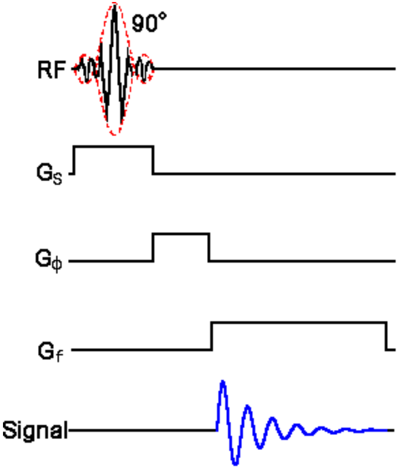




nice overview of NMR: http://www.cis.rit.edu/htbooks/mri/inside.htm

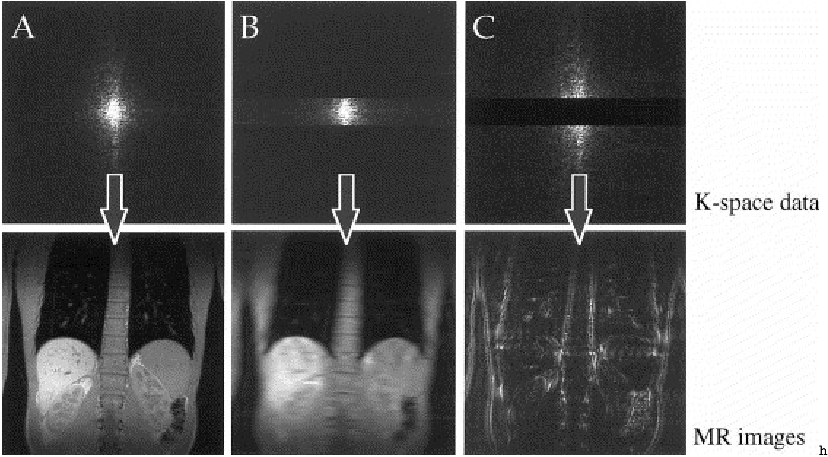
NMR imaging: example of imaging sequence II

System is excited at different strengths of phase encoding gradient pulse ⇒ various precession signal are detected.
Fourier transform can recovers both phase and frequency of a signal ⇒ by determining frequency and phase, one can determine strength of oscillation in each position of the slice.



nice overview of NMR: `http://www.cis.rit.edu/htbooks/mri/inside.htm`

Example of *k*-space to *r*-space conversion by Fourier trans.



http://www.sciencedirect.com/science/article/pii/S0720048X98001727
http://www.ajronline.org/doi/full/10.2214/AJR.07.2874