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X-ray Nano Probes for Nano Materials

Tseng, Shao-Chin

2015/3/6

Outline

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

“Light” is indispensable to man‘s exploration of nature.

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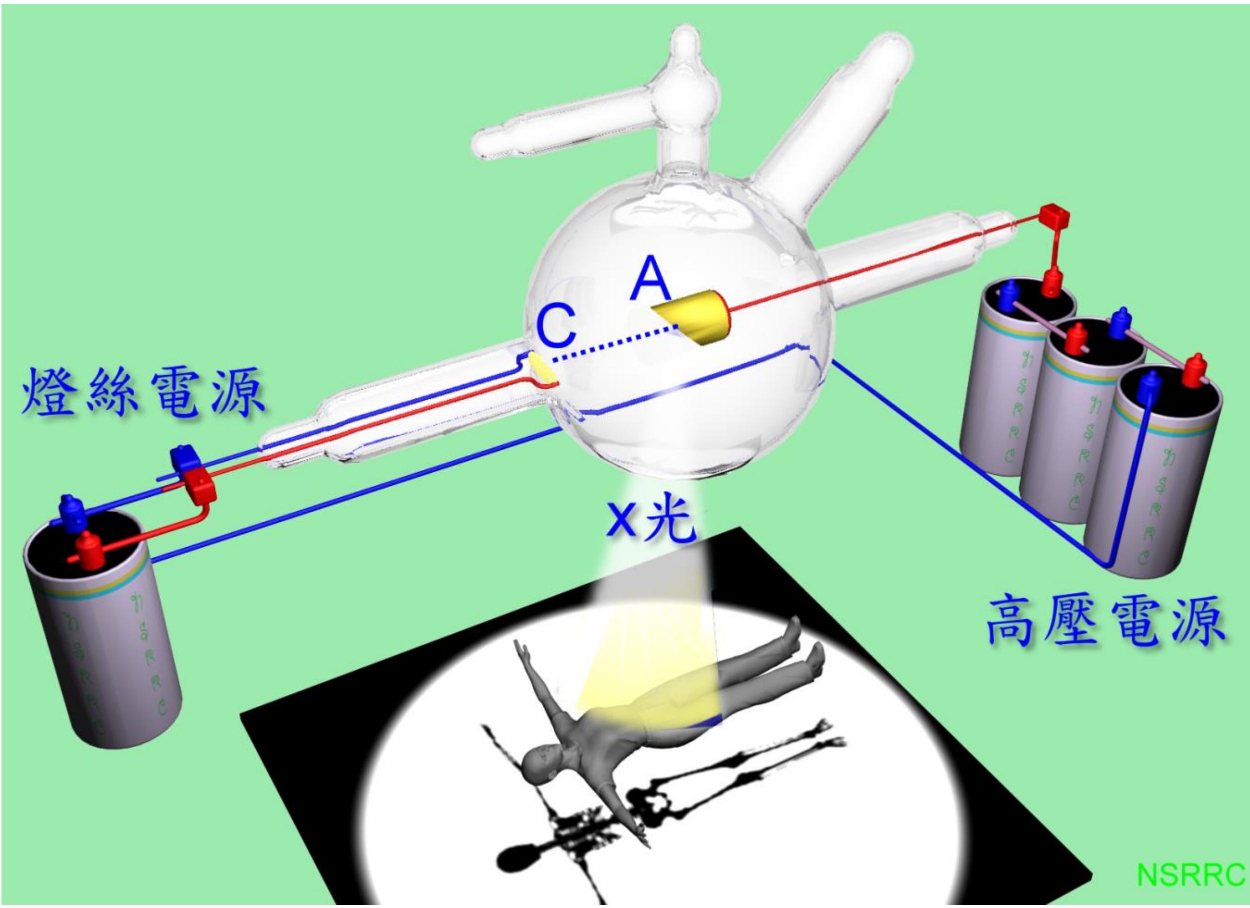
Rontgen used a simple accelerator to discover X-rays



1895

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

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

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http://snallabolaget.com/?page_id=666

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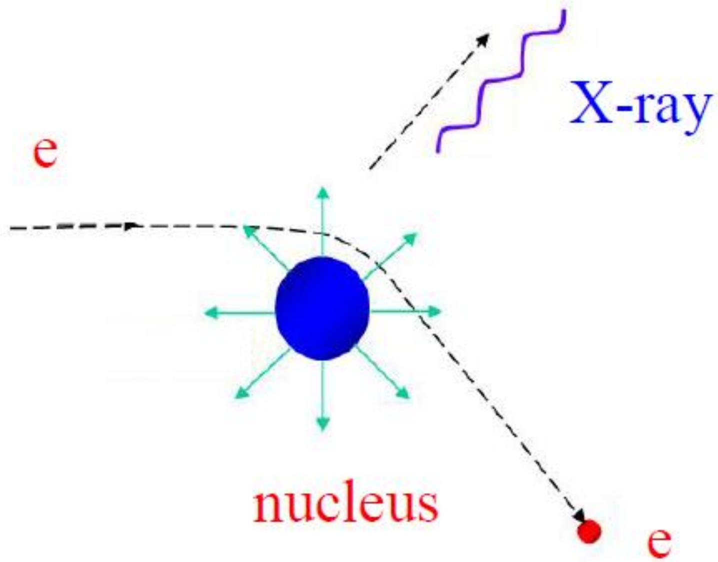
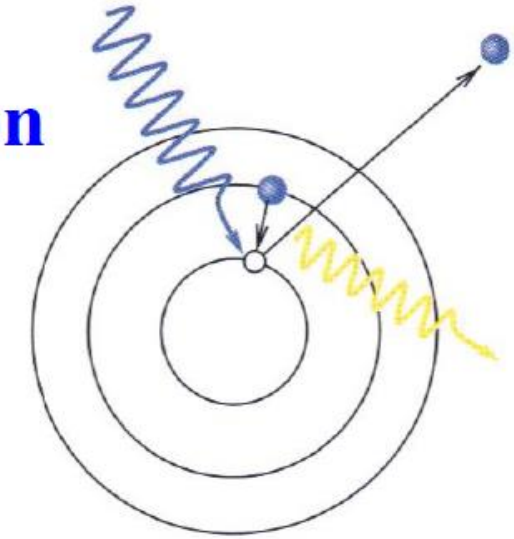
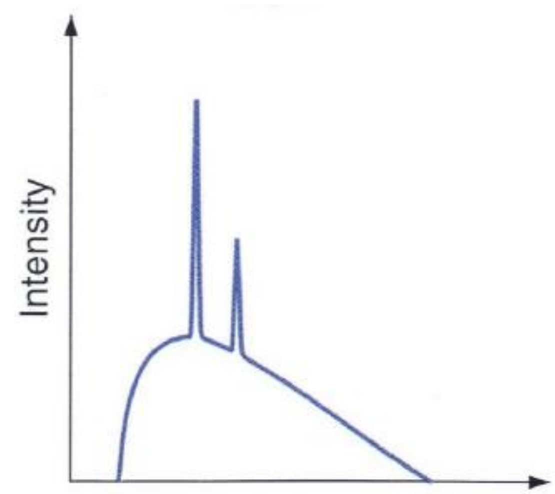
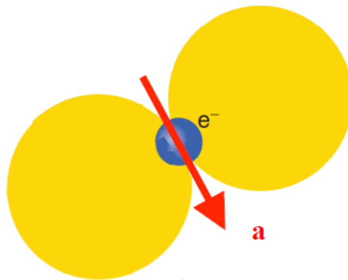
Characteristic X-ray emission



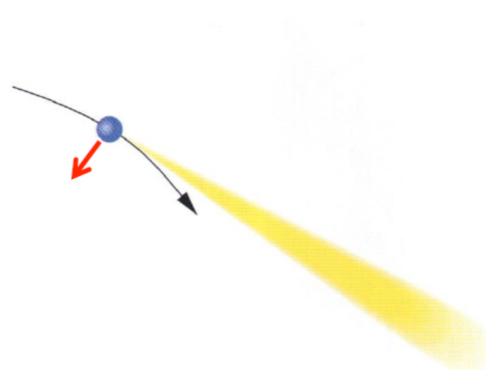




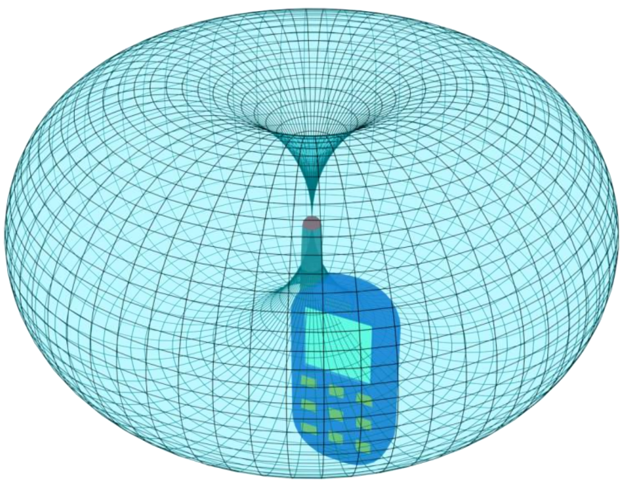
Electromagnetic wave from a moving charge

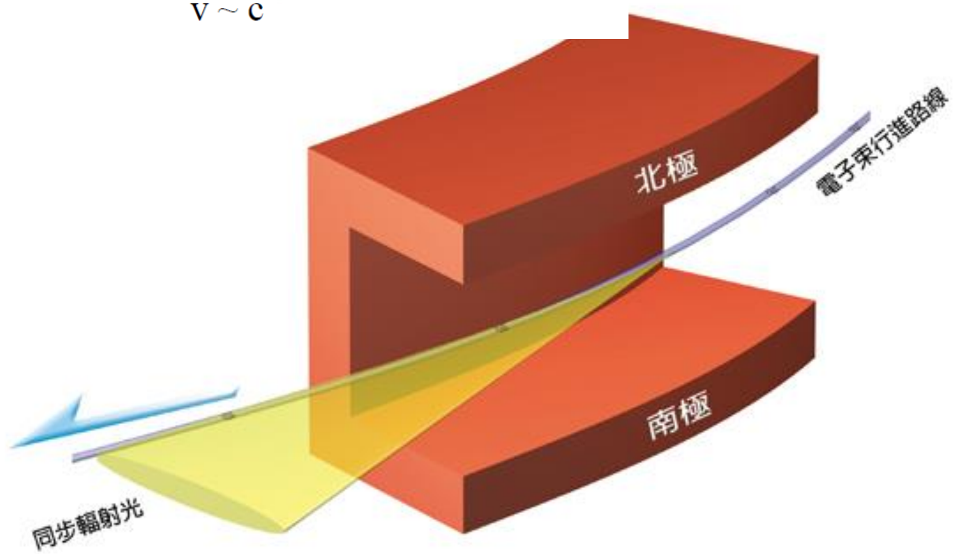


v << c



v ~ c

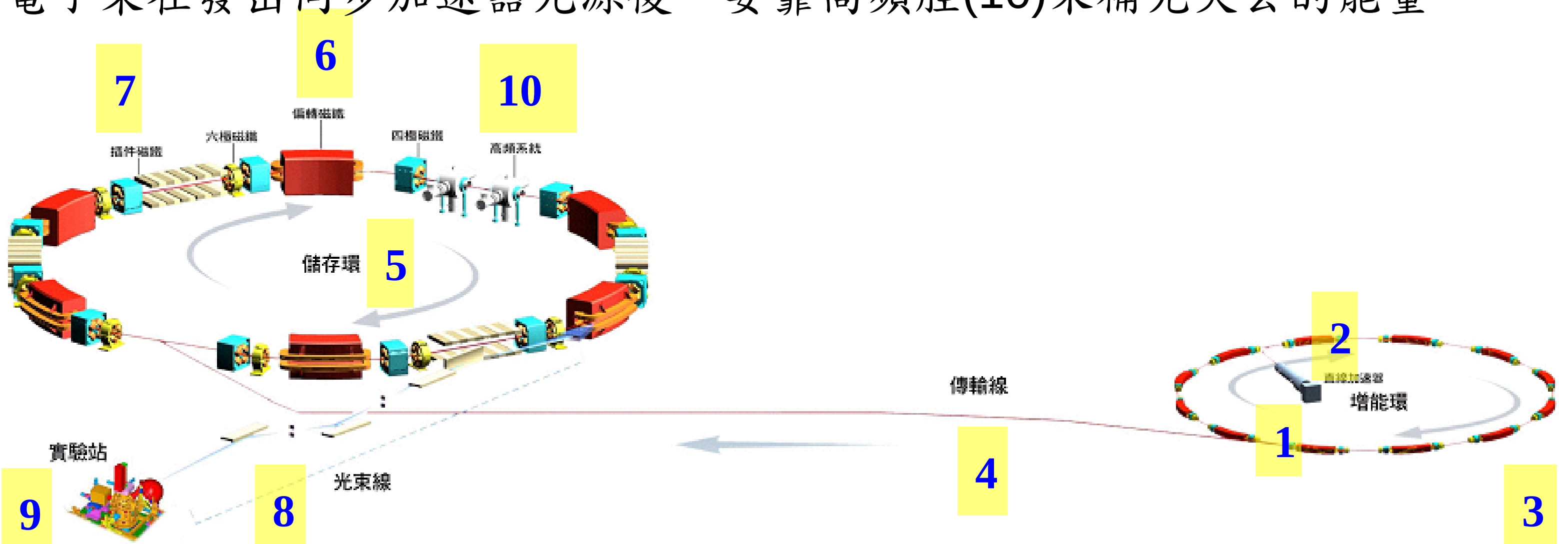




二極偏轉磁鐵

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。



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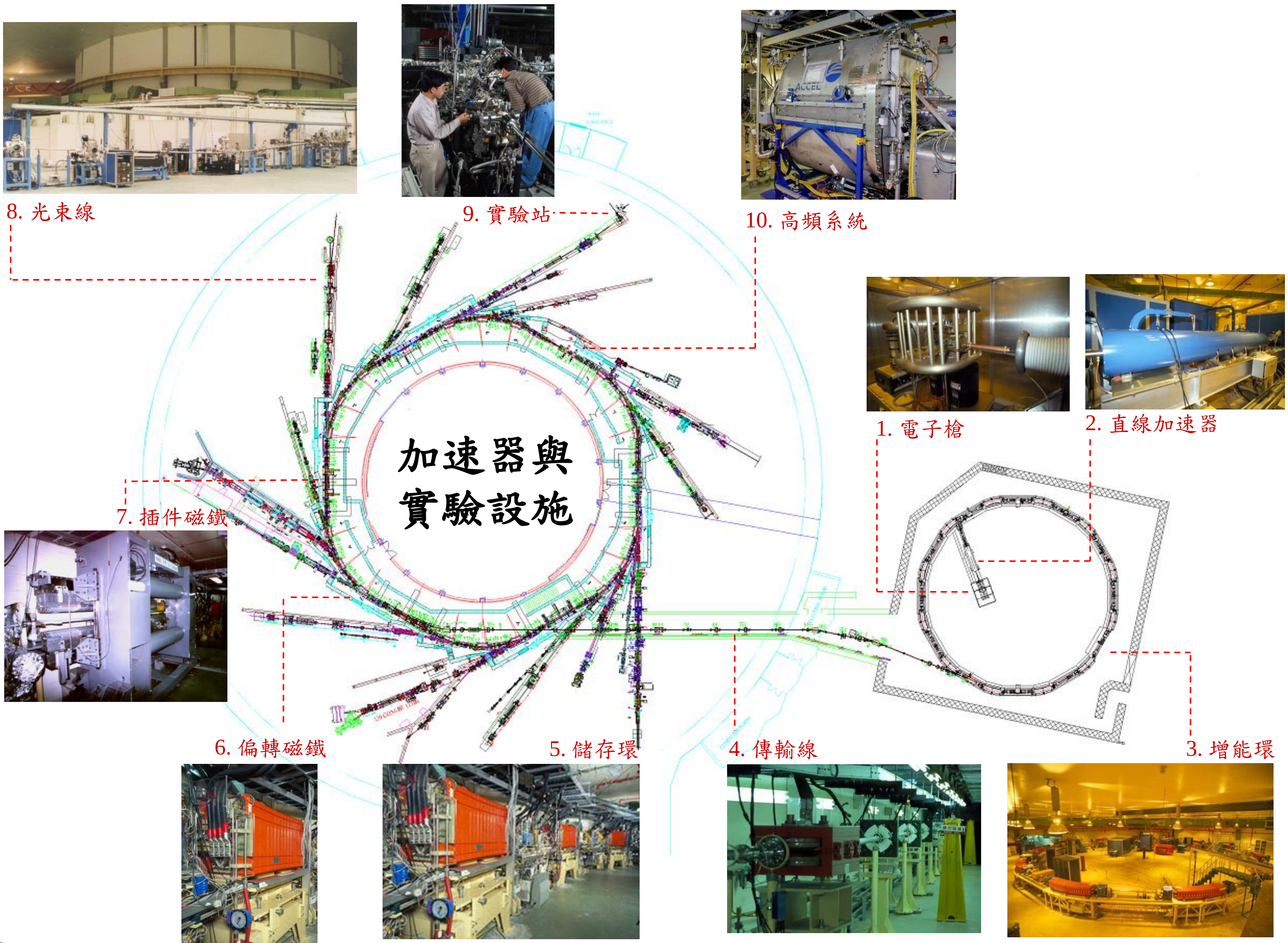
加速器與實驗設施



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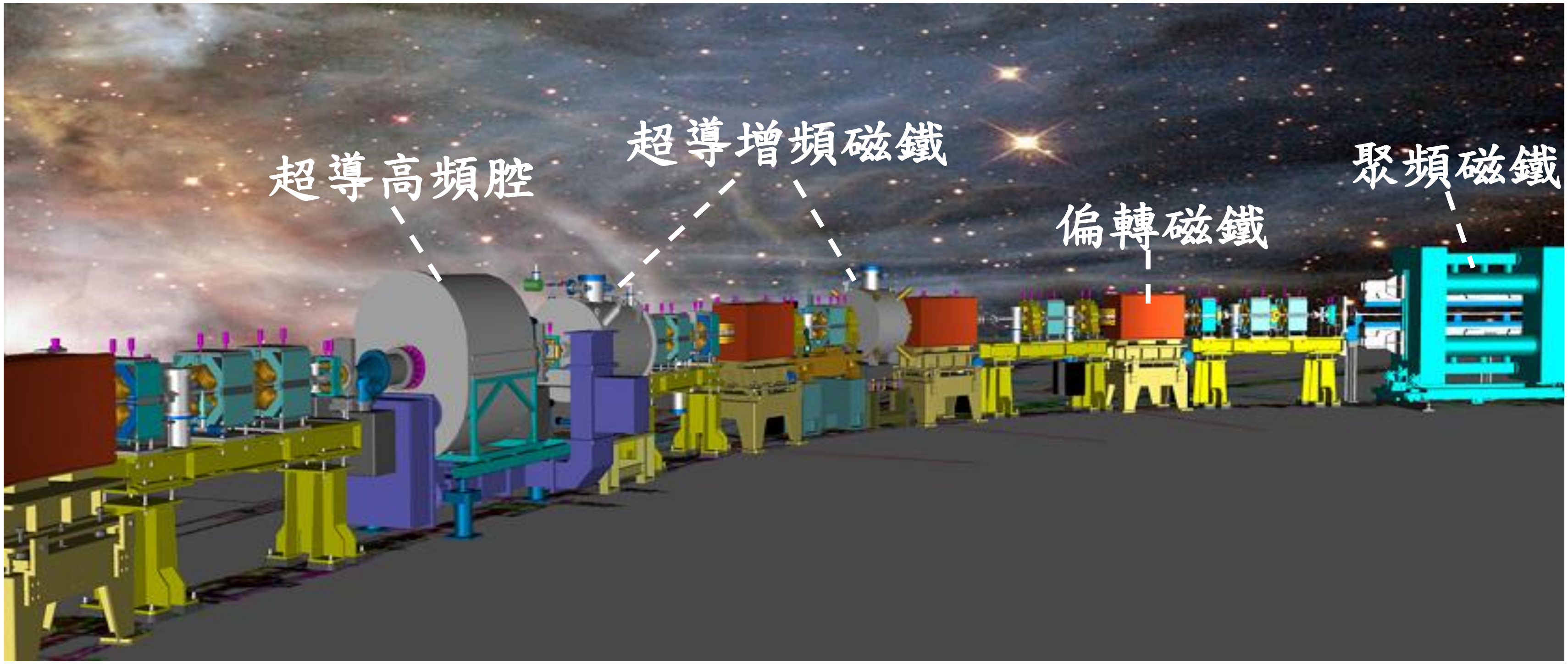
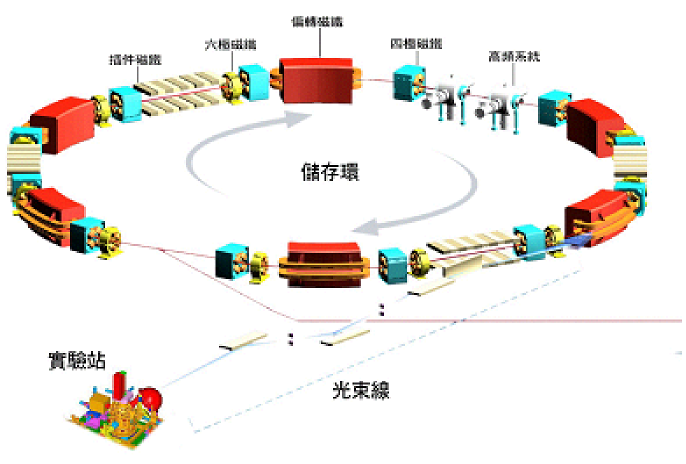
儲存環 3D 圖





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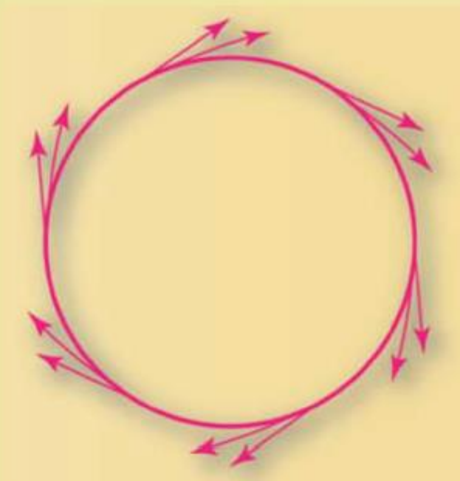
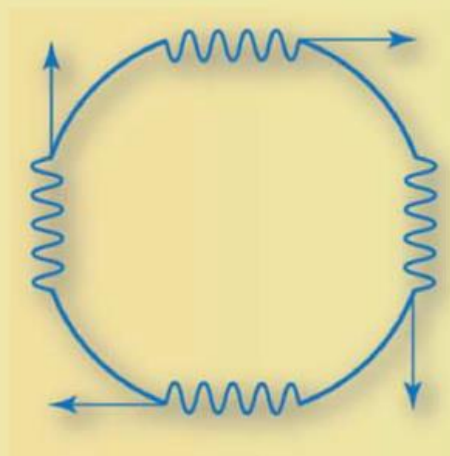
Generations of Synchrotron Light Source

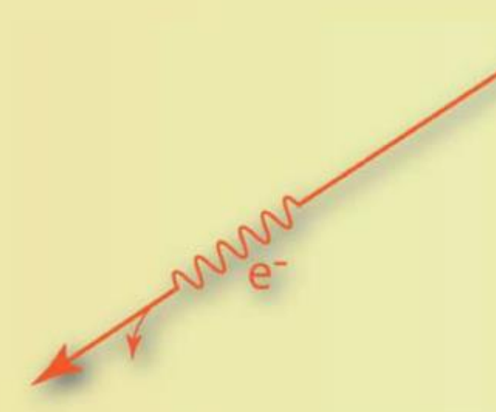
1st generation: parasitic source



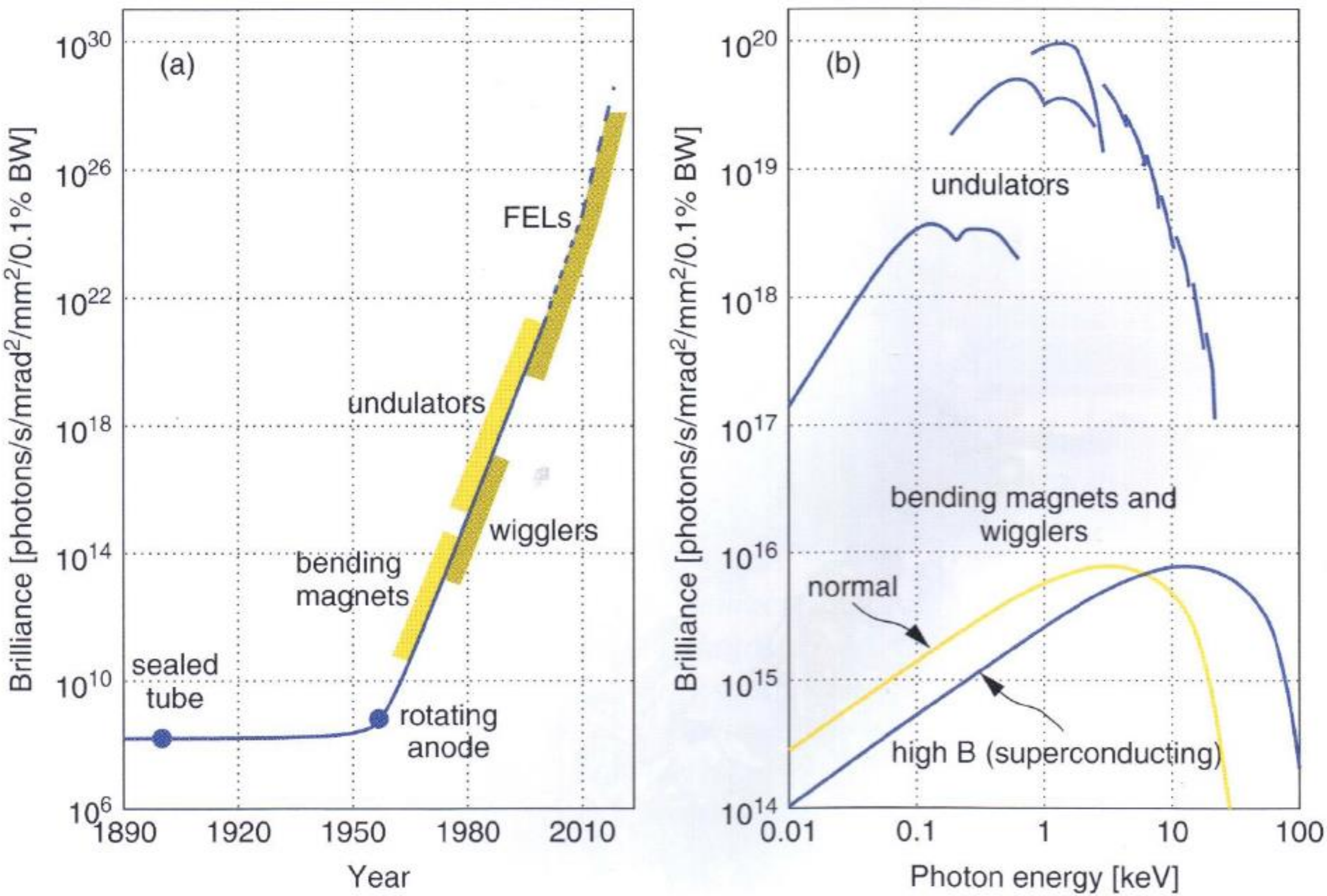
2nd generation:
dedicated source



3rd generation:
low emittance
with ID's



4th generation:
free electron laser



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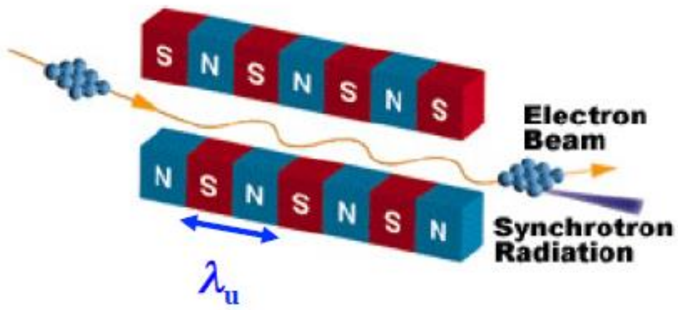
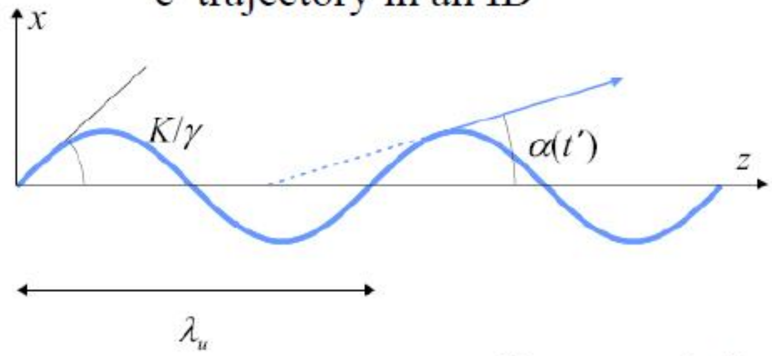
Angular distribution of synchrotron radiation emitted from various magnets

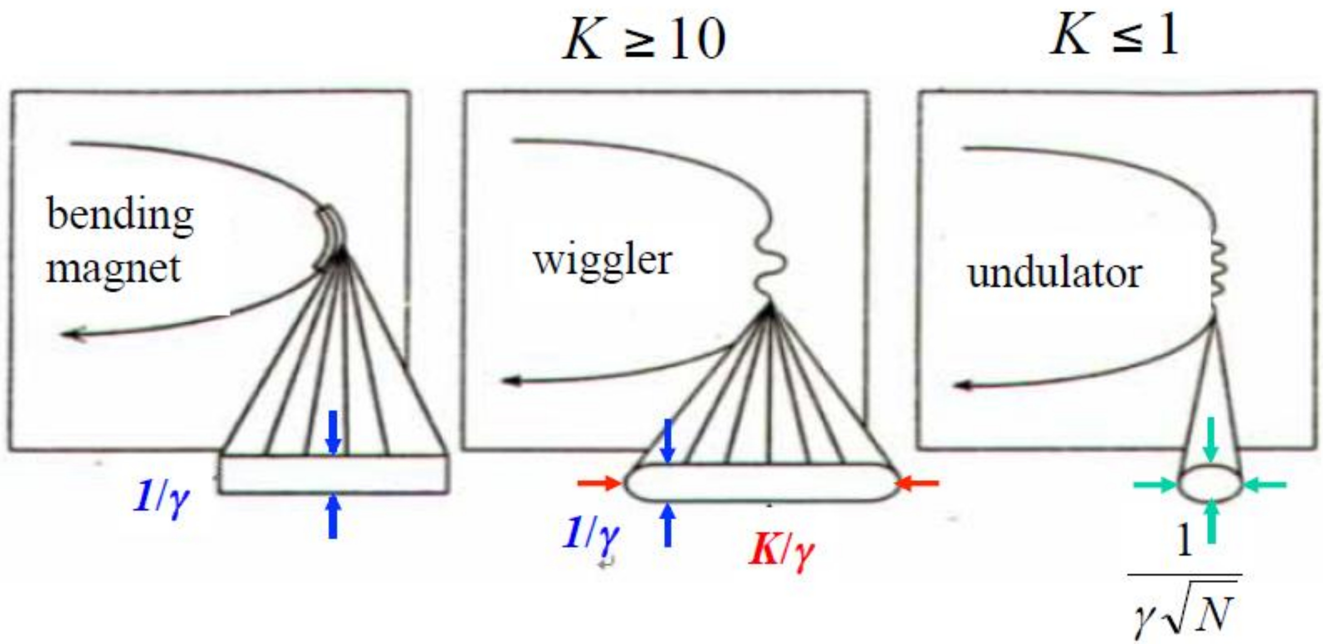
Wiggler or undulator



e⁻ trajectory in an ID



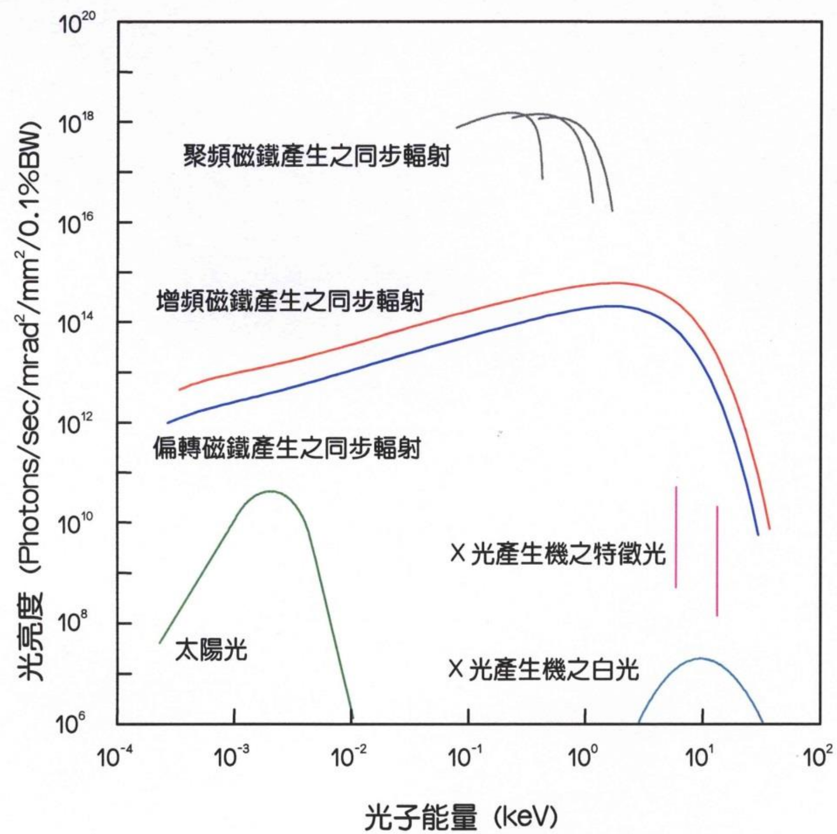
$$K = \alpha_{max.} / \gamma^{-1}$$



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：一般單位爲電子伏特(eV)，一電子伏特爲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。

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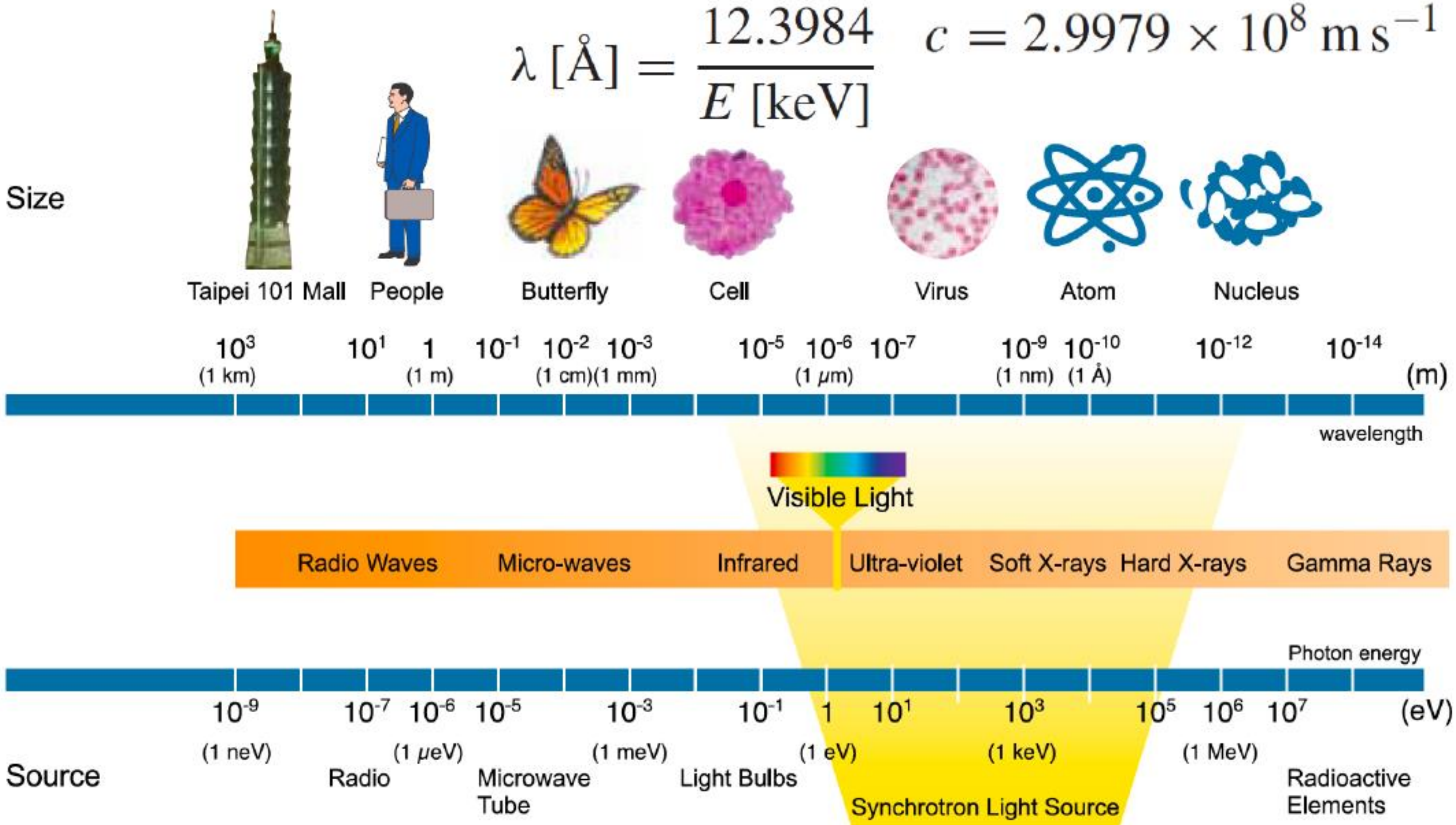
$$E = h\nu = hc/\lambda,$$

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

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

Electromagnetic Spectrum

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



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World Map of Synchrotron Facilities

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Outline

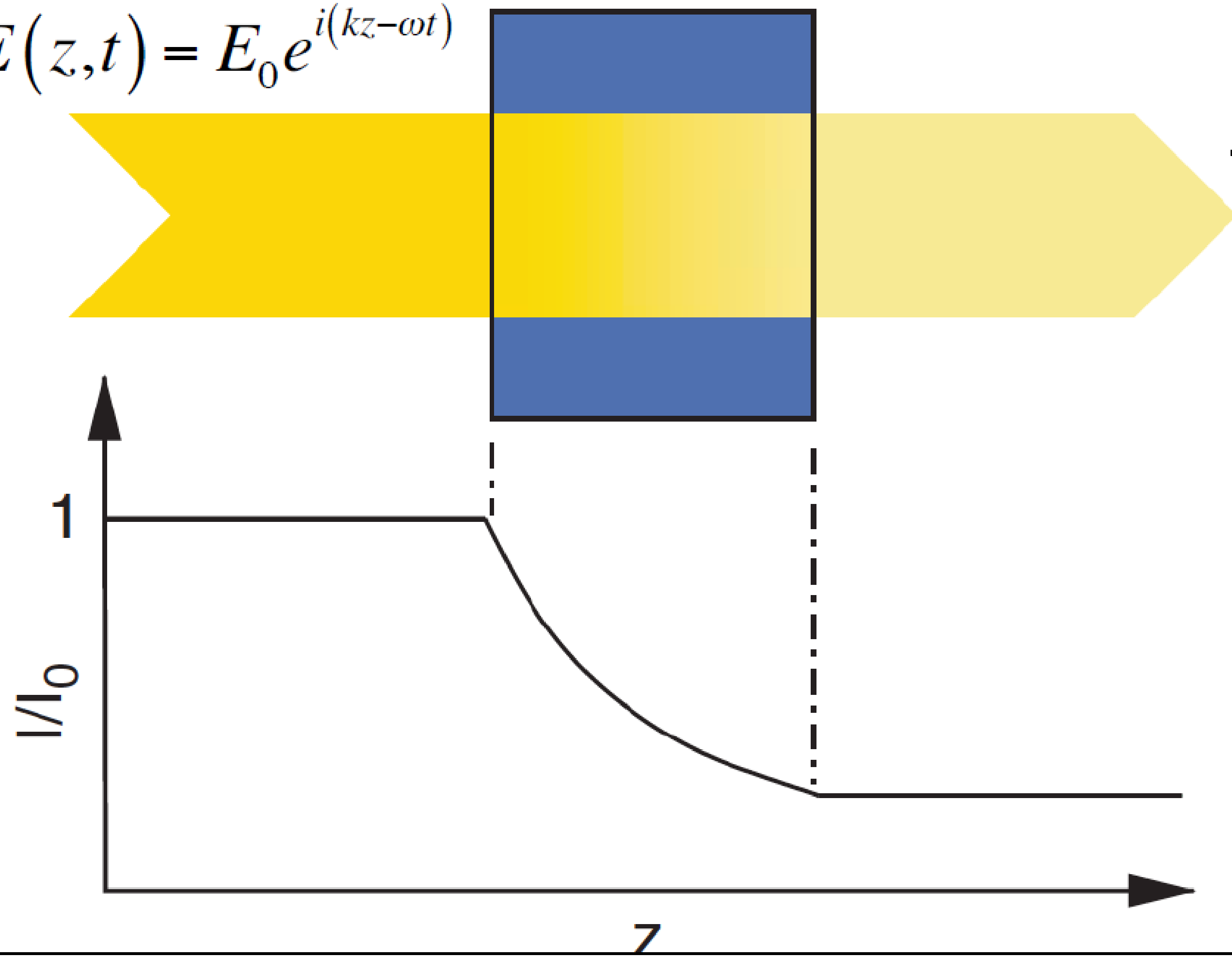
- Synchrotron Light Source
- Application of Synchrotron Light
- X-ray nano probe at TPS

Absorption

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

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

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



absorption coefficient

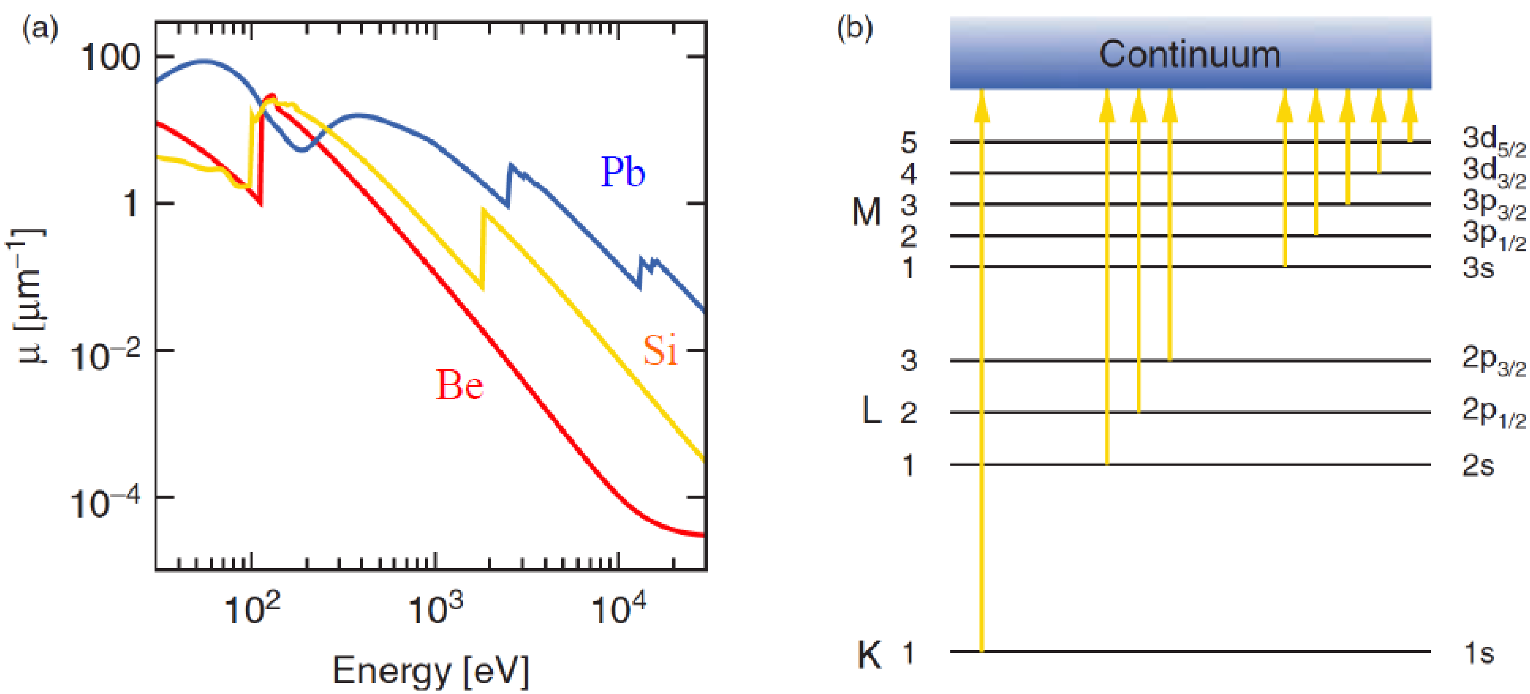
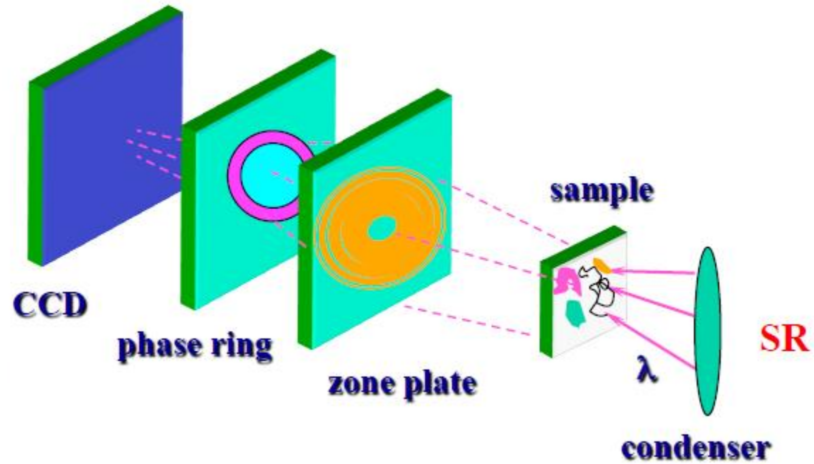


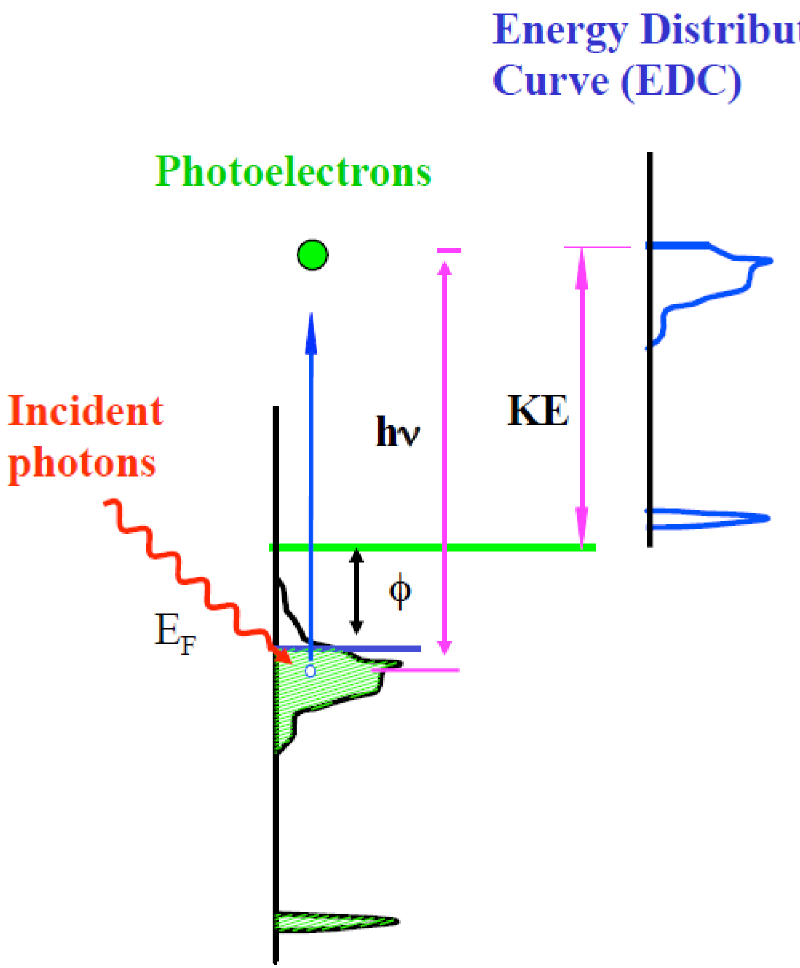
Figure 2.16 *(a) The x-ray absorption coefficient μ for beryllium (red curve), silicon (yellow) and lead (blue) as a function of the photon energy. (b) Sharp increases in the absorption occur when the photon energy is just sufficient to eject the electron from the electronic orbital to the continuum.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



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

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

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

$\Delta m_l = 0$ (linearly polarized)

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

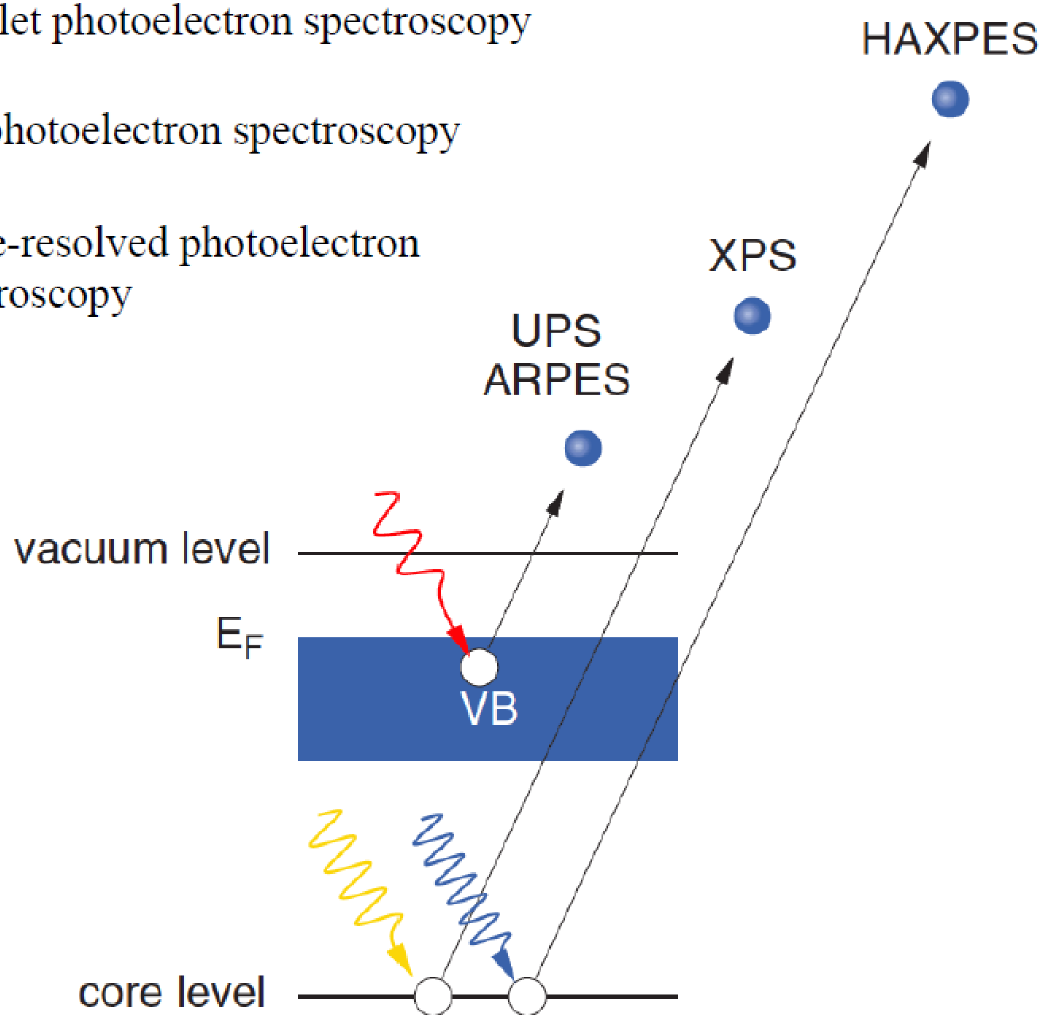
$\Delta m_l = -1$ (R. circularly polarized)

HAXPES = Hard X-ray photoelectron spectroscopy

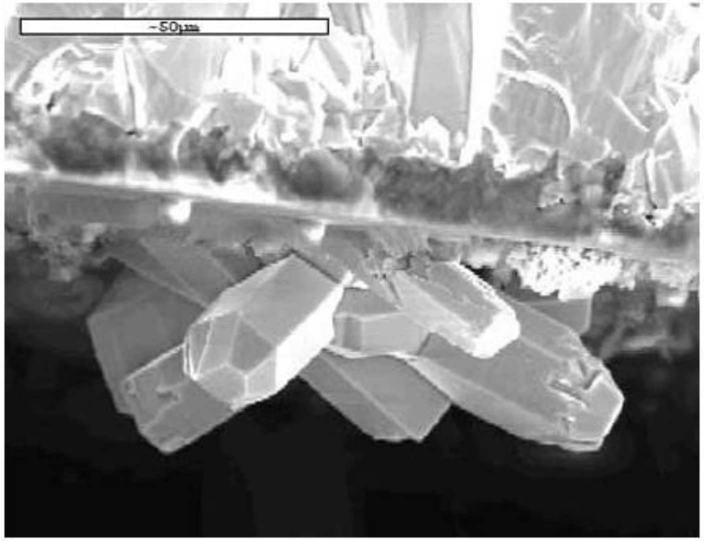
UPS = ultraviolet photoelectron spectroscopy

XPS = X-ray photoelectron spectroscopy

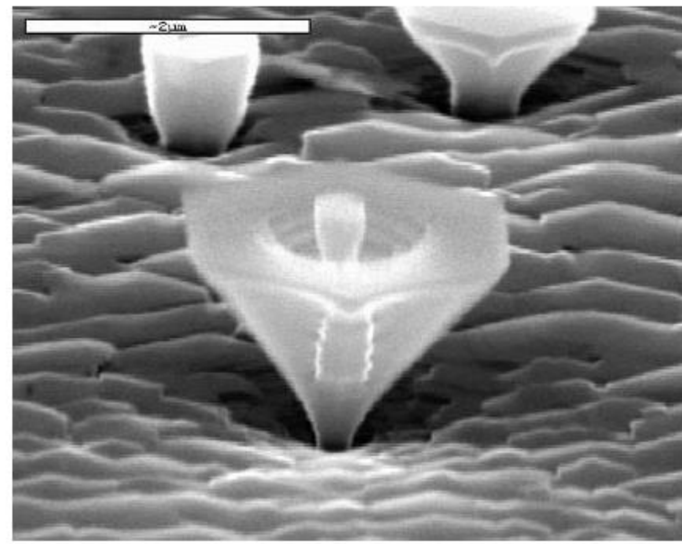
ARPES = angle-resolved photoelectron spectroscopy



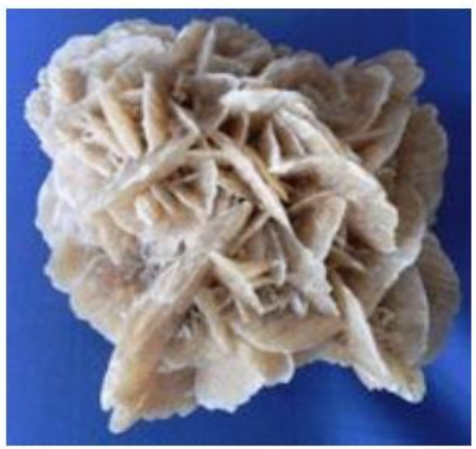
“Crystals”



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



AlN pyramids grown by MBE



Sand Rose of gypsum (石膏) crystals

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

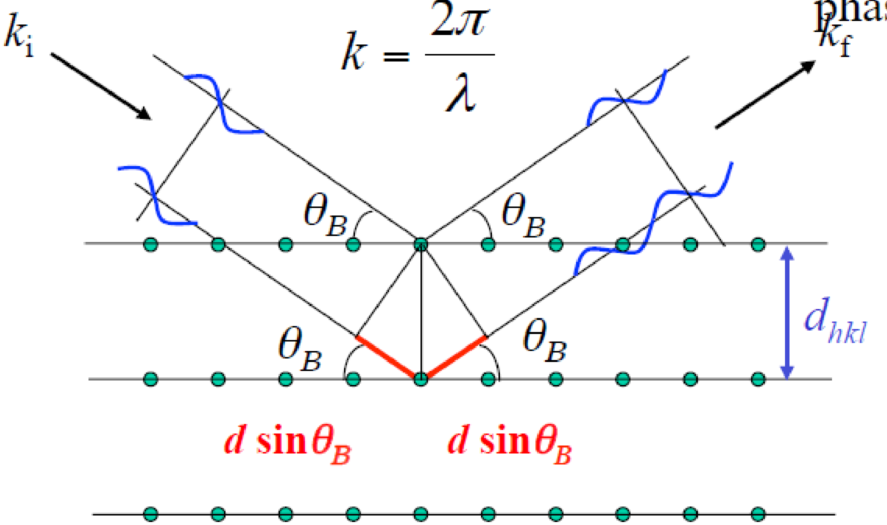
$$\vec{E} = E_0 e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

$$k = \frac{2\pi}{\lambda}$$

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

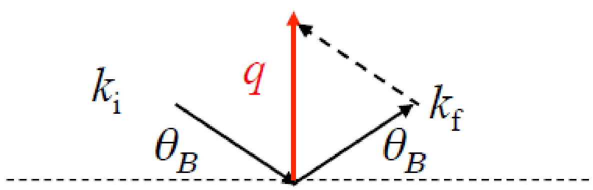
Constructive interference: $L = n\lambda$

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

$$q = G_{hkl}$$

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

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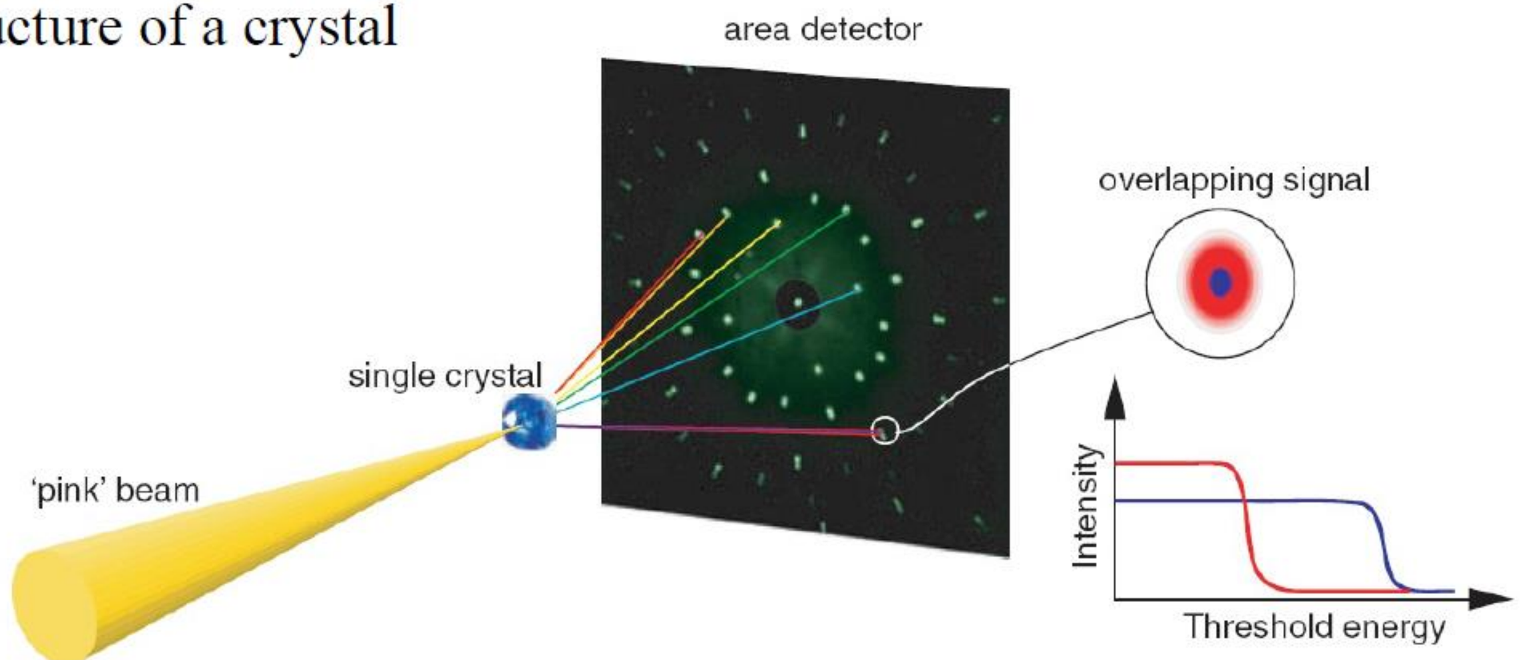
Single Crystal Diffraction - Laue Diffraction

- Method: stationary
- Light source: a polychromatic 'pink' beam (e.g. ΔE <1 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



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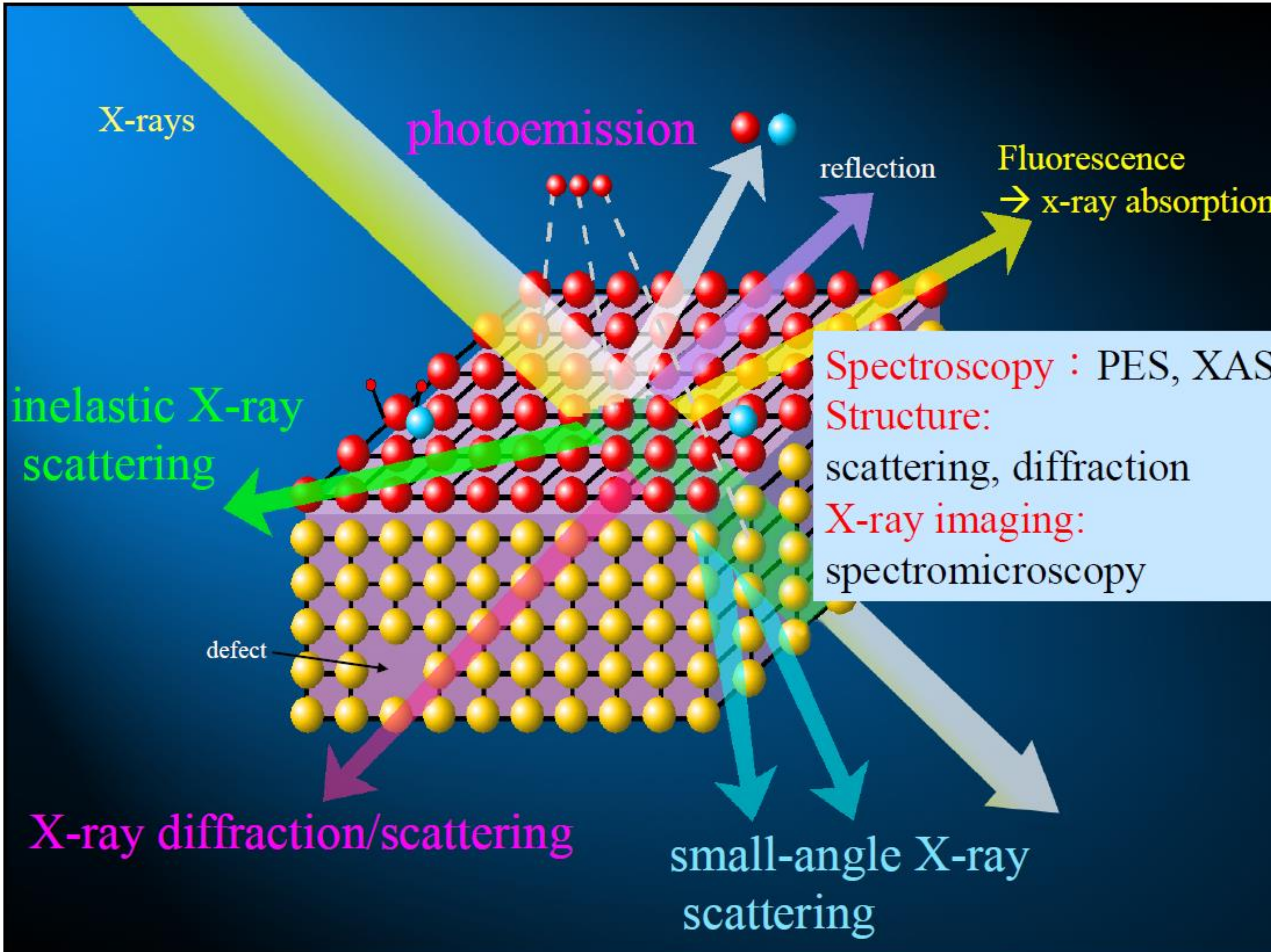

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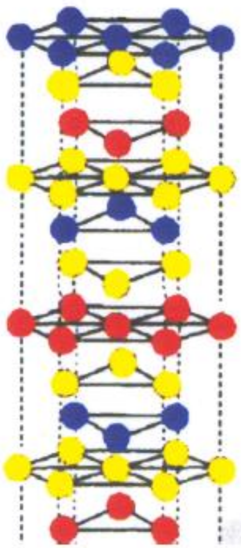

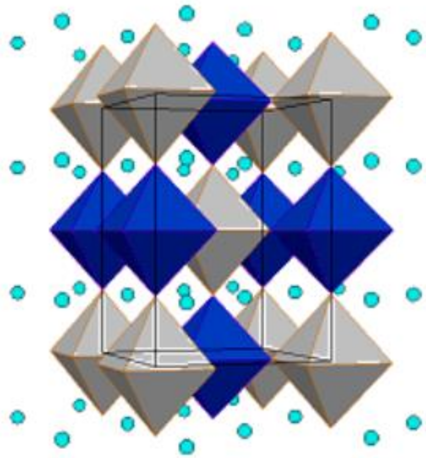

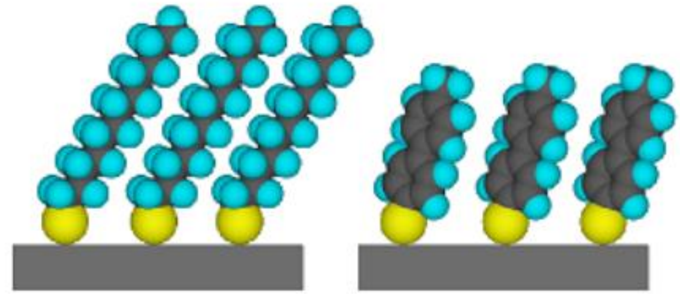

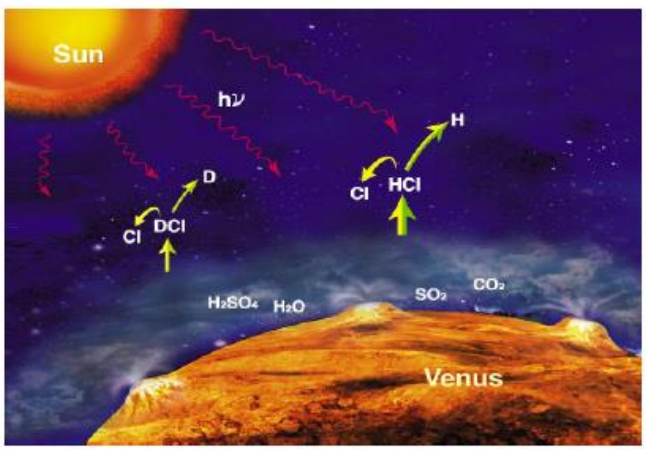

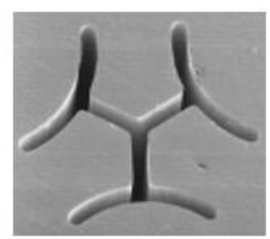

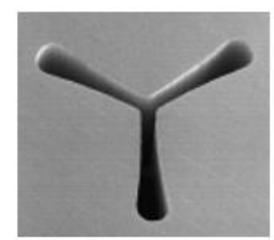

Synchrotron light source is a powerful tool for basic and applied studies in physics, chemistry, materials, biology and medicine, and their many subfields.

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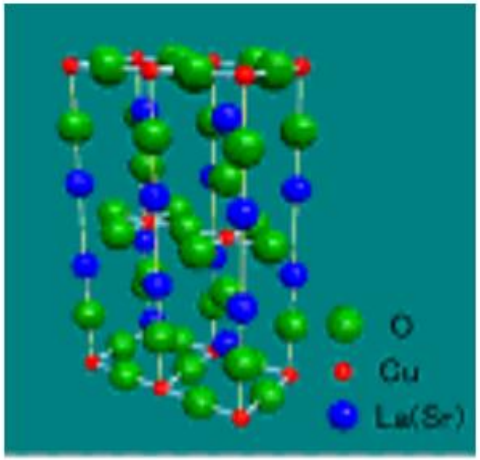
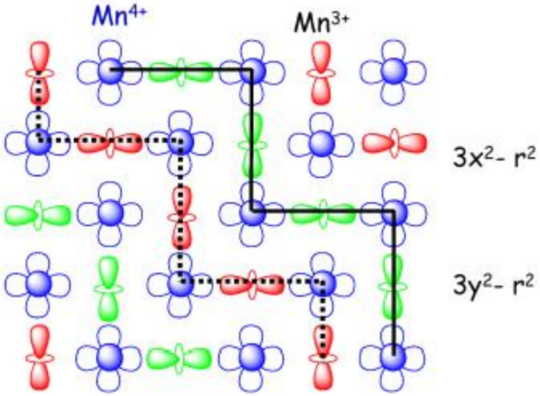
Condensed-Matter Physics



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



$La_{0.5}Sr_{1.5}MnO_4$

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

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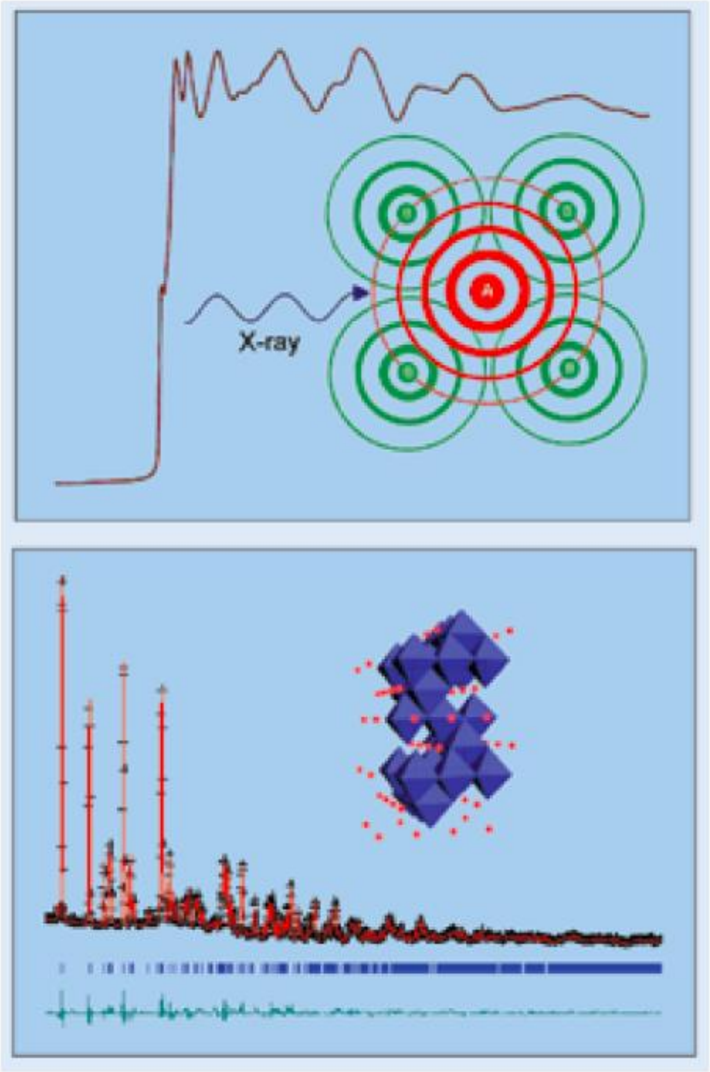
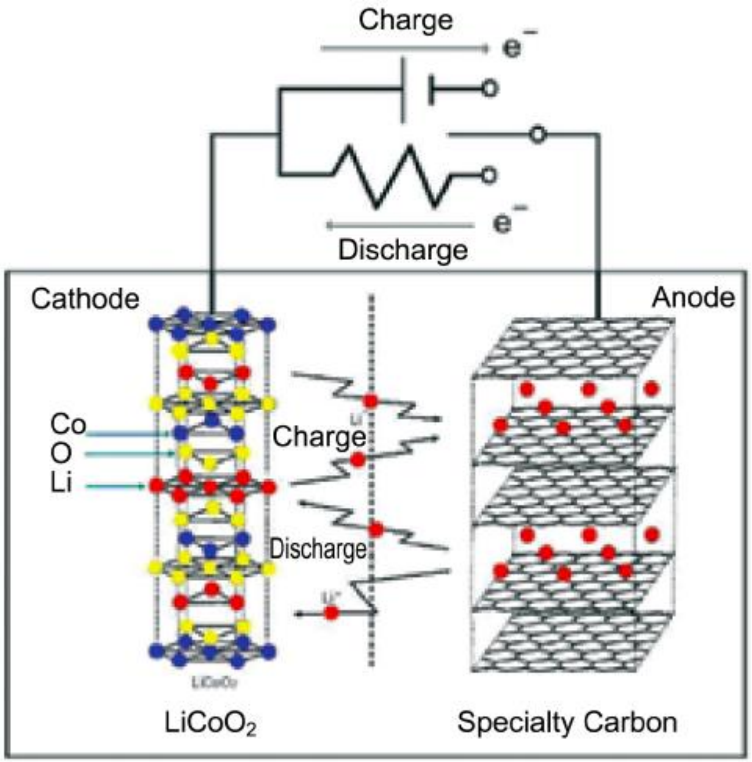
Energy Science





structure ←→ electrochemical properties of electrode

➡ develop novel electrode materials.

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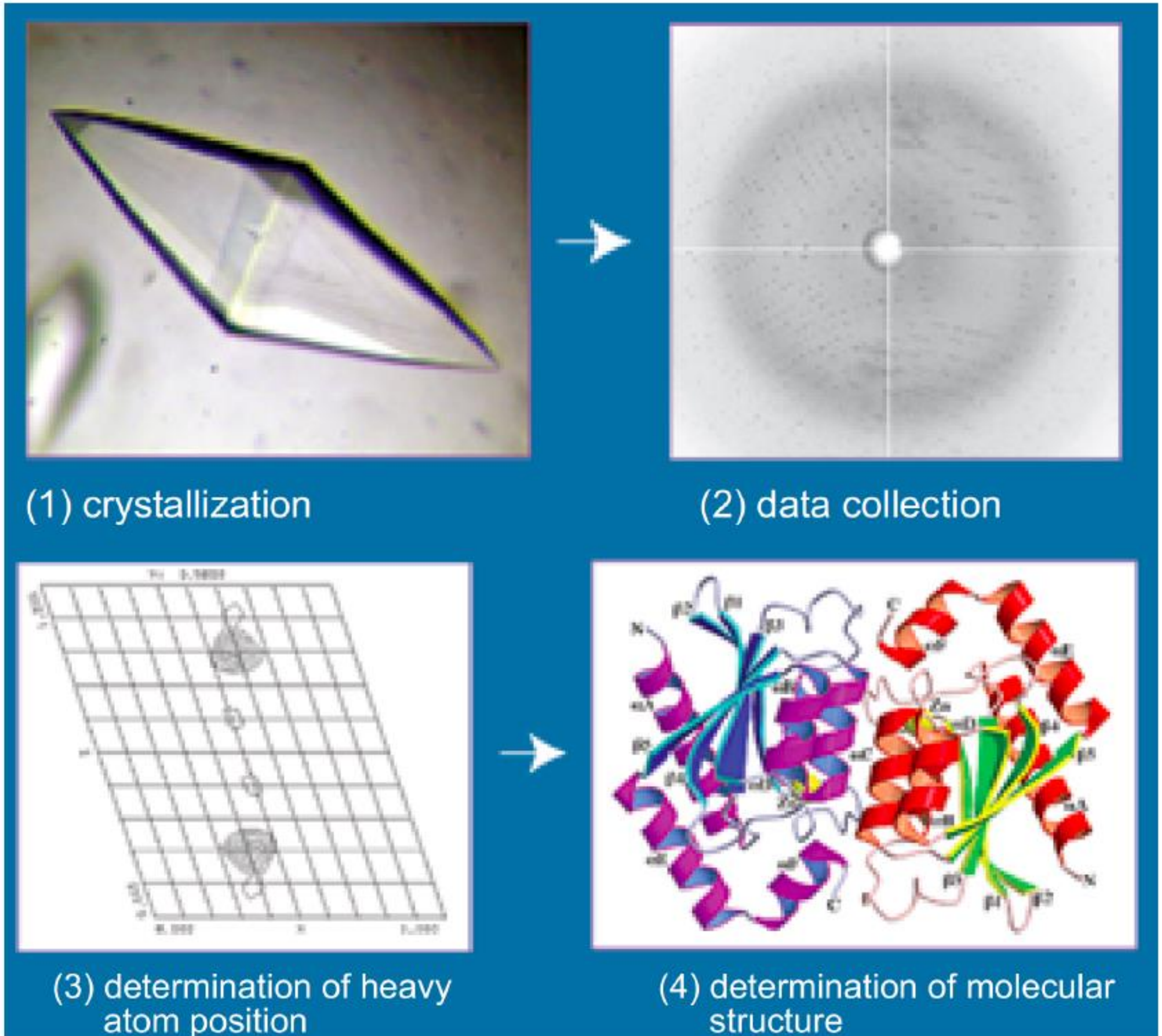
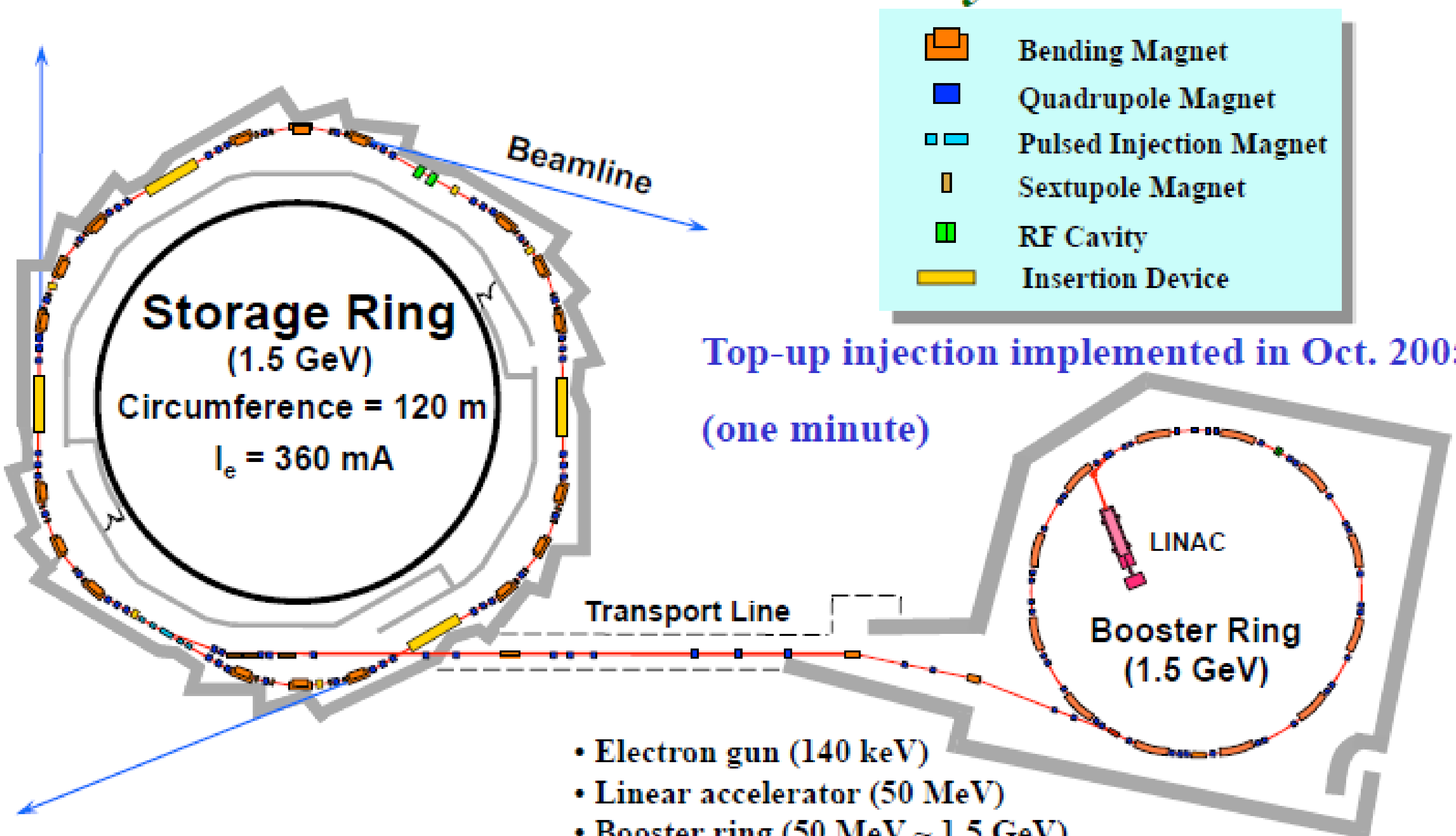
Biological structure: protein crystallography



Taiwan Light Source (TLS)

Accelerator Facility



Top-up injection implemented in Oct. 2005

(one minute)

- Electron gun (140 keV)
- Linear accelerator (50 MeV)
- Booster ring (50 MeV ~ 1.5 GeV)

TLS Experimental Hall

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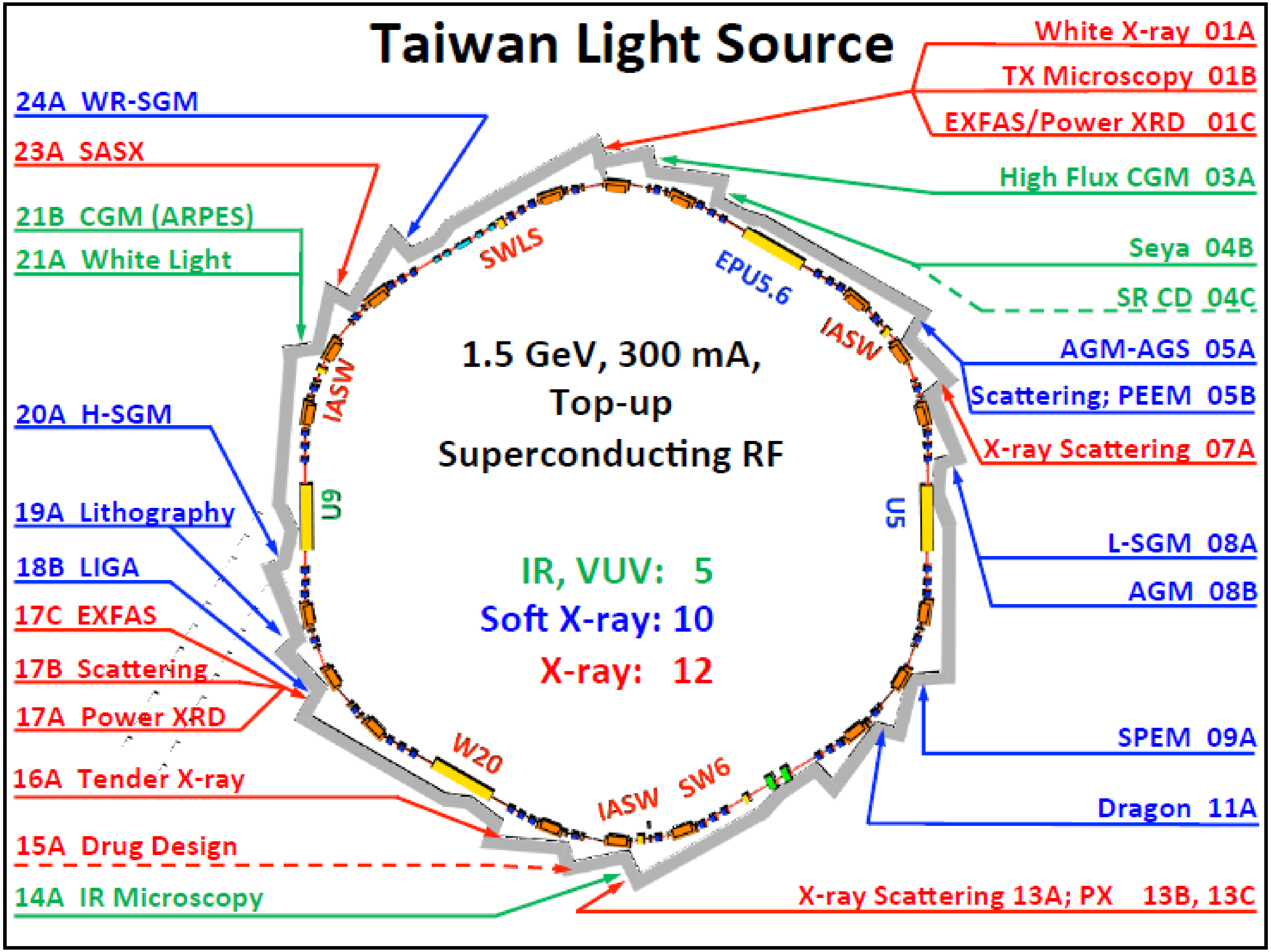

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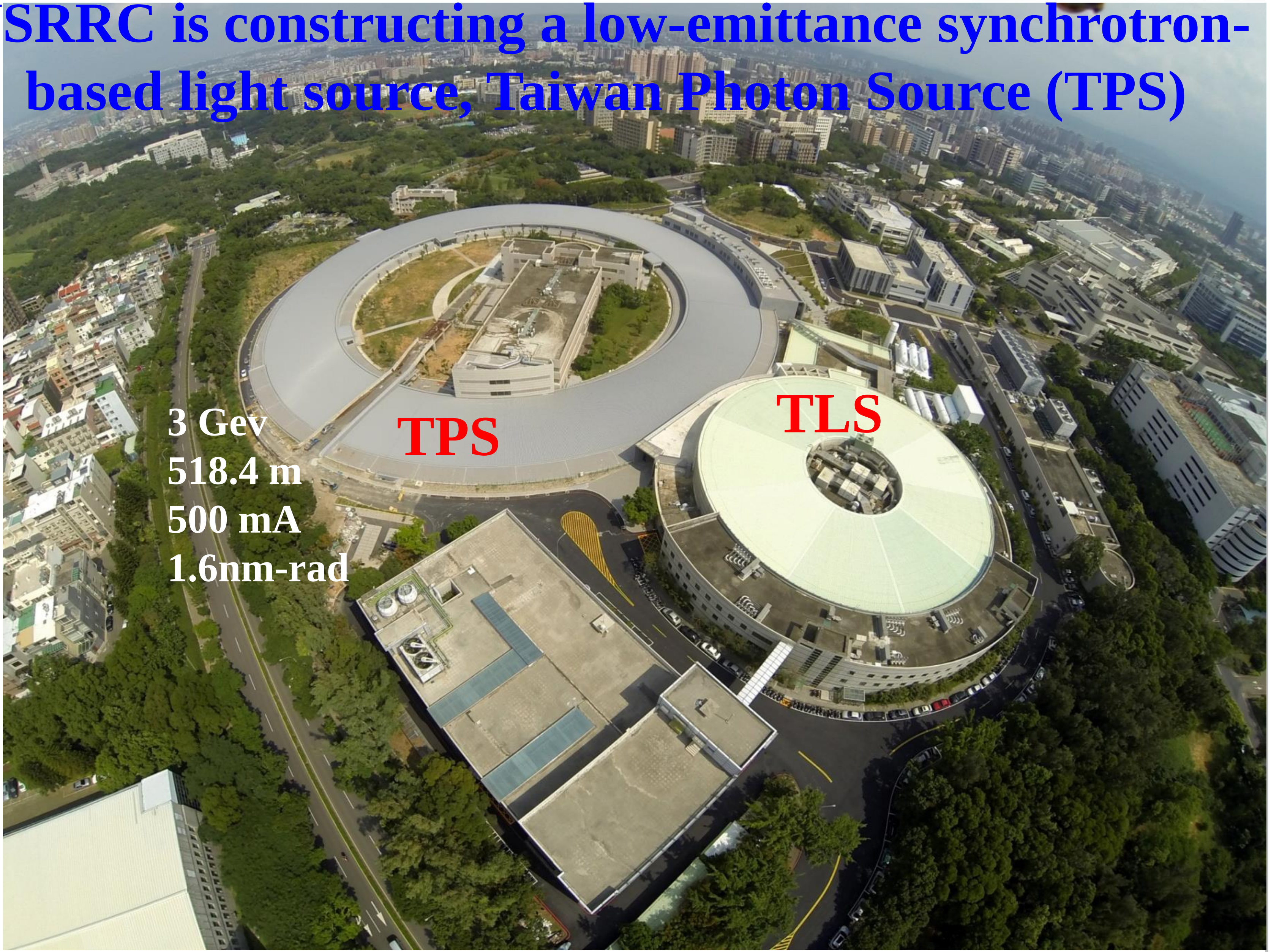
NSRRC is constructing a low-emittance synchrotron-based light source, Taiwan Photon Source (TPS)

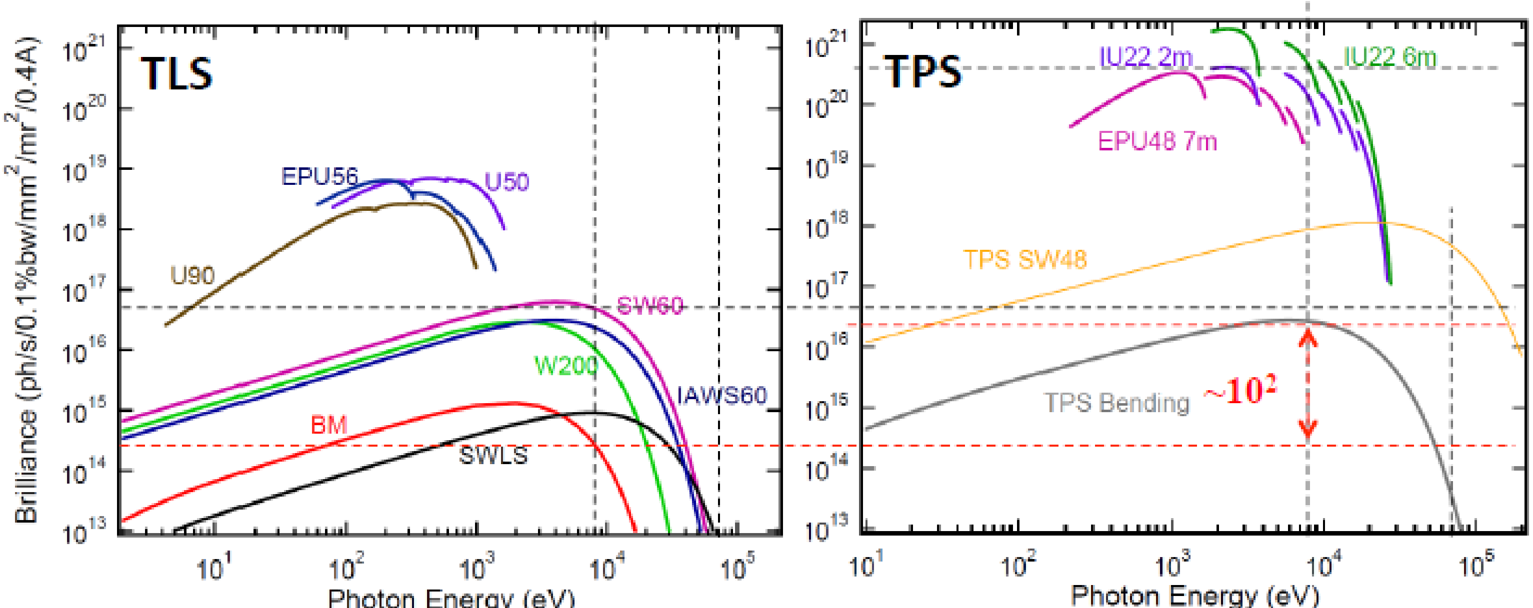


Comparison of Brilliance between TLS and TPS

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.

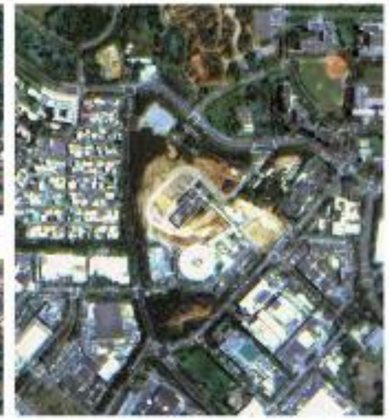


中心現址衛星圖
(太空中心提供)

Groundbreaking
2010-02-07

2010-02-10

2010-05-21



2010-08-04

2011-02-05

2011-09-27

2012-05-14

2013-01-16

Civil Construction of TPS

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Taiwan Photon Source (TPS)

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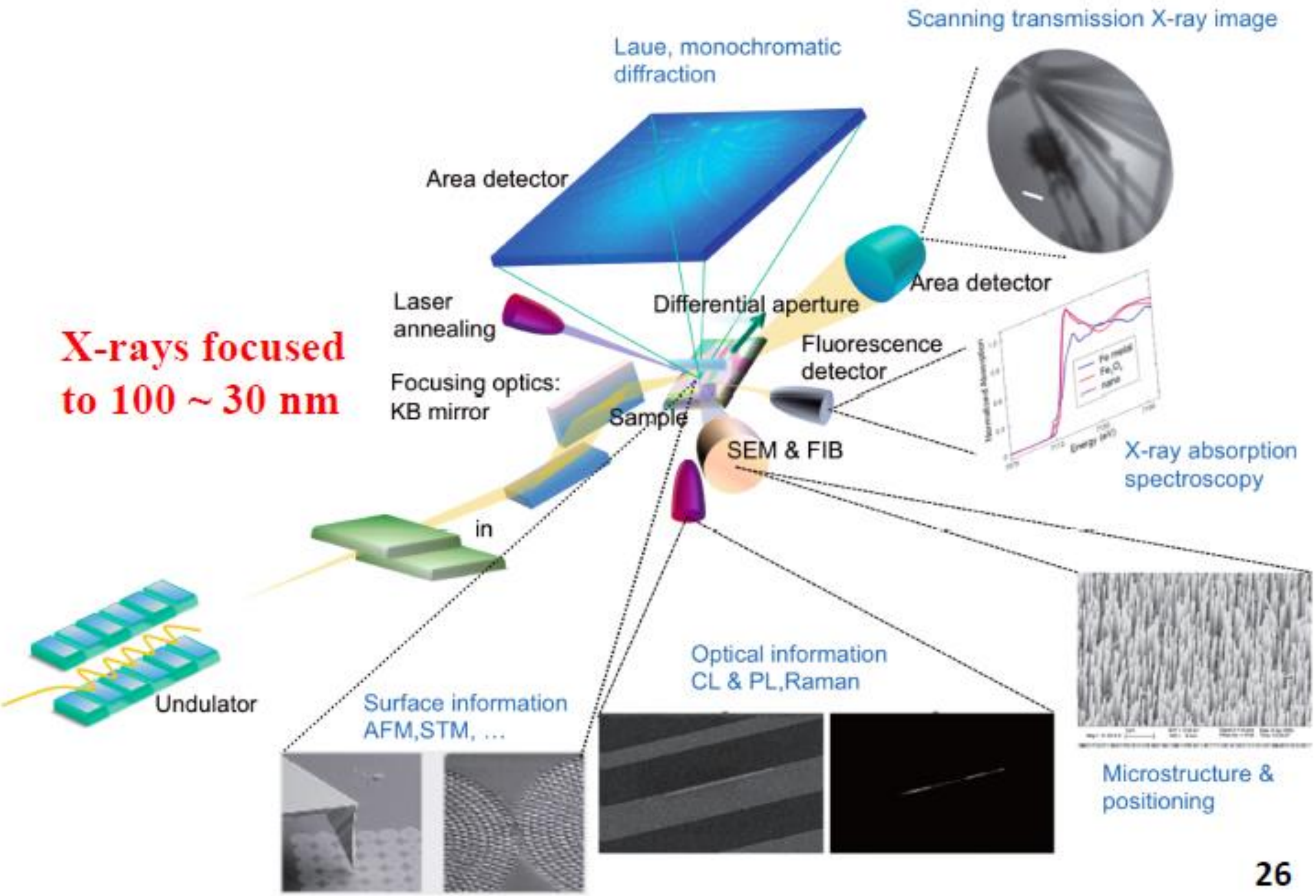
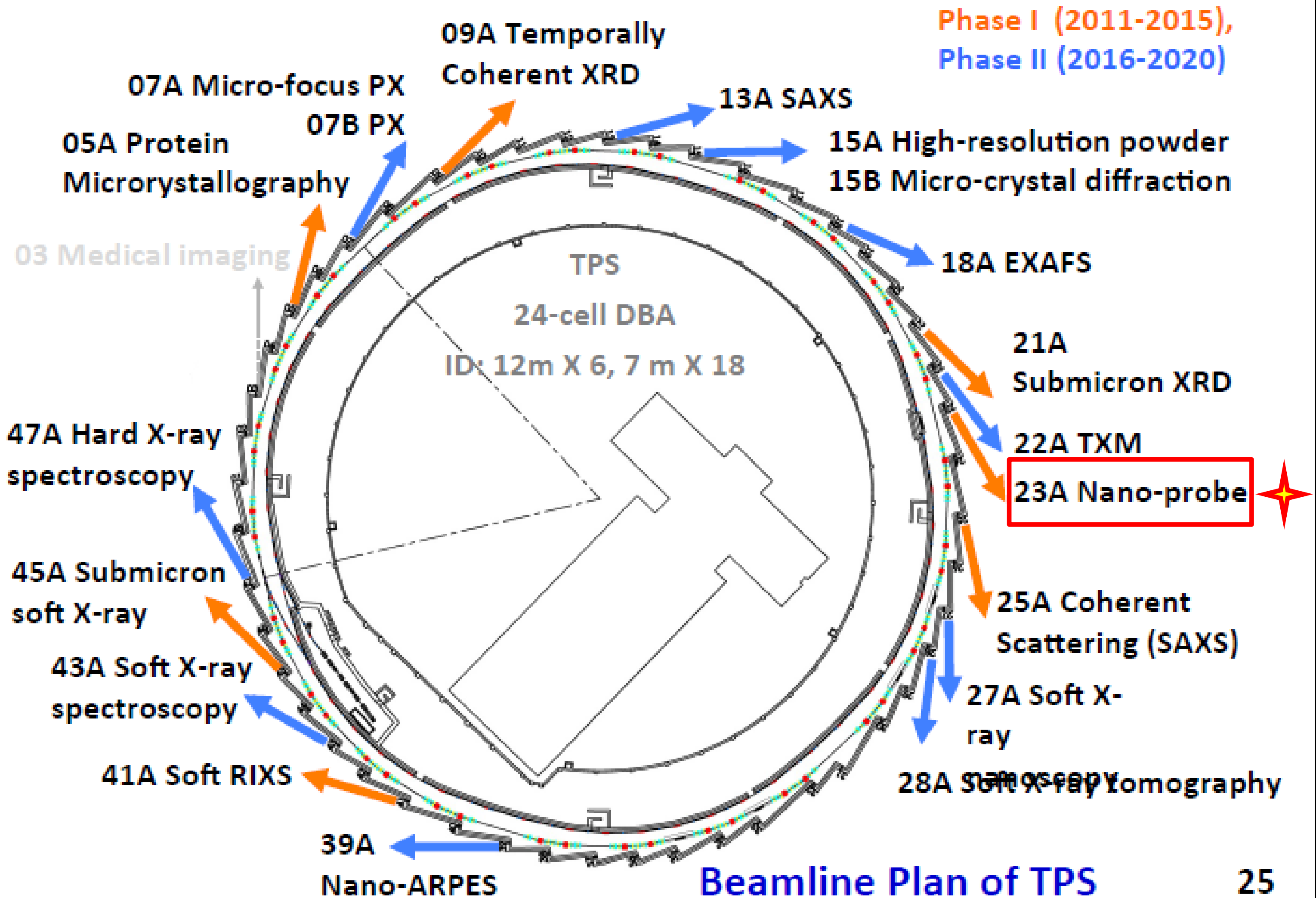
TPS will brighten the future of scientific discovery.

X-rays focused to 100 ~ 30 nm



The user operation of the TPS will begin in 2015.



Beamline Plan of TPS

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-ptychograpgy
  - strain dynamics in nano-devices

Beamline specification

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

Other than X-rays

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

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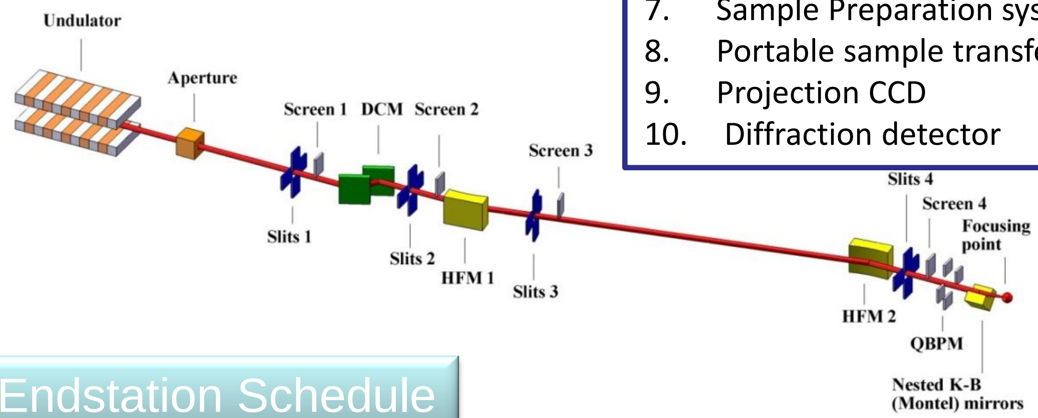
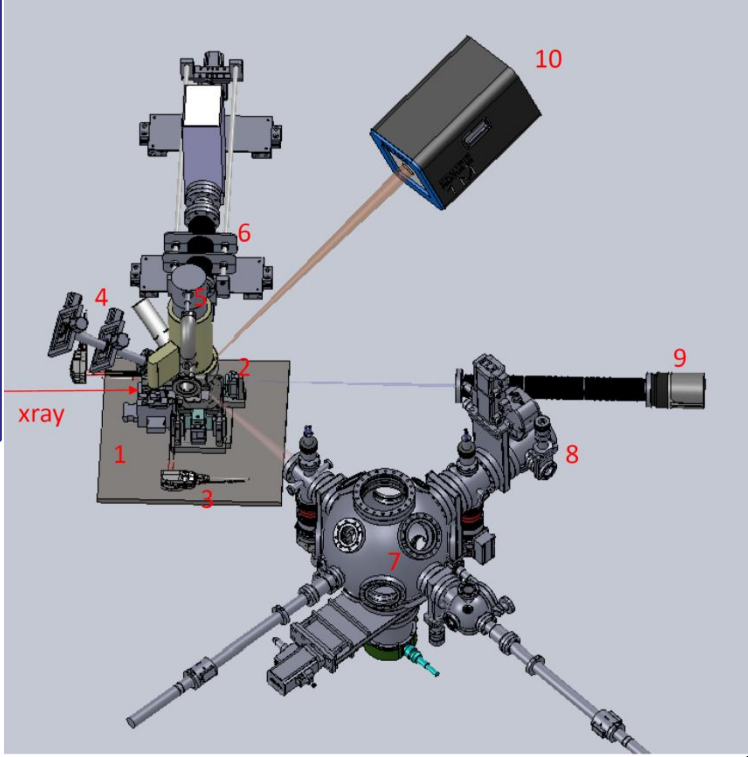
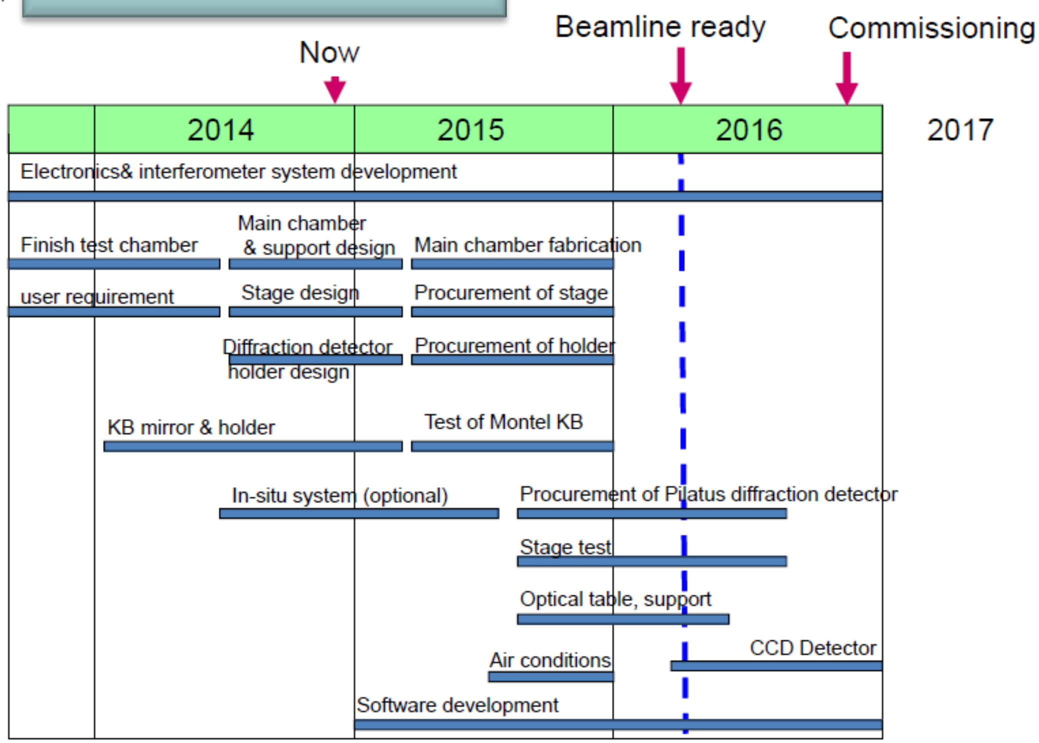
TPS 23A XNP

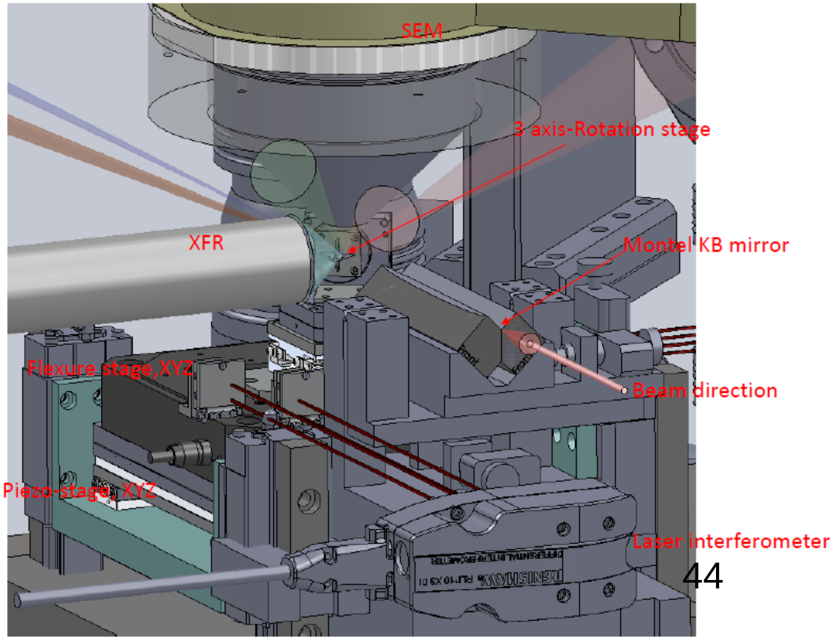
1. Montel mirror
2. Sample Stage
3. Laser interferometer
4. XEOL
5. SEM
6. EDS
7. Sample Preparation system
8. Portable sample transfer
9. Projection CCD
10. Diffraction detector

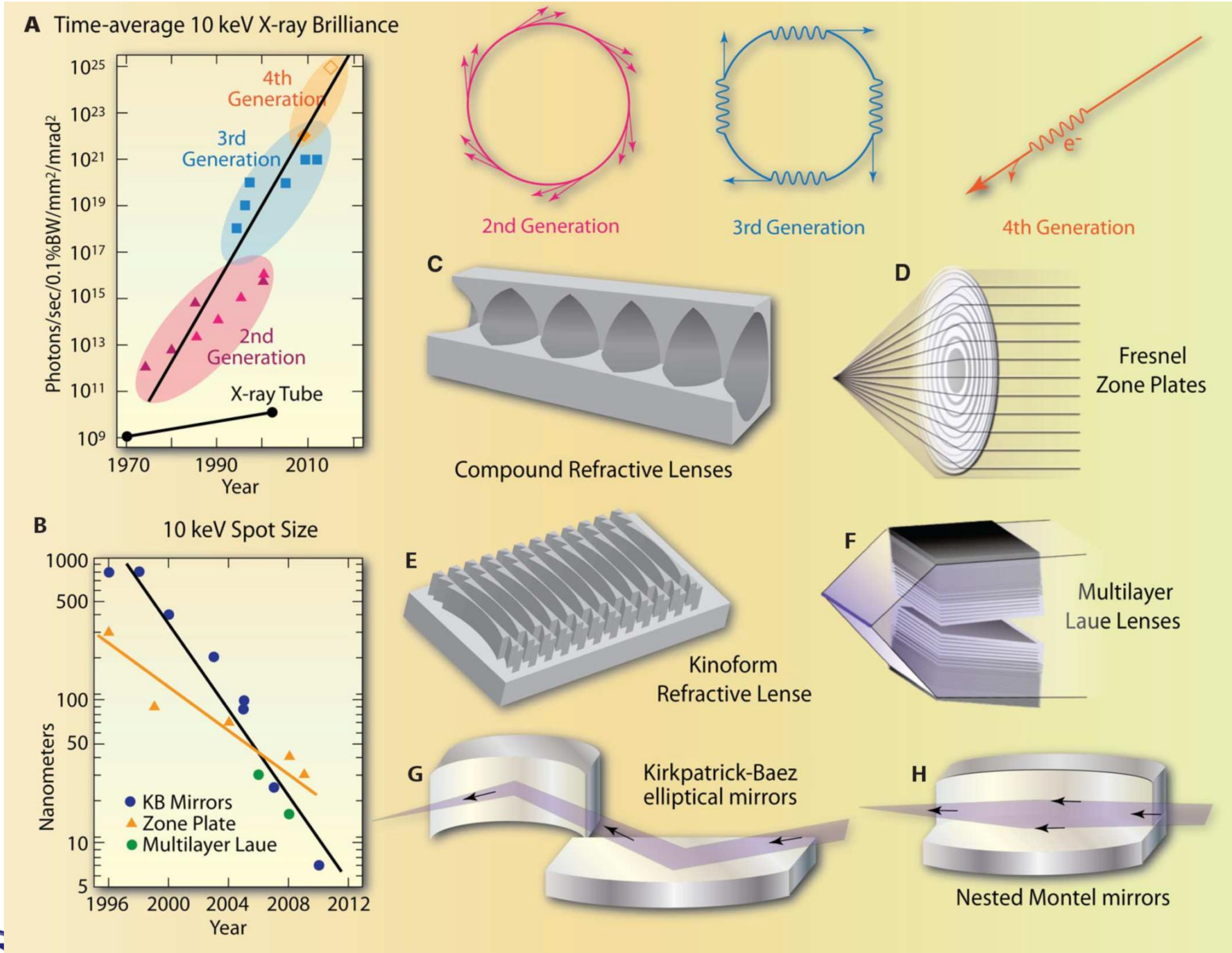




Endstation Schedule





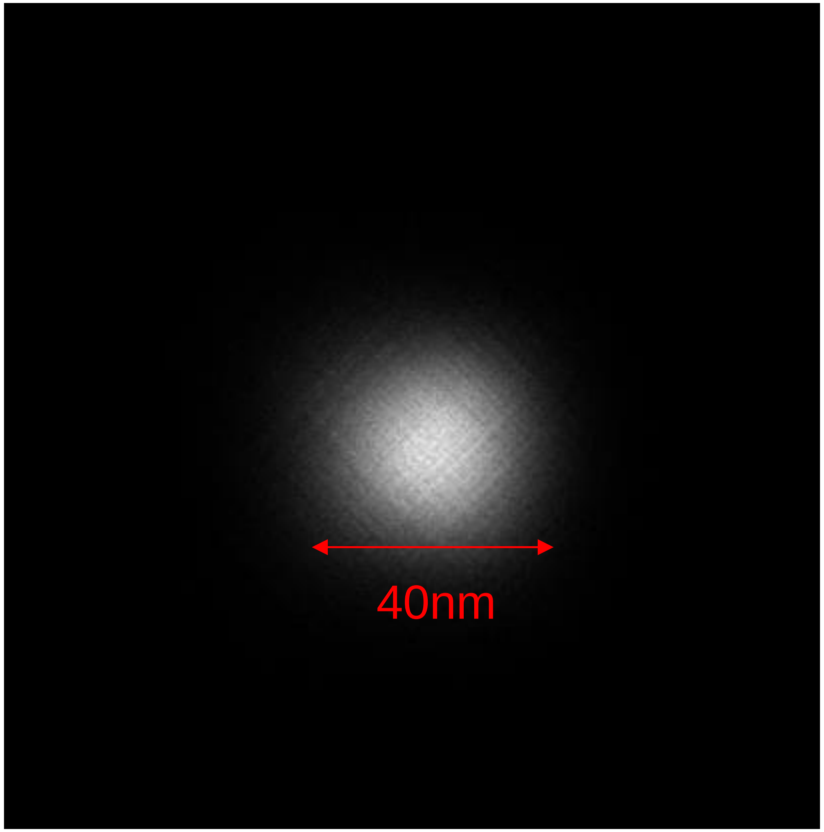


A Time-average 10 keV X-ray Brilliance
Photons/sec/0.1%BW/mm²/mrad²
10²⁵
10²³
10²¹
10¹⁹
10¹⁷
10¹⁵
10¹³
10¹¹
10⁹
4th Generation
3rd Generation
2nd Generation
X-ray Tube
1970
1990
2010
Year
2nd Generation
3rd Generation
4th Generation
e-
B
10 keV Spot Size
Nanometers
1000
500
100
50
10
5
KB Mirrors
Zone Plate
Multilayer Laue
1996
2000
2004
2008
2012
Year
C
Compound Refractive Lenses
D
Fresnel Zone Plates
E
Kinoform Refractive Lense
F
Multilayer Laue Lenses
G
Kirkpatrick-Baez elliptical mirrors
H
Nested Montel mirrors

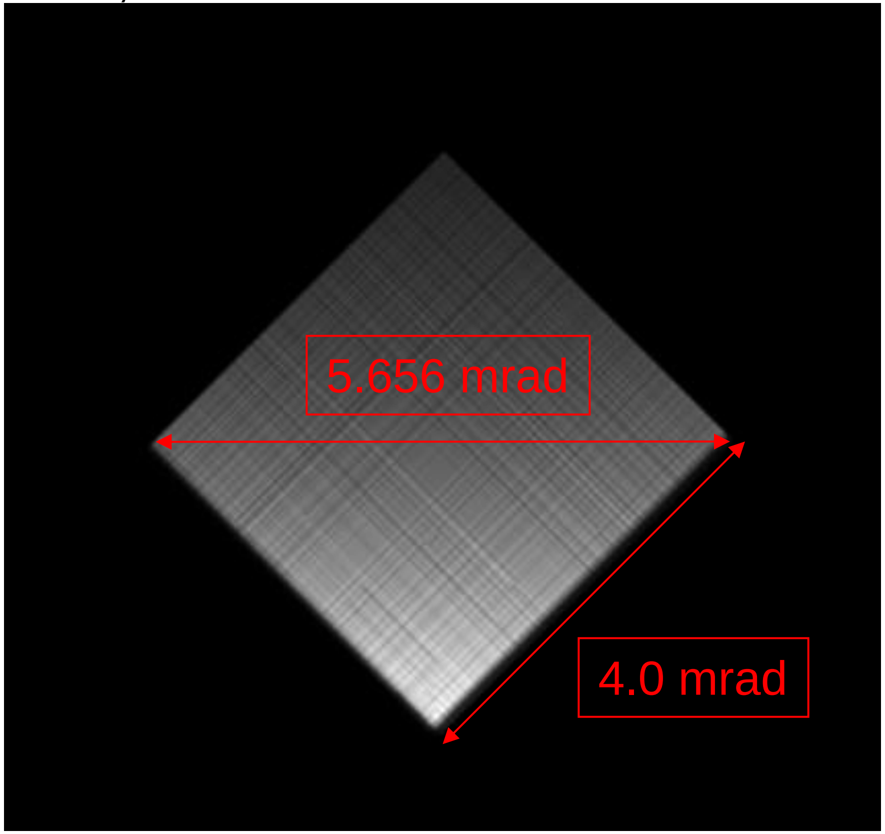
Simulation of Focus Spot

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

Source size	12.5 μm x 12.5 μm
Source divergence	6μrad x 6μrad
FHWM	32nm x 32nm,



Simulated
Focus spot size



Simulated
Divergence

By Gung-Chian Yin

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nano-XRF (x-ray fluorescence)

Element-specific nano-imaging

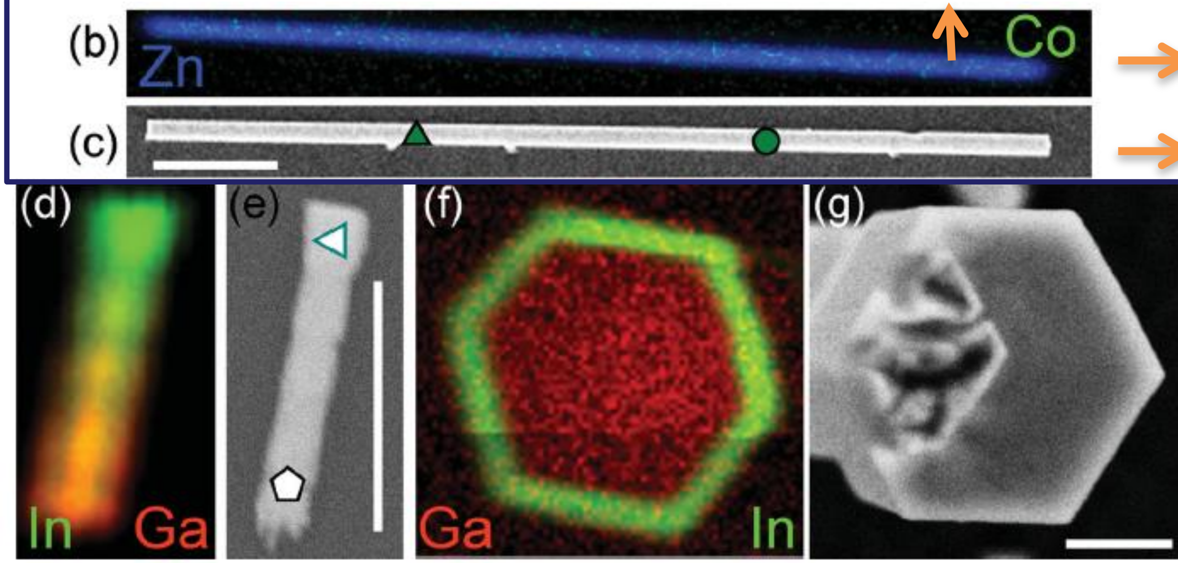
Doping of ZnO NWs by transition metal Co.
Application : Spintronic device
Want to know:

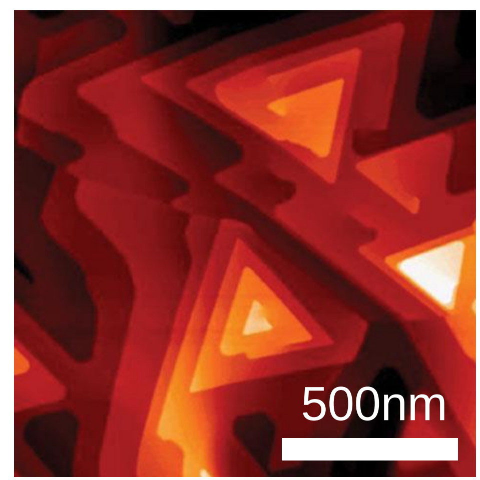
- Distribution
- Short structure order
- Elemental composition

- Pink beam mode at 12 KeV
- Pixel size : 25 x 25 nm^2
- Accumulation time : 0.5 sec/point
- beam size : 60 x 60 nm^2 (V x H)

Vapour-liguid-solid process
Nano Lett. 2011, 11, 5322–5326

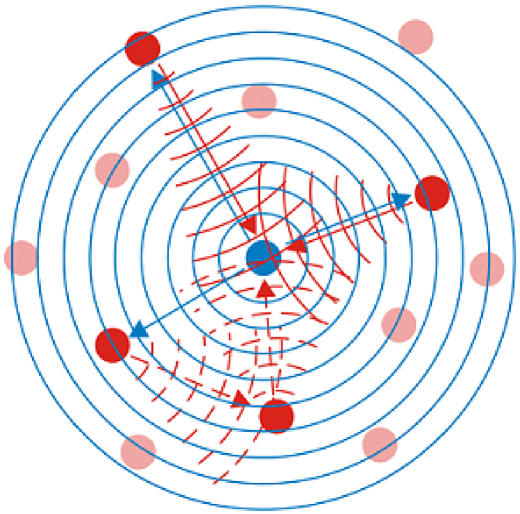
Doping method:
Ion implantation
and thermal annealing
Elemental map of XRF
SEM

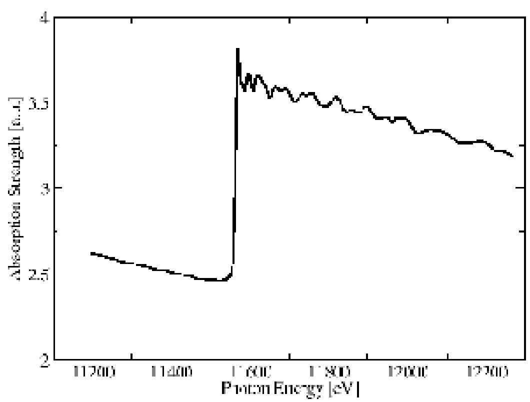


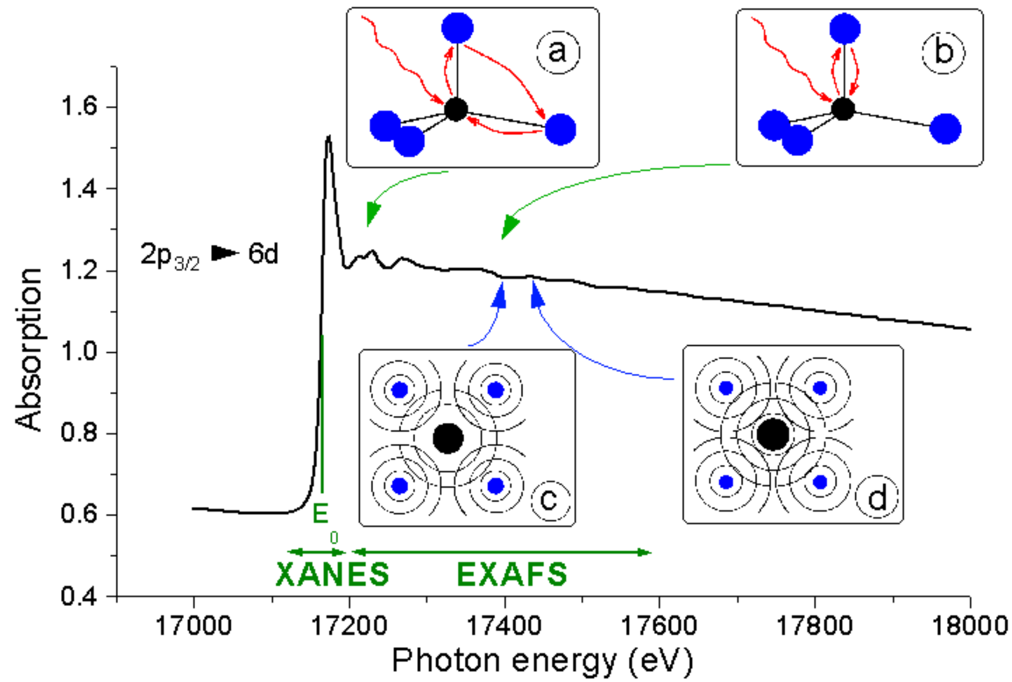


nano-XAFS (x-ray absorption fine structures)

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







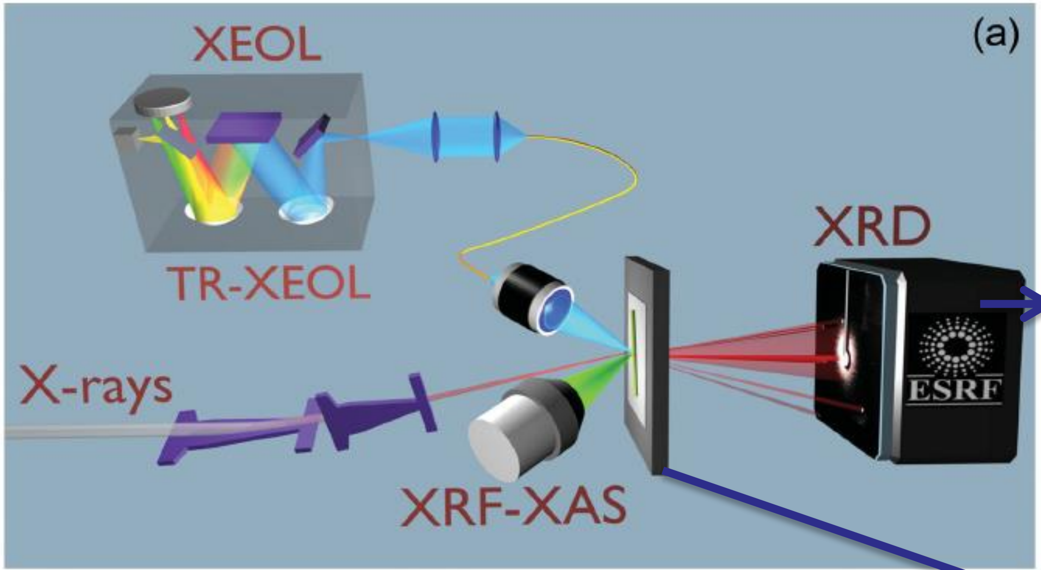
XEOL

•Multimode optical fiber

• UV-VIS : linear CCD Si detector

•Si avalanche photodiode (id100 from id-Quantique)

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 Al2O3 reference sample.

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.

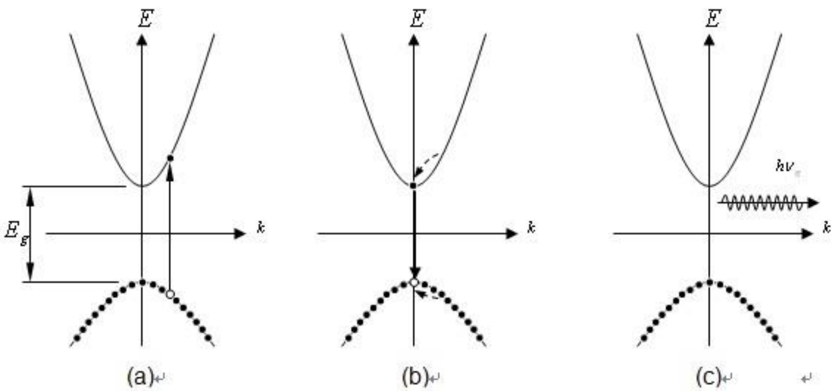
• 200 nm thick SiN membranes.

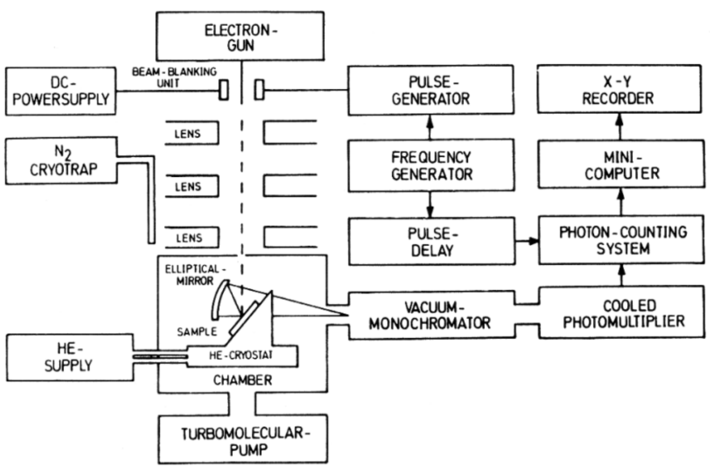
• Without XRF background signal

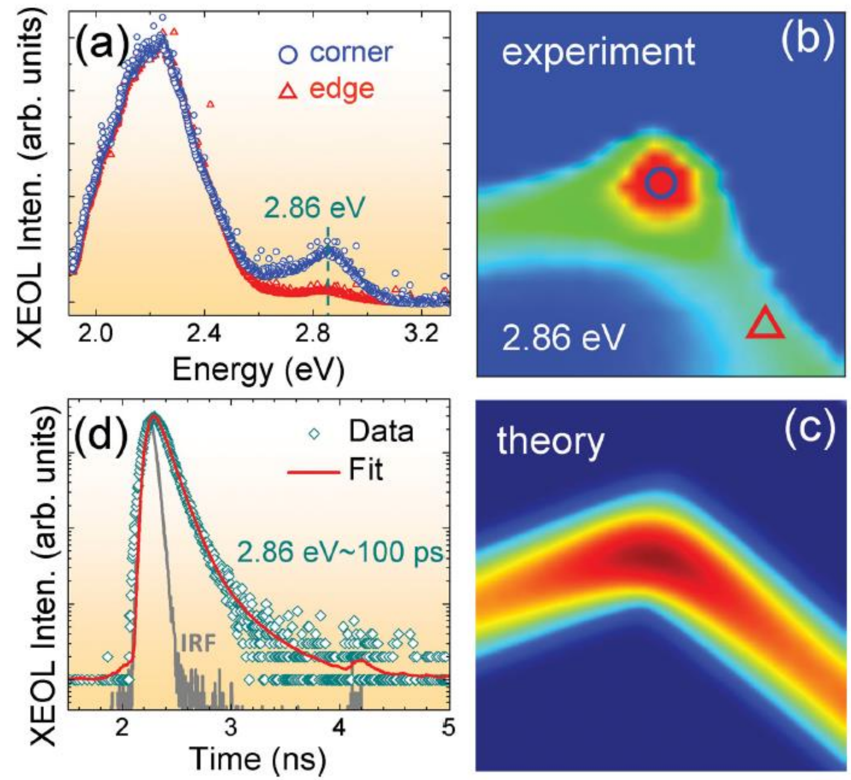
• X-ray diffraction can be transmitted

Adv. Mater. **2014**,
DOI: 10.1002/adma.201304345

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







XEOL: 1.nano-area

2.multi-layer, buried layer

Doping species, Band gap, Defect band, Charge transport

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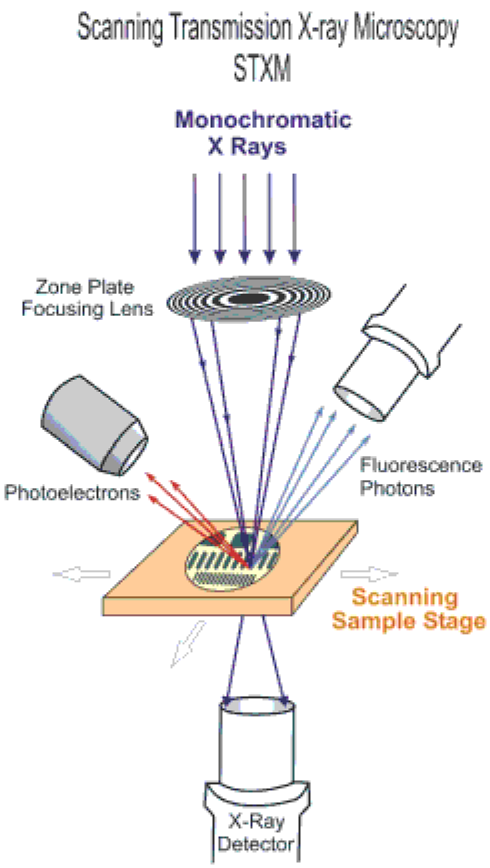
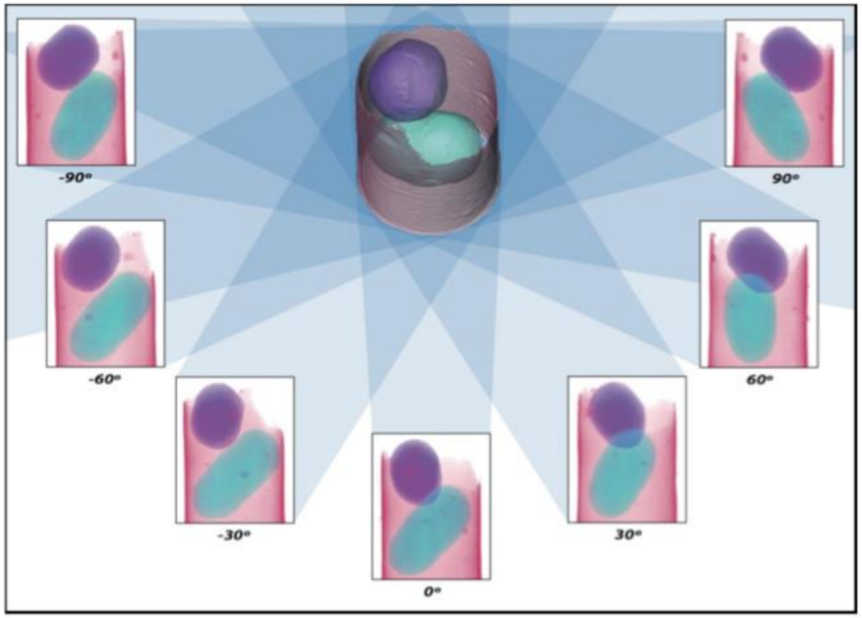
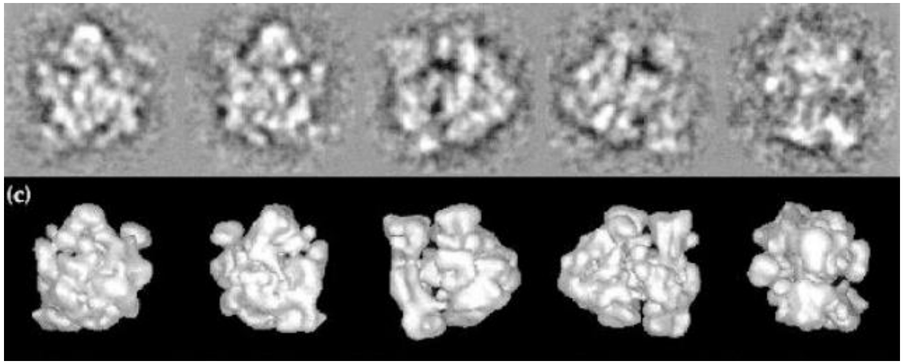
nano-PXM (projection x-ray microscopy)

– Absorption and phase contrast x-ray images





TRENDS in Cell Biology



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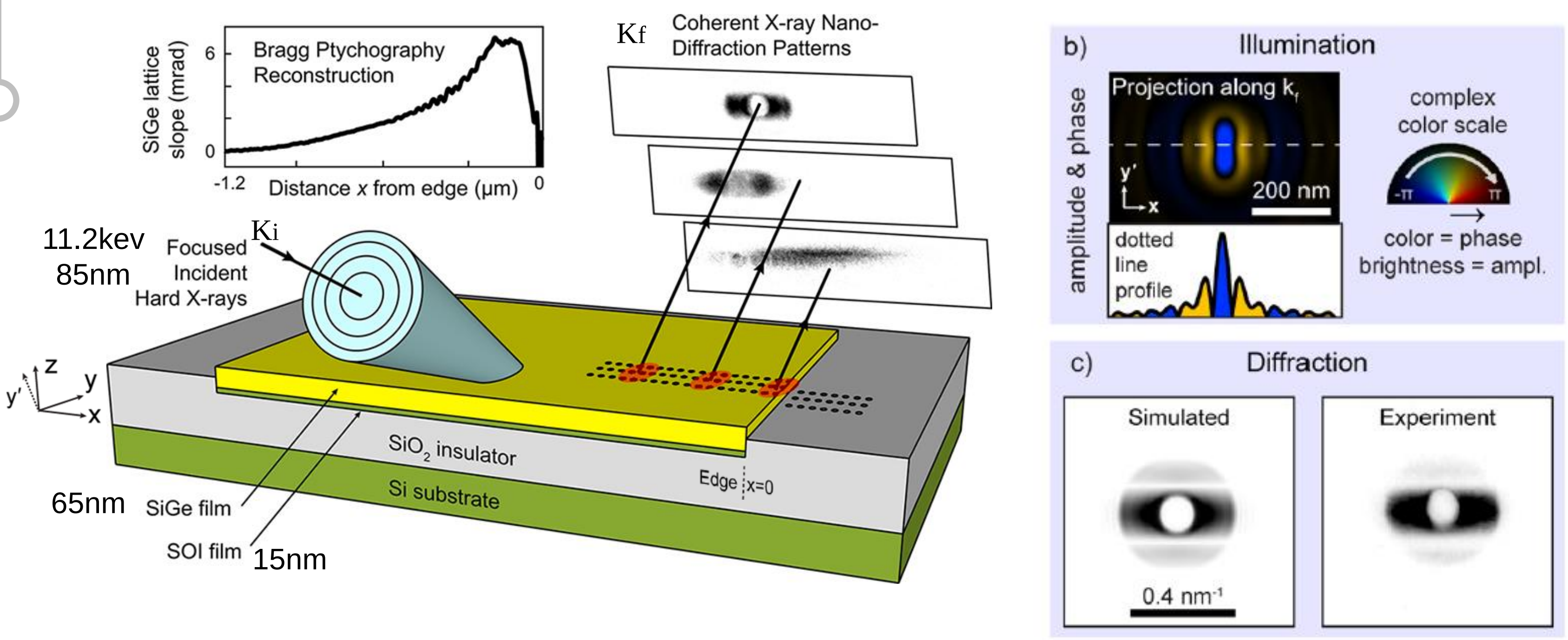
X-ray Bragg projection ptychography from thin film heterostructures



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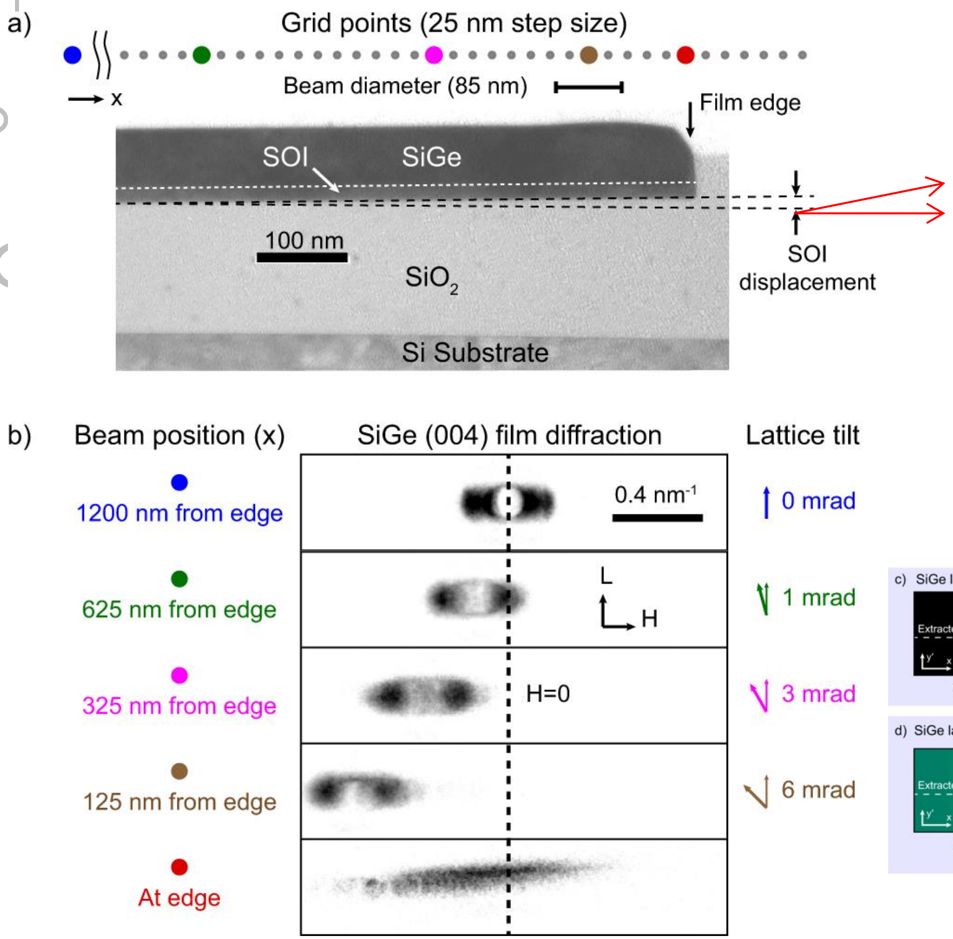
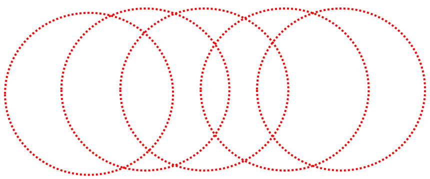
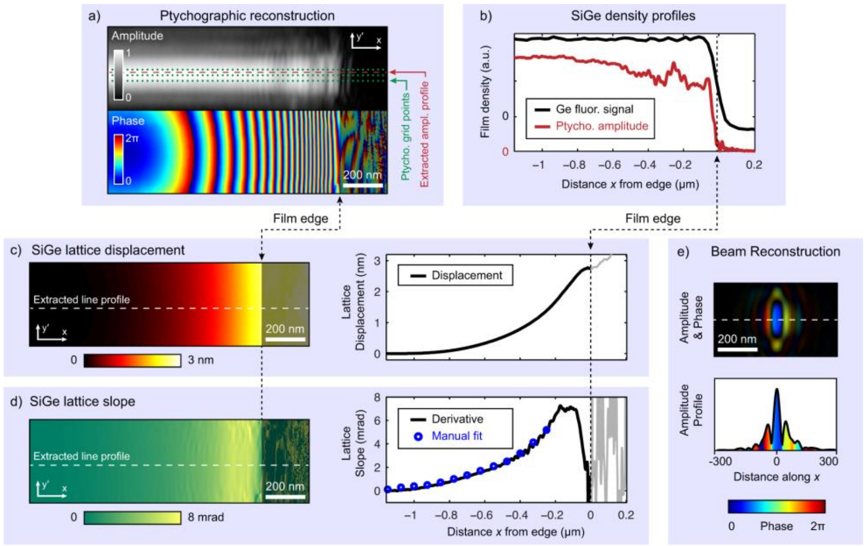
Focused beam Bragg diffraction near the device edge





70% spatial overlap



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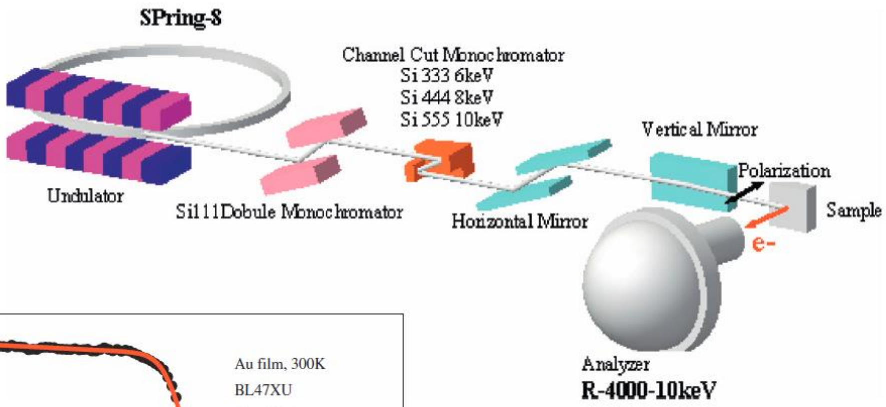
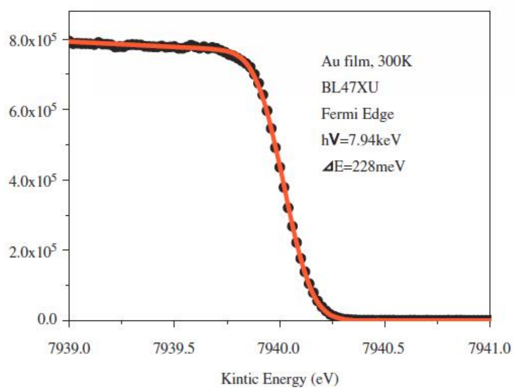
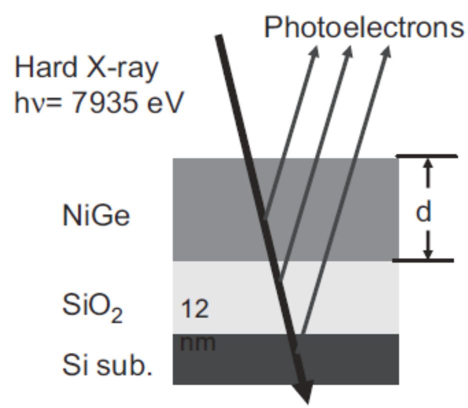
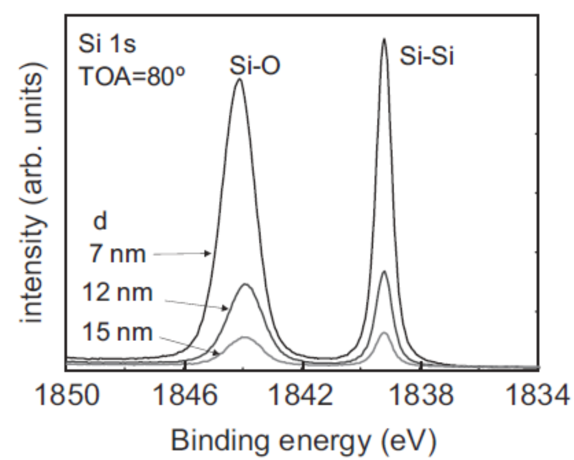
Upgrade: Hard X-ray photoelectron spectroscope(HXPS) at XNP



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







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K. Kobayashi, *Nuclear Instruments and Methods in Physics Research* A 601 (2009) 32–47

Applications

Solid state physics

- Strongly correlated electron systems

YbAl3, YbInCu4, YbCu2Si2

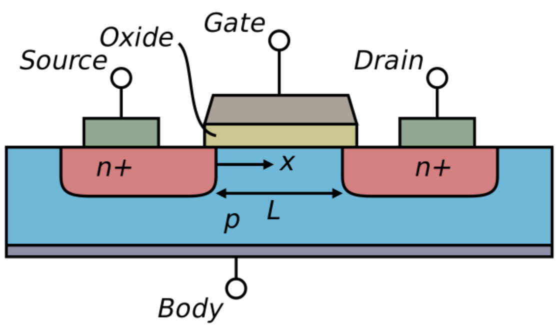
La1-xSrxMnO3 (LSMO)

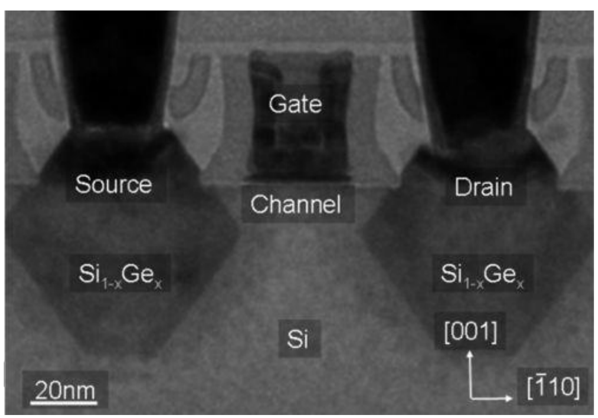
- Spintronics

LaVO3, LaAlO3, Fe3-xMxO4(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

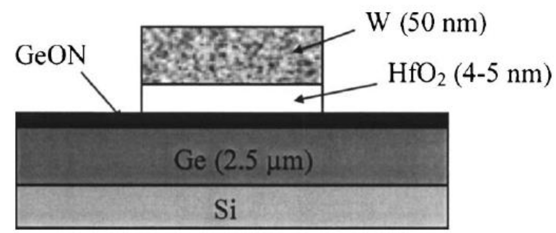
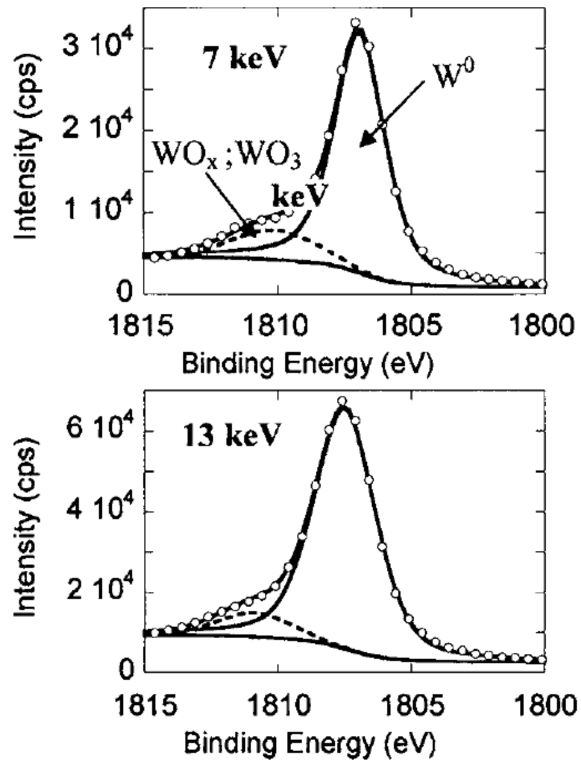
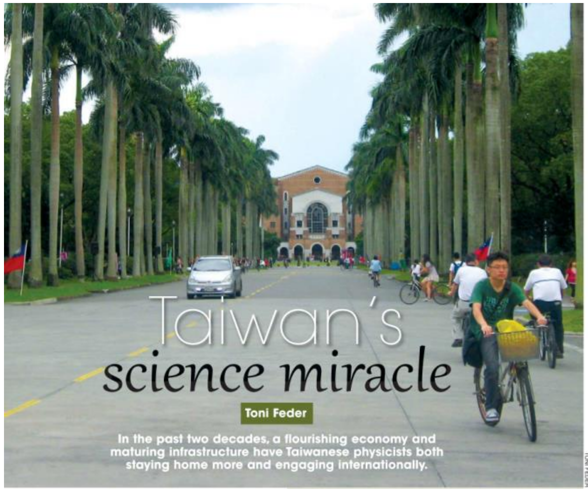


FIG. 1. Diagram of the W/HfO_2/GeON/Ge stack.





March 2014 Physics Today

A state-of-the-art synchrotron light source

The Taiwan Photon Source (TPS), designed to provide high-intensity, low-emittance beams at both hard- and soft-x-ray wavelengths, is set to open in mid 2015. It is intended to support users from Taiwan and abroad in industrial and basic research, especially in the areas of biology and nanotechnology—among the initial beamlines are ones optimized for protein microcrystallography, low-energy excitation of materials with atomic specificity, and scanning nanoprobe studies that resolve structures with 40- to 50-nm resolution. The Taiwanese government footed the $235 million tab for construction, plus $62 million for the first 7 beamlines; the machine can accommodate a total of 44 beamlines.

The storage ring is about 518 meters in circumference, with an electron beam energy of 3 GeV. It will have three superconducting RF cavities to power high-current (500 mA) operation. The TPS will provide coherent x rays in a narrow spectral bandwidth, which is key for high-resolution spectroscopic measurements. Similar machines are in operation in Australia, France, Spain, South Korea, Switzerland, and the UK and are being built in Brazil, Sweden, and the US. Thanks to advances in electron storage rings and undulators, such intermediate-energy rings perform on a par with older, more expensive, higher-energy ones.

Located next to the Taiwan Light Source (TLS), which opened more than 20 years ago at the National Synchrotron Radiation Research Center in Hsinchu Science Park on the island's northwestern coast, the TPS storage ring circulates a beam that is double the energy and two to five orders of magnitude brighter than the TLS beam. For the first few years, at least, both light sources will operate—the TLS at visible UV and IR wavelengths, and the new TPS in the hard- and soft-x-ray regimes.

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Thanks for your attentions