

X-ray Nano Probes for Nano Materials at Taiwan Photon Source



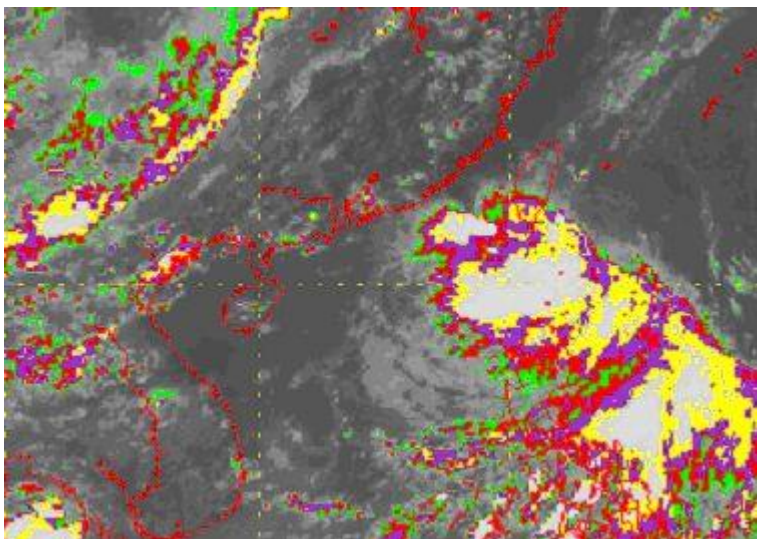
Outline

- Synchrotron Light Source
- Application of Synchrotron Light
- X-ray nano probe at TPS

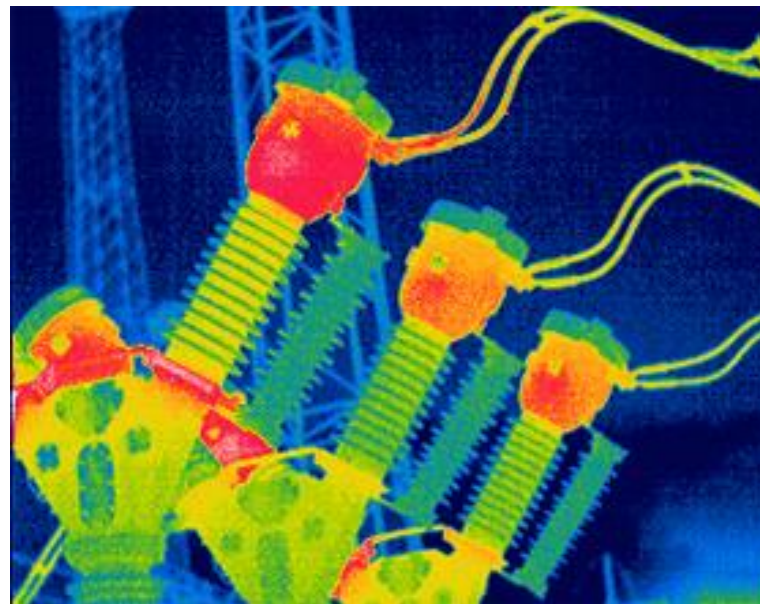
“Light” is indispensable to man’s exploration of nature



Invisible light: IR and X-ray...



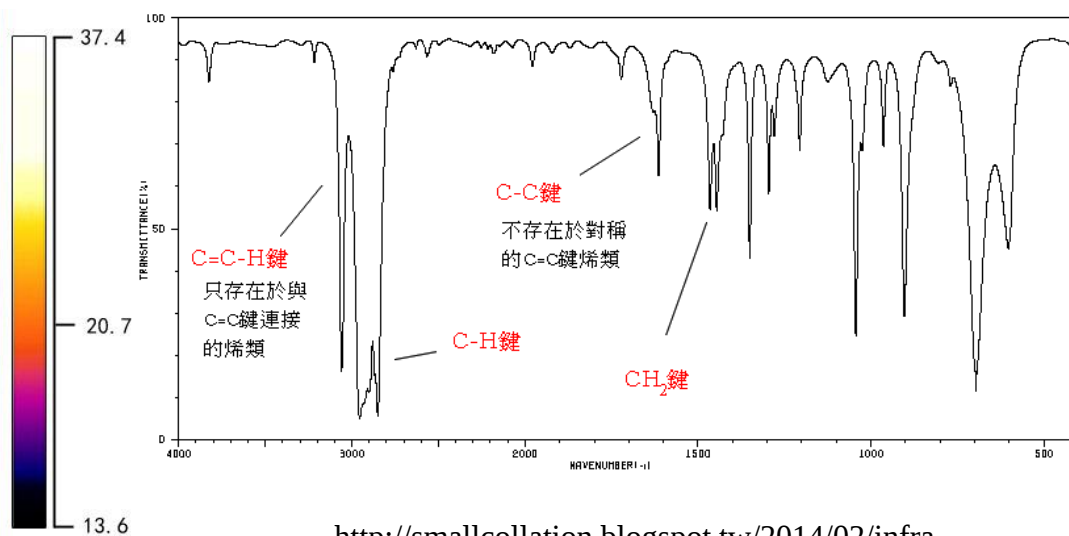
http://www.hko.gov.hk/prtver/html/docs/education/edu02rga/radiation/radiation_02-c.shtml



<http://www.yingfukeji.com/appl/grid.html>

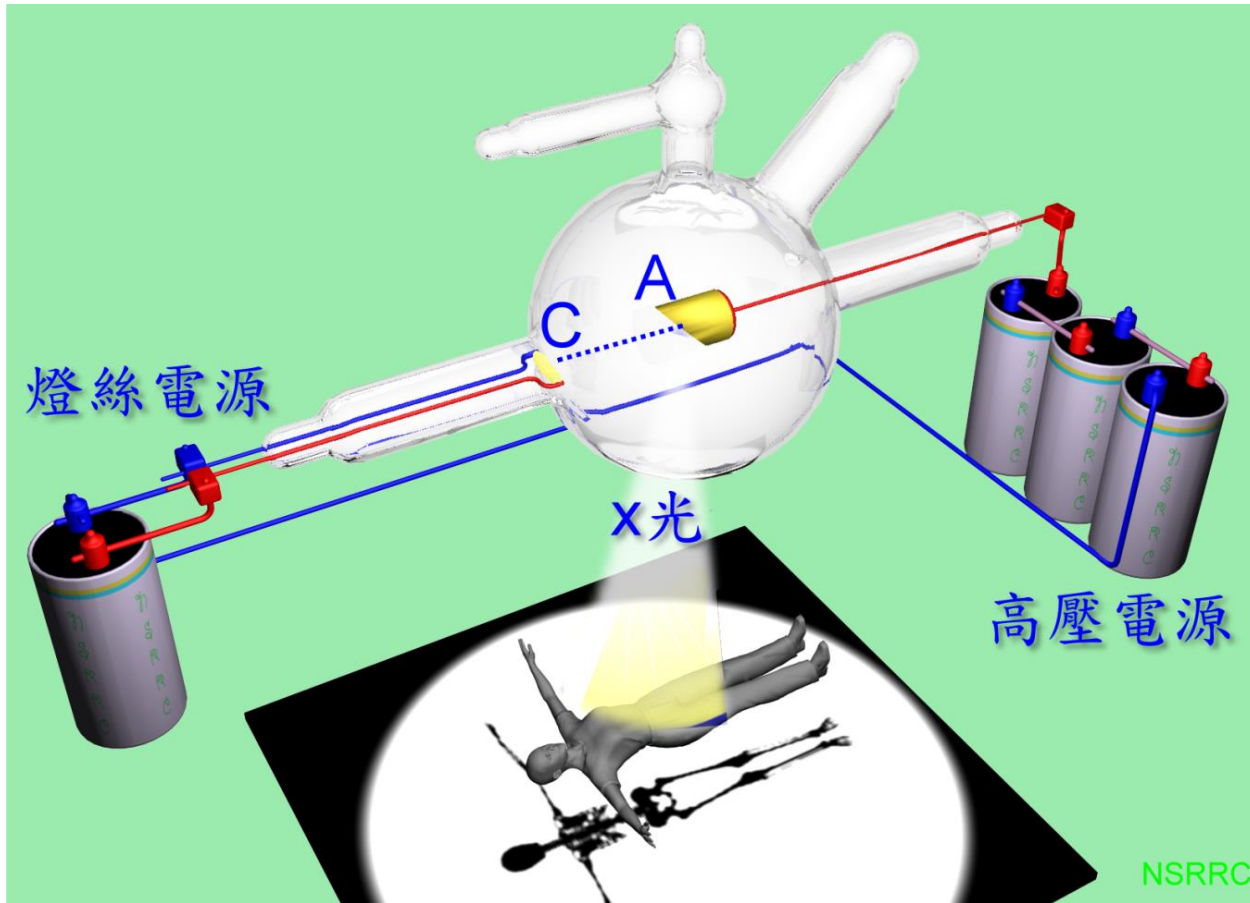


<http://www.uv-teck.com/Ttwjy>



<http://smallcollation.blogspot.tw/2014/02/infrared-spectroscopy-of-alkanes.html#gsc.tab=0>

Rontgen used a simple accelerator to discover X-rays



1895

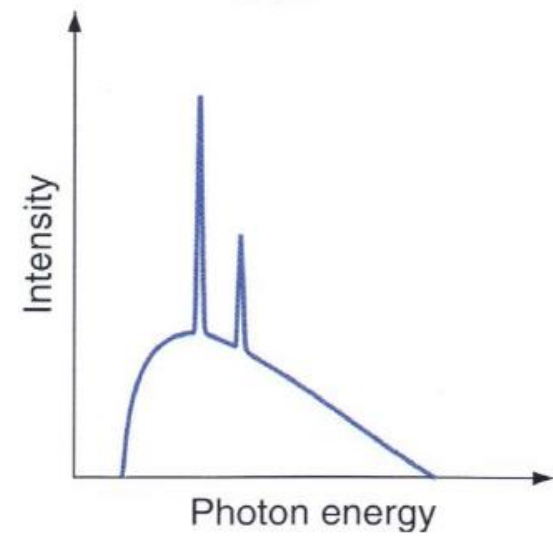
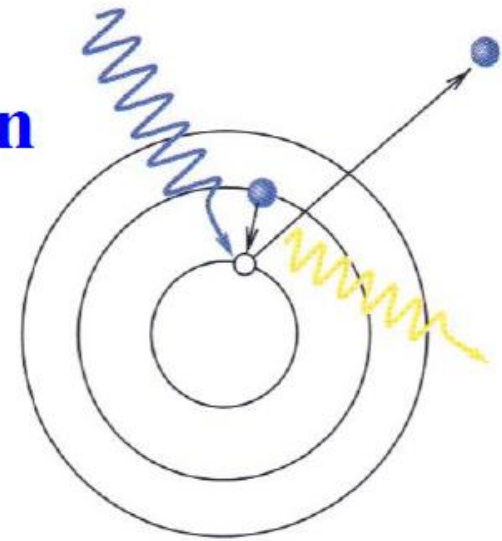
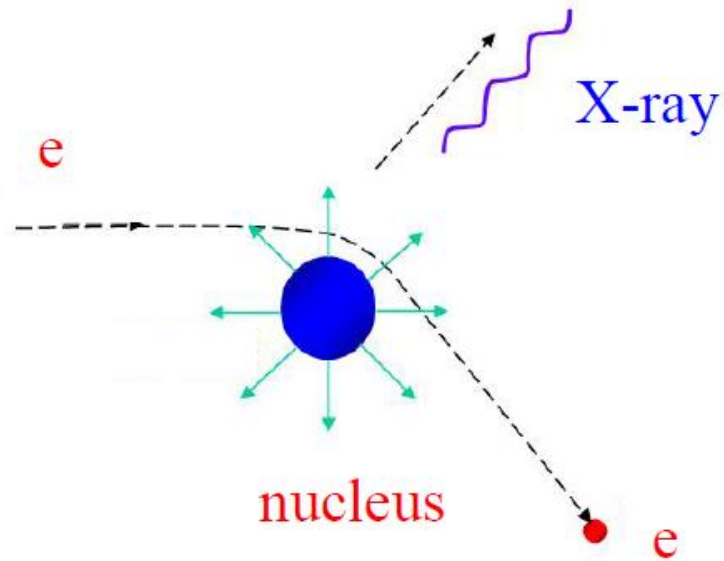




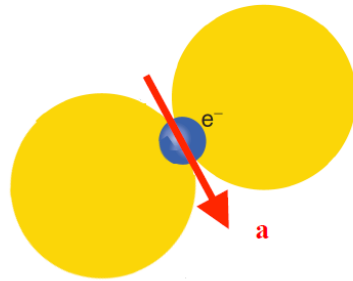
Hand mit Ringen (Hand with Rings): Wilhelm Röntgen's first "medical" X-ray, of his wife's hand, taken on 22 December 1895 and presented to Ludwig Zehender of the Physik Institut, University of Freiburg, on 1 January 1896.

<http://en.wikipedia.org/wiki/X-ray>

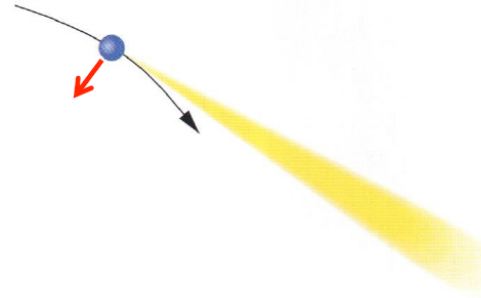
Characteristic X-ray emission



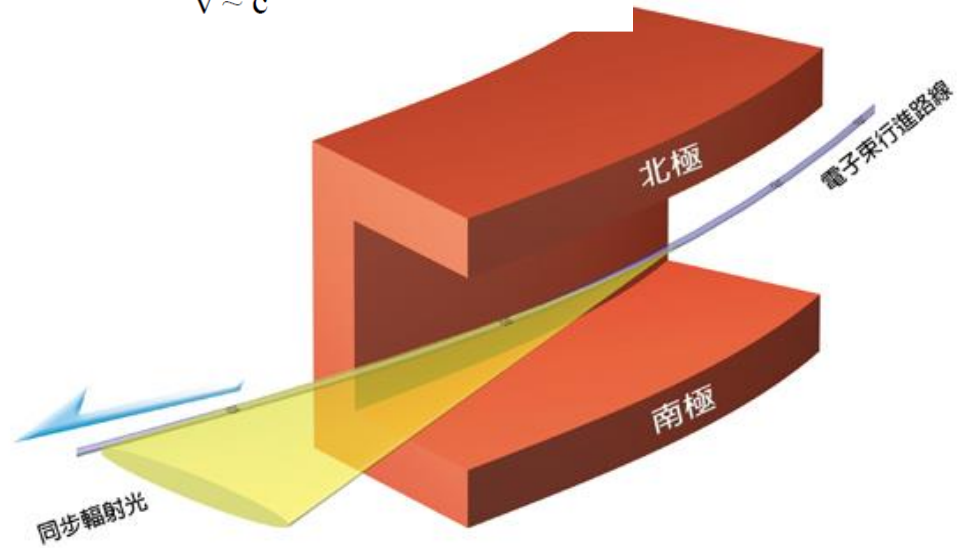
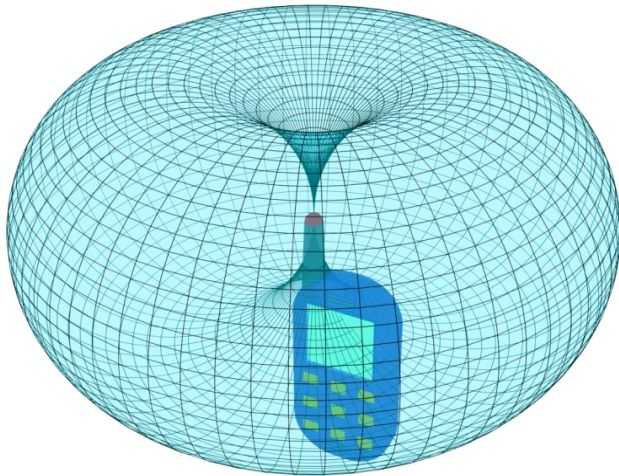
Electromagnetic wave from a moving charge



$v \ll c$



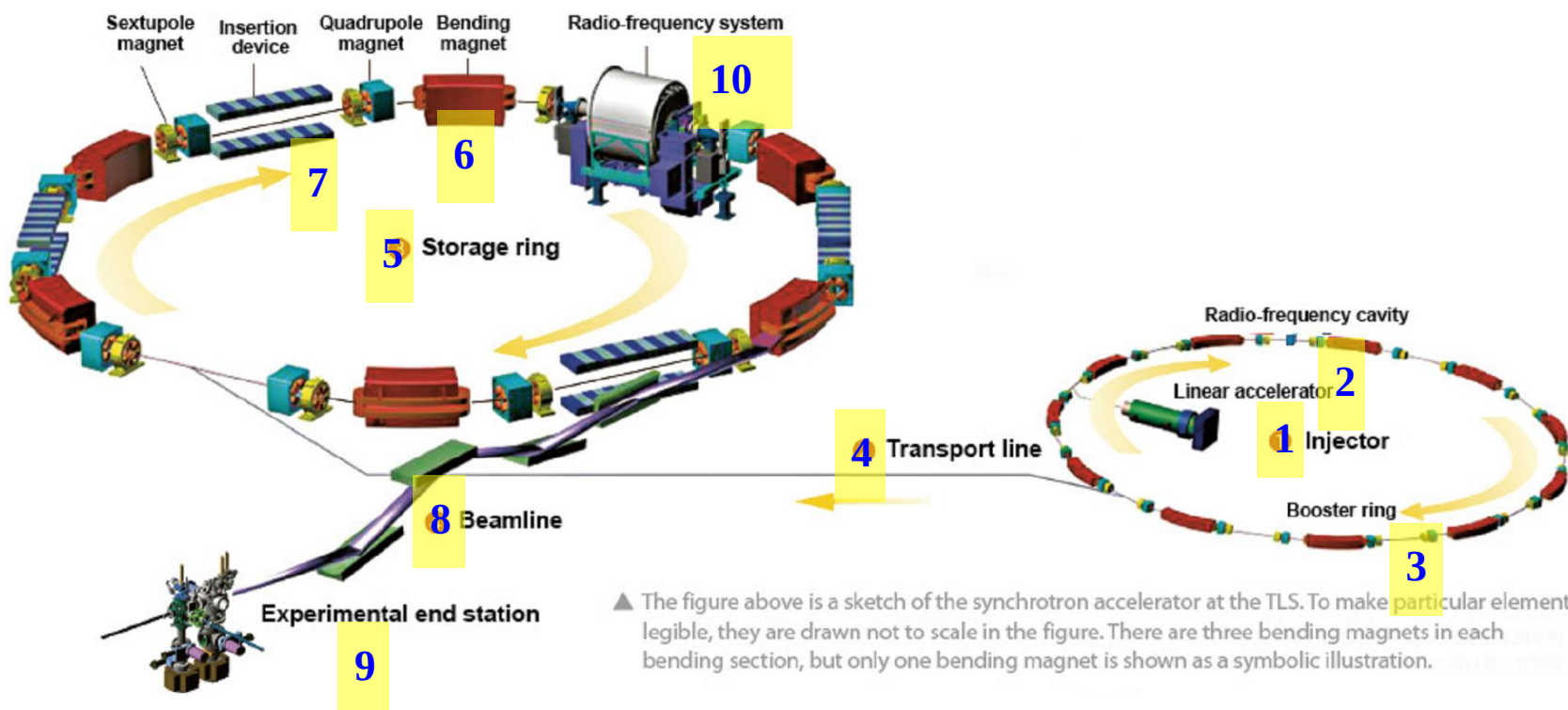
$v \sim c$



二極偏轉磁鐵

同步加速器光源的原理

- 電子在電子槍(1)內產生，經過直線加速器(2)加速至能量為5,000萬電子伏特。
- 電子束進入增能環(3)後，繼續增加能量至15億電子伏特(1.5GeV)，速度非常接近光速(0.99999995倍)。
- 電子束經由傳輸線(4)進入儲存環(5)。
- 當儲存環累積足夠的電子束後，經由各個磁鐵的導引與聚焦，電子束在偏轉磁鐵(6)及插件磁鐵(7)發出同步加速器光源，經由光束線(8)將光源引導至實驗站(9)進行實驗。
- 電子束在發出同步加速器光源後，要靠高頻腔(10)來補充失去的能量。





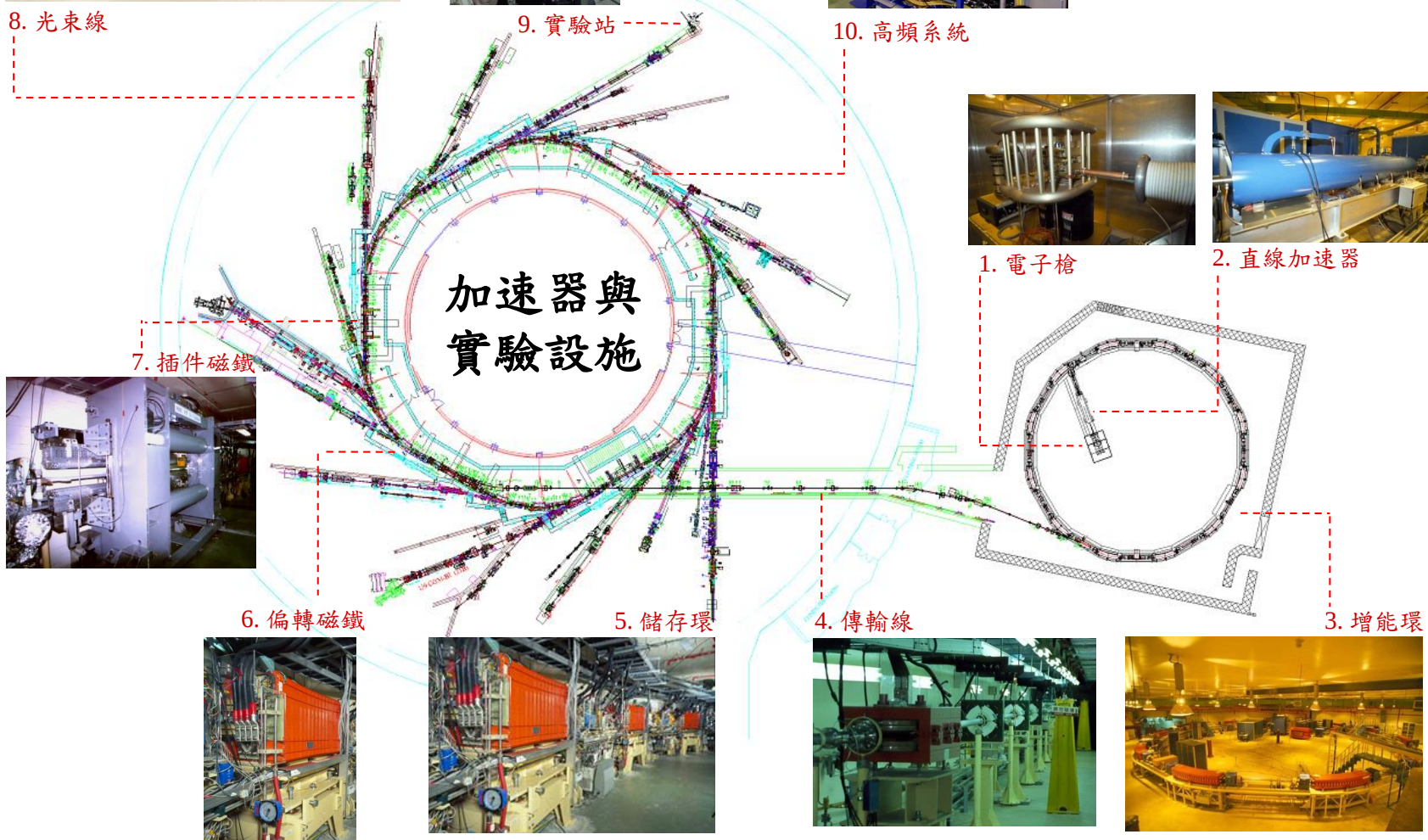
8. 光束線



9. 實驗站



10. 高頻系統



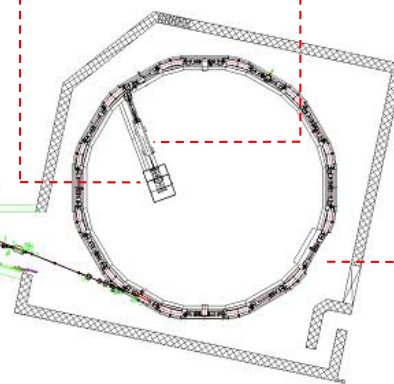
7. 插件磁鐵



1. 電子槍



2. 直線加速器



3. 增能環



6. 偏轉磁鐵



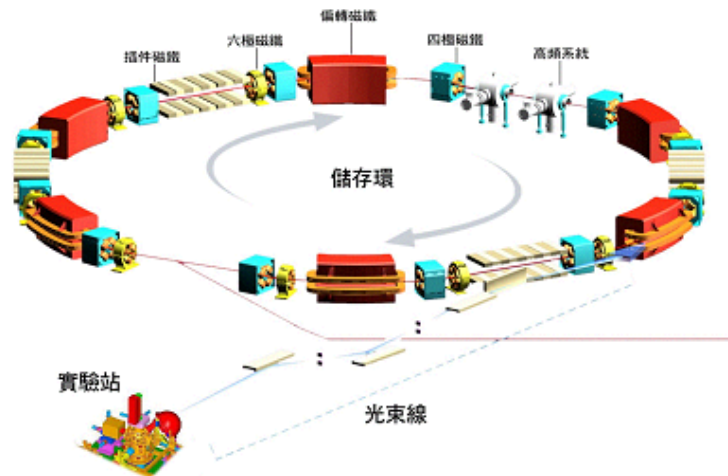
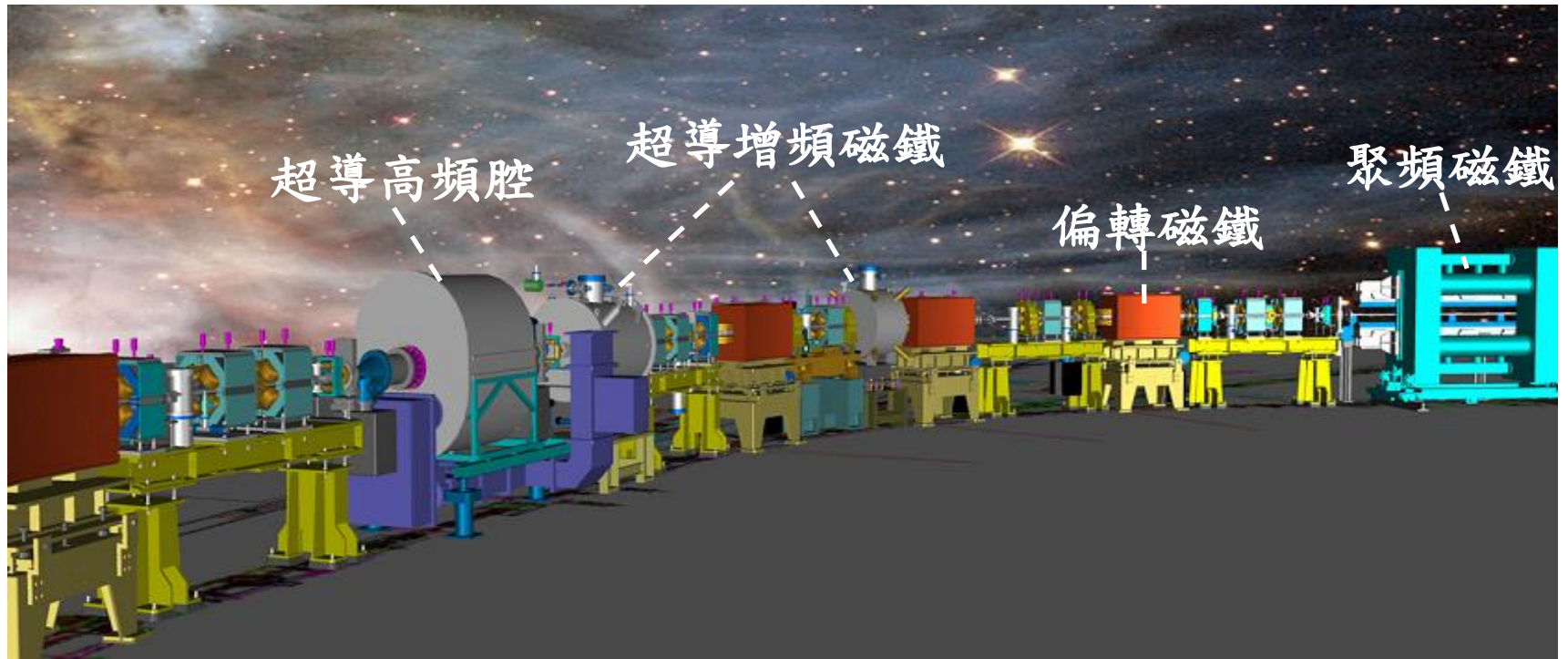
5. 儲存環



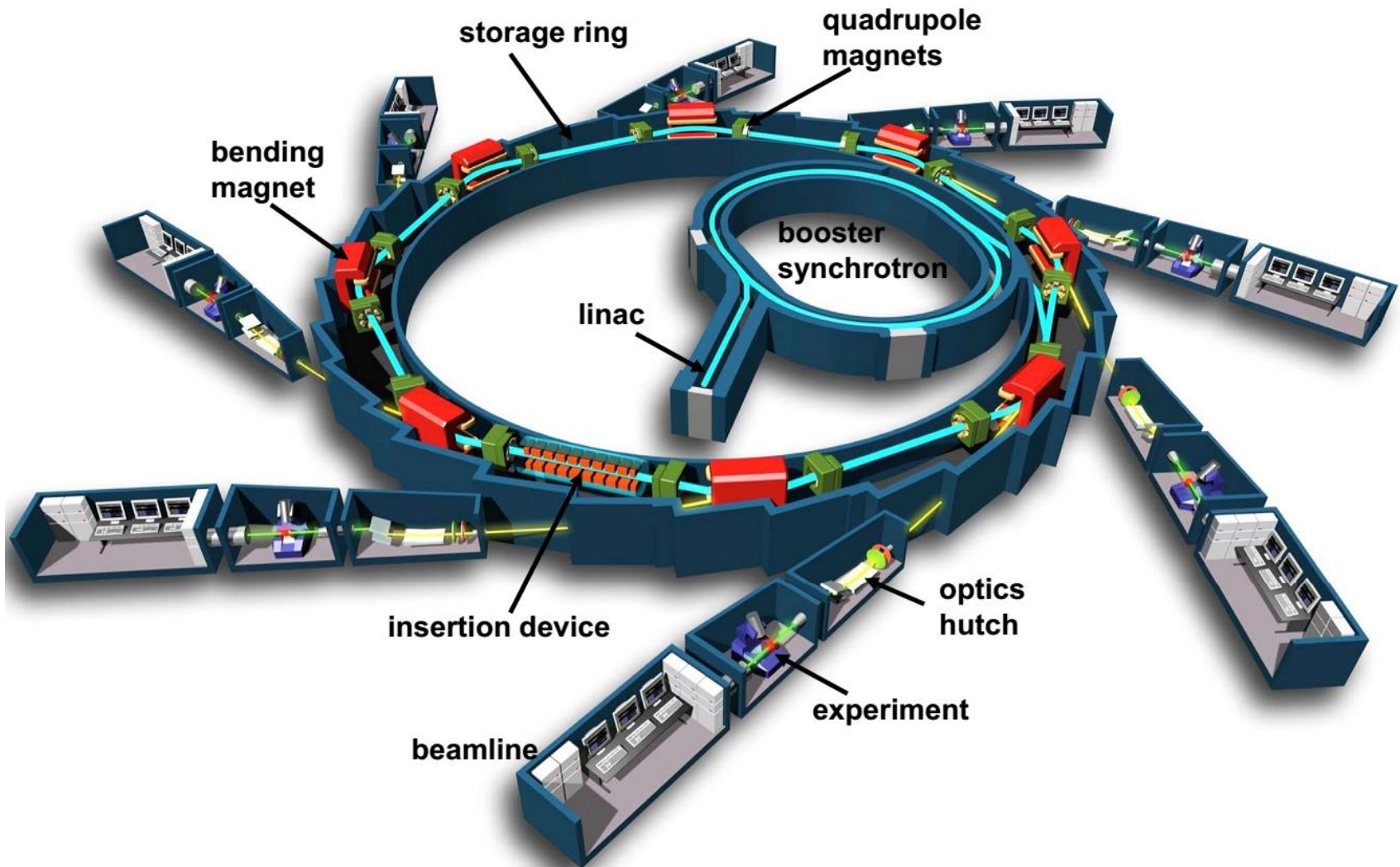
4. 傳輸線



儲存環 3D 圖

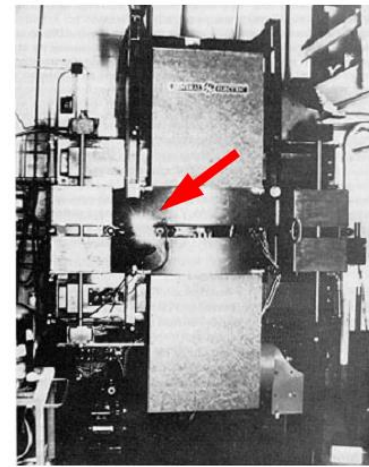


A Synchrotron Step by Step

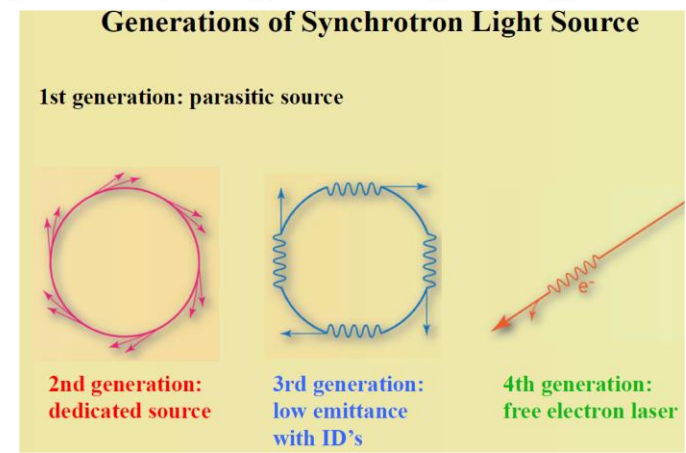


A brief history

- First observed:
1947, General Electric, 70 MeV synchrotron
- First user experiments:
1956, Cornell, 320 MeV synchrotron
- First insertion Device:
1979, 7 pole wiggler, SSRL
- 1st generation light sources: high energy physics synchrotrons and storage rings used parasitically for synchrotron radiation – eg DESY (Germany), INS-SOR (Tokyo), SPEAR (USA), (1960's, 1970's)
- 2nd generation light sources: purpose built synchrotron light sources, eg Photon Factory, NSLS, Daresbury (1980s onwards)
- 3rd generation light sources: optimised for high brilliance with low emittance and Insertion Devices; SPRing-8, ESRF, APS, Diamond, ... (1990's onwards)
- Free Electron Laser sources: FLASH (Germany), LCLS (USA), SACLA (Japan), FERMI (Italy) ... (2000's)
- Next??

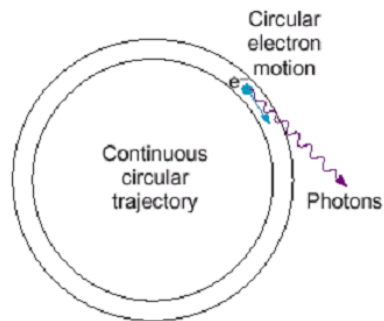


2015 Cheiron School

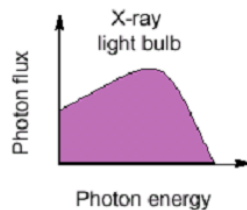


Third Generation Sources: Undulator Insertion Devices

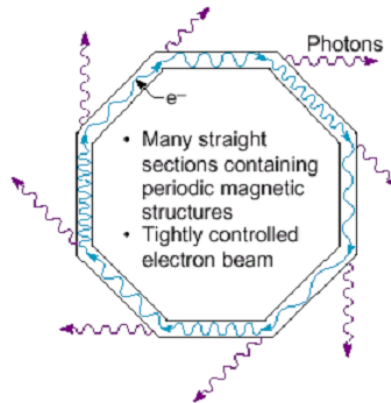
1st, 2nd Generation



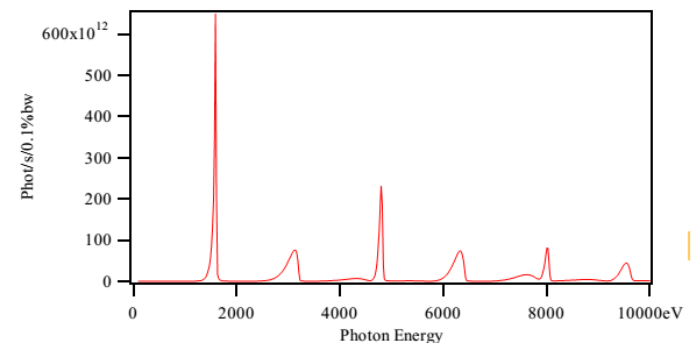
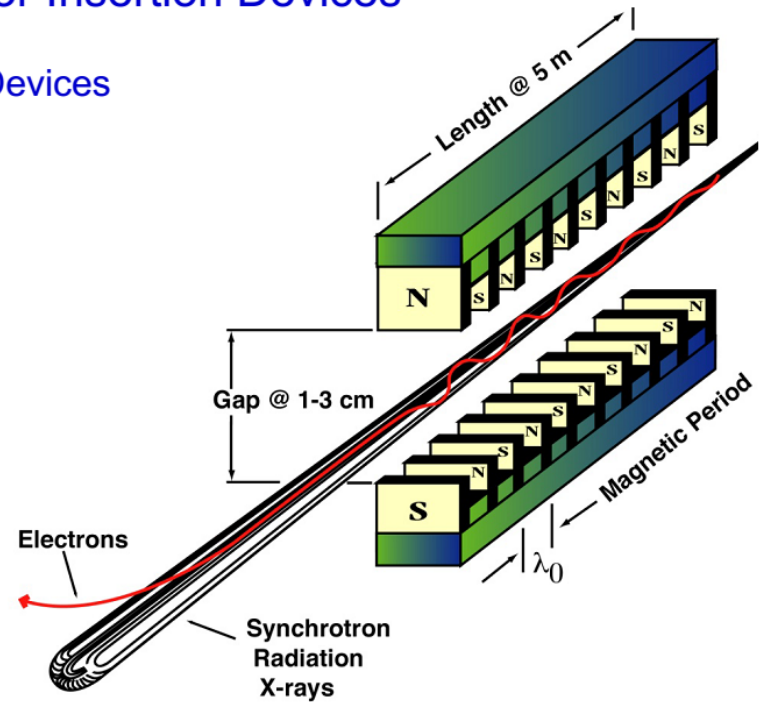
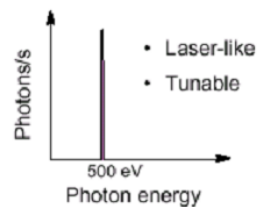
Bend Magnet Radiation



3rd Generation: Insertion Devices

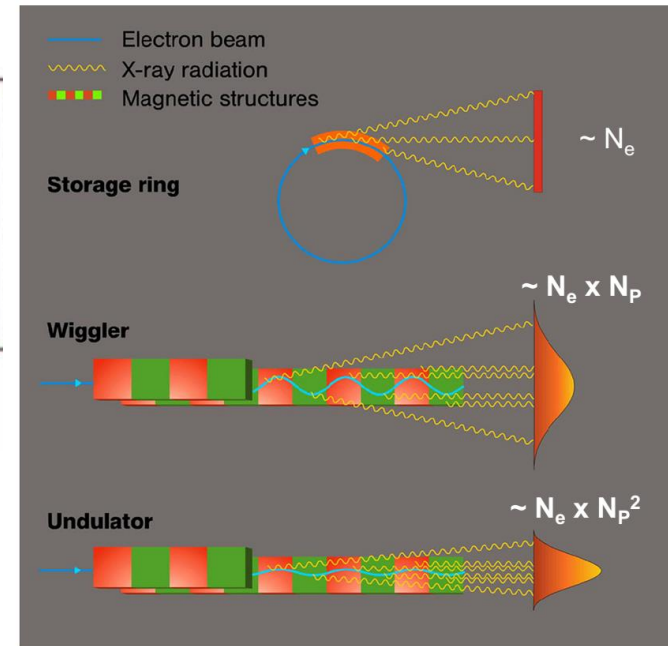
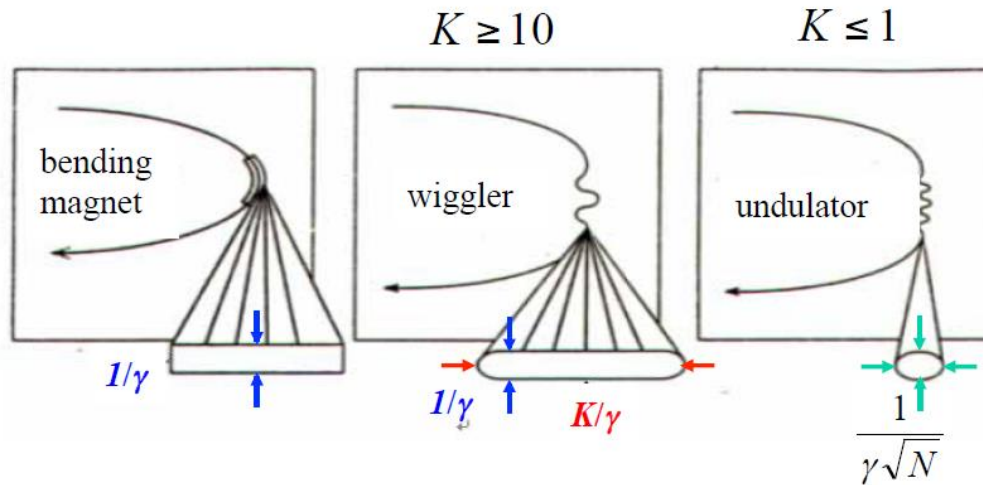
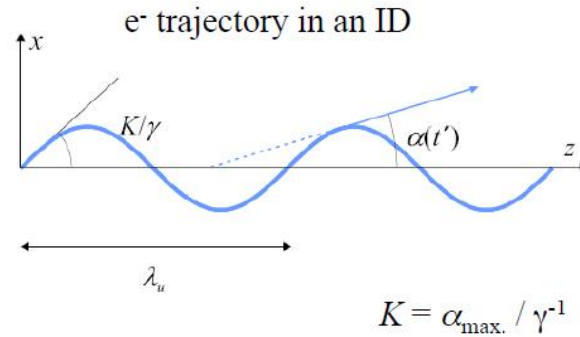
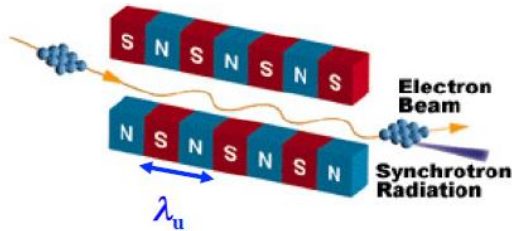


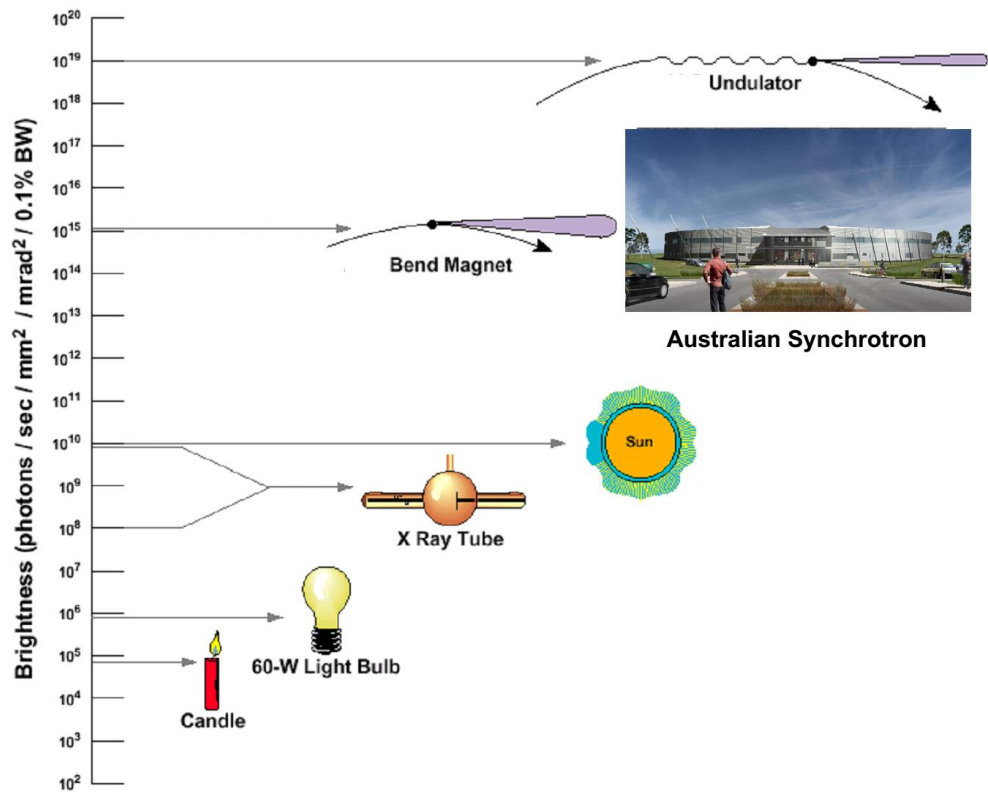
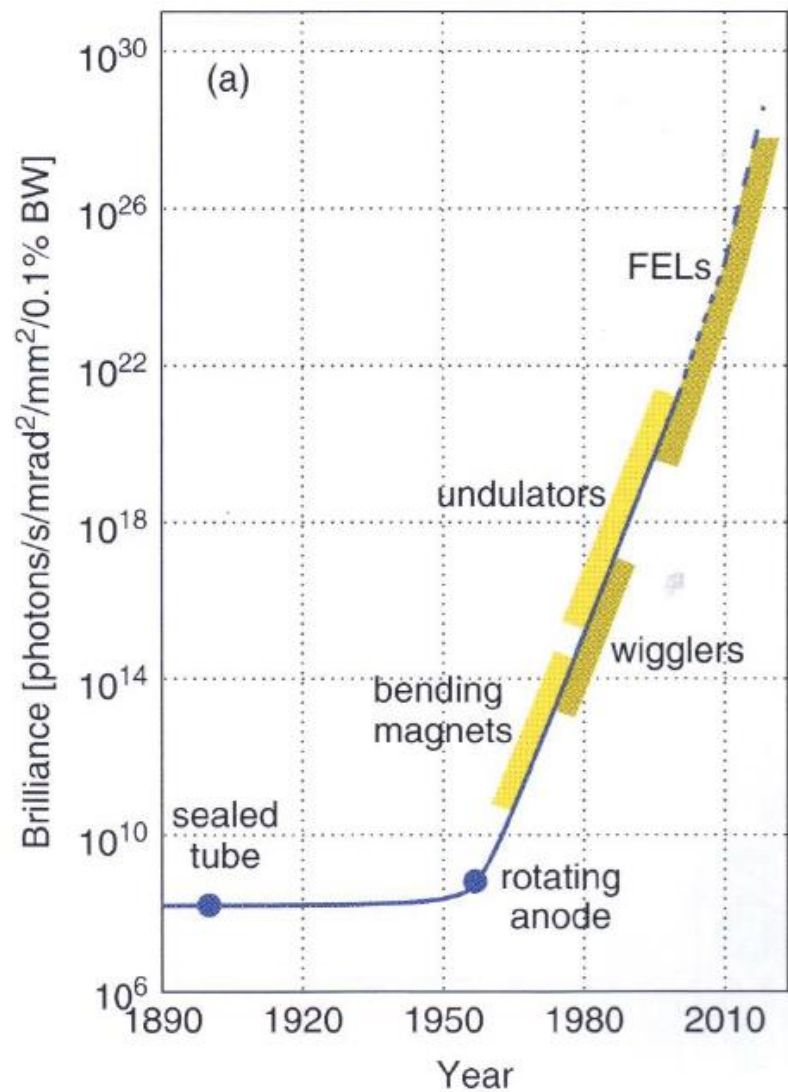
Undulator Radiation



Angular distribution of synchrotron radiation emitted from various magnets

Wiggler or undulator

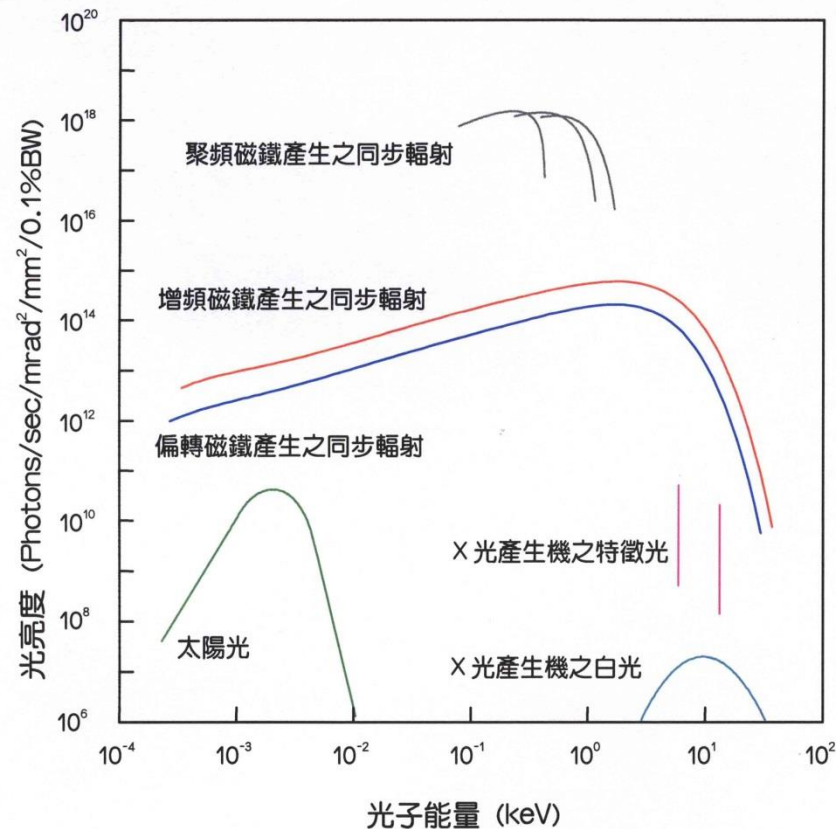




Unique Features of Synchrotron Light Source

- High intensity
- Continuous spectrum
- Excellent collimation
- High polarization
- Pulsed-time structure

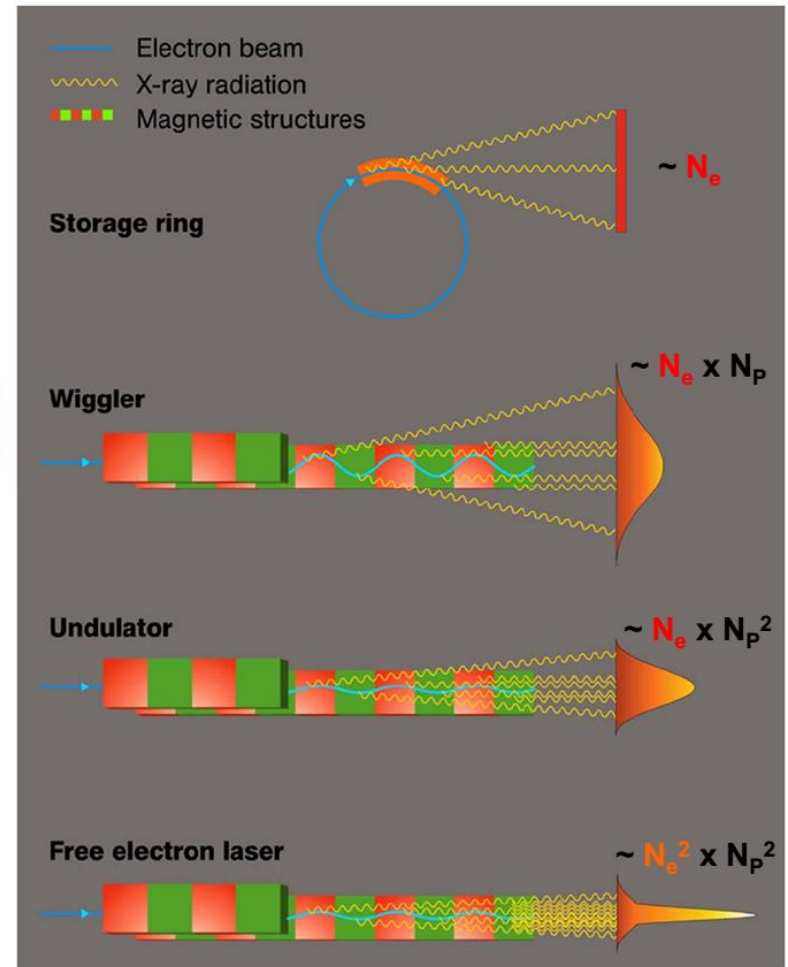
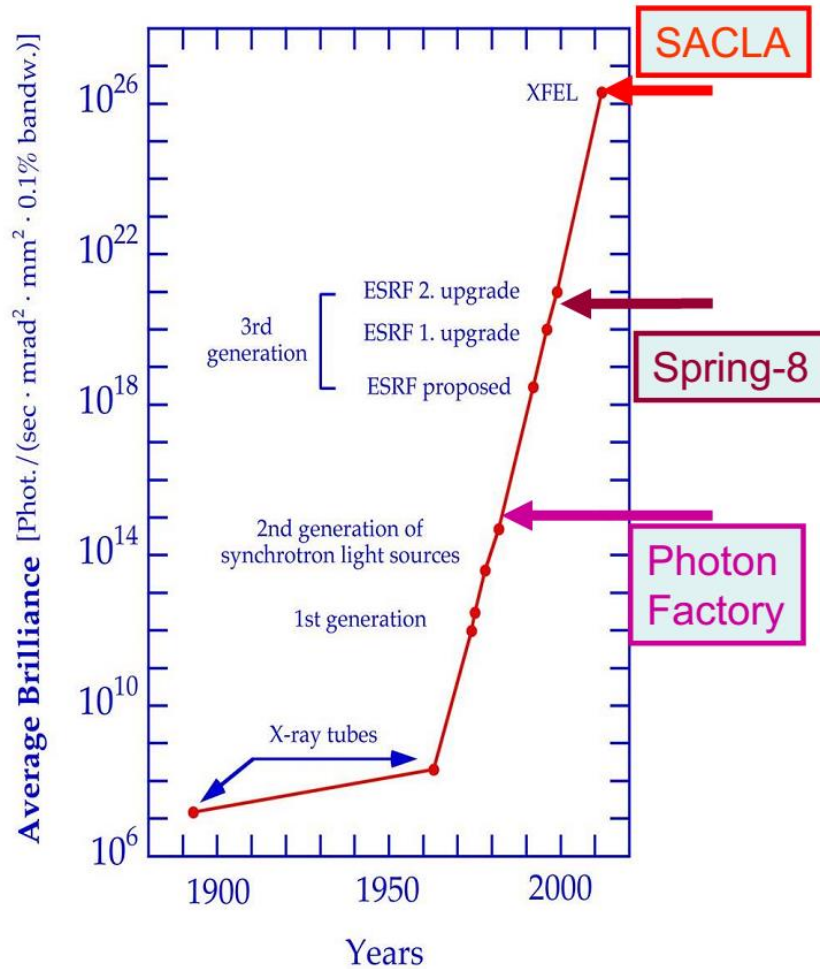
以X光為例，同步加速器光源在這個波段的亮度比傳統X光機還要強百萬倍以上！過去需要幾個月才能完成的實驗，現在只需幾分鐘便能得到結果。以往因實驗光源亮度不夠而無法探測的結構，現在藉由同步加速器光源，都可分析得一清二楚，也因此得以開發新的研究領域。



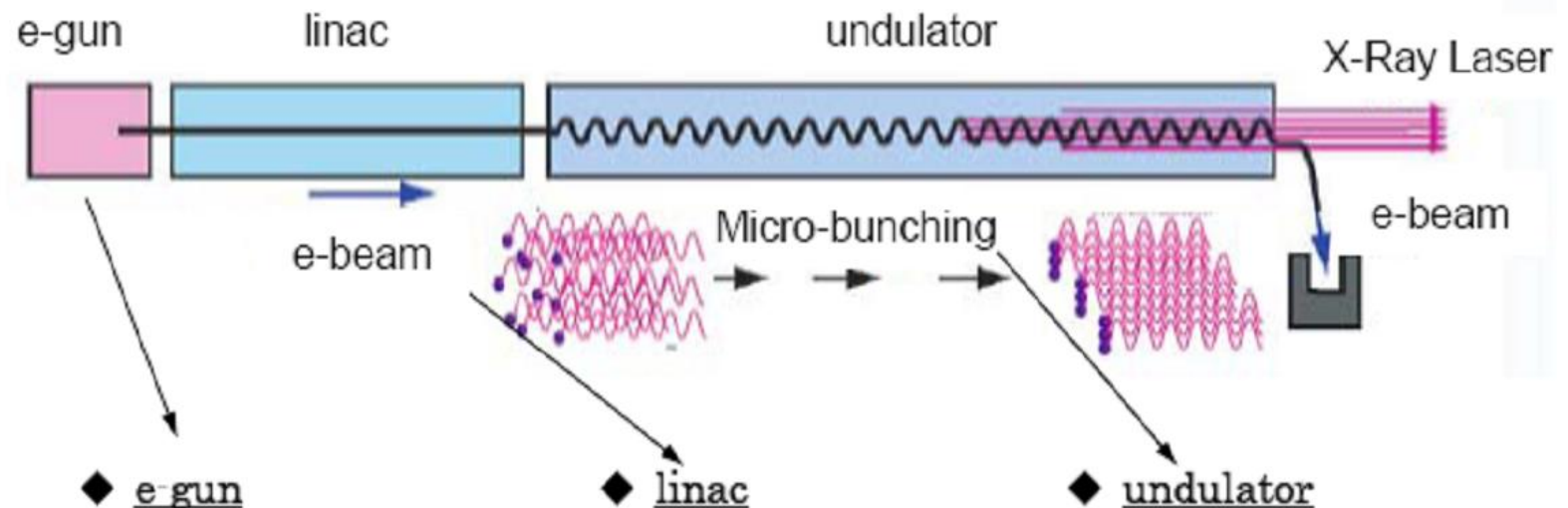
光子能量：一般單位為電子伏特(eV)，一電子伏特為電子在真空中通過一伏特電位差所獲得的能量。

光亮度：指單位時間內通過單位立體角的單位頻寬光子數。

Next Step - X-ray Lasers? Yes → FELs



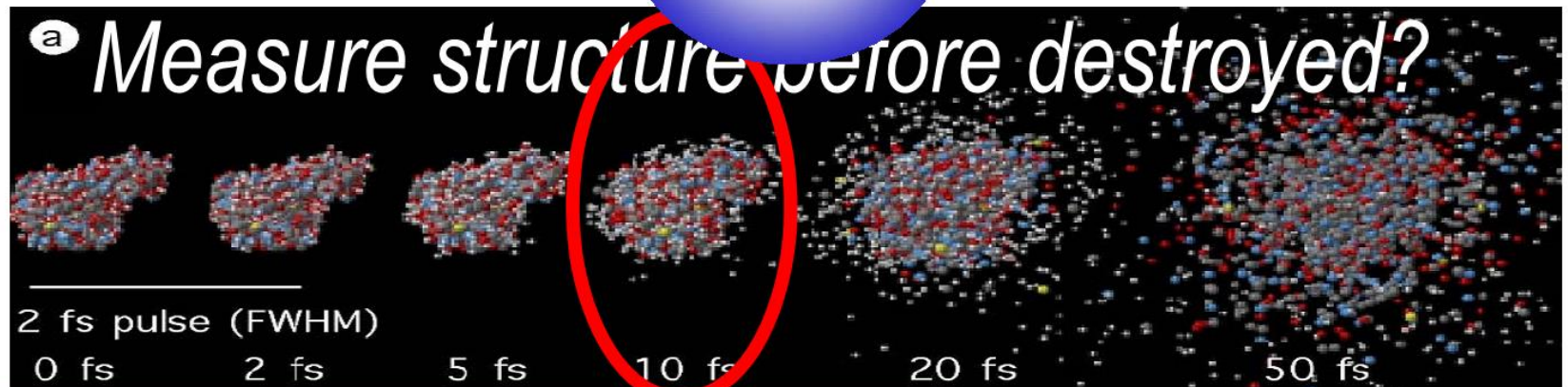
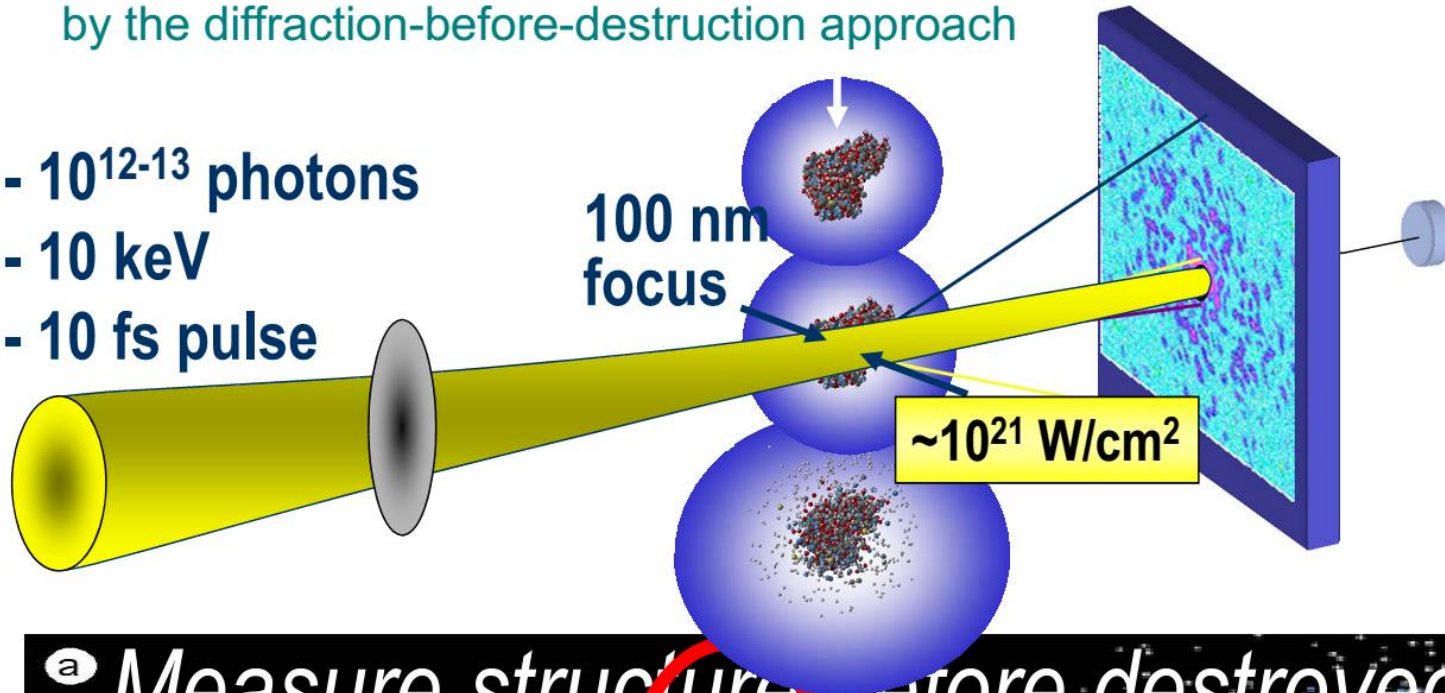
Linac-Based Free Electron Laser Self-Amplified Spontaneous Emission (SASE)



Coherent diffractive imaging of single particles

by the diffraction-before-destruction approach

- 10^{12-13} photons
- 10 keV
- 10 fs pulse



Calculations. in vacuum Neutze et al., Nature 2000

$$E = h\nu = hc/\lambda,$$

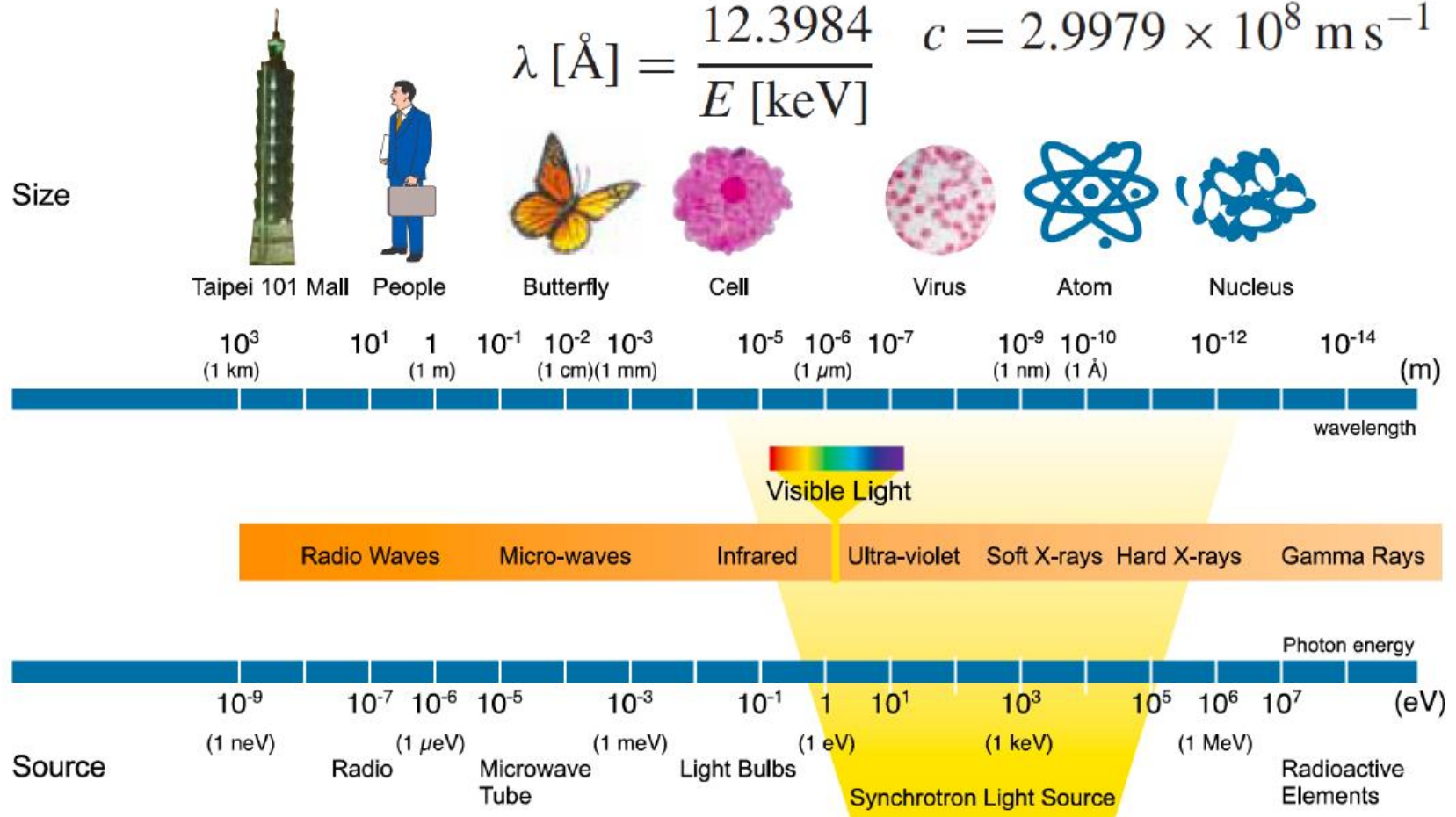
$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$c = 2.9979 \times 10^8 \text{ m s}^{-1}$$

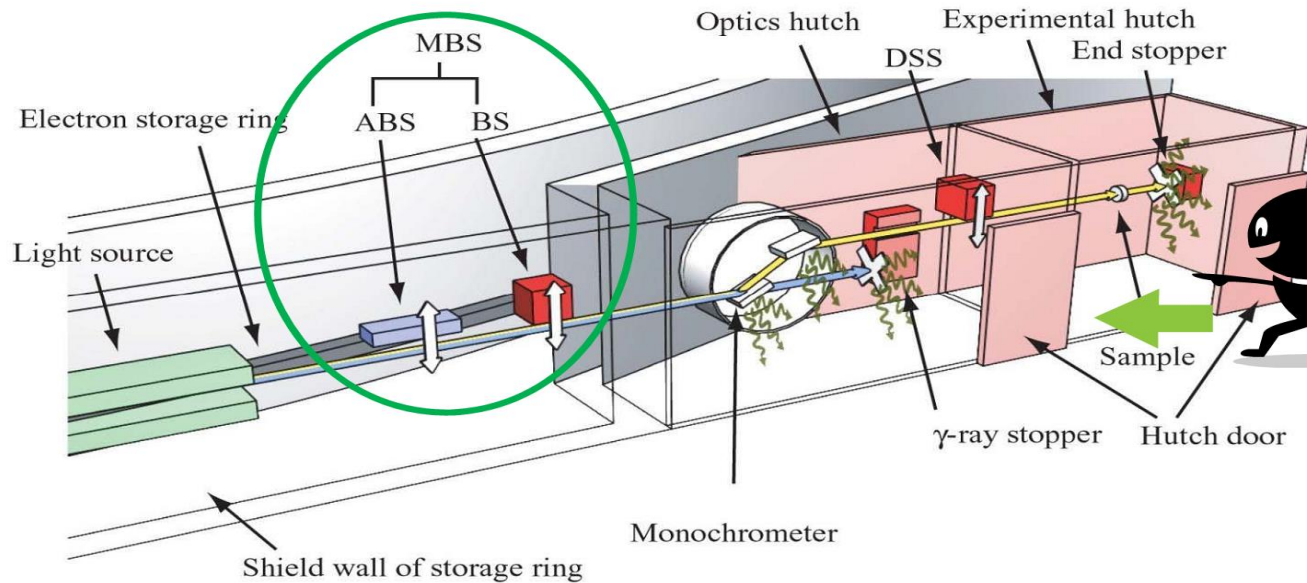
Electromagnetic Spectrum

$$\lambda [\text{\AA}] = \frac{12.3984}{E [\text{keV}]}$$

Size



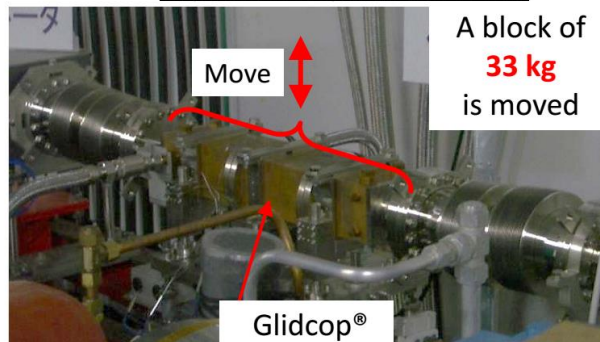
Beamline



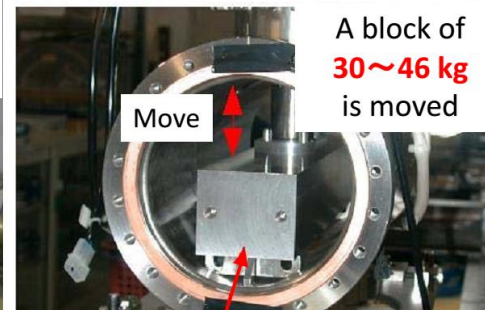
When we operate a main beam shutter (MBS), what happens ?

For safety

X-ray → **Absorber (Abs)** → **Beam shutter (BS)**
to protect BS from heat load to shield you against radiation



(copper that is dispersion-strengthened with ultra-fine particles of aluminum oxide)

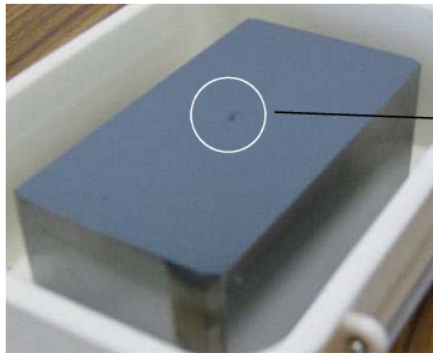


Heavy metal (alloy of tungsten) the thermal conductivity not so high

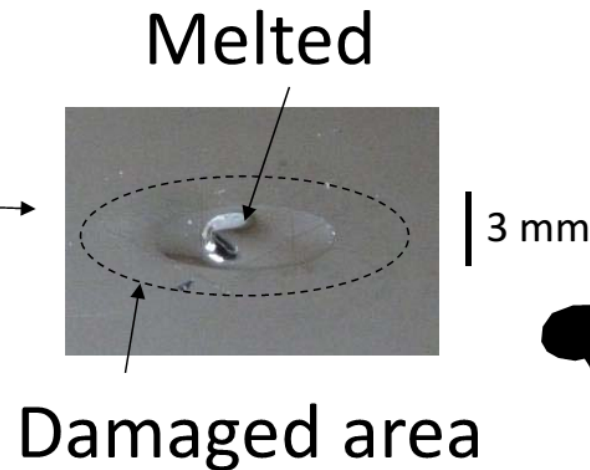
If an optical component is irradiated
by too much power

One user opened FE slit excessively.

2kW

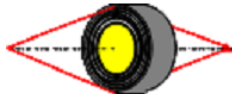
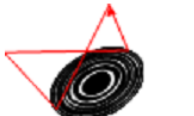
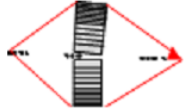


LN2-cooled
Si crystal

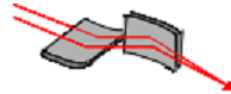
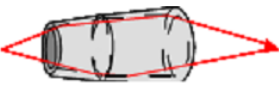
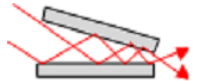


Slit : *“Too much is as bad as too little”*

Overview of x-ray focusing devices

Diffraction	focus size, focal length [energy]	energy range	aberration -coma -chromatic -figure error
 Fresnel Zone Plate	12 nm, $f = 0.16$ mm [0.7 keV], 30 nm, $f = 8$ cm [8 keV]	soft x-ray hard x-ray	-coma small -chromatic exist -figure error small
 Sputter sliced FZP	0.3 μ m, $f = 22$ cm [12.4 keV], 0.5 μ m, $f = 90$ cm [100 keV]	8-100 keV	-coma small -chromatic exist -figure error large $\rightarrow$ small
 Bragg FZP	2.4 μ m, $f = 70$ cm [13.3 keV]	mainly hard x-ray	-coma small -chromatic exist -figure error small
 Multilayer Laue Lens	16 nm(1D), $f = 2.6$ mm [19.5 keV], 25nm $\times$ 40nm, $f = 2.6$ mm, 4.7mm [19.5 keV]	mainly hard x-ray	-coma large -chromatic exist -figure error small

Refraction	focus size, focal length [energy]	energy range	aberration -coma -chromatic -figure error
 Pressed Lens	1.5 μ m, $f = 80$ cm [18.4 keV], 1.6 μ m, $f = 1.3$ m [15 keV]	mainly hard x-ray	-coma small -chromatic exist -figure error large
 Etching Lens	47nm $\times$ 55nm, $f = 1$ cm, 2cm [21 keV]	mainly hard x-ray	-coma small -chromatic exist -figure error small

Reflection	focus size, focal length [energy]	energy range	aberration -coma -chromatic -figure error
 Kirkpatrick-Baez Mirror	7 nm $\times$ 8nm, $f = 7.5$ cm [20 keV]	soft x-ray hard x-ray	-coma large -chromatic not exist -figure error small
 Wolter Mirror	0.7 μ m, $f = 35$ cm [9 keV]	<10 keV	-coma small -chromatic not exist -figure error large
 X-ray Waveguide	95 nm, [10 keV]	soft x-ray hard x-ray	-coma large -chromatic not exist -figure error large

Outline

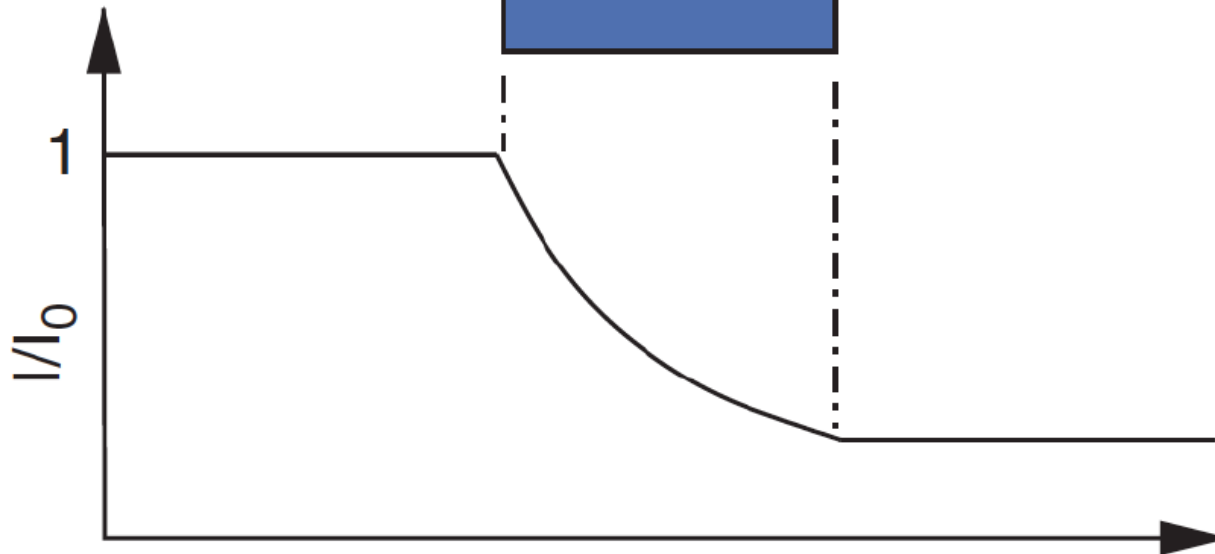
- Synchrotron Light Source
- Application of Synchrotron Light
- X-ray nano probe at TPS

Absorption

$$E(z,t) = E_0 e^{-n_I k z} e^{i(n_R k z - \omega t)}$$

$$E(z,t) = E_0 e^{i(kz - \omega t)}$$

$$\frac{I}{I_0} = e^{-\mu z}$$



z

absorption coefficient

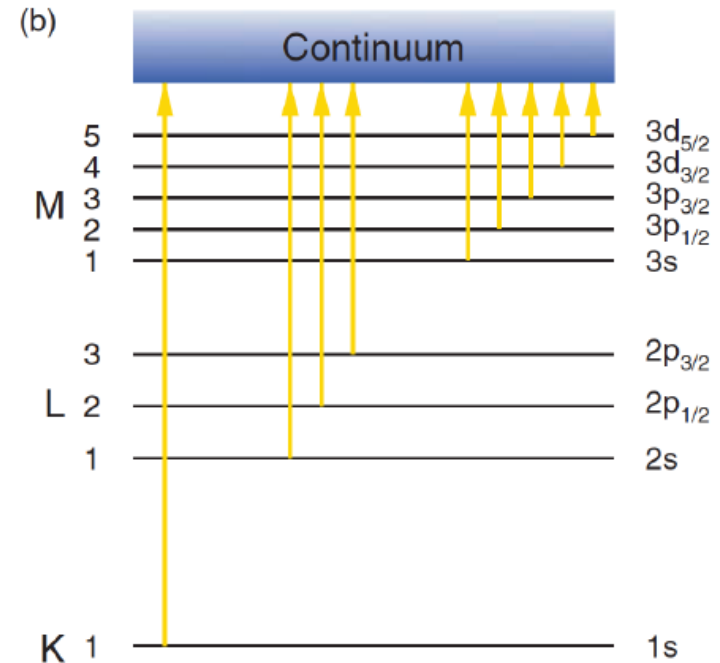
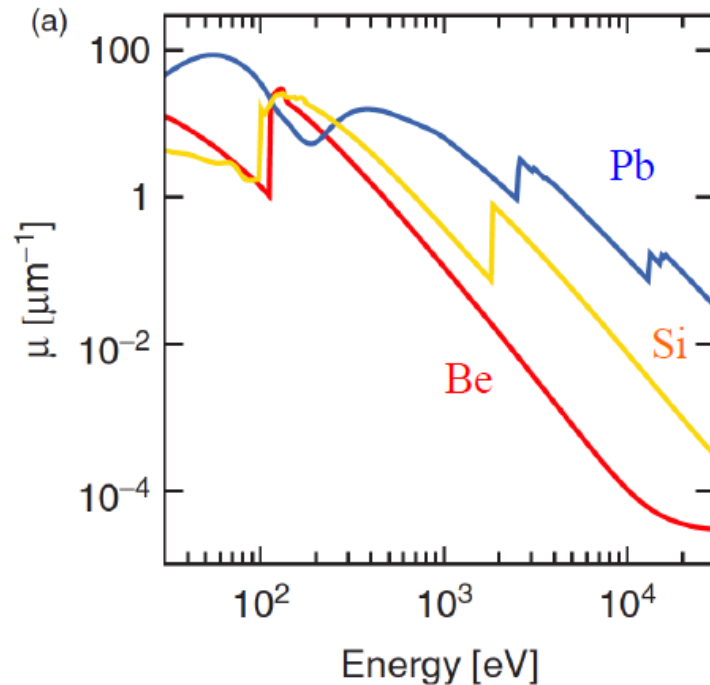
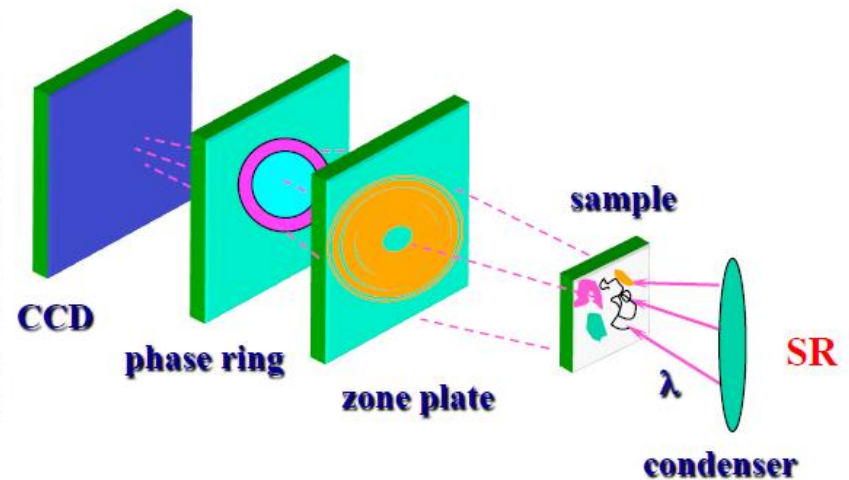


Figure 2.16 (a) The x-ray absorption coefficient μ for beryllium (red curve), silicon (yellow) and lead (blue) as a function of the photon energy. (b) Sharp increases in the absorption occur when the photon energy is just sufficient to eject the electron from the electronic orbital to the continuum. The x-ray absorption (left) and atomic orbital labellings (right) are shown.

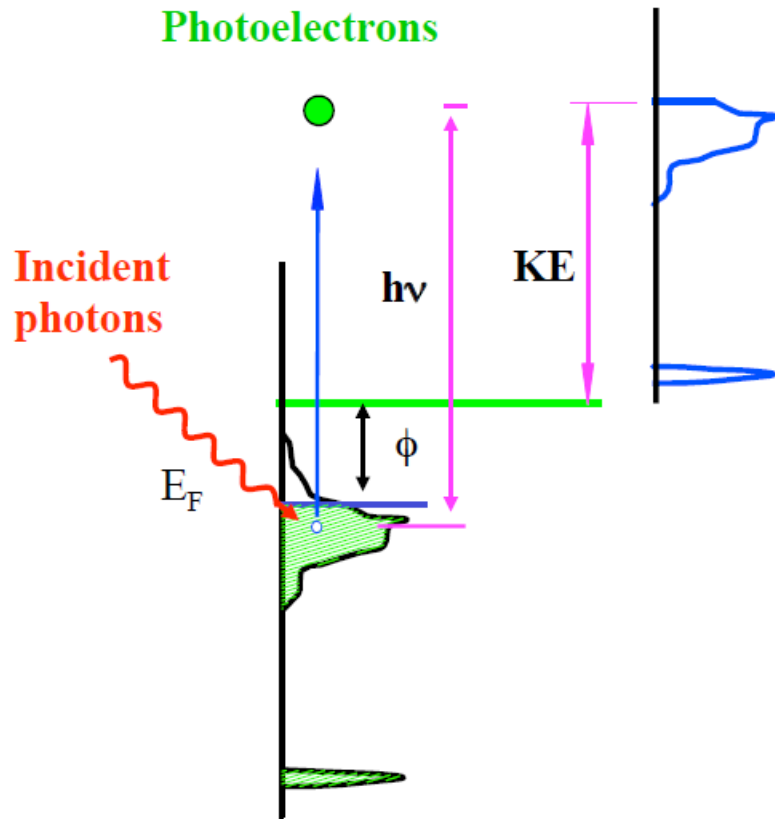
Transmission X-ray Microscope (TXM)



energy: 8 keV
3D tomography
spatial resolution = 60 nm

Photoemission Spectroscopy

Energy Distribution Curve (EDC)



$$KE = h\nu - BE - \phi$$

$$\frac{d\sigma}{d\Omega} \propto \sum \left| \langle \Psi_f | A \cdot P | \Psi_i \rangle \right|^2 \cdot \delta(E_f - E_i - h\nu)$$

Selection rule: $\Delta l = \pm 1$

$\Delta m_l = 0$ (linearly polarized)

$\Delta m_l = +1$ (L. circularly polarized)

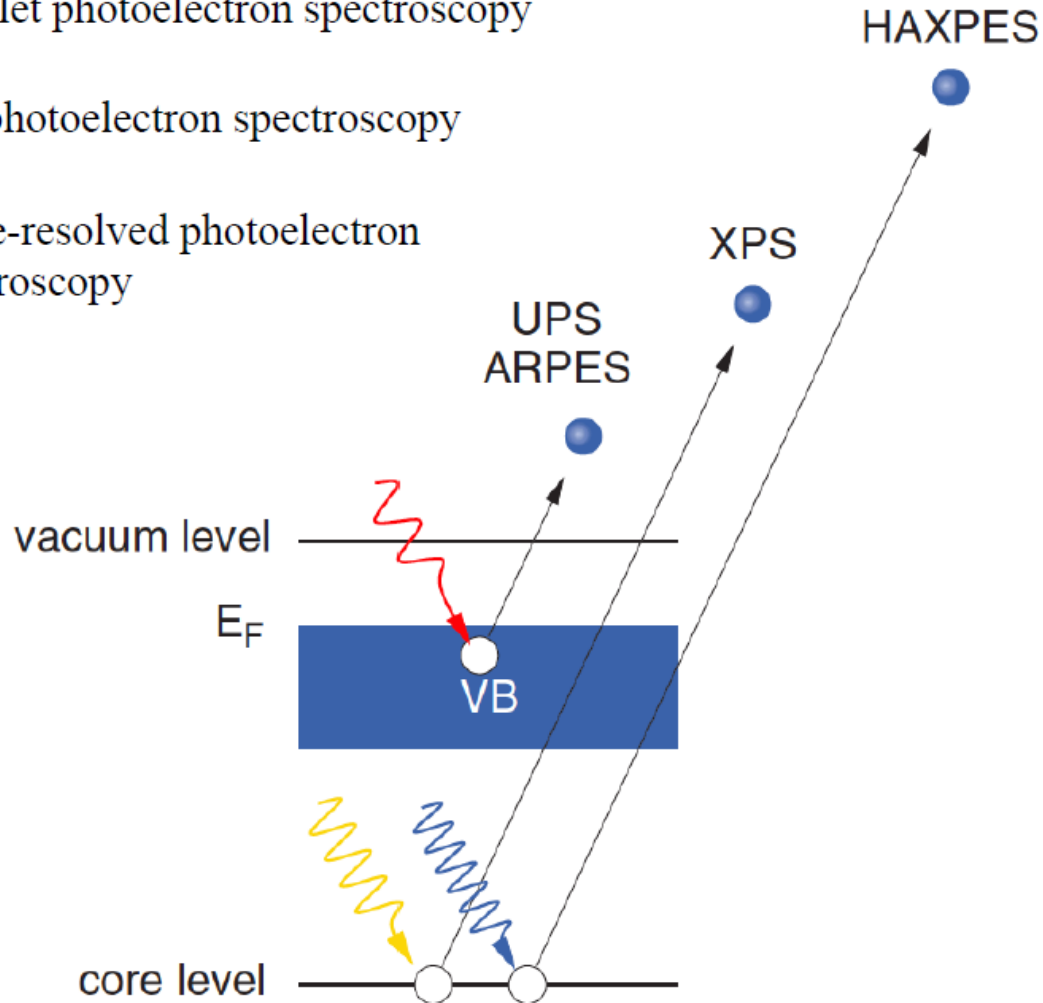
$\Delta m_l = -1$ (R. circularly polarized)

HAXPES = Hard X-ray photoelectron spectroscopy

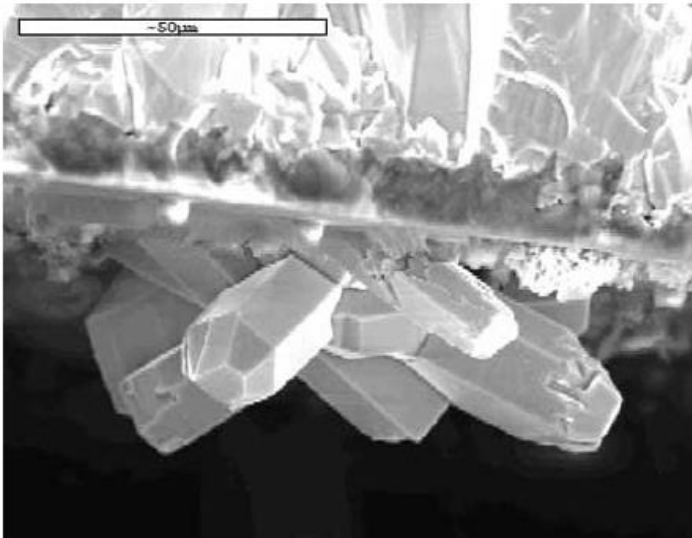
UPS = ultraviolet photoelectron spectroscopy

XPS = X-ray photoelectron spectroscopy

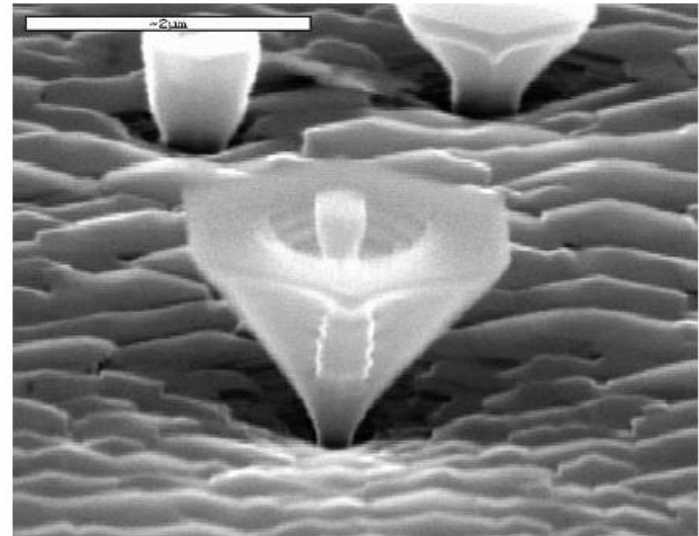
ARPES = angle-resolved photoelectron spectroscopy



“Crystals”



GaN (hexagonal) crystal cluster grown by hydride vapor phase epitaxy



AlN pyramids grown by MBE

Sand Rose of gypsum
(石膏) crystals



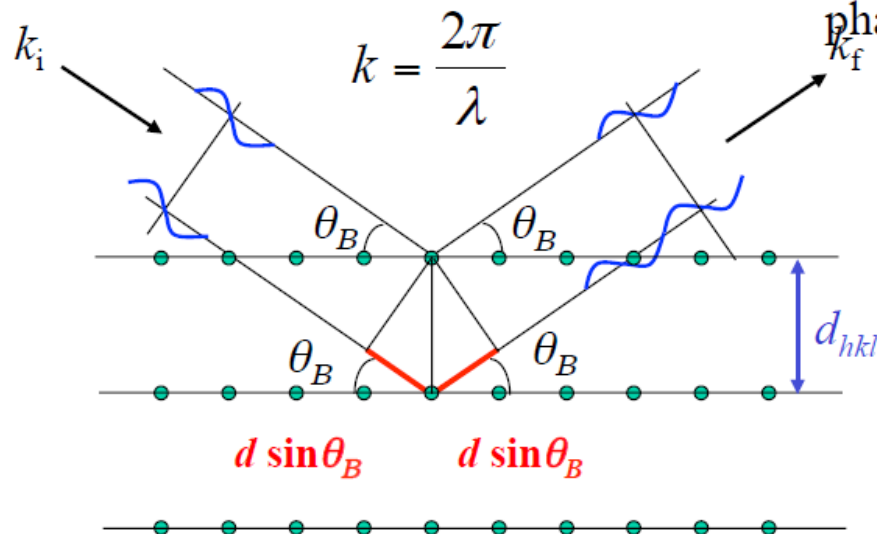
Bragg Law - X-ray reflected by the (hkl) planes

$$\vec{E} = E_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

Path Difference $L = 2d_{hkl} \sin \theta_B$

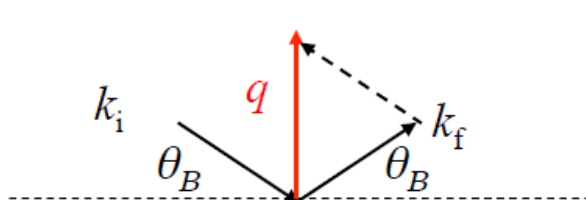
Constructive interference: $L = n\lambda$

phase difference $\phi = k L$



Bragg Law: $2d_{hkl} \sin \theta_B = n\lambda$

$$2\pi \frac{2}{\lambda} \sin \theta_B = 2\pi \frac{1}{d_{hkl}} = G_{hkl}$$



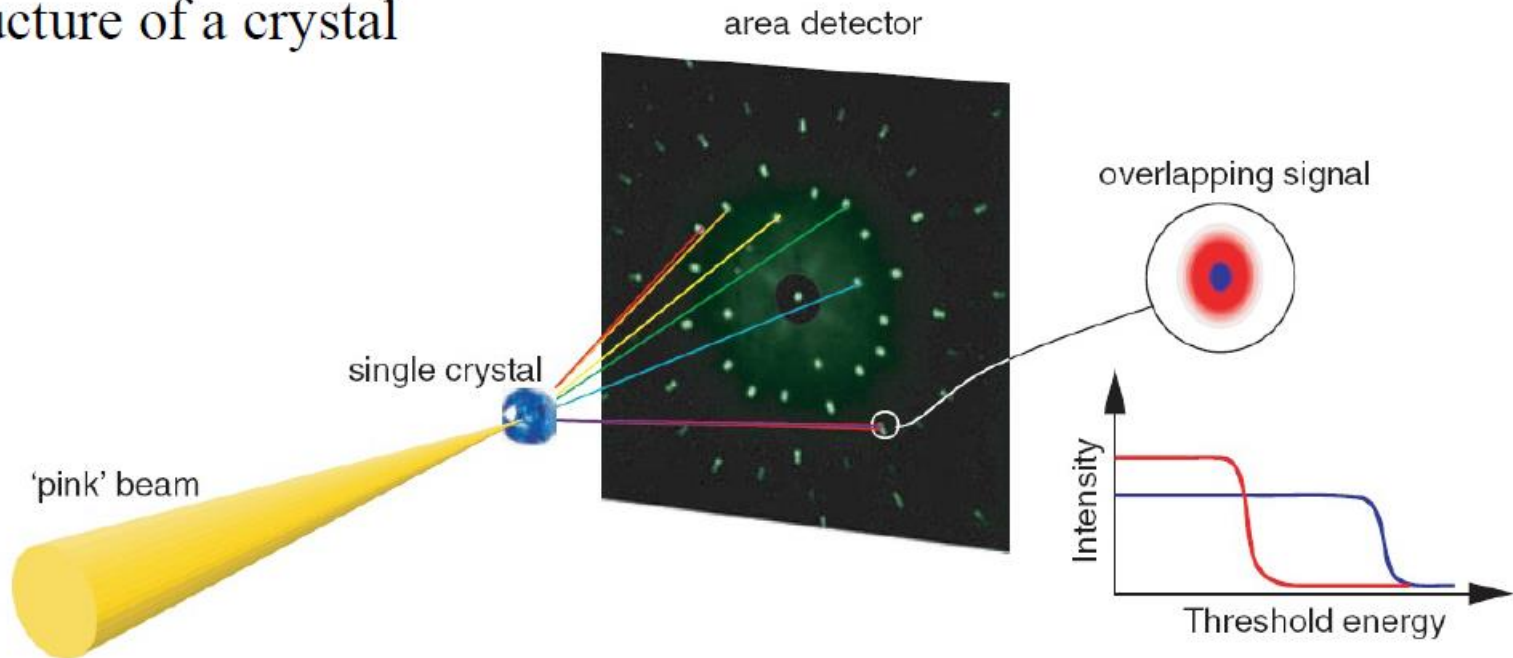
scattering vector $\vec{q} = \vec{k}_f - \vec{k}_i$ $q = 2 \frac{2\pi}{\lambda} \sin \theta_B$

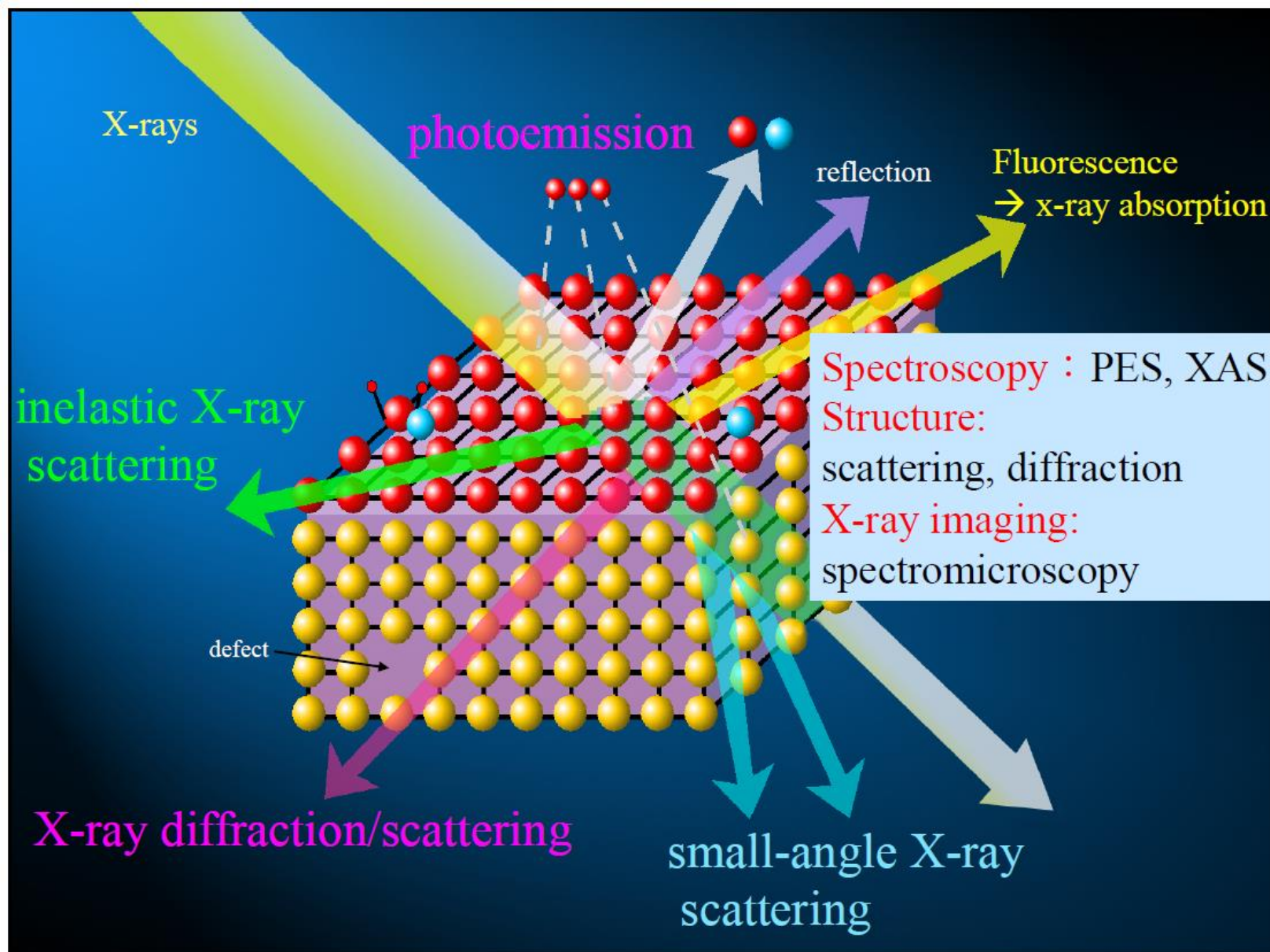
$q = G_{hkl}$

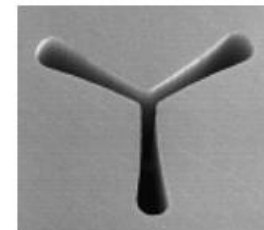
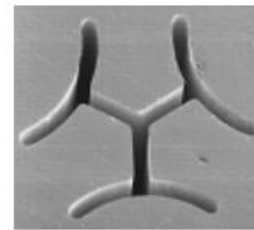
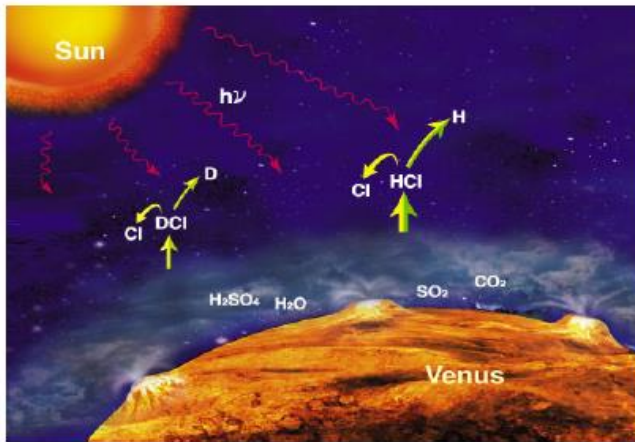
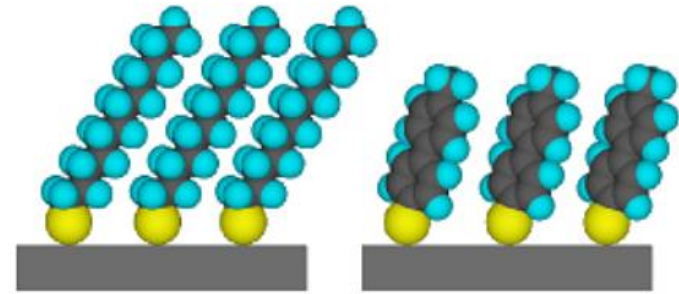
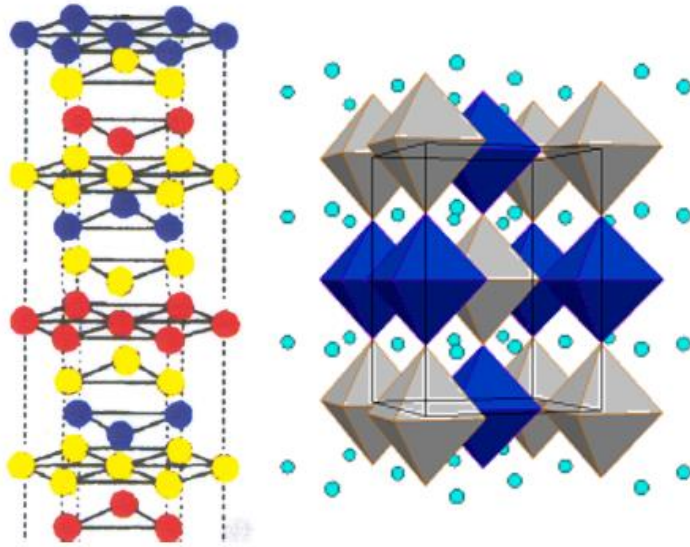
In terms of diffraction, two key characteristics of a set of crystal planes :
 $1/d$ and orientation

Single Crystal Diffraction - Laue Diffraction

- Method: stationary
- Light source: a polychromatic 'pink' beam (e.g. $\Delta E < 1 \text{ keV}$ @ 10 keV)
- Applications: orient single crystals, determine their crystal quality, dynamical studies of transient crystalline states (time-resolved study)
- Disadvantage: not well-suited for determining the full atomic structure of a crystal

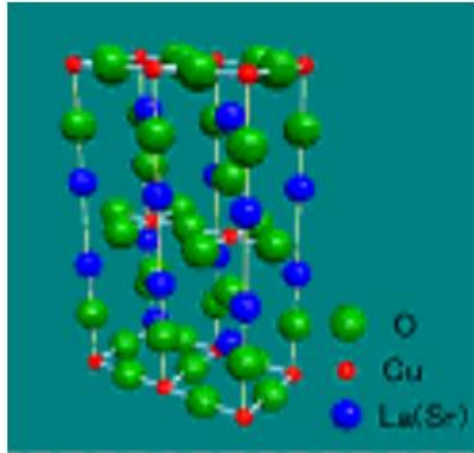




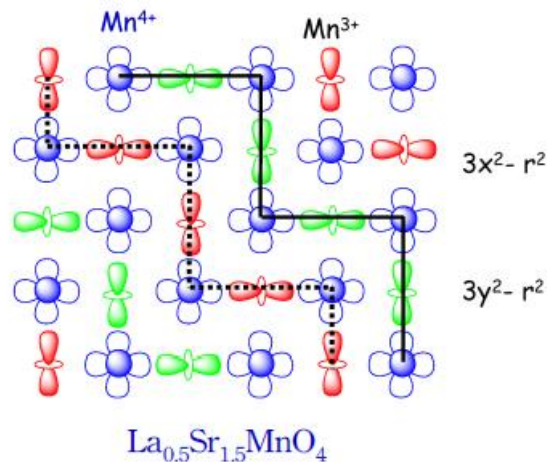


Synchrotron light source is a powerful tool for basic and applied studies in physics, chemistry, materials, biology and medicine, and their many subfields.

Condensed-Matter Physics

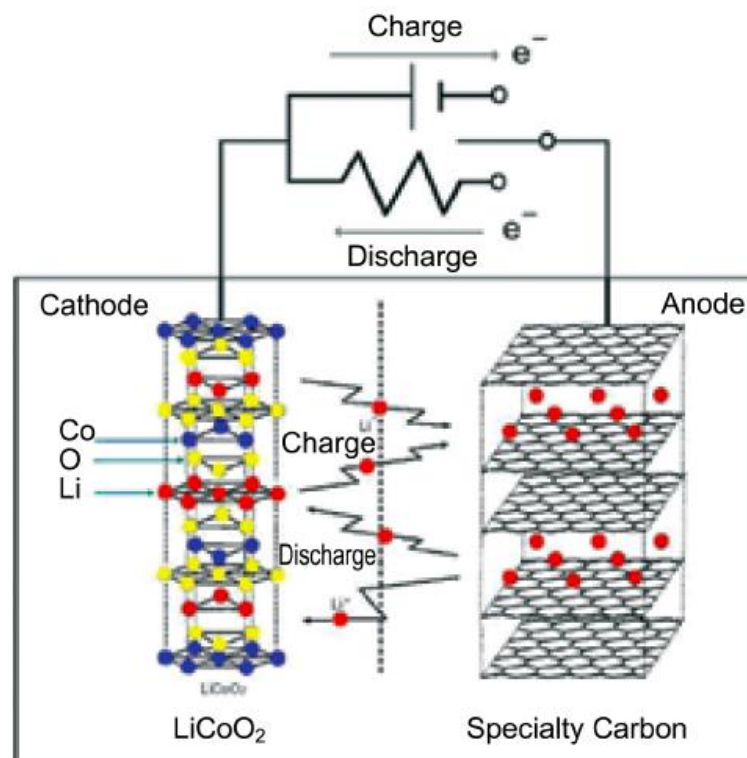
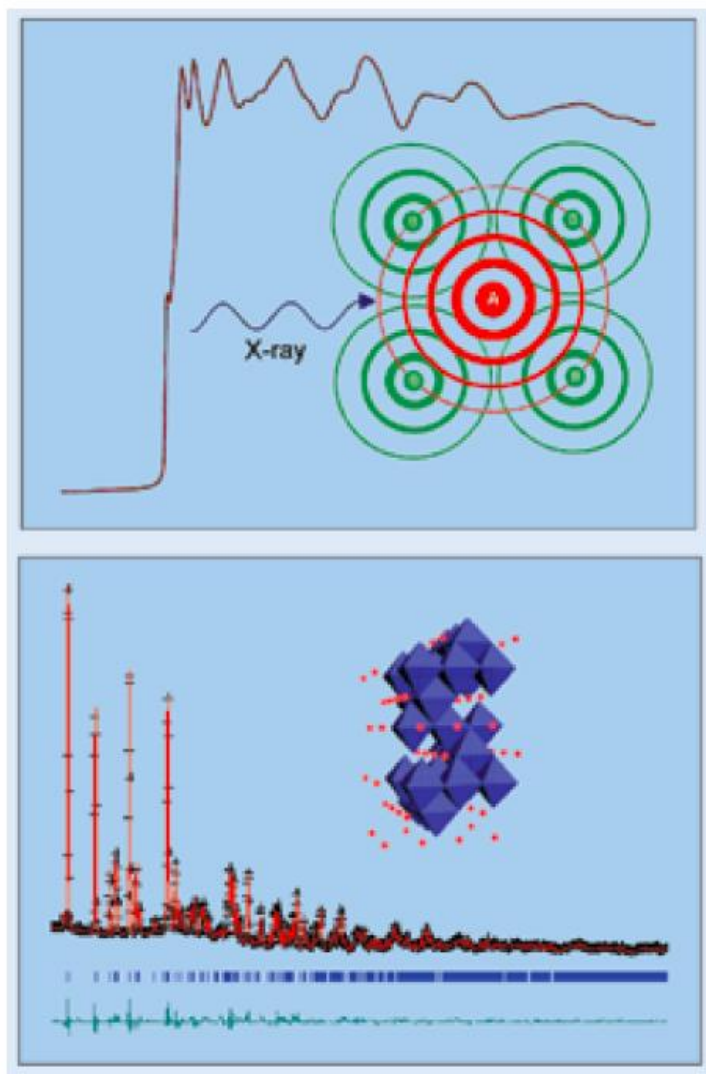


Electronic properties of novel materials can be revealed with X-ray scattering.



(Source: website of Railway Technical Research Institute, Japan)

Energy Science



structure $\leftrightarrow$ electrochemical properties of electrode

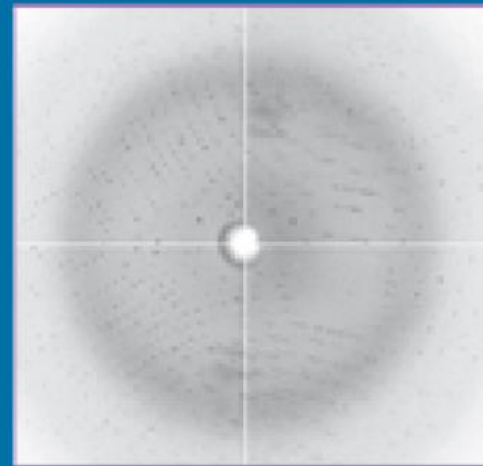


develop novel electrode materials.

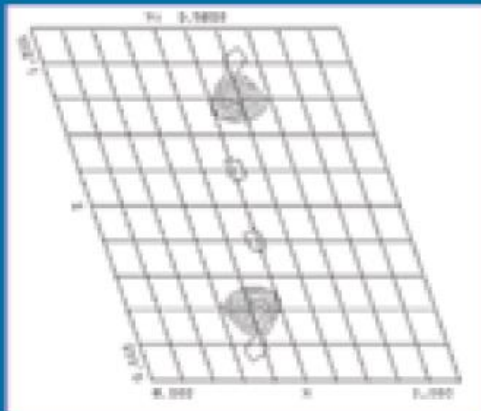
Biological structure: protein crystallography



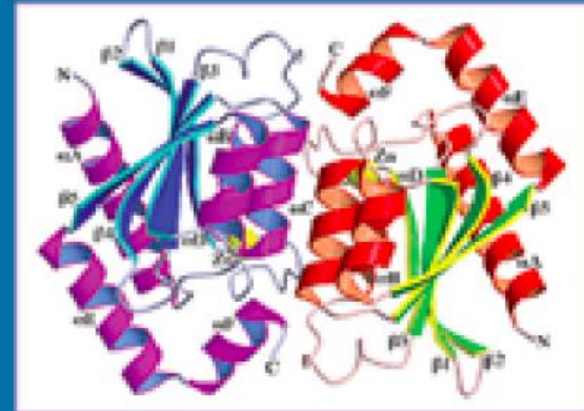
(1) crystallization



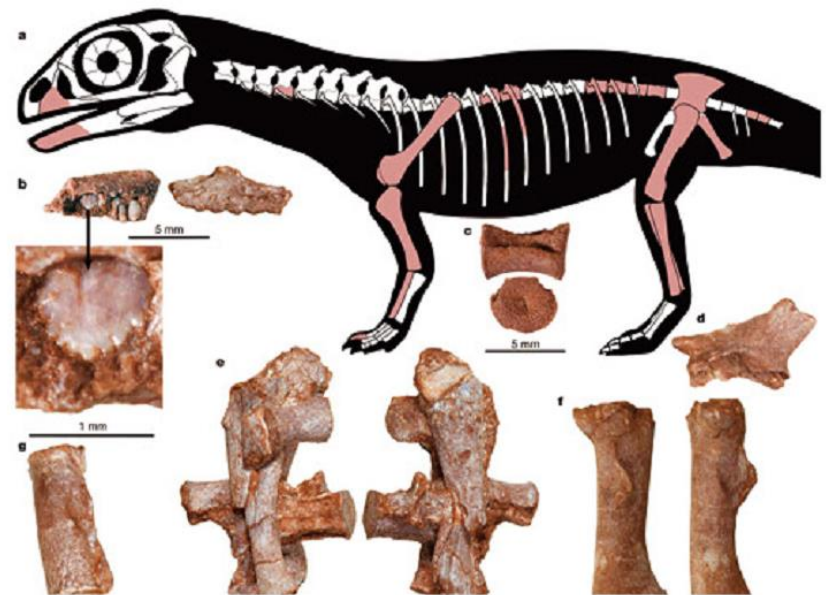
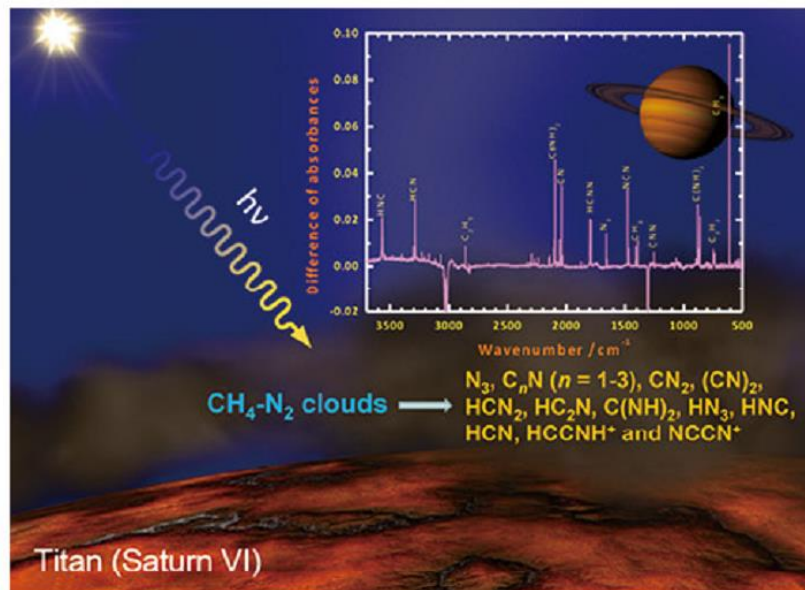
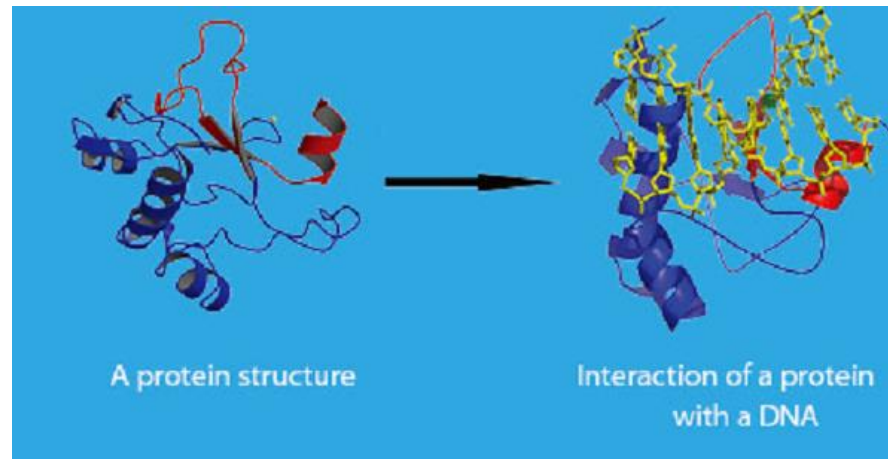
(2) data collection



(3) determination of heavy atom position

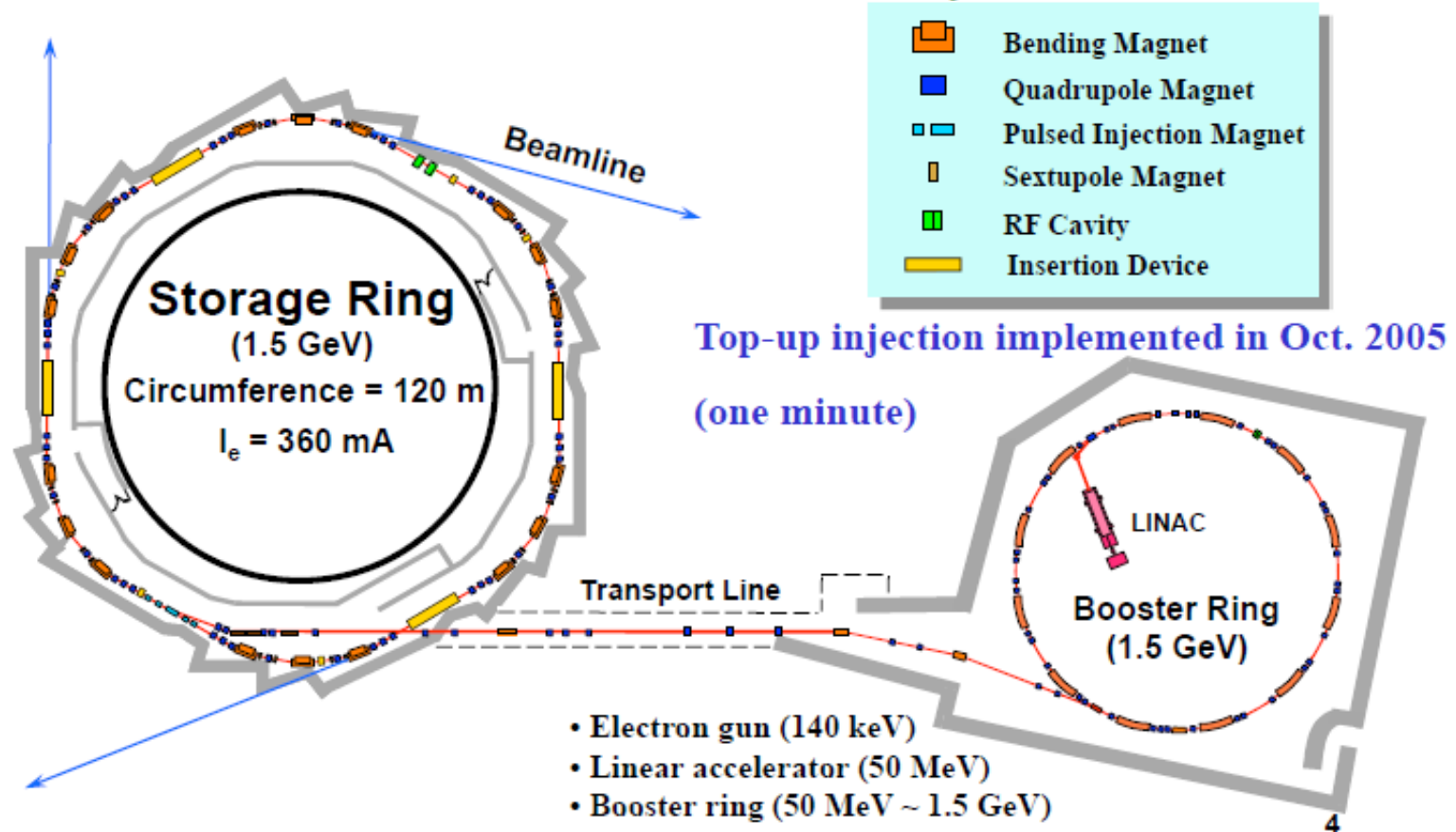


(4) determination of molecular structure



Taiwan Light Source (TLS)

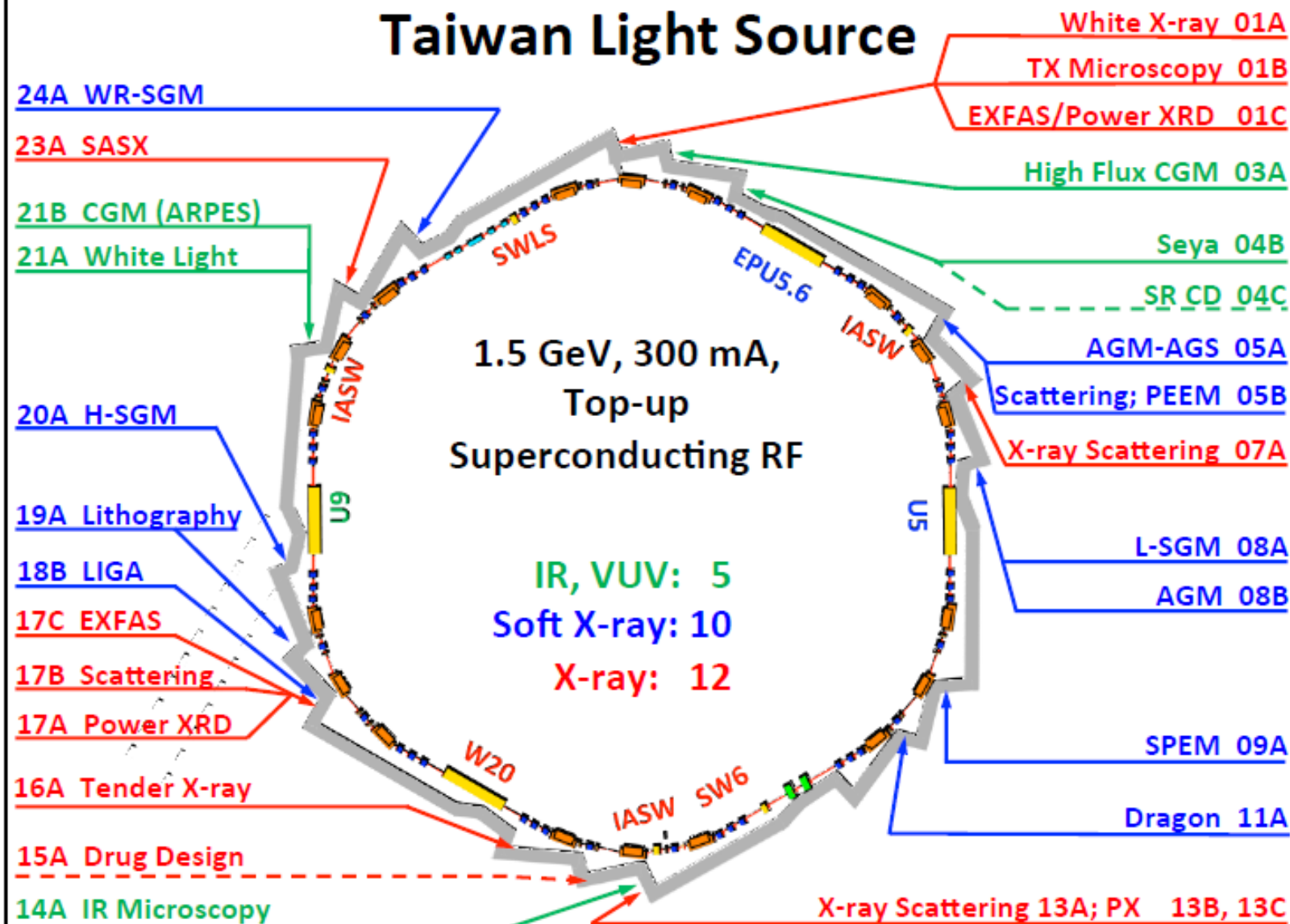
Accelerator Facility



TLS Experimental Hall



Taiwan Light Source



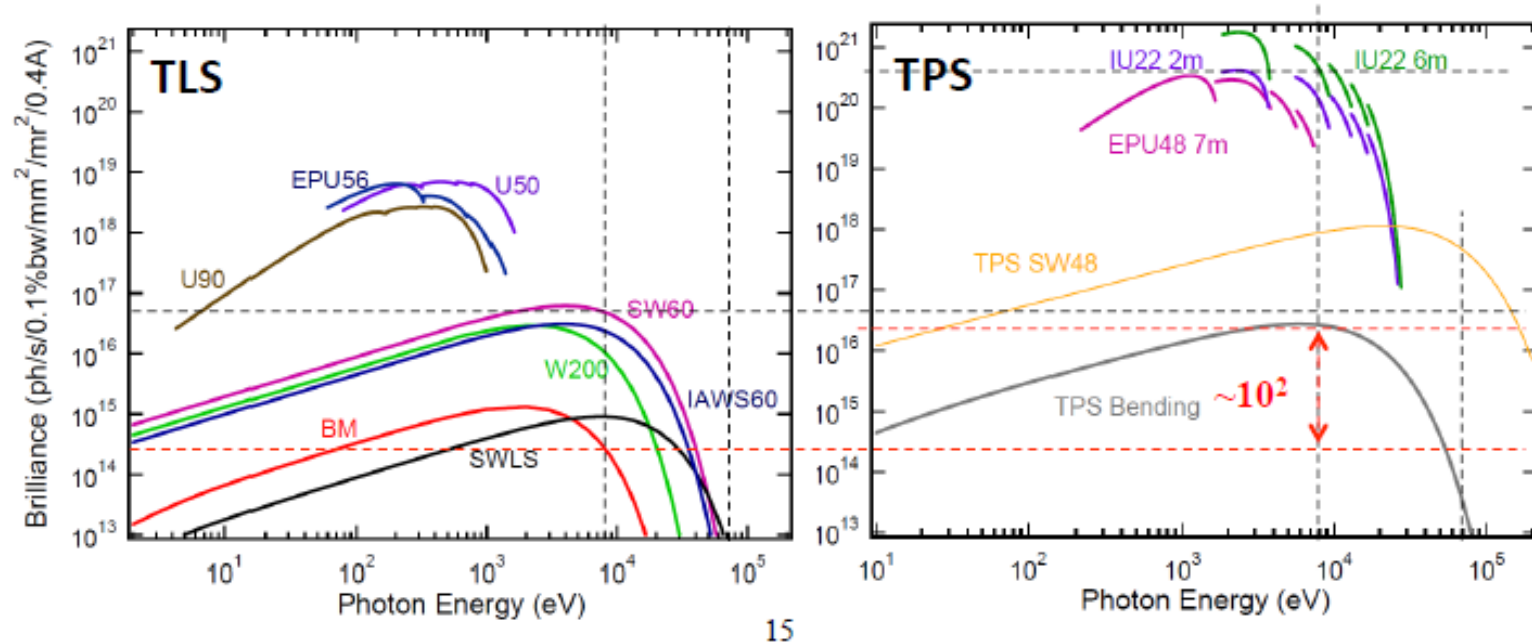
NSRRC is constructing a low-emittance synchrotron-based light source, Taiwan Photon Source (TPS)



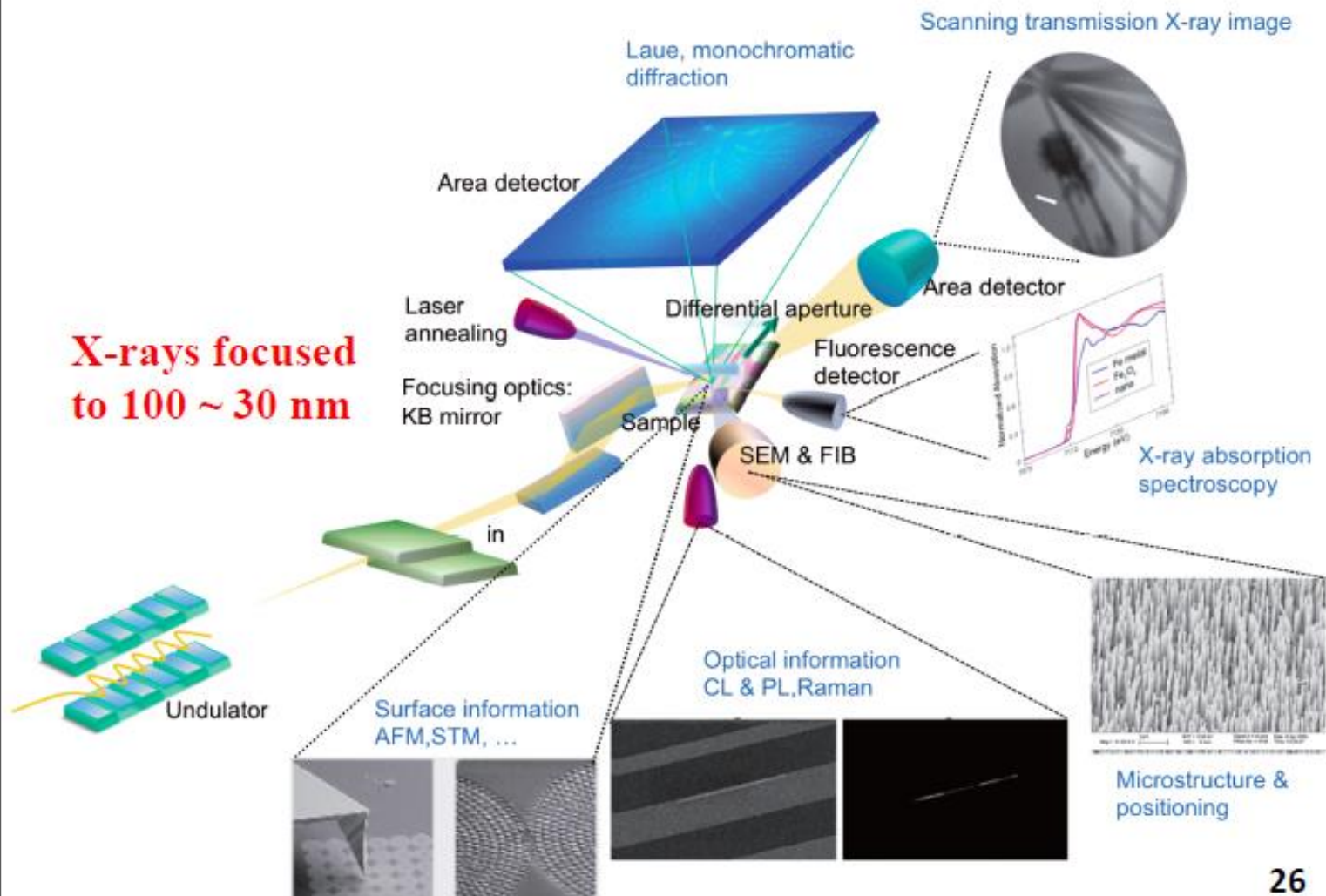
Comparison of Brilliance between TLS and TPS

The X-ray spectrum (photon energy 8 keV - 70 keV):
the brightness of bending magnet $>10^2$.

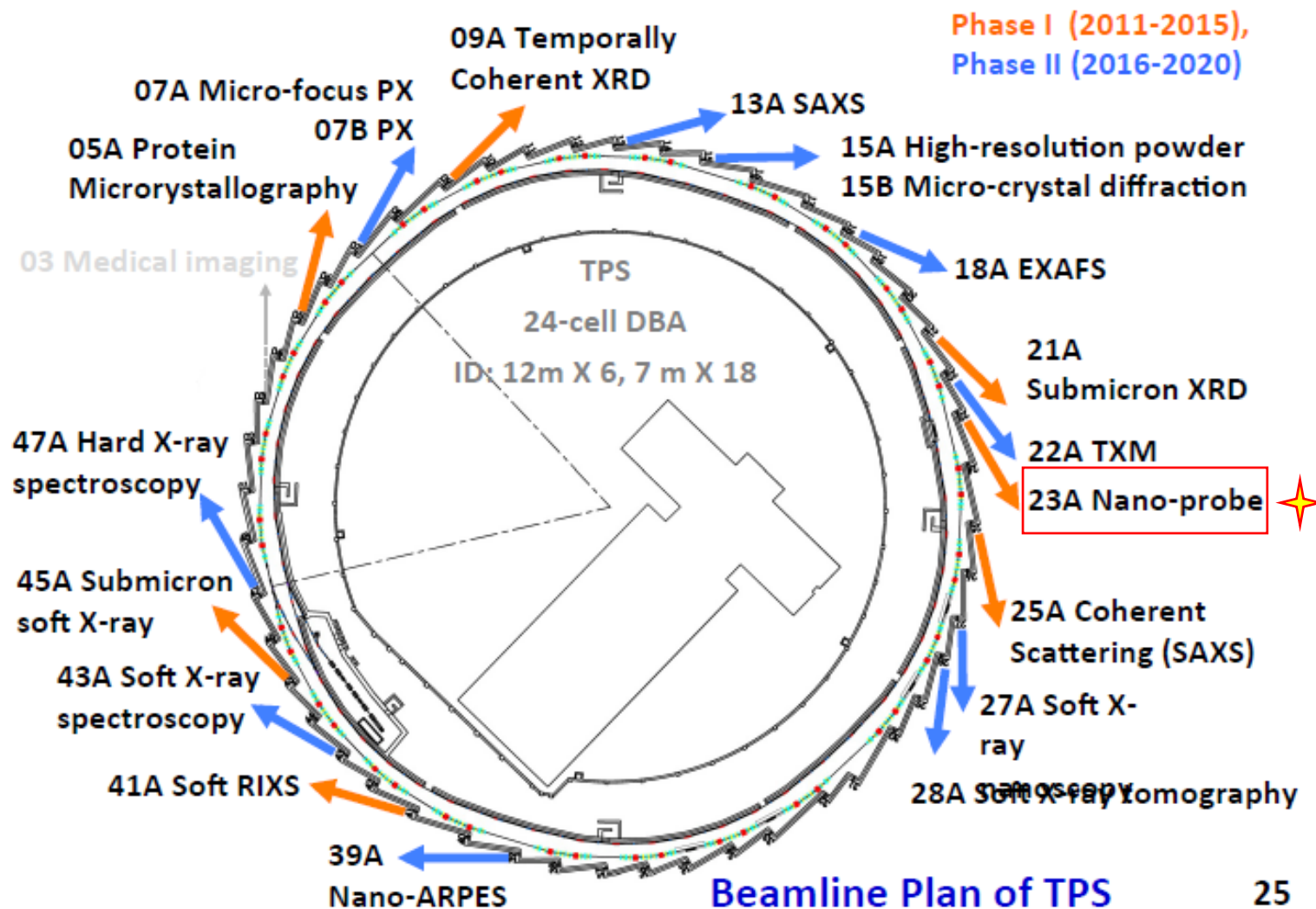
the brightness of IDs: 4~6 orders of mag.



TPS will brighten the future of scientific discovery.



The user operation of the TPS will begin in 2015.



Outline

- Synchrotron Light Source
- Application of Synchrotron Light
- X-ray nano probe at TPS

X-ray Methods:

With tens-nm resolution (incoherent)

TAIWAN TPS 23A

- nano-XRF (x-ray fluorescence)
 - Element-specific nanoimaging
- nano-XAFS (x-ray absorption fine structures)
 - Local electronic structure
 - Local chemical environments
 - Element-specific, averaged over nano-size area
- nano-XEOL (x-ray excited optical luminescence)
 - X-ray-to-visible down-conversion efficiency in nano phosphor
- nano-PXM (projection x-ray microscopy)
 - Absorption and phase contrast x-ray images

Beyond sub-ten-nm resolution (coherent)

- nano-CXDI (coherent x-ray diffraction imaging)
- Bragg-ptychography
 - strain dynamics in nano-devices

Other than X-rays

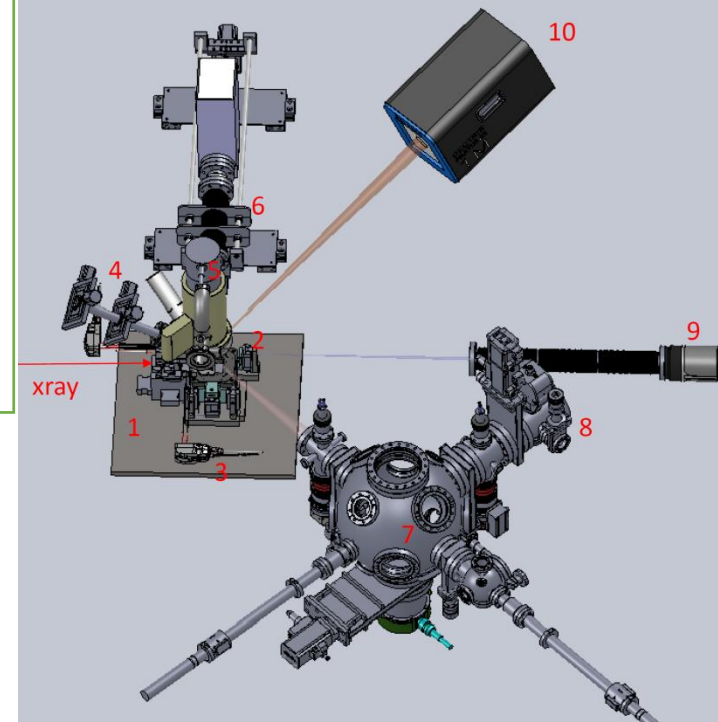
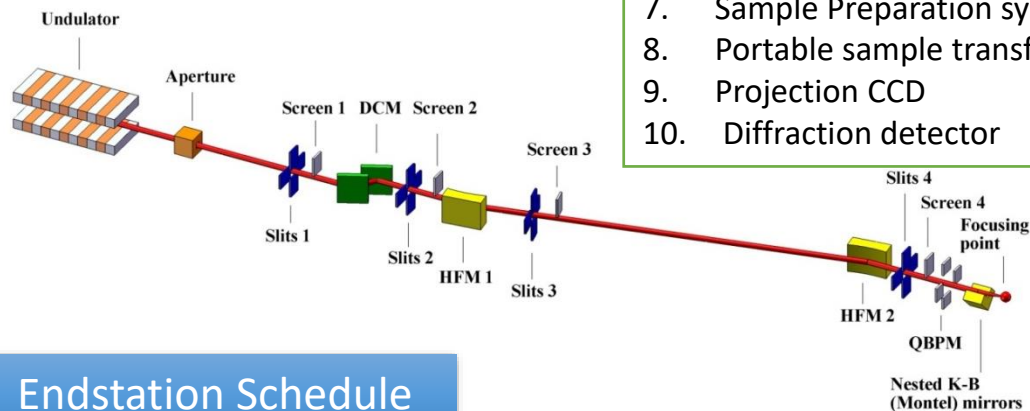
- SEM (SE, EDS, CL with high spatial resolution)
- Fly scanning
- Nanomotors (optional)
- Sample environment -heat, electric, L-He (optional)

Beamline specification

- ◆ Energy range : 4 - 15 keV
- ◆ Photon flux :
 $10^{10} \sim 10^{11}$ photons/sec
- ◆ Energy resolution :
 $< 2 \times 10^{-4}$ with Si(111) crystals
- ◆ Beam size :
 ~ 40 nm at 10 keV (H $\times$ V, FWHM)
- ◆ High-order harmonic contamination :
 $\leq 1 \times 10^{-4}$
- ◆ Energy scanning capabilities.

TPS 23A XNP

1. Montel mirror
2. Sample Stage
3. Laser interferometer
4. XEOL
5. SEM
6. EDS
7. Sample Preparation system
8. Portable sample transfer
9. Projection CCD
10. Diffraction detector



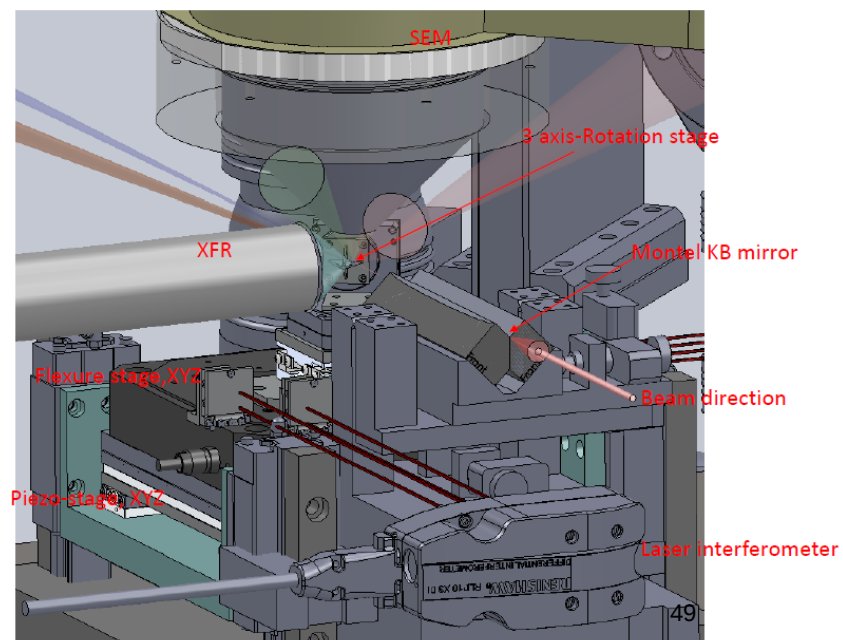
Endstation Schedule

Now

Beamline ready

Commissioning

	2014	2015	2016	2017
Electronics & interferometer system development				
Finish test chamber	Main chamber & support design	Main chamber fabrication		
user requirement	Stage design	Procurement of stage		
	Diffraction detector holder design	Procurement of holder		
	KB mirror & holder	Test of Montel KB		
	In-situ system (optional)	Procurement of Pilatus diffraction detector		
		Stage test		
		Optical table, support		
		Air conditions		
		Software development		
			CCD Detector	

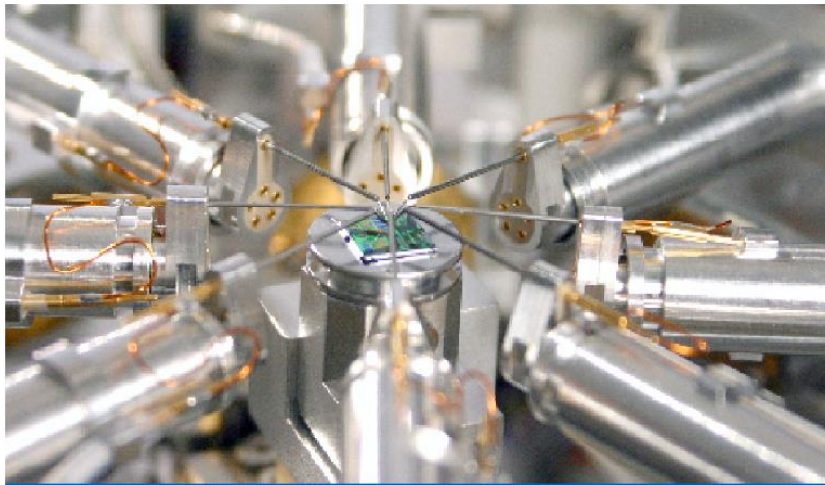


Nanomotor probe

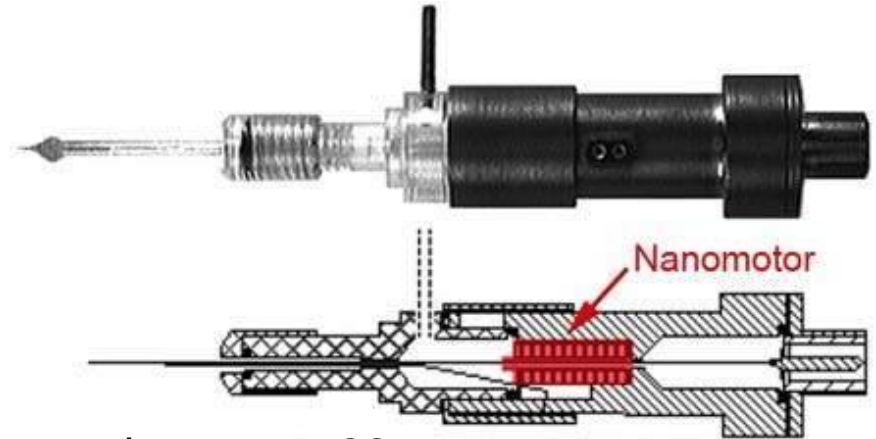
Cone Angle: 16.5° , Diameter: 25nm



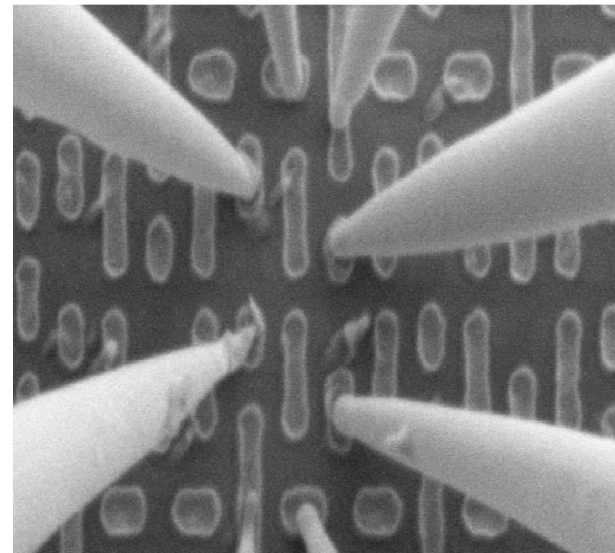
Cone Angle: 5.4° , Diameter: 6nm



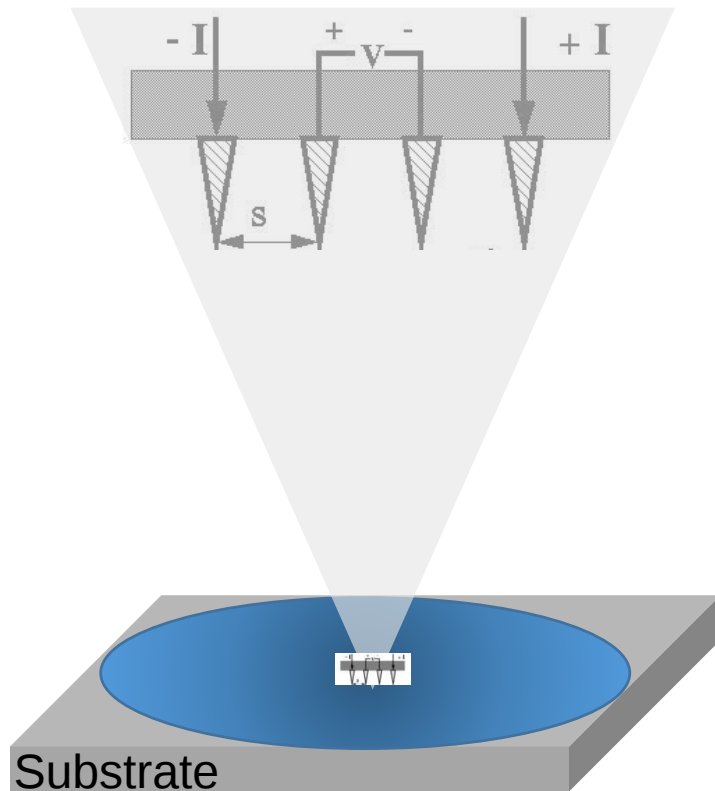
NT:600,000



Moving 5nm-100um

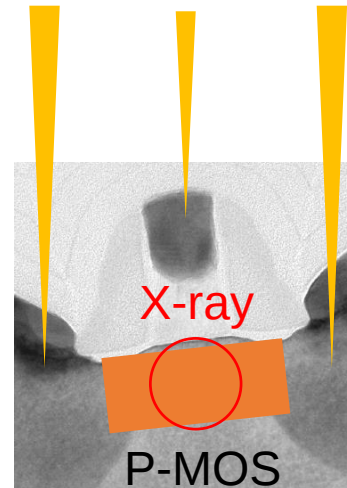


Nanomotor Probe Application

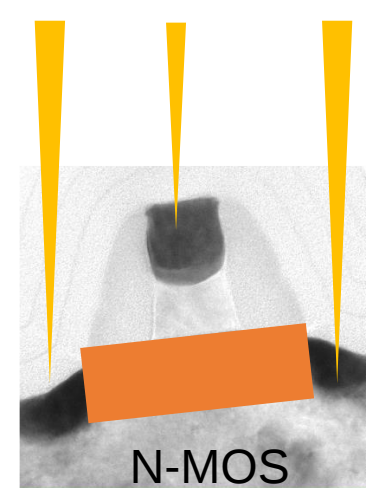


Nanometer can construct
the 4-point probe

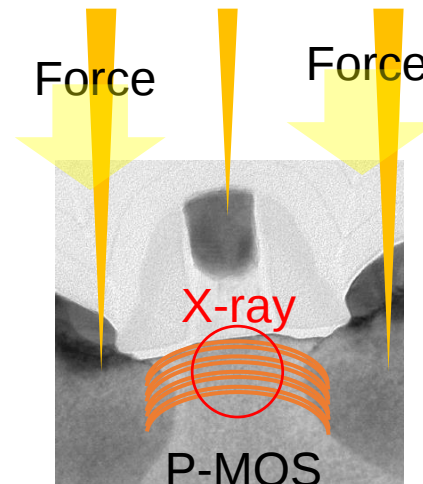
I-V measurement



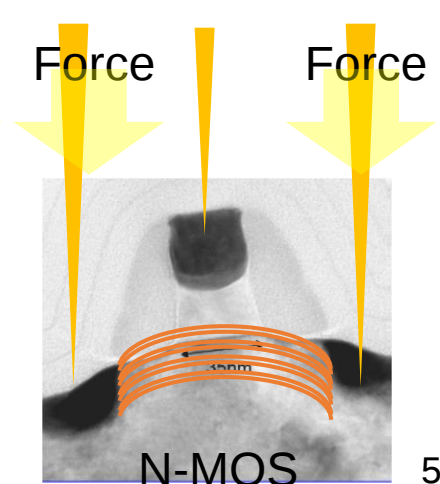
I-V measurement

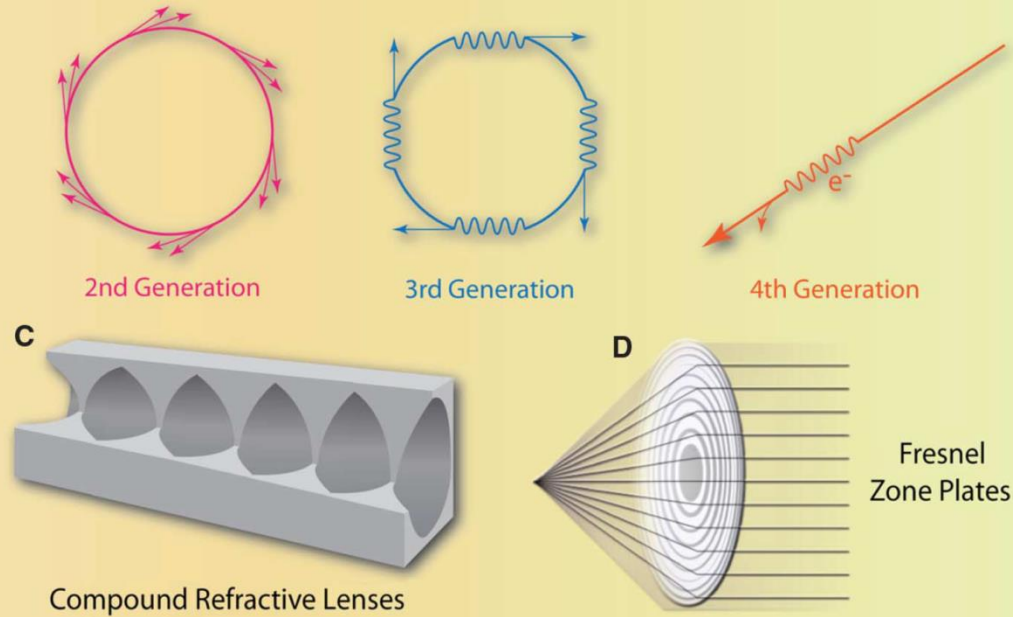
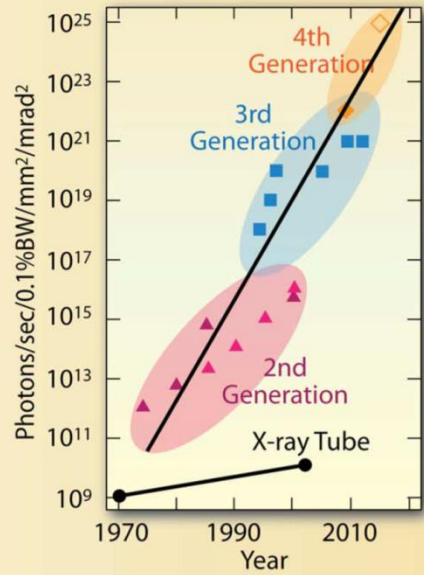
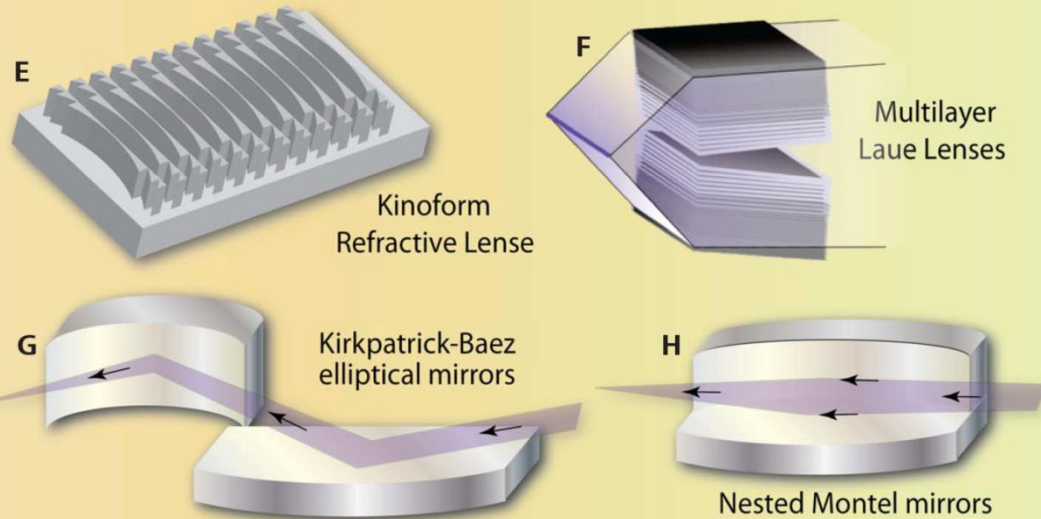
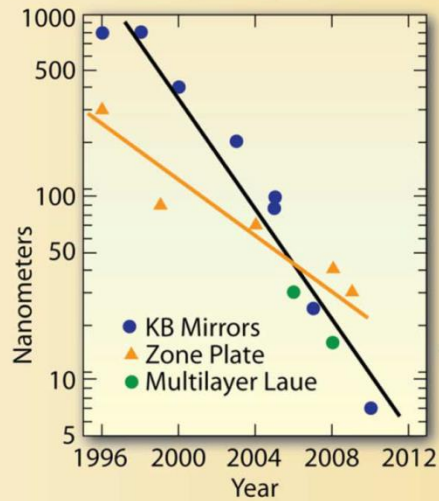


I-V measurement



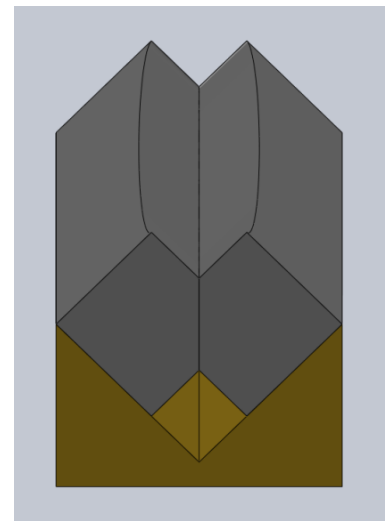
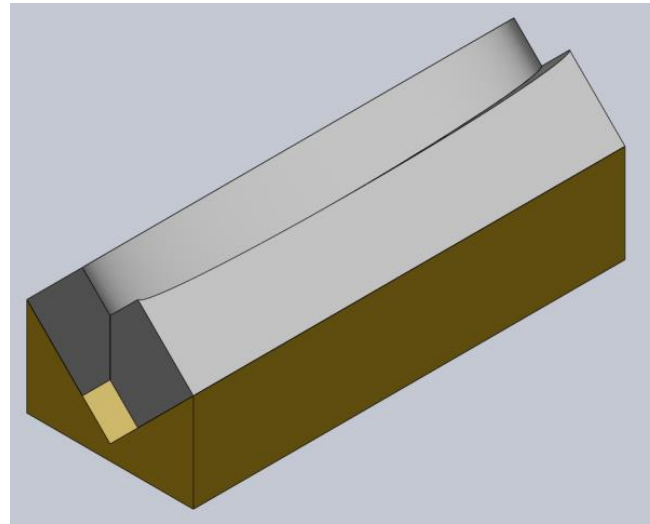
I-V measurement



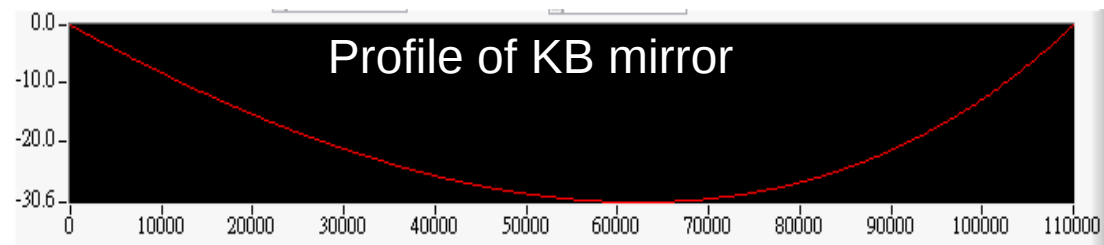
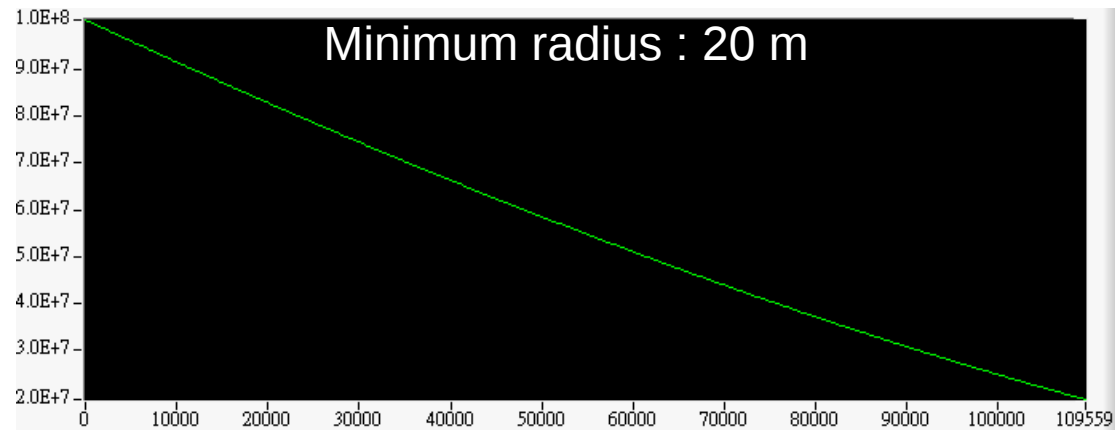
A Time-average 10 keV X-ray Brilliance**B** 10 keV Spot Size

Montel Nested KB Mirror @TPS-23A

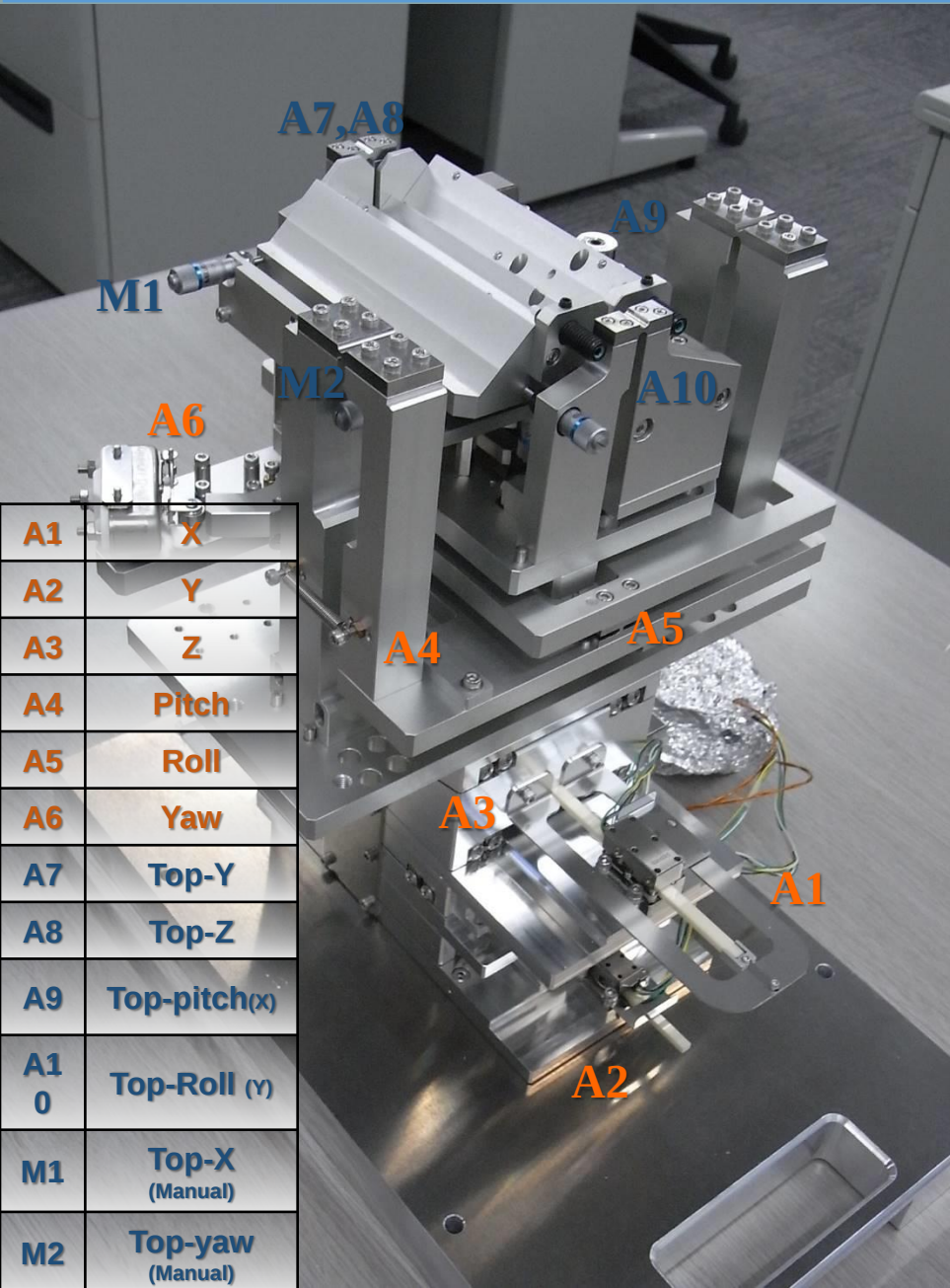
- **Montel nested KB mirror @ APS:**
 - Focal spot: 100 nm
 - **Challenges:**
 - Gap between mirrors
 - Slope error
- Overcome by **Elastic Emission Machining (EEM)**
- **Montel nested KB mirror @ TPS:**



Objective distance	69 m
Focus length	11 cm
Mirror length	11 cm
Slope error (RMS)	< 0.05 μ rad
Incident angle	4 mrad
Coating	Rh
Material	silica
Working Distance	5.5 cm



Montel KB Montel Mirror and Holders



Montel Mirror on the holder



Gap imaged by microscope

June 2015, at JTEC

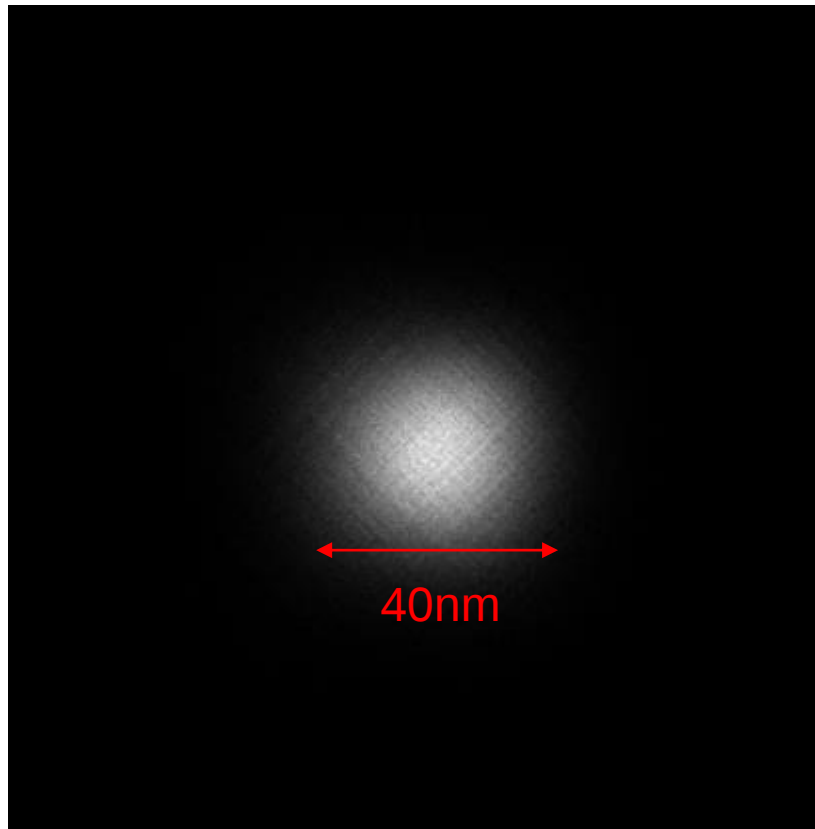
Simulation of Focus Spot

Simulation at 10 keV, average reflection=0.802, by ray tracing

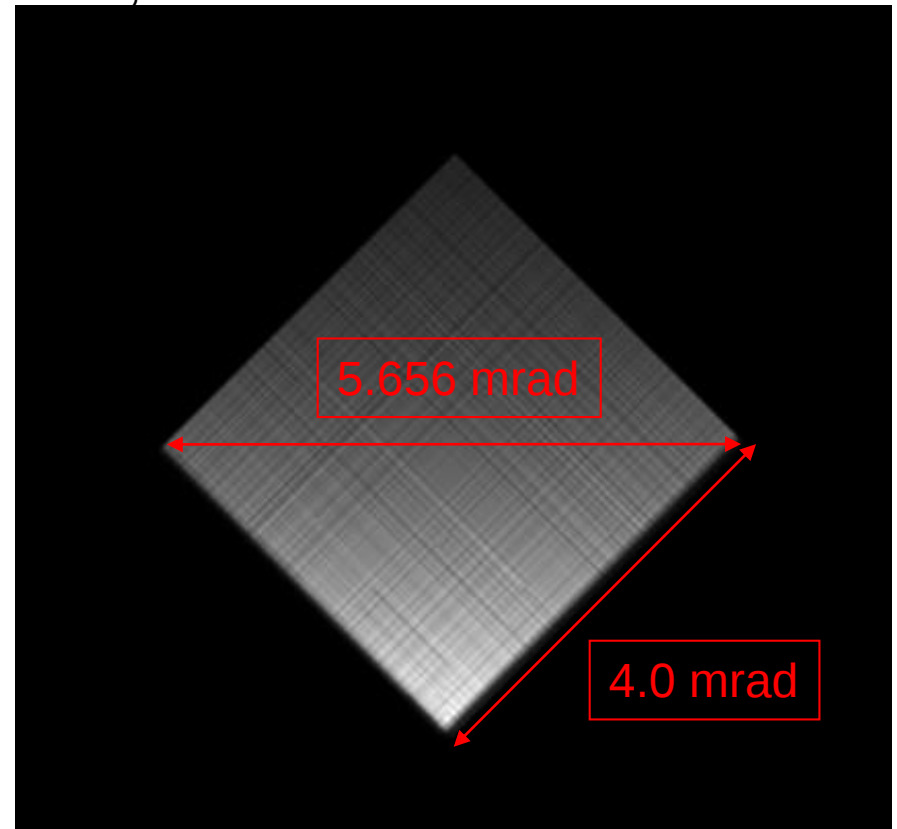
Source size 12.5 μm x 12.5 μm

Source divergence 6 μrad x 6 μrad

FHWM 32nm x 32nm,



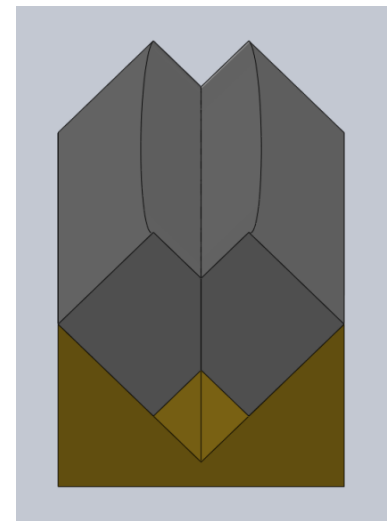
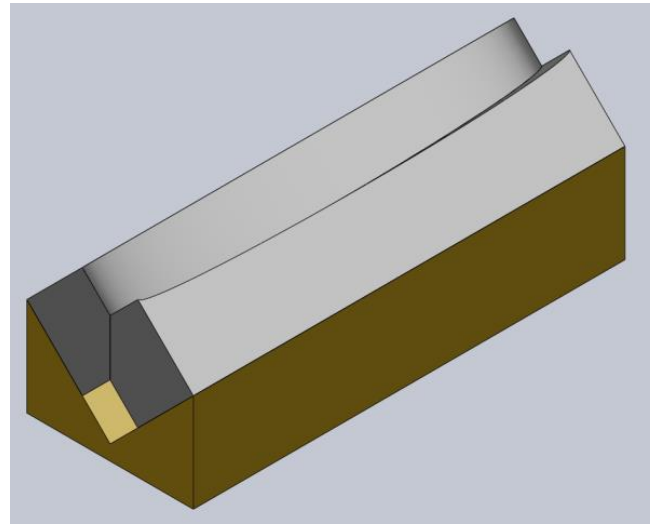
Simulated
Focus spot size



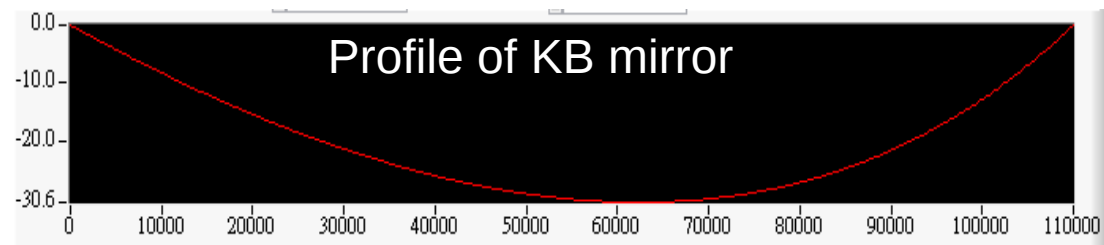
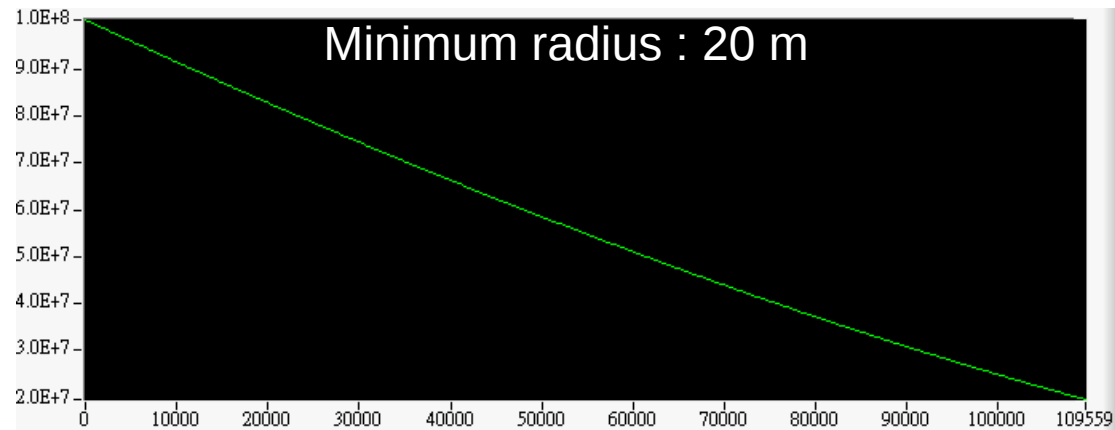
Simulated
Divergence
By Gung-Chian Yin

Montel Nested KB Mirror @TPS-23A

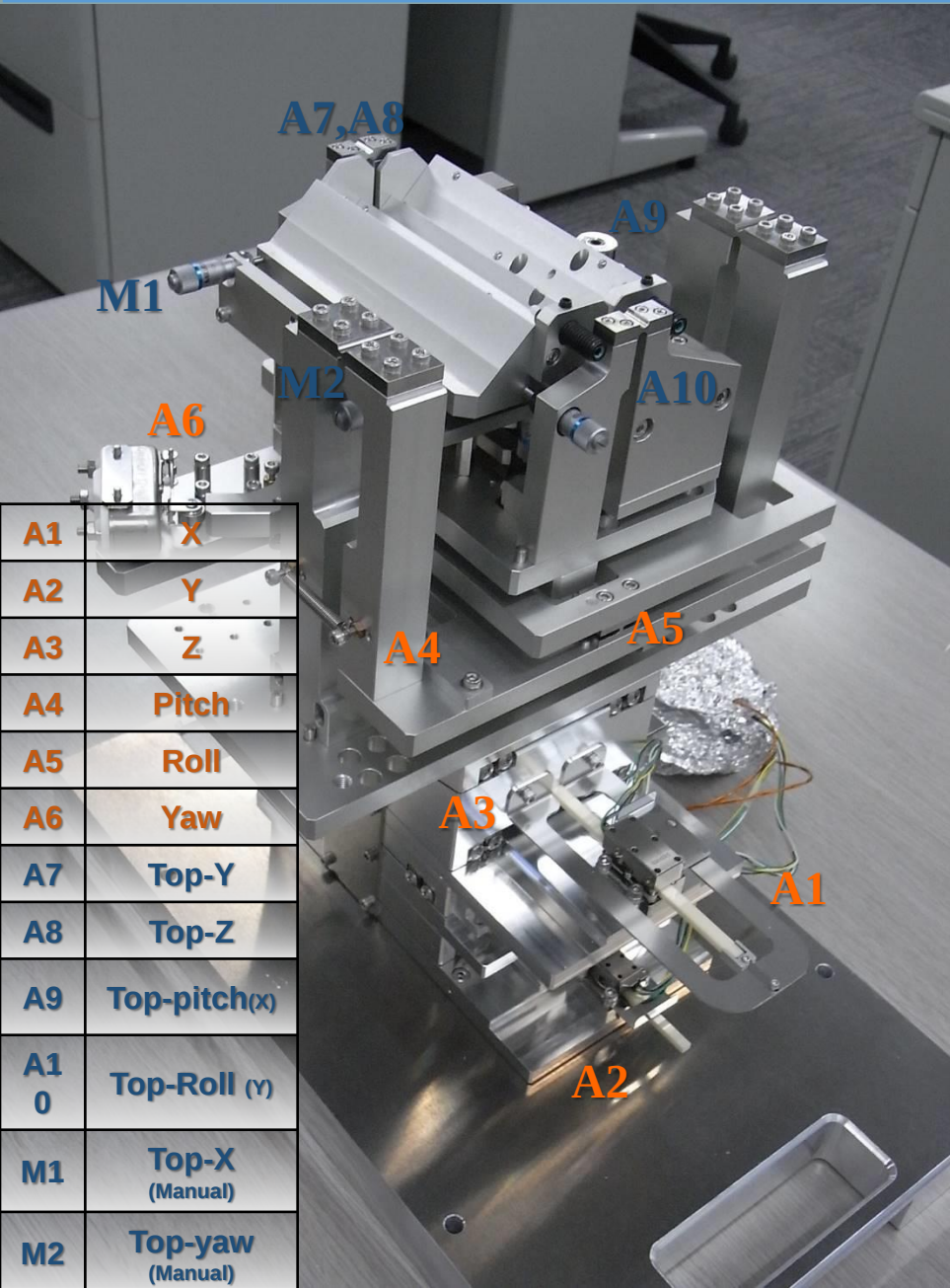
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Montel KB Montel Mirror and Holders

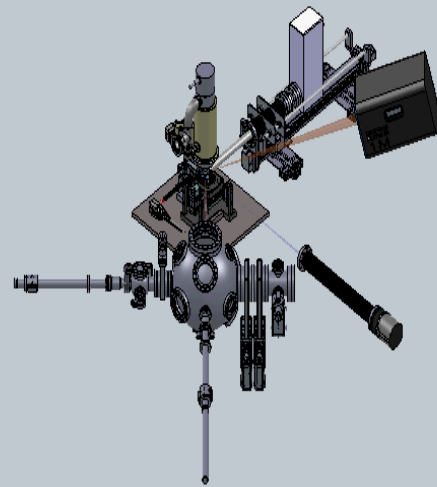


Montel Mirror on the holder



Gap imaged by microscope

June 2015, at JTEC



nano-XRF (x-ray fluorescence)

Element-specific nano-imaging

Doping of ZnO NWs by transition metal Co.

Application : [Spintronic device](#)

Want to know:

- Distribution
- Short structure order
- Elemental composition

Vapour-liquid-solid process

Nano Lett. 2011, 11, 5322–5326

Doping method:

Ion implantation

and thermal annealing

Elemental map of XRF

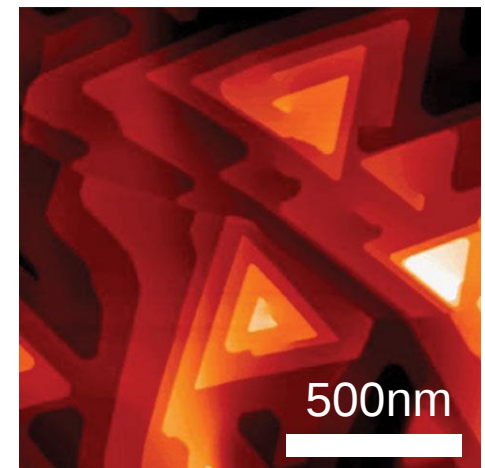
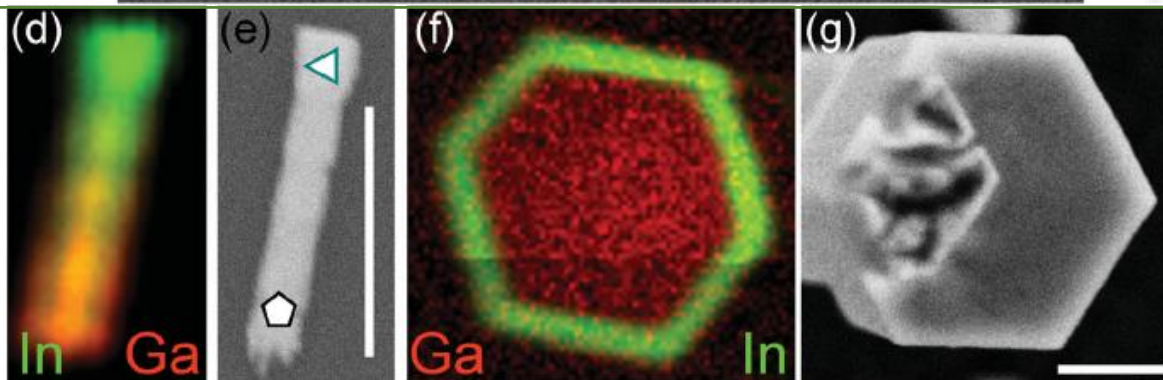
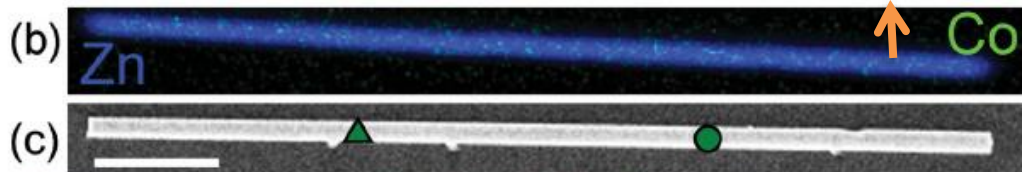
SEM

➤ Pink beam mode at 12 KeV

➤ Pixel size : $25 \times 25 \text{ nm}^2$

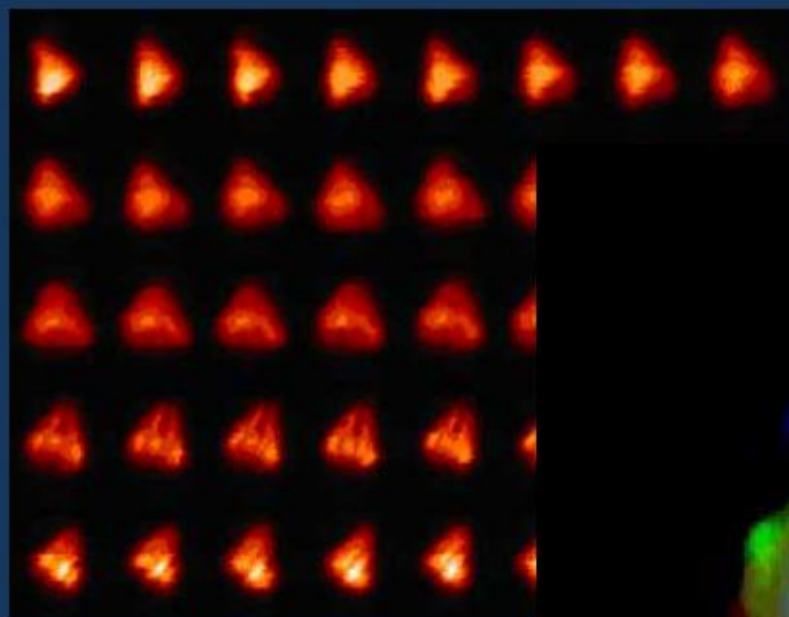
➤ Accumulation time : 0.5 sec/point

➤ beam size : $60 \times 60 \text{ nm}^2$ (V x H)

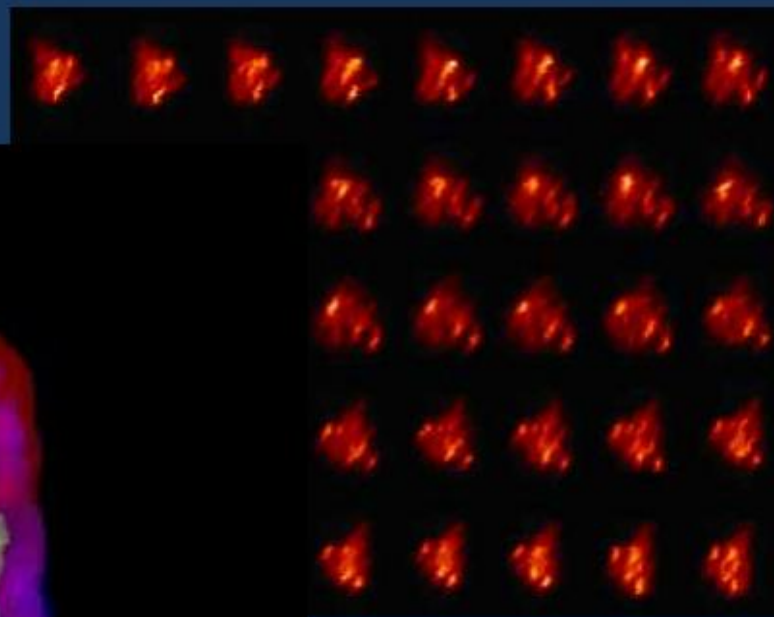


High resolution XRF tomography

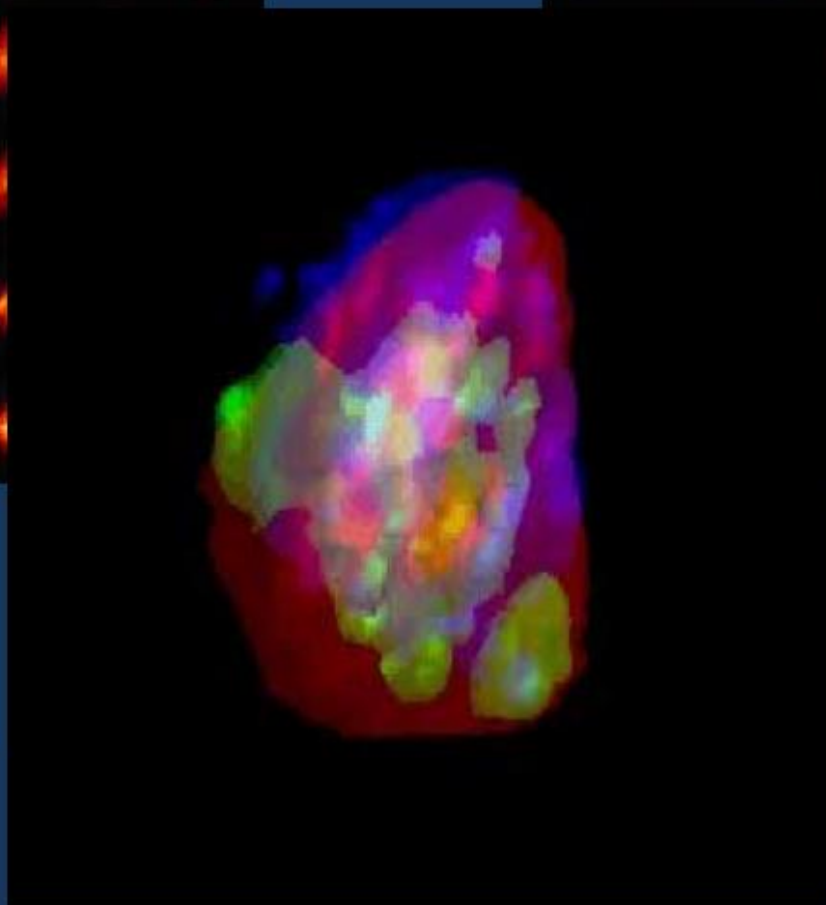
Pixel size: 100 nm, sample rotation 0-180° (4.5° / image)



Fe



Cr

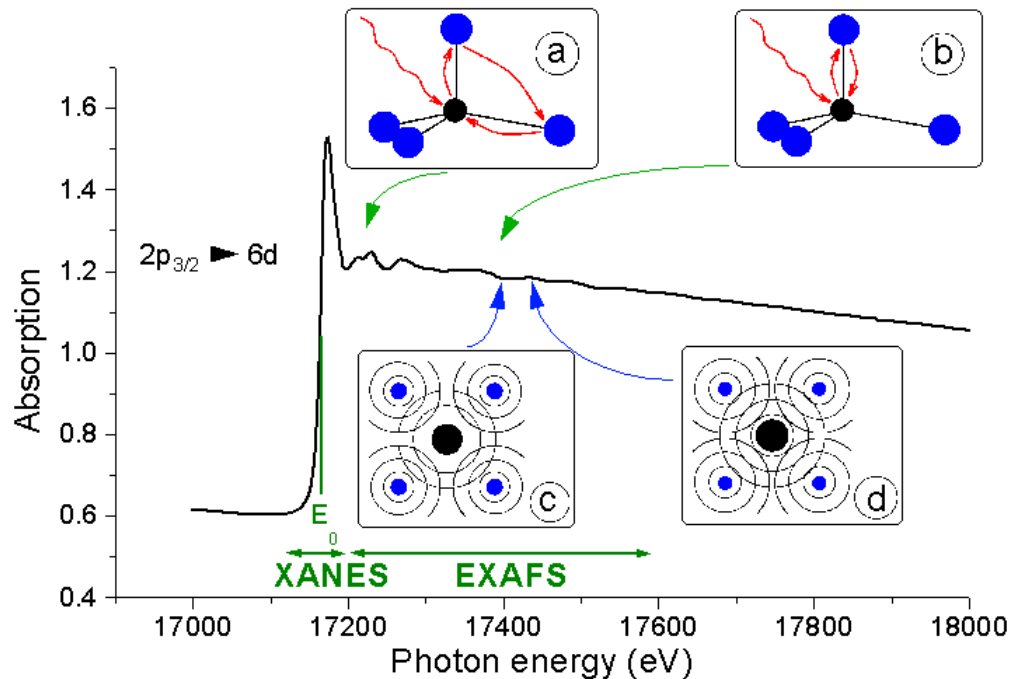
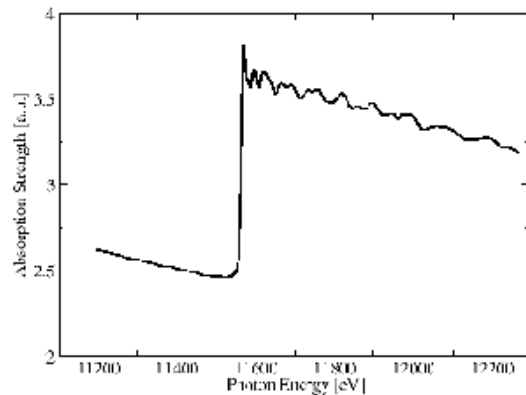
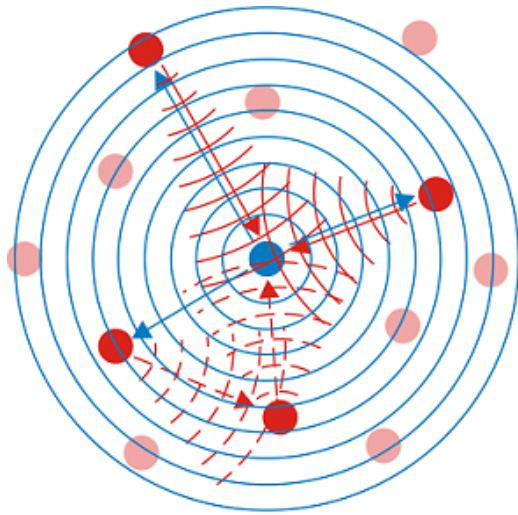


Composite
Fe-Cr-Se

Silversmit *et al.*, *Anal. Chem.* 81 (2009)

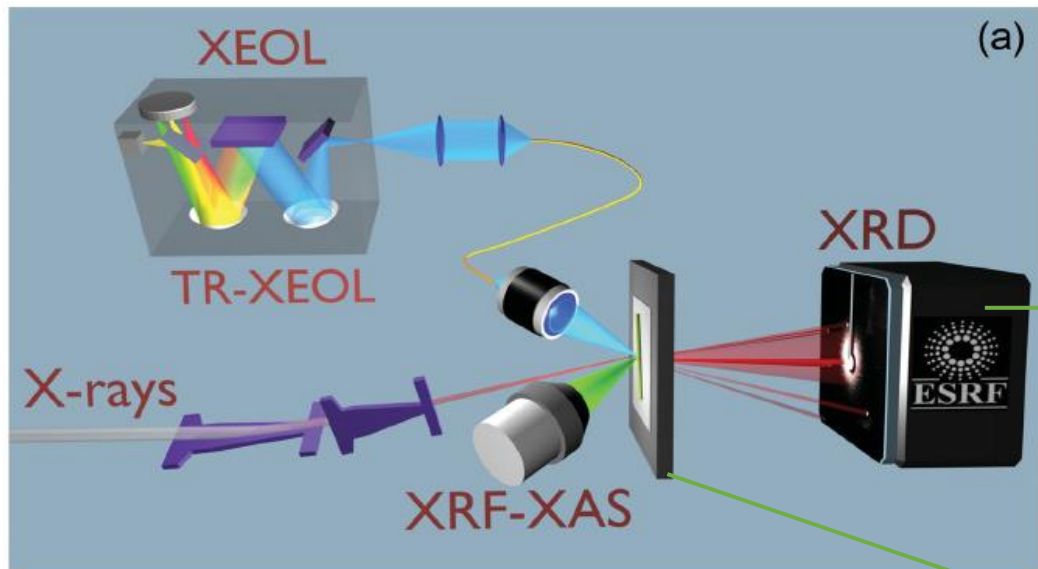
nano-XAFS (x-ray absorption fine structures)

- Local electronic structure
- Local chemical environments
- Element-specific, averaged over nano-area



XEOL

- Multimode optical fiber
- UV-VIS : linear CCD Si detector
- Si avalanche photodiode (id100 from id-Quantique)



XRF

- XRF signal was collected at 15°
- The elemental composition of the NWs was estimated by fitting the XRF spectra using the [PyMca](#) program.
- XANES spectra were recorded in X-ray fluorescence mode with a step size of 1 eV and integration times determined by the counting statistics.
- The data analysis was performed using the IFEFFIT package.

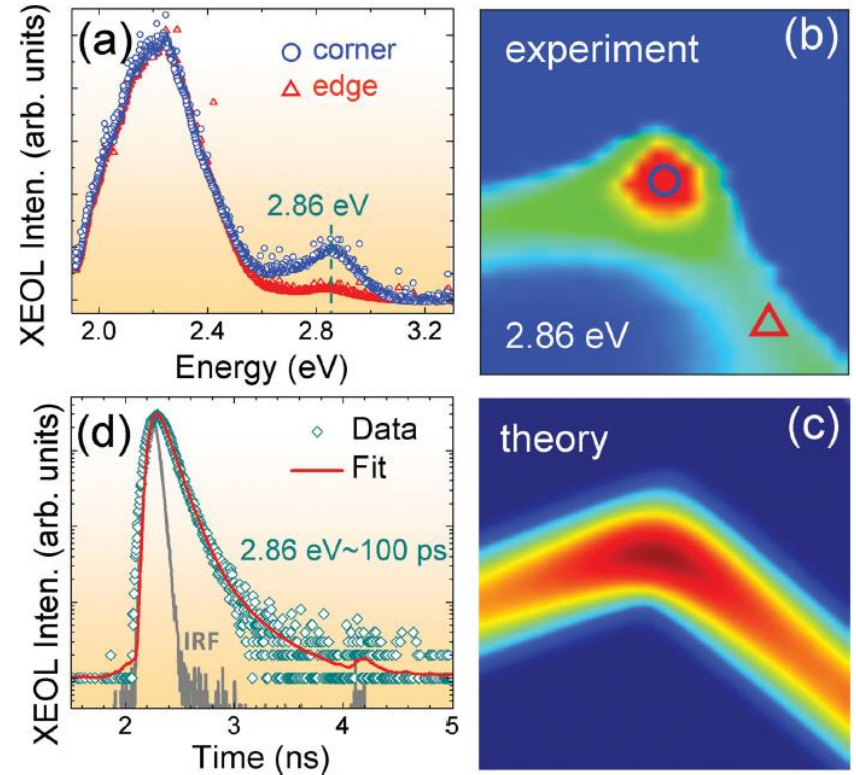
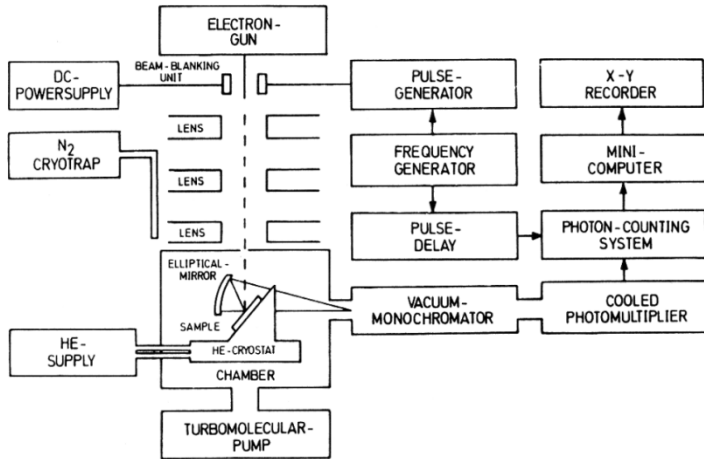
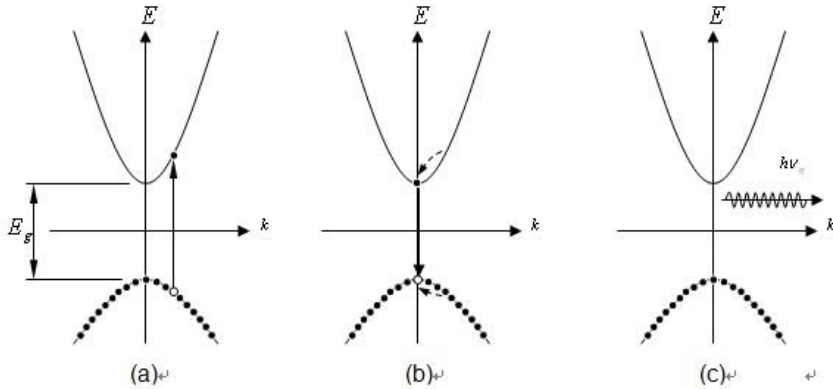
ESRF ID16B methods

XRD

- The XRD signal was measured using a fast readout low noise (FReLoN) CCD detector.
- The CCD images were processed using Fit2D software to generate the standard diffractograms.
- Using the experimental parameters derived from the measurement of an Al_2O_3 reference sample.

- 200 nm thick SiN membranes.
- Without XRF background signal
- X-ray diffraction can be transmitted

**nano-XEOL (x-ray excited optical luminescence) &
CL (cathodoluminescence)**

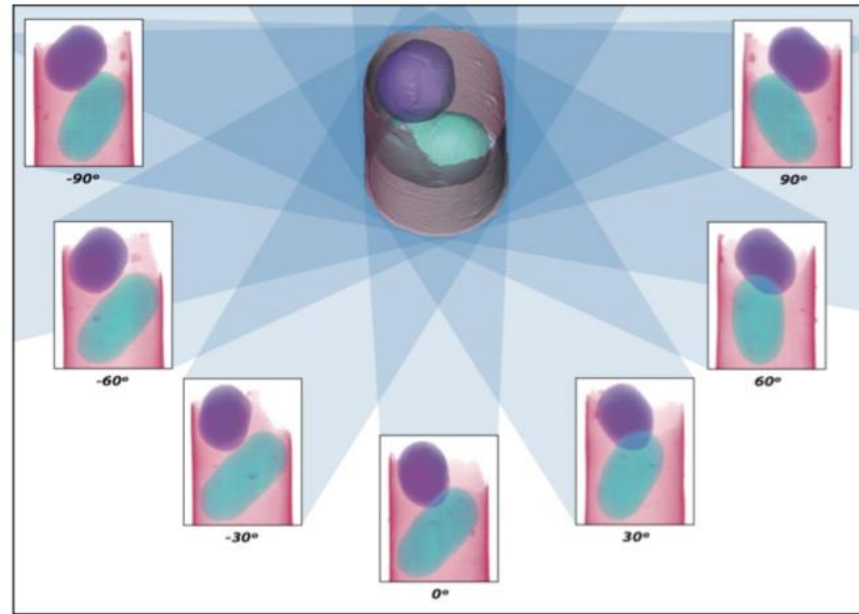
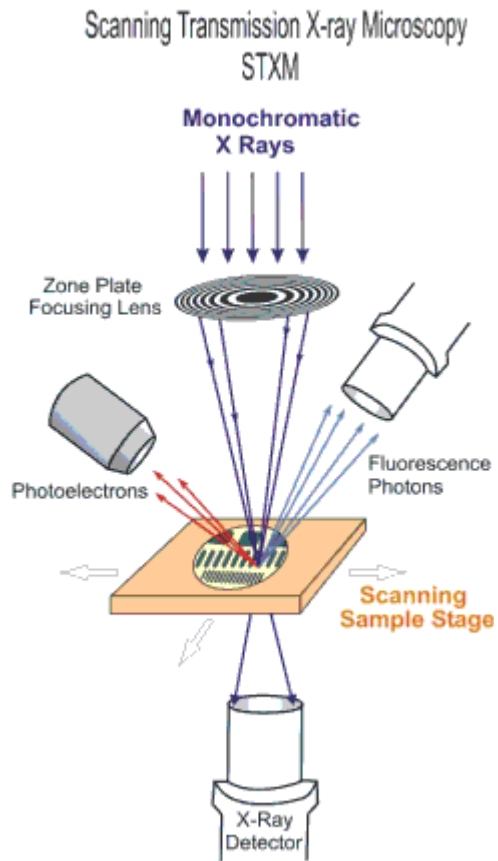


XEOL: 1.nano-area
2.multi-layer, buried layer

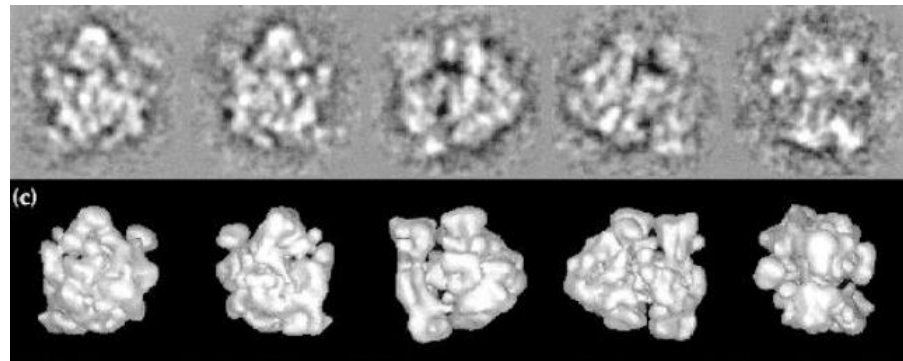
Doping species, Band gap, Defect band,
Charge transport

nano-PXM (projection x-ray microscopy)

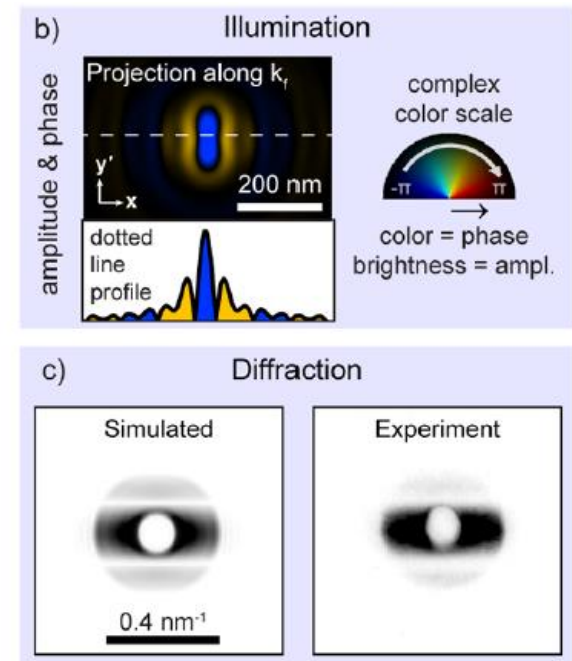
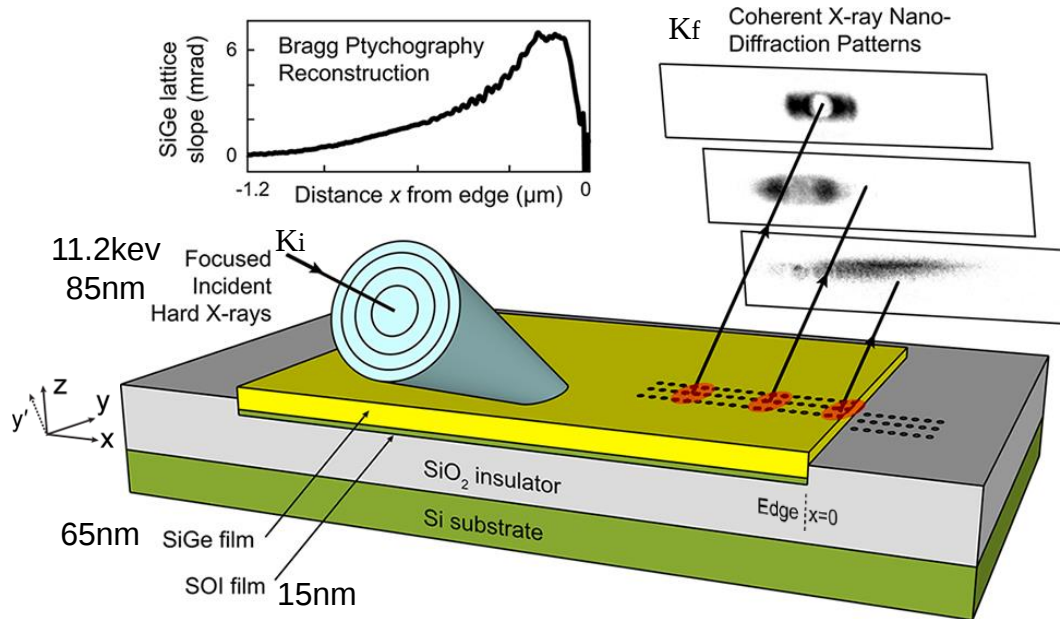
– Absorption and phase contrast x-ray images



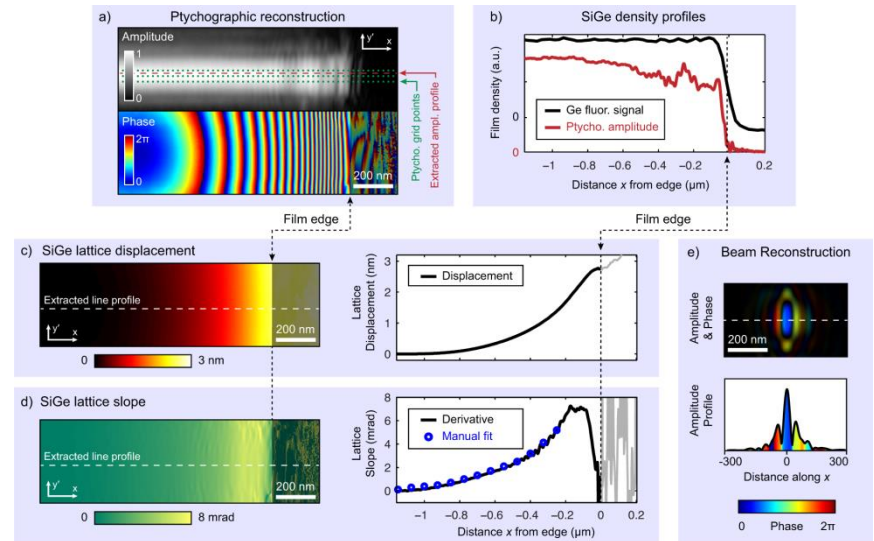
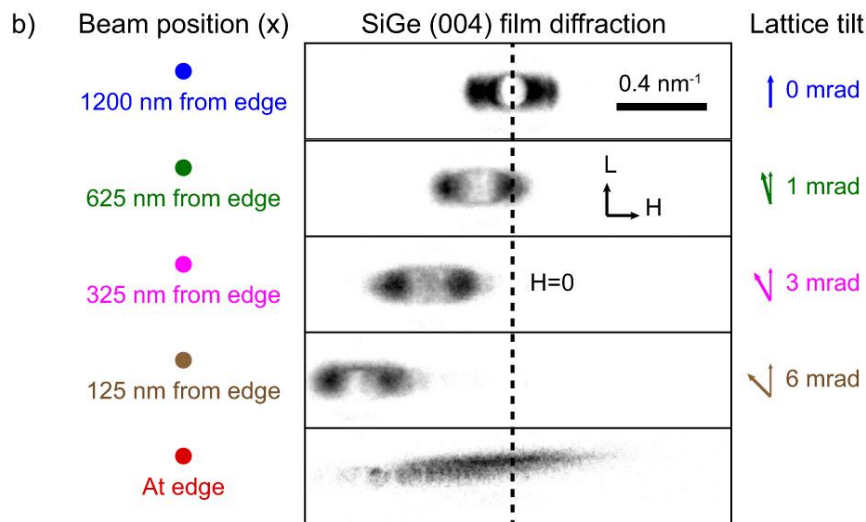
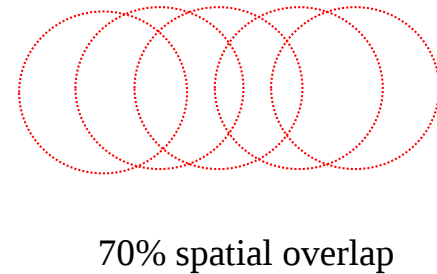
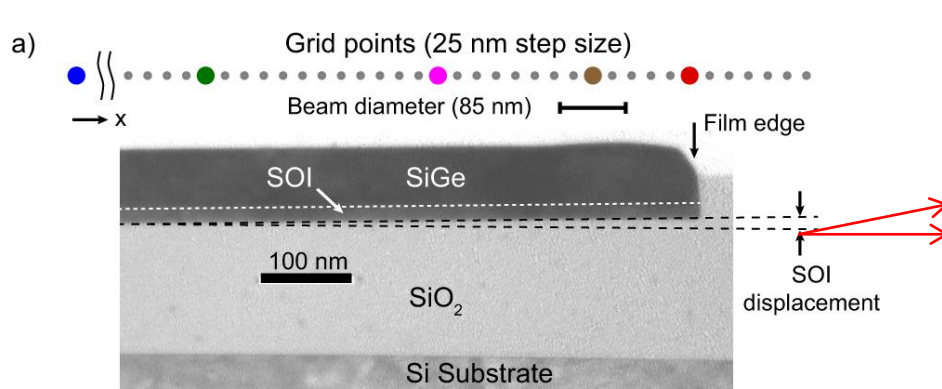
TRENDS in Cell Biology



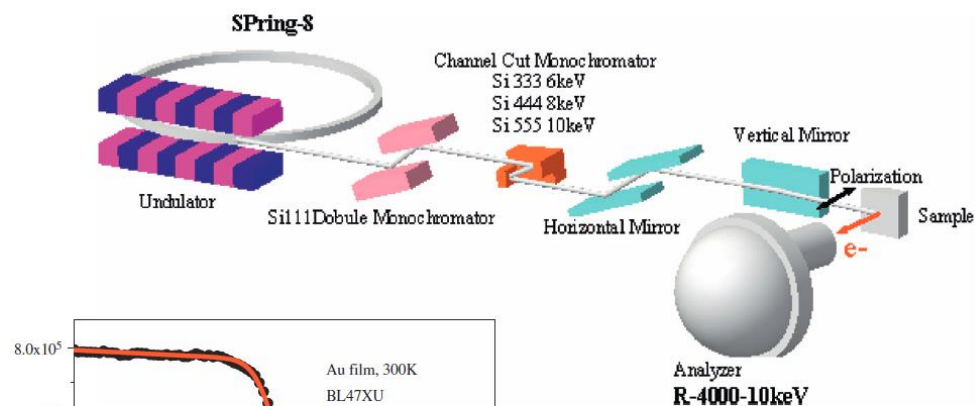
X-ray Bragg projection ptychography from thin film heterostructures



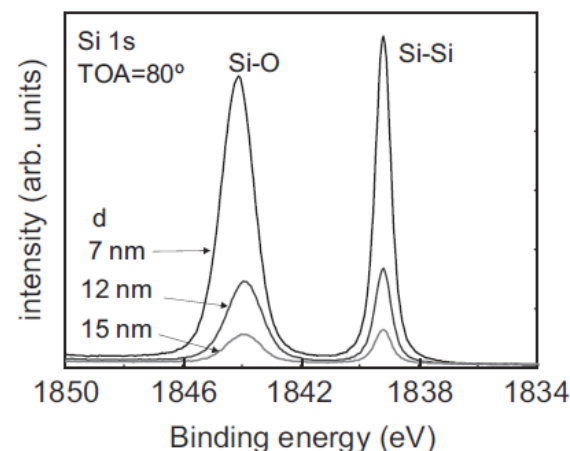
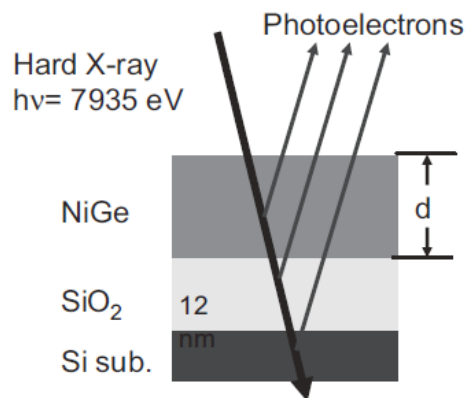
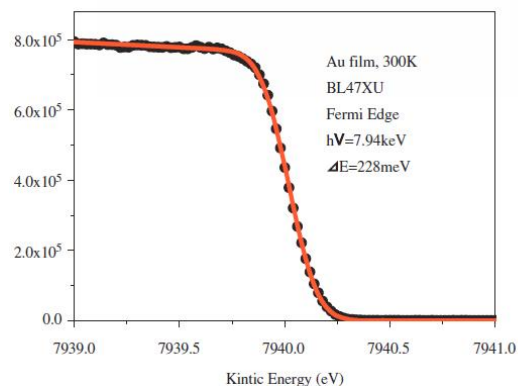
Focused beam Bragg diffraction near the device edge



Upgrade: Hard X-ray photoelectron spectroscopy(HXPS) at XNP



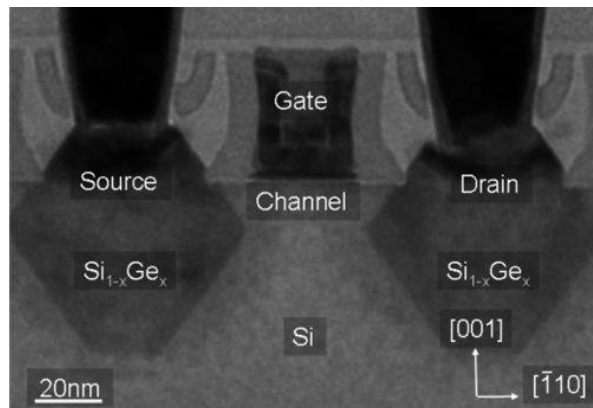
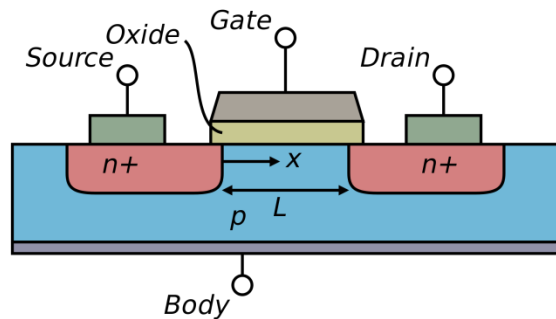
HXPS: Several keV to 15 keV to increase bulk sensitivity for bulk electronic structure and buried interface.



Applications

Solid state physics

- Strongly correlated electron systems
YbAl₃, YbInCu₄, YbCu₂Si₂
La_{1-x}Sr_xMnO₃ (LSMO)
- Spintronics
LaVO₃, LaAlO₃, Fe_{3-x}M_xO₄ (M=Mn, Zn)
- Compound semiconductors
InGaZnO, GaCrN, InN, ZnMgO



M. Chu, *et al.*, *Annu. Rev. Mater. Res.*
39 (2009) 203-229

High-k gate stacks

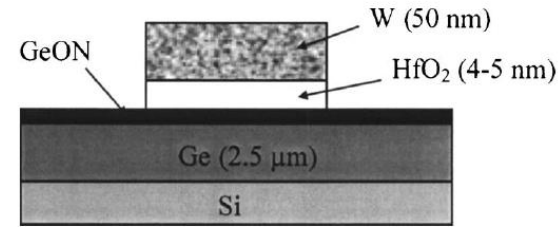


FIG. 1. Diagram of the W/HfO₂/GeON/Ge stack.

