Overview of spectroscopies III

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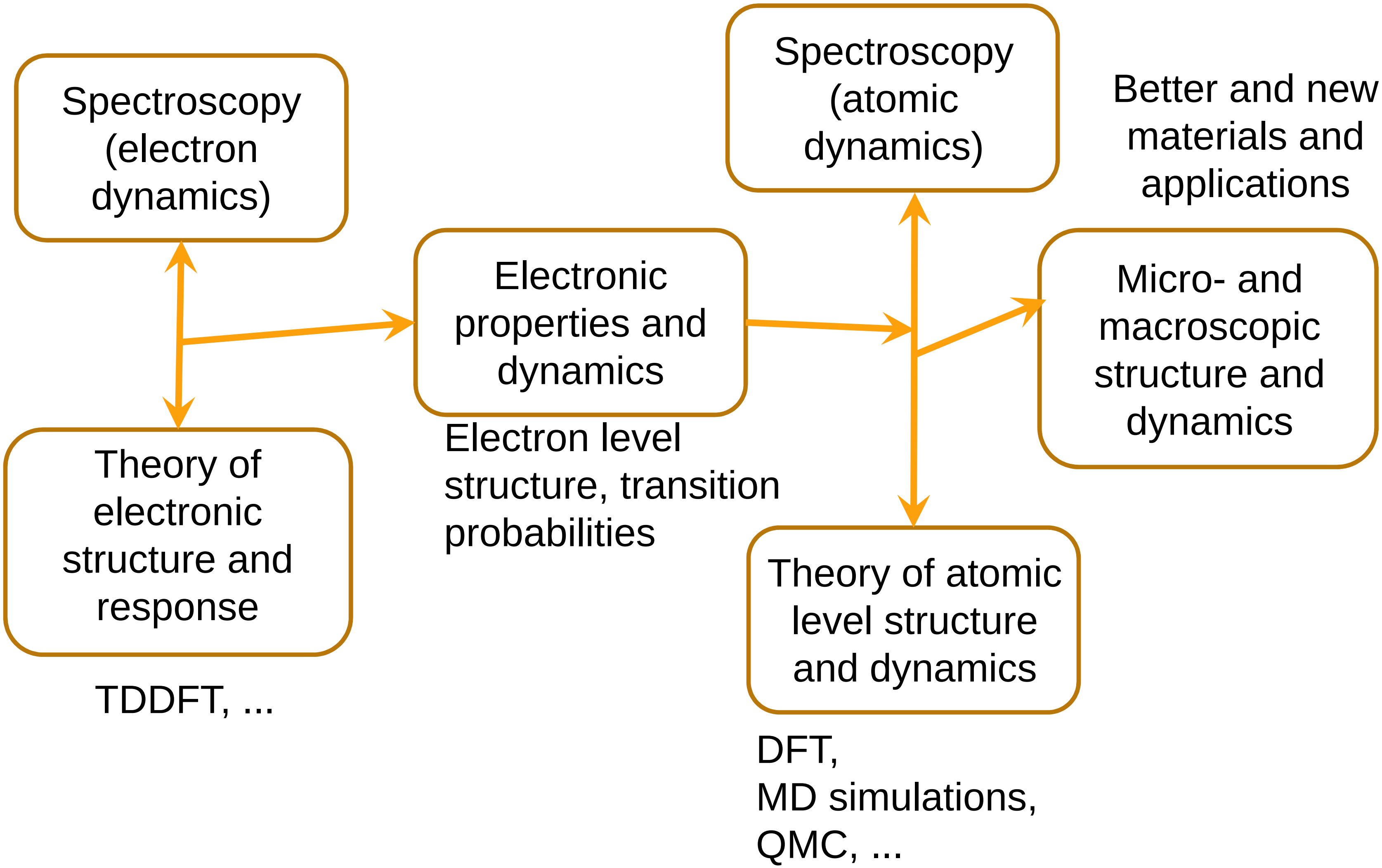
TDDFT school, Benasque, Spain, January 2012

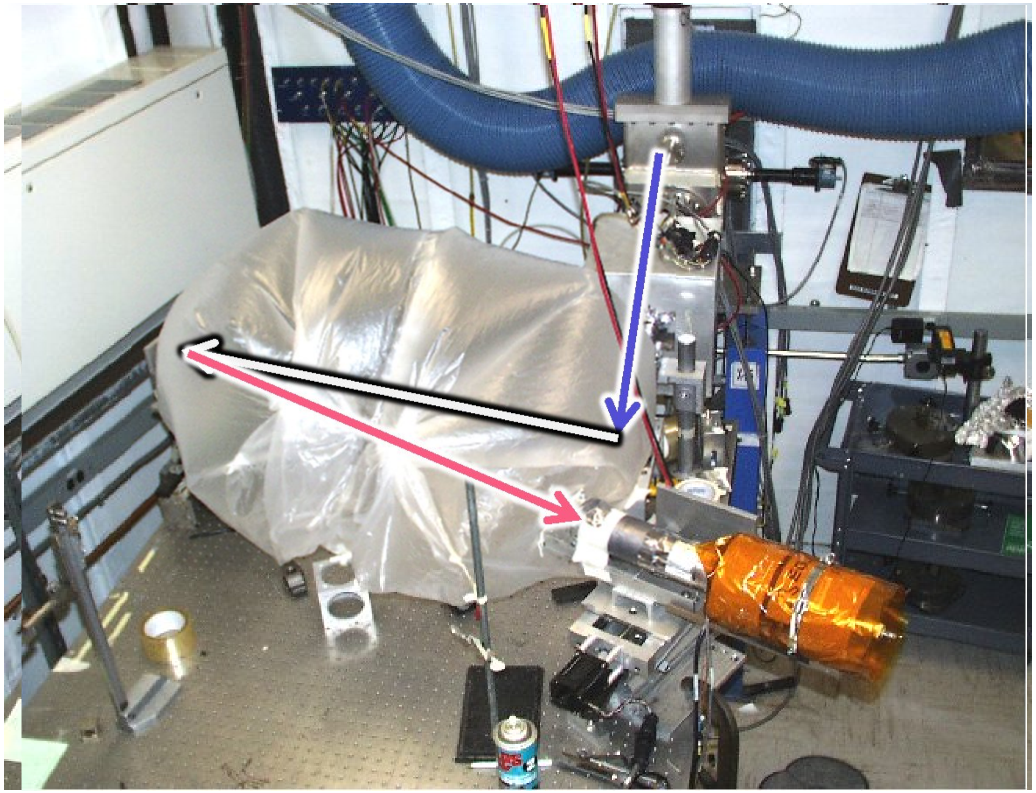
Motivation: why we need theory



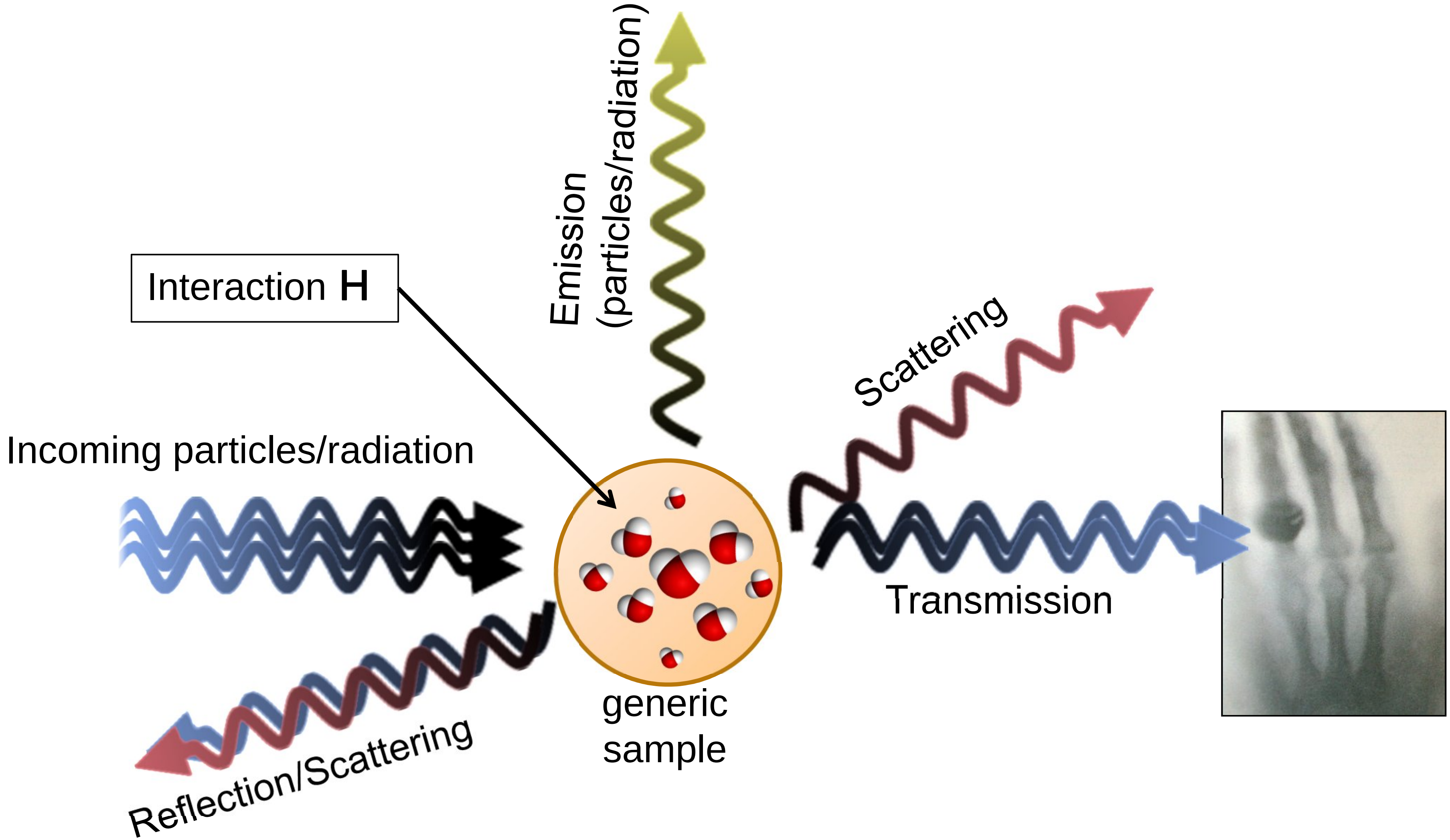
Measurement vs. experiment

Equipment for measurements

Equipment for experiments



Probes and messengers



Outline

Part 1 – Excitations and properties

Part 2 – Techniques (general)

Part 3 – Sample environments

Tomorrow – Techniques (examples)

Classification of excitations

(non-exhaustive)

	Collective	**”Single particle”**
Vibrational	Sound waves (phonons)	Molecular bending, stretching...
Spin	Magnons, spin waves	Spin flip
Electronic	Plasmons, orbitons, polarons	Crystal fields, excitons, Compton, electron removal

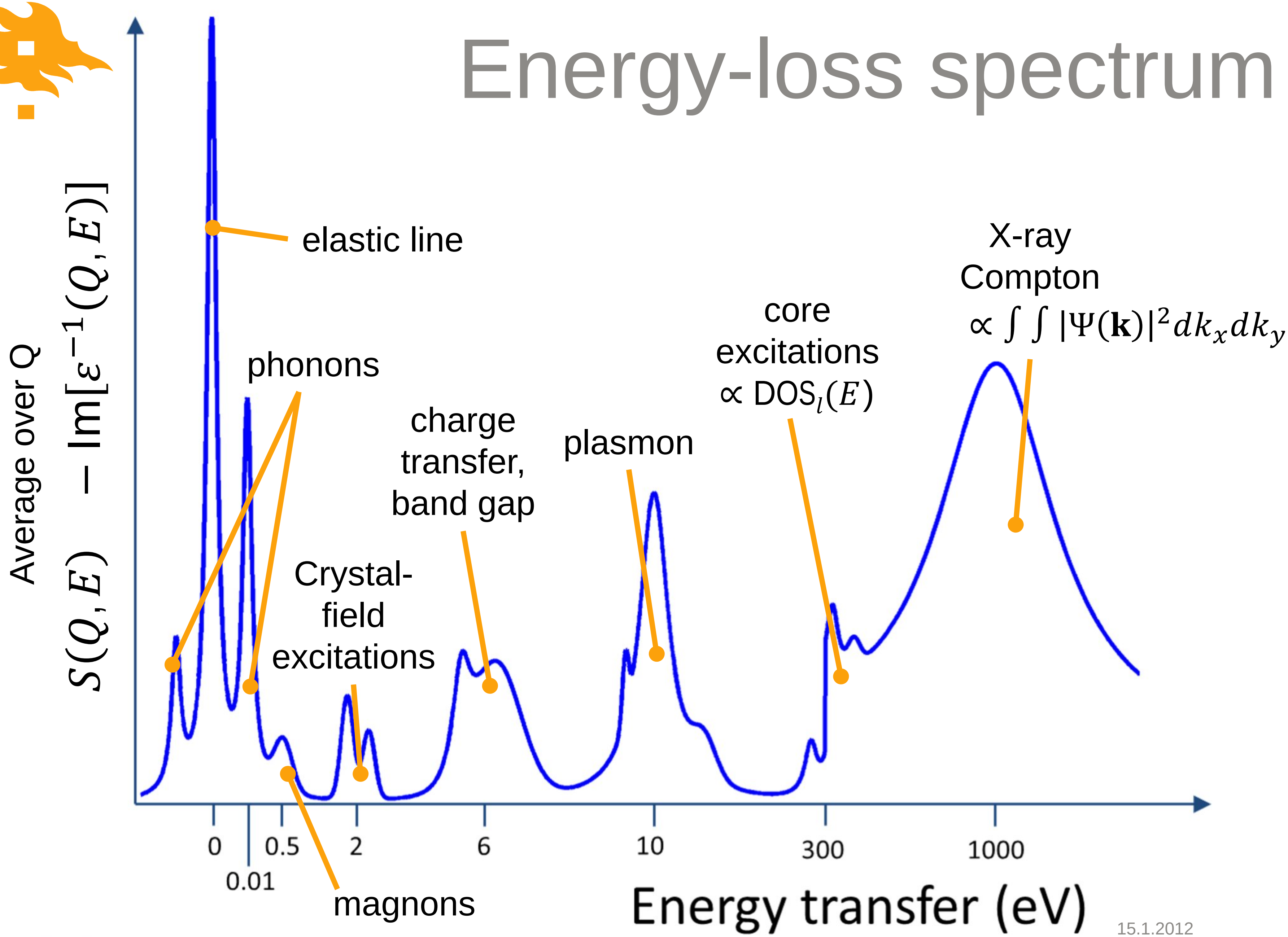
+ multiples (bimagnons, double plasmons, ...)

Properties

Macroscopic **dielectric function** $\varepsilon_M(Q,E) = \varepsilon_1(Q,E) + i\,\varepsilon_2(Q,E)$
Complex **refractive index** $n + i\,\kappa$
Reflectivity R
Absorption coefficient $\alpha = 4\pi\kappa/\lambda$
Loss function $-\mathrm{Im}[\varepsilon_M{}^{-1}(\mathbf{Q},E)]$
Dynamic structure factor $S(\mathbf{Q},E) = -\left(\frac{Q^2}{4\pi^2 e^2 n}\right)\,\mathrm{Im}[\varepsilon_M{}^{-1}(\mathbf{Q},E)]$
Spectral density function $A(k,\omega)$
Resonant Raman spectra

Dynamic structure factor is also the Fourier transform of the **density correlation function** - which is the probability to find two different particles separated by $\mathbf{r}$ and t.

Energy-loss spectrum

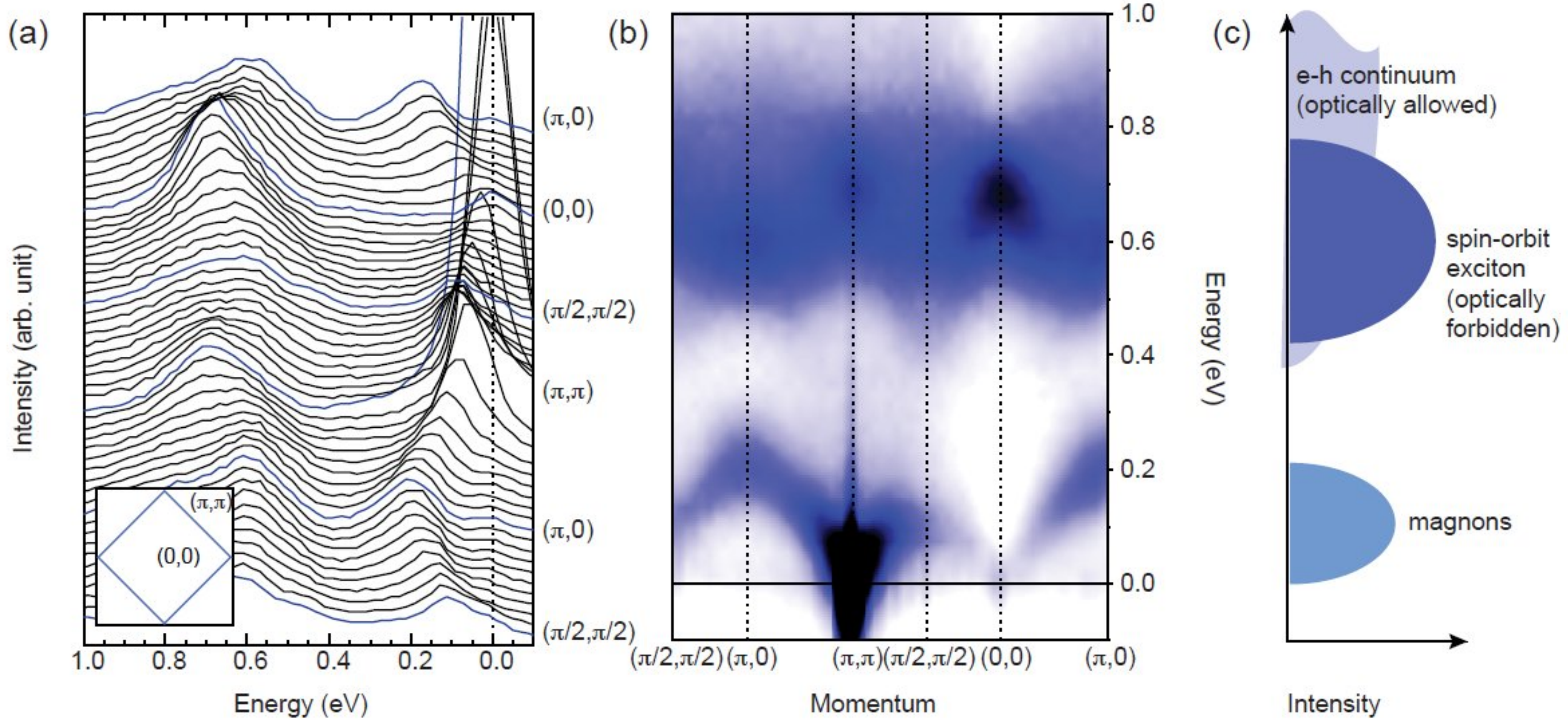


Magnons: spin waves

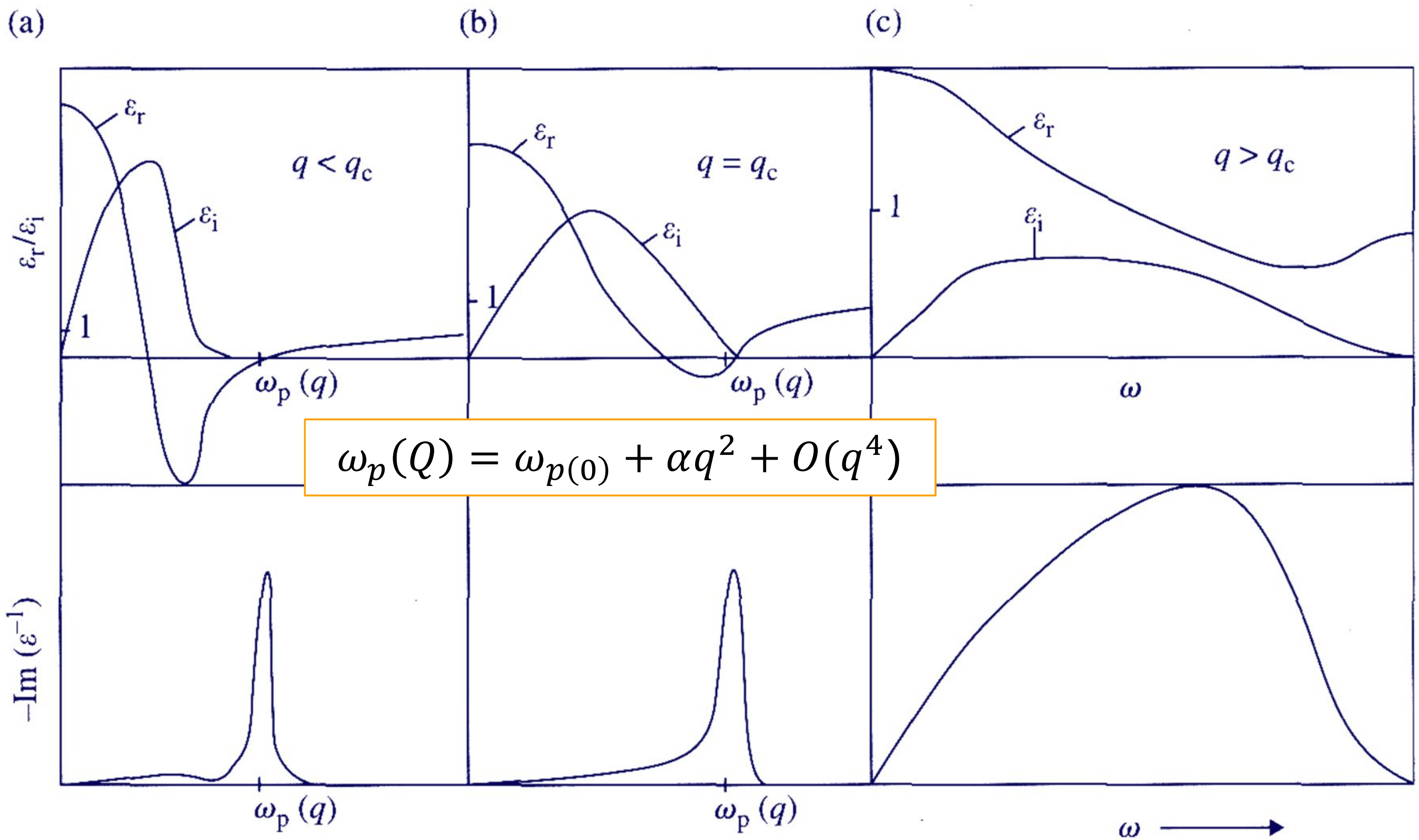
Magnetic excitations: orbital physics in transition metal oxides

Sr_2IrO_4

J. Kim et al. 2011, arXiv:1110.0759v1 [cond-mat.str-el]



Plasmons



$$\omega_p(Q) = \omega_{p(0)} + \alpha q^2 + O(q^4)$$

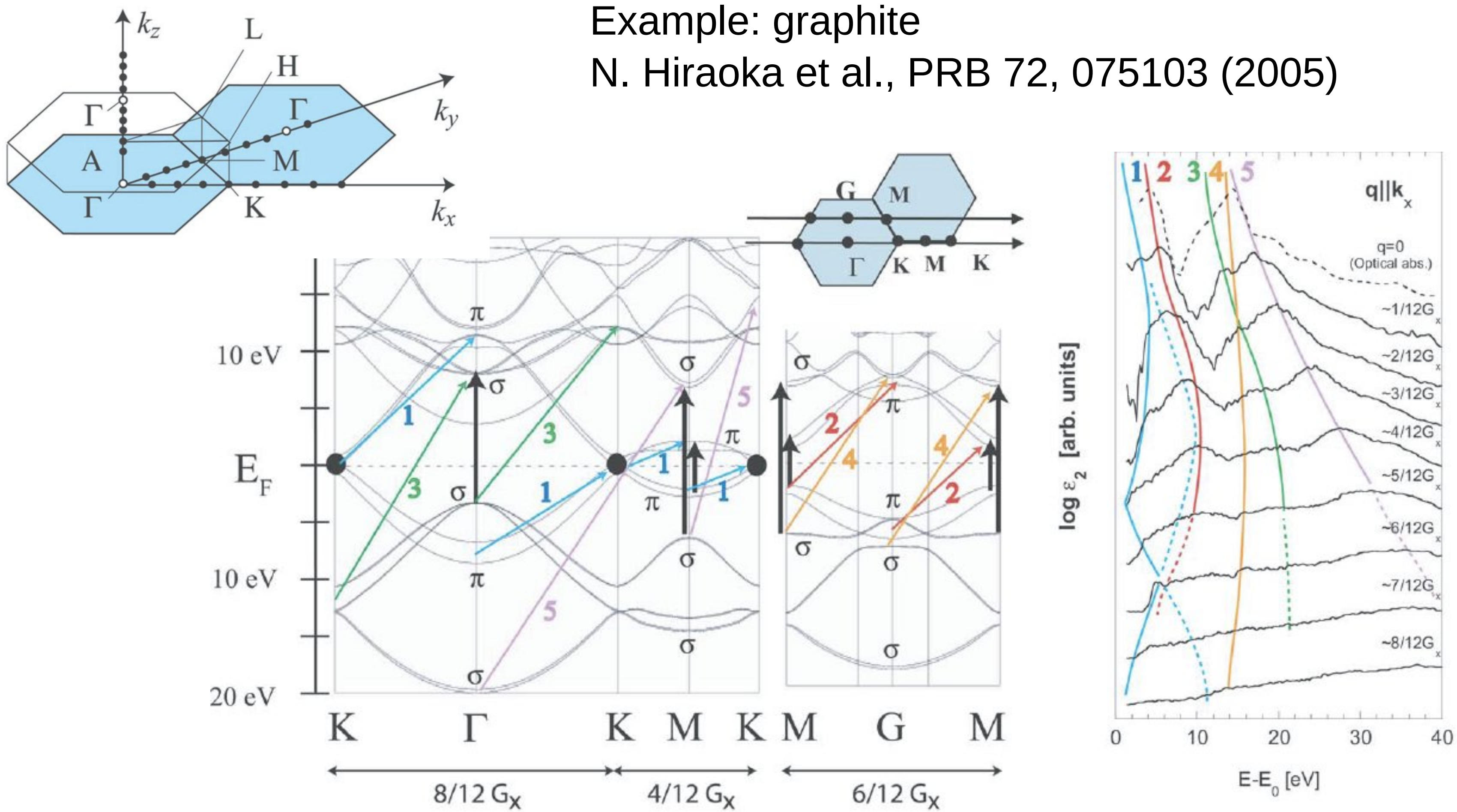
W. Schülke: Electron dynamics by inelastic x-ray scattering (Oxford Univ. Press)

Band structure picture

Both ***energy*** and ***momentum*** can be controlled

Example: graphite

N. Hiraoka et al., PRB 72, 075103 (2005)



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Outgoing particle

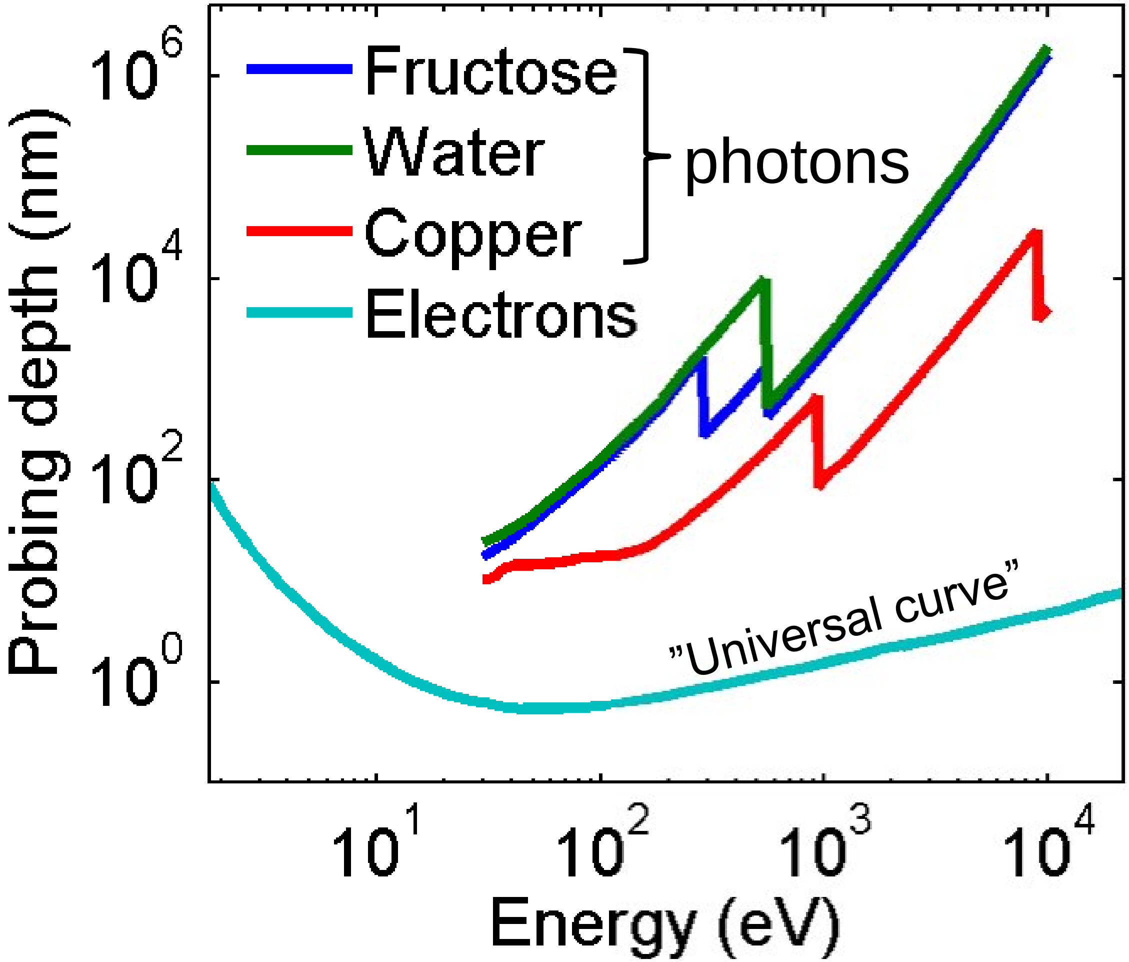
Incoming particle

	Nothing	Photon	Electron
Nothing	Skiing at the Pyrenees	Light emission, photoluminescence	Electron emission
Photon	Absorption (IR, UV/vis, vacuum UV, x-ray..) CD; XMCD	Ellipsometry, reflectometry, ATR, Raman, Brillouin, x-ray scattering, Compton scattering	Photoemission Auger spectroscopy
Electron	Electron absorption	Inverse photoemission Cathodo-luminescence	Electron energy loss Tunneling

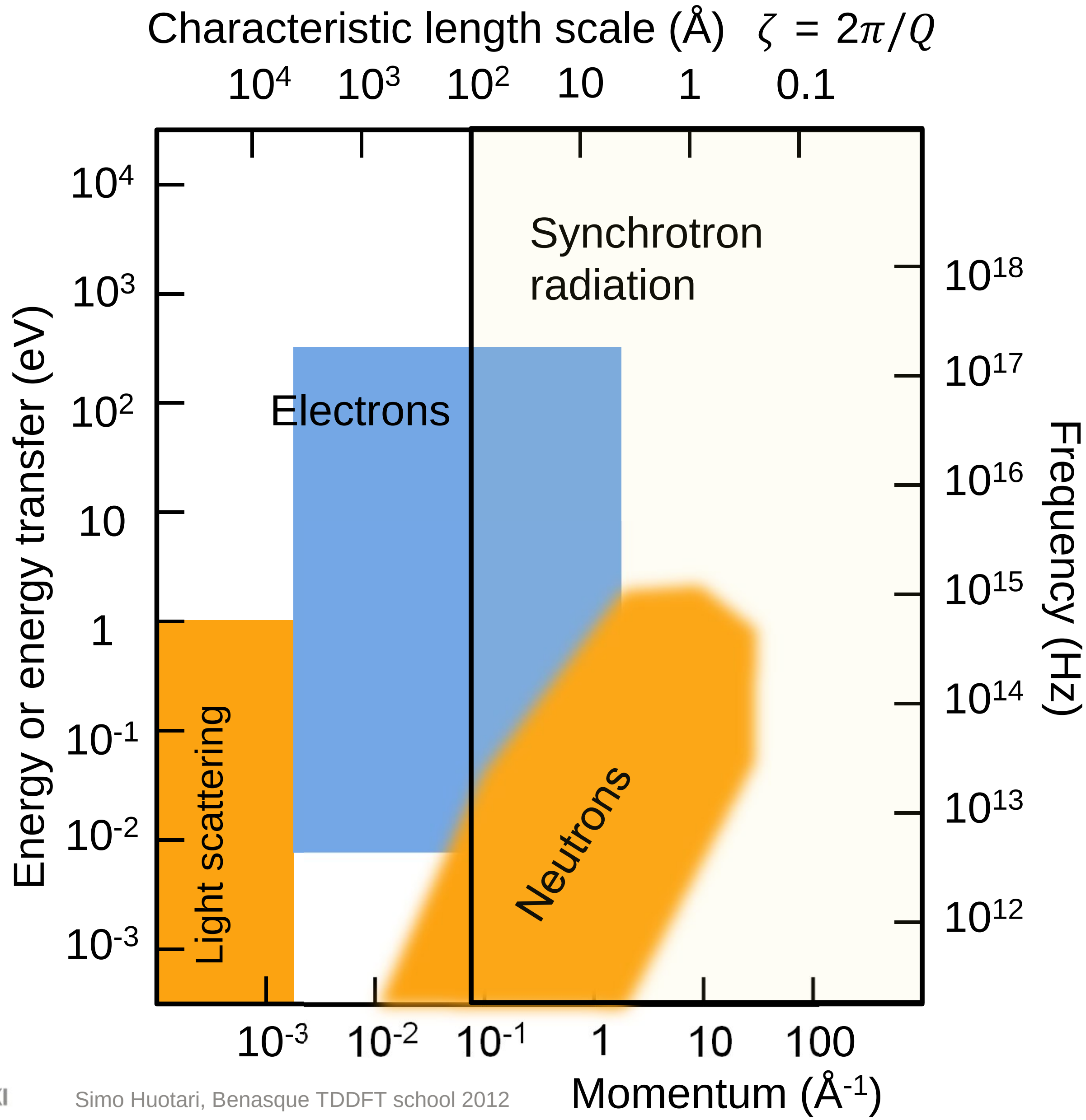
+ Time-of-flights
+ Non-linear phenomena

Differences in:
- Dynamic range of Q and E, coupling to spin, nuclei, …
- Bulk or surface sensitivity
- Resolving power in energy, momentum, time, space…
- Element specifity (useful for complicated systems)

Particle probing depth

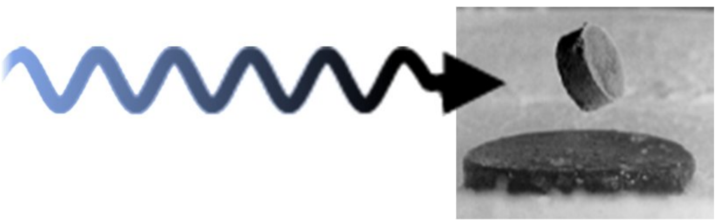


Dynamic ranges for scattering



Spectroscopy - interaction

Photon-electron $$H = \frac{e^2}{2mc^2}\mathbf{A}^2 + \frac{e}{mc}\mathbf{A}\cdot\mathbf{p}$$



Scattering

Absorption and emission in first order, resonant scattering in second order

Electron-electron $$V = e^2/|\mathbf{r} - \mathbf{r}_i|$$

Transition rate from state |A> to state |B>
is given by the Fermi's Golden Rule:

$$W_{BA} = \frac{2\pi}{\hbar}\left|\langle B|H|A\rangle + \sum_I \frac{\langle B|H|I\rangle\langle I|H|A\rangle}{E_A - E_I + i\Gamma/2}\right|^2 \delta(E_B - E_A) + O(H^3)$$

Kramers-Heisenberg formula

From $\mathbf{A}\cdot\mathbf{A}$ - Non-resonant scattering (Raman, inelastic x-ray, ...)

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega_2} = r_0^2\left(\frac{\omega_2}{\omega_1}\right)\left| < \Psi_f|e^{i\mathbf{Q}\cdot\mathbf{r}}|\Psi_i > (\boldsymbol{\epsilon}_1\cdot\boldsymbol{\epsilon}_2) + \frac{1}{m}\sum_n \left[\frac{\langle\Psi_f \mid \boldsymbol{\epsilon}_2\cdot\mathbf{p}\; e^{-i\mathbf{k}_2\cdot\mathbf{r}} \mid \Psi_n\rangle\langle\Psi_n \mid \boldsymbol{\epsilon}_1\cdot\mathbf{p}\; e^{i\mathbf{k}_1\cdot\mathbf{r}} \mid \Psi_i\rangle}{E_i - E_n + \omega_1 + i\Gamma_n} + \frac{\langle\Psi_f \mid \boldsymbol{\epsilon}_1\cdot\mathbf{p}\; e^{i\mathbf{k}_1\cdot\mathbf{r}} \mid \Psi_n\rangle\langle\Psi_n \mid \boldsymbol{\epsilon}_2\cdot\mathbf{p}\; e^{-i\mathbf{k}_2\cdot\mathbf{r}} \mid \Psi_i\rangle}{E_i - E_n - \omega_2}\right]\right|^2 \delta(E_i - E_f + \omega)$$

From $\mathbf{p}\cdot\mathbf{A}$ - Resonant scattering (Resonant Raman, resonant inelastic x-ray, fluorescence....)

Dynamic structure factor

Average density-density correlation function

$$G(\mathbf{r},t) = \frac{1}{N}\int \langle \rho(\mathbf{r}' - \mathbf{r}, t)\rho(\mathbf{r}', 0)\rangle d\mathbf{r}'$$

Dynamic structure factor

$$S(\mathbf{Q},E) = \int\int G(\mathbf{r},t)e^{i\mathbf{Q}\cdot r}e^{-iEt}$$

Small *Q*
interference effects are important
(collective excitations)

Large *Q*
independent particle picture
(Compton scattering)

Absorption and scattering

Absorption $P(\omega) \propto \sum_f \left|\langle \Psi_f | \mathbf{p} \cdot \mathbf{A} | \Psi_i \rangle\right|^2 \delta(E_i - E_f + \omega)$ Dipole selection rule

Scattering $S(\mathbf{Q}, \omega) \propto \sum_f \left|\langle \Psi_f | \sum_j e^{i\,\mathbf{Q}\cdot\mathbf{r}_j} | \Psi_i \rangle\right|^2 \delta(E_i - E_f + \omega)$

Use the momentum transfer dependence of the scattering matrix element: as $q \to 0$ then

$$e^{i\mathbf{Q}\cdot\mathbf{r}} = 1 + i\mathbf{Q}\cdot\mathbf{r} - (\mathbf{Q}\cdot\mathbf{r})^2/2 + \cdots$$

dipole

Higher order multipoles

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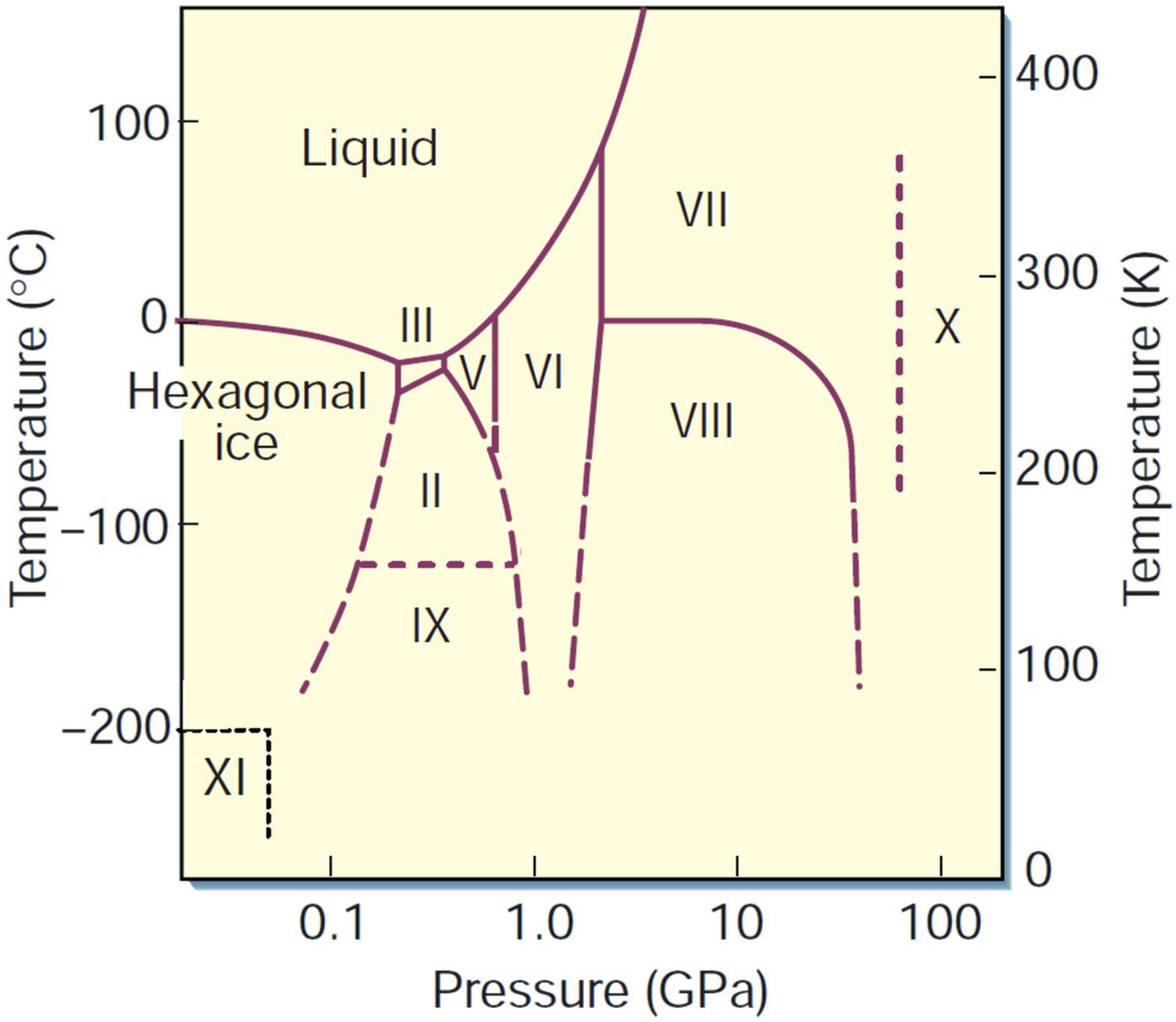
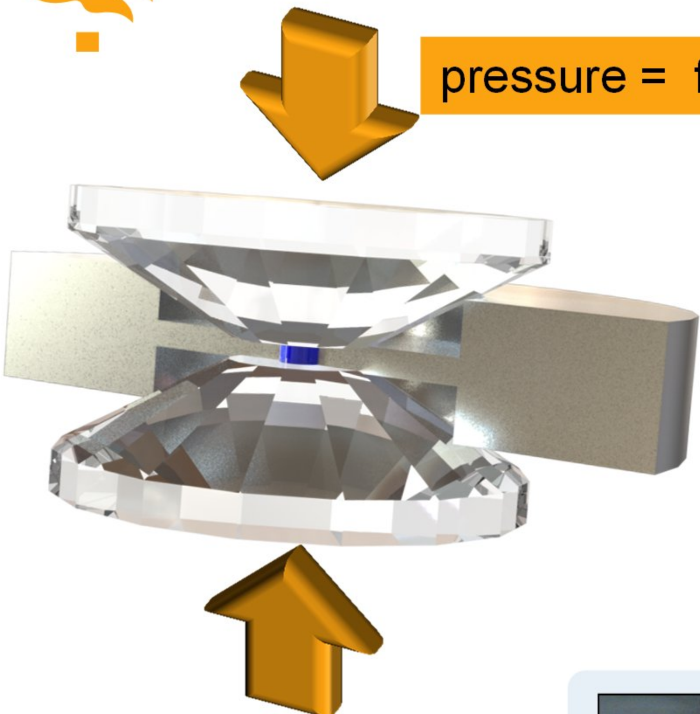
Phase diagram of water

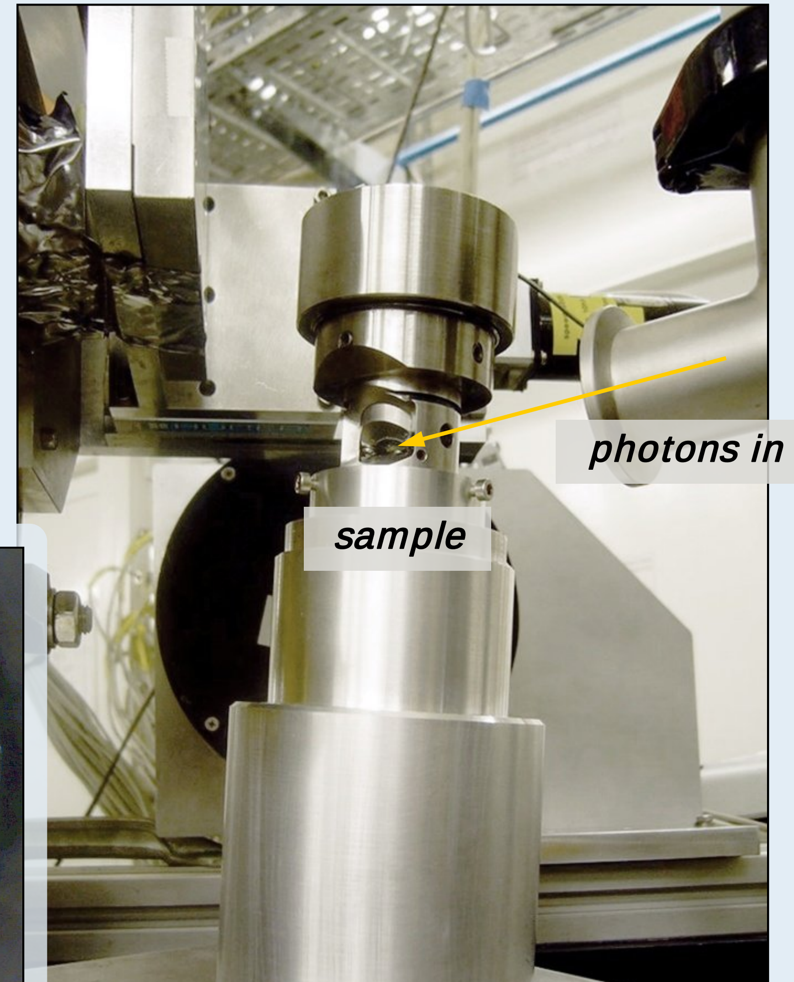


Extremely high pressures

pressure = force / area

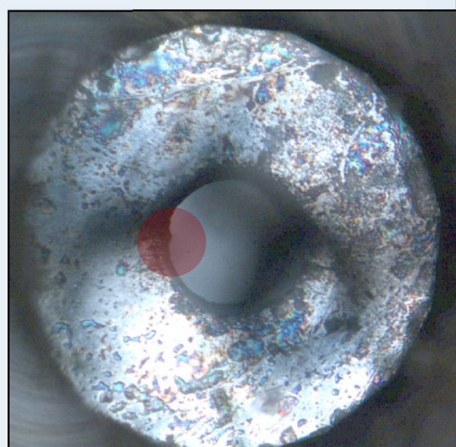
V.M.Giordano, T. Pylkkänen et al. ESRF ID16





Experimental details

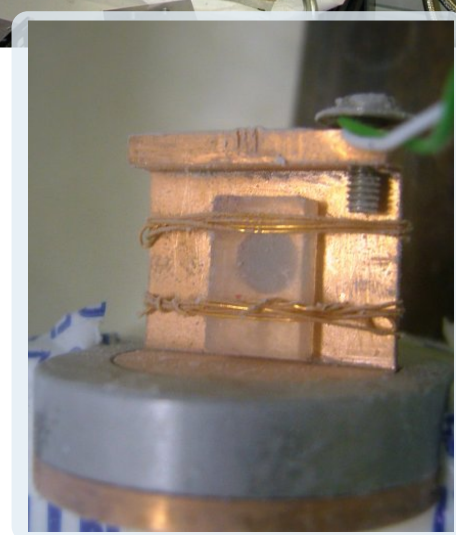
- 1 mm diamond tip (culet)
- ∅ 5 mm Be gasket
- ∅ 350 micron sample size
- X-ray beam 100 × 50 μm^2
- Ruby chip for *P* calibration



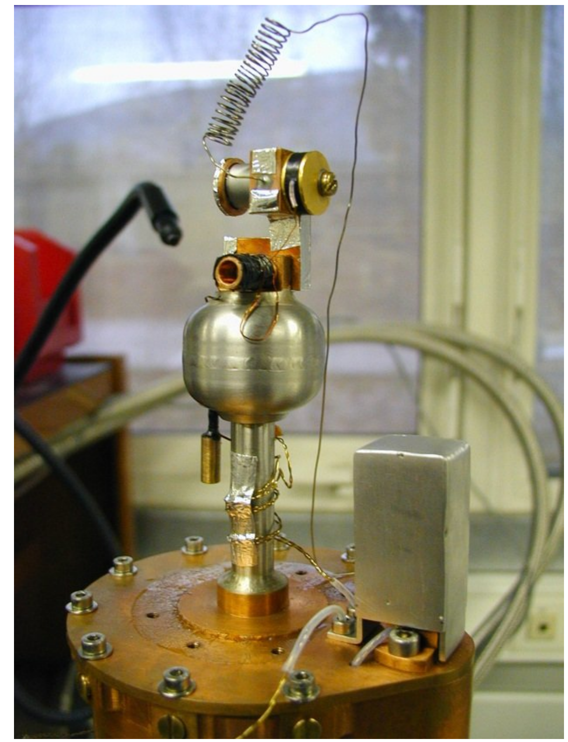
Low temperatures

Liquid nitrogen cryo-jet (77 K)

Liquid He Cryostat (4 K)



He sorption pump (1 K)

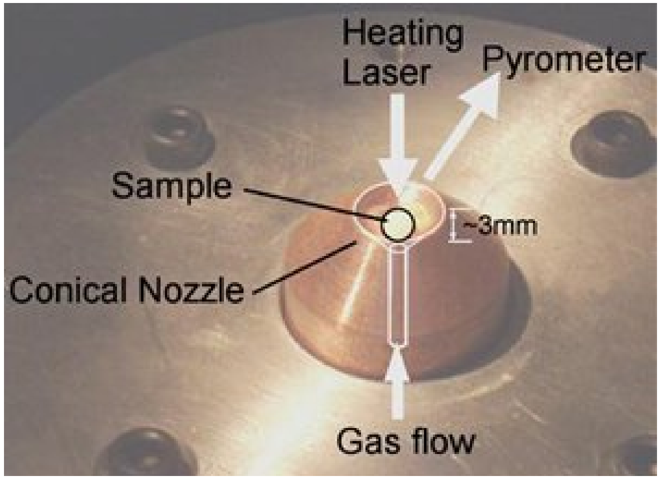


F. Albergamo et al., ESRF

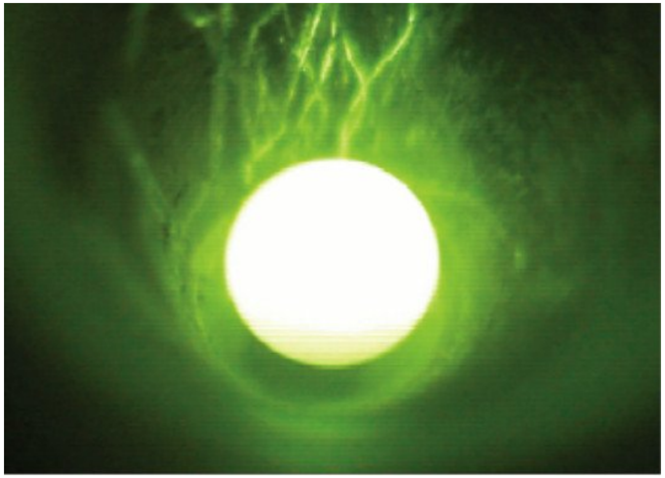
Extremely high temperatures (thousands of deg): Laser heating and aerodynamic levitation

High temperatures
(up to 1000 deg C):
furnaces, hot air guns

ESRF, Sample group



Wikipedia: Aerodynamic levitation



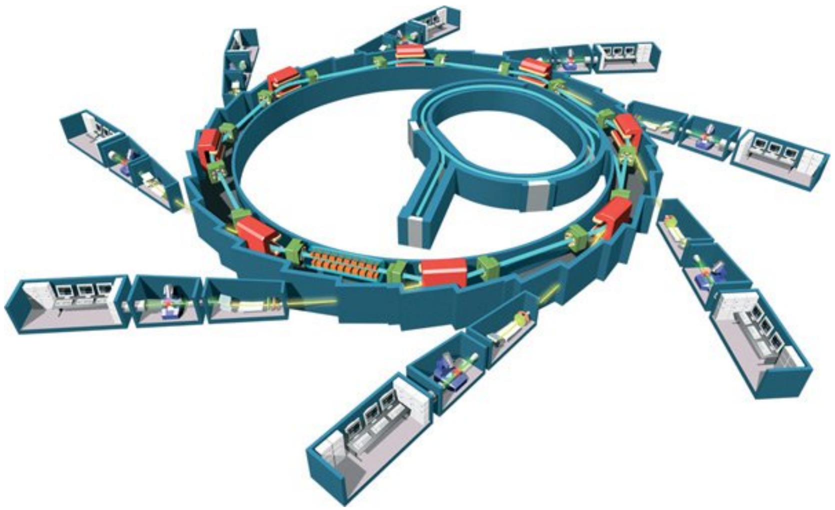
Droplet of liquid basalt BCR-2 during levitation. The sample was heated from the top using a CO_2-laser. The diameter of the sphere was ~2 mm. A. Pack et al., Geochemical transactions 2010, 11:4

Modern 3rd generation synchrotrons

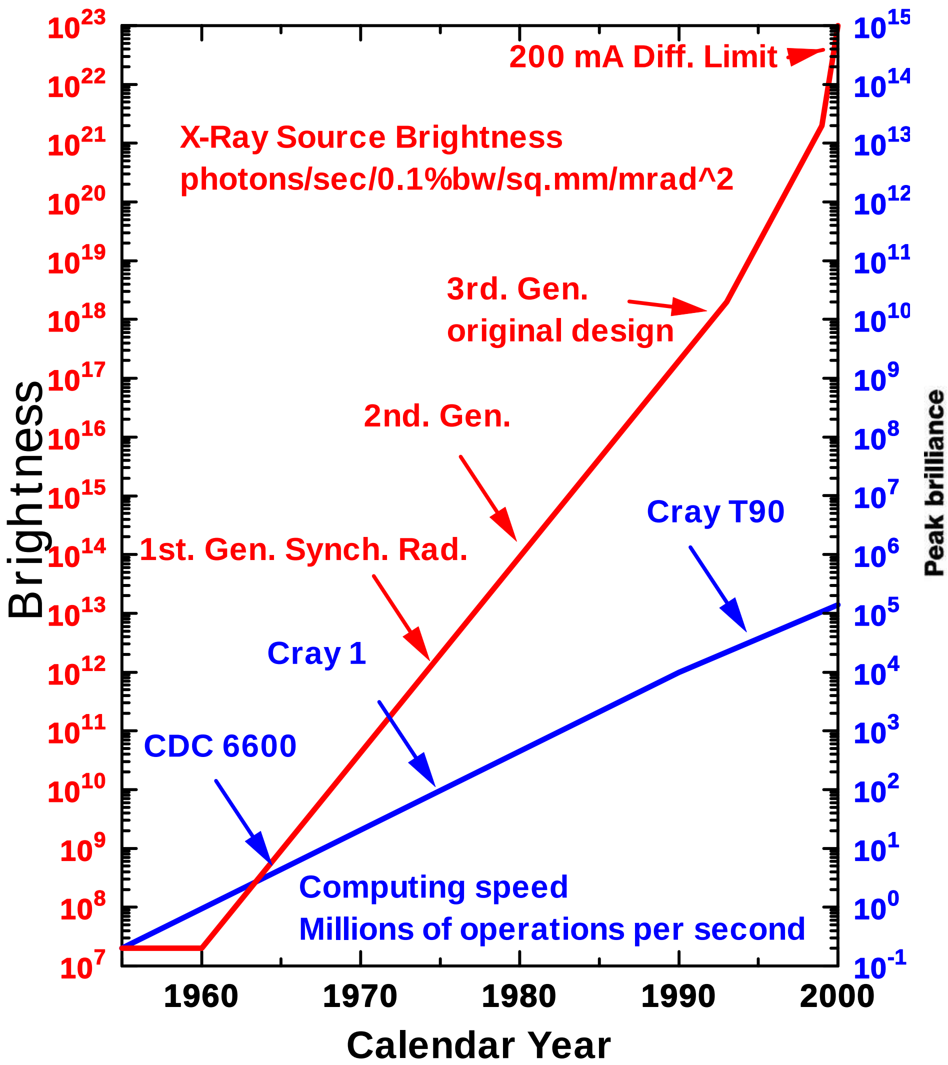
Advanced Photon Source, USA

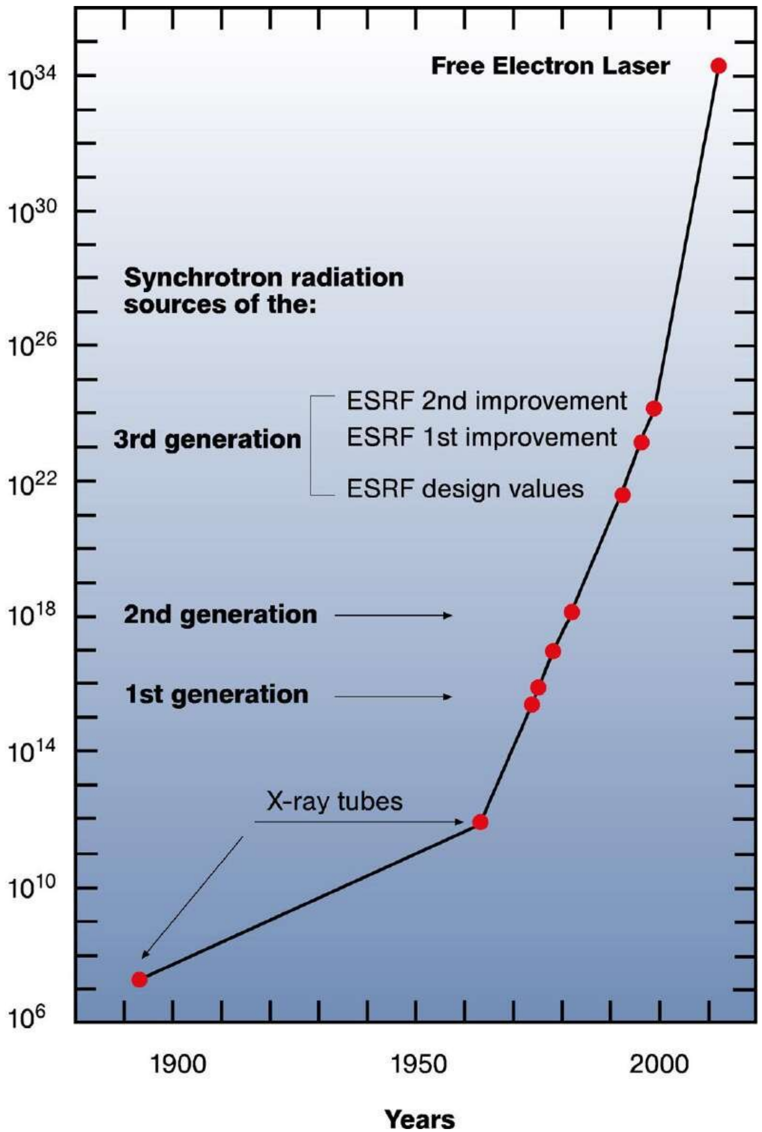
Super Photon Ring 8 (Spring-8), Japan

European Synchrotron Radiation Facility, France



Moore’s law


X-Ray Source Brightness
photons/sec/0.1%bw/sq.mm/mrad^2
200 mA Diff. Limit
3rd. Gen.
original design
2nd. Gen.
1st. Gen. Synch. Rad.
Cray T90
Cray 1
CDC 6600
Computing speed
Millions of operations per second
Brightness
Calendar Year
1960
1970
1980
1990
2000


Free Electron Laser
Synchrotron radiation
sources of the:
3rd generation
ESRF 2nd improvement
ESRF 1st improvement
ESRF design values
2nd generation
1st generation
X-ray tubes
Peak brilliance
Years
1900
1950
2000