New Scientific Possibilities & Directions

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Key words:

-*In situ*

- Dynamics

Why SR?

Realization of abundant, secure, sustainable society

Growth of industry

Natural environment

Socila welfare

Persistent energy

Sophisticated medicine

Sophisticated infor. & comm. tech.

Tech. of Solar, hydrogen energy use

Manufacturing tech. of materials

Biomedicine

Quantum dot, optoelectronics

Hydrogen storage materials

catalyst

Nano-tube

molecular・Bio-materials

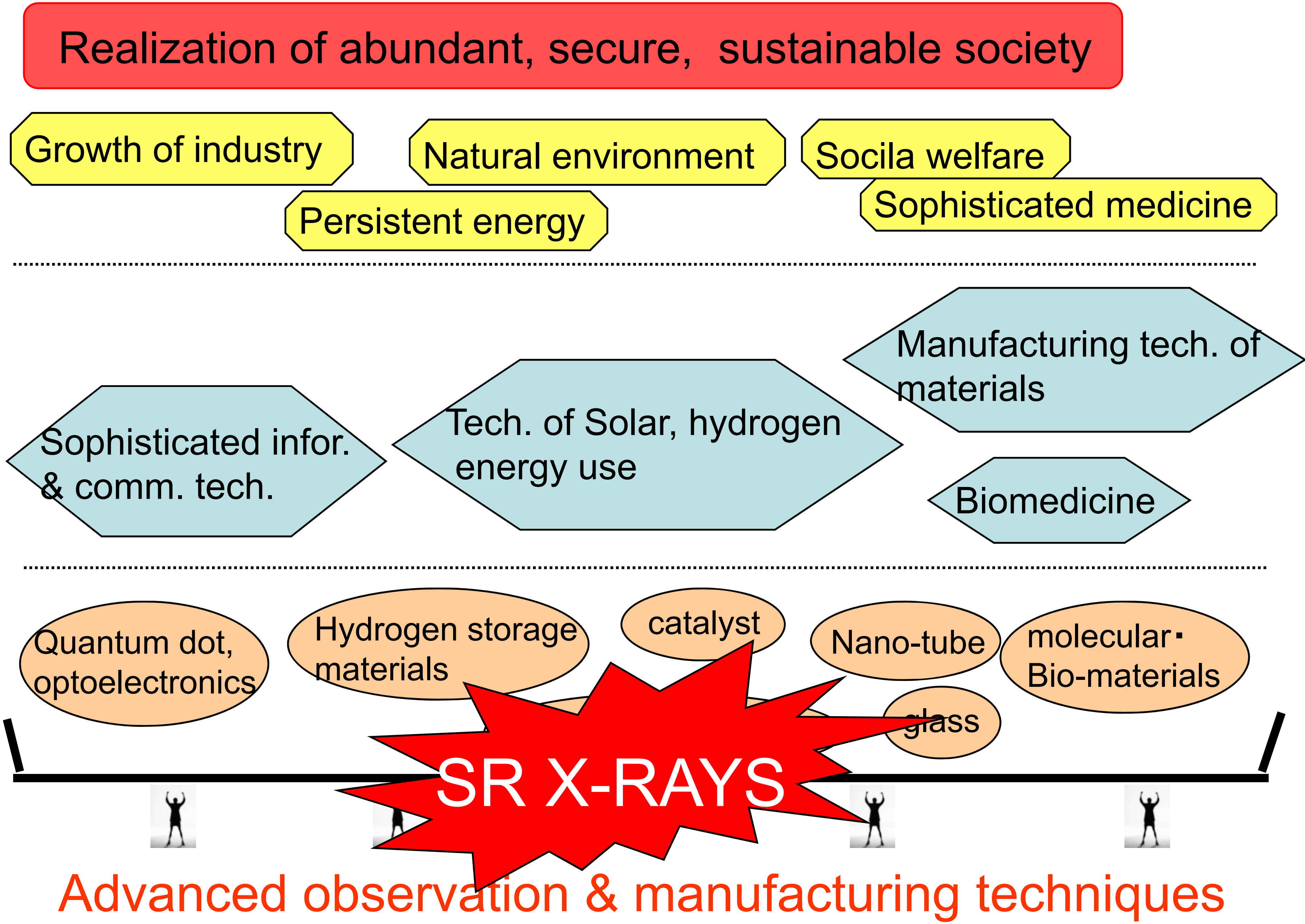
Spintronics materials

glass

Advanced observation & manufacturing techniques

Why SR?



Realization of abundant, secure, sustainable society
Growth of industry
Natural environment
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Sophisticated medicine
Manufacturing tech. of materials
Sophisticated infor. & comm. tech.
Tech. of Solar, hydrogen energy use
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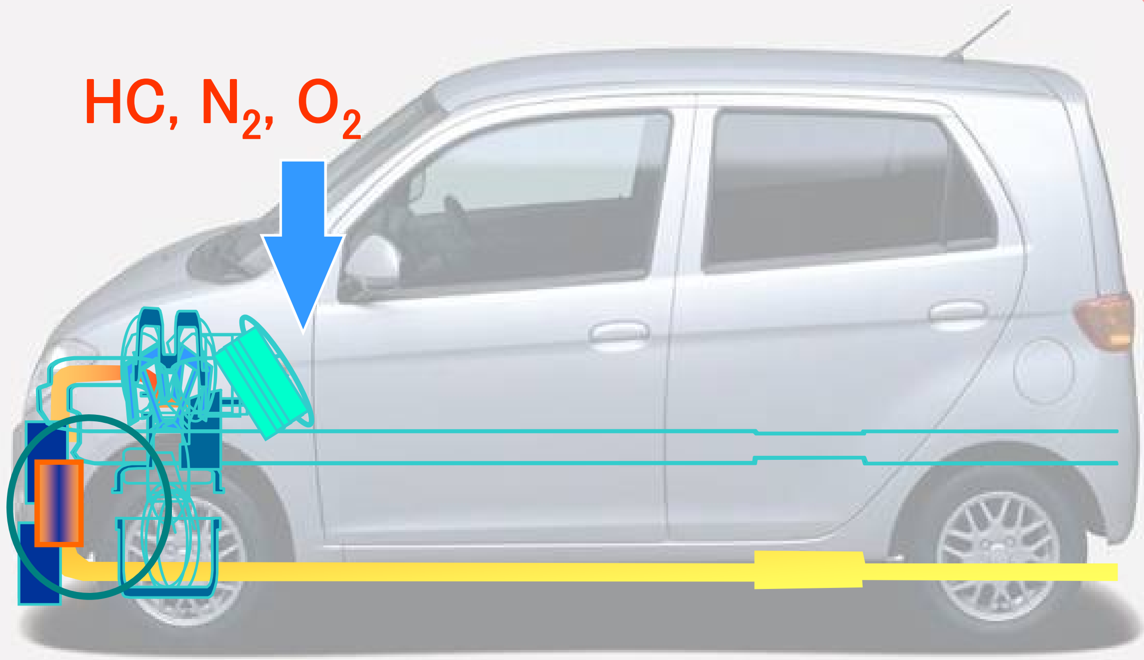
Quantum dot, optoelectronics
Hydrogen storage materials
catalyst
Nano-tube
molecular･Bio-materials
glass
SR X-RAYS
Advanced observation & manufacturing techniques

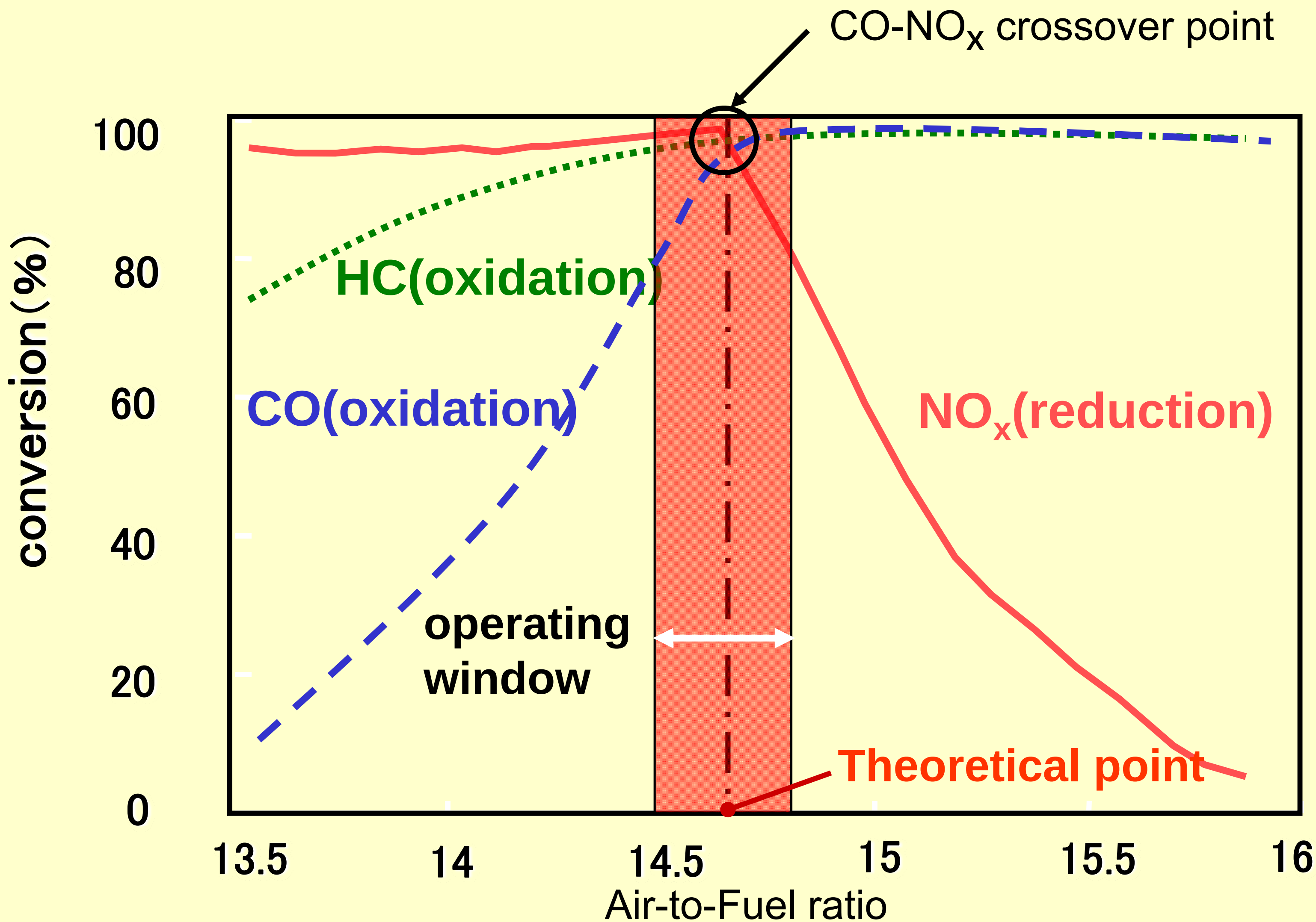
We would like to live in pollution-free environment

Three-way catalyst



Pd, Pt, Rh

HC	$\longrightarrow$	H_2O+C	oxidation
CO	$\longrightarrow$	CO_2	oxidation
NO_X	$\longrightarrow$	N_2+O_2	reduction

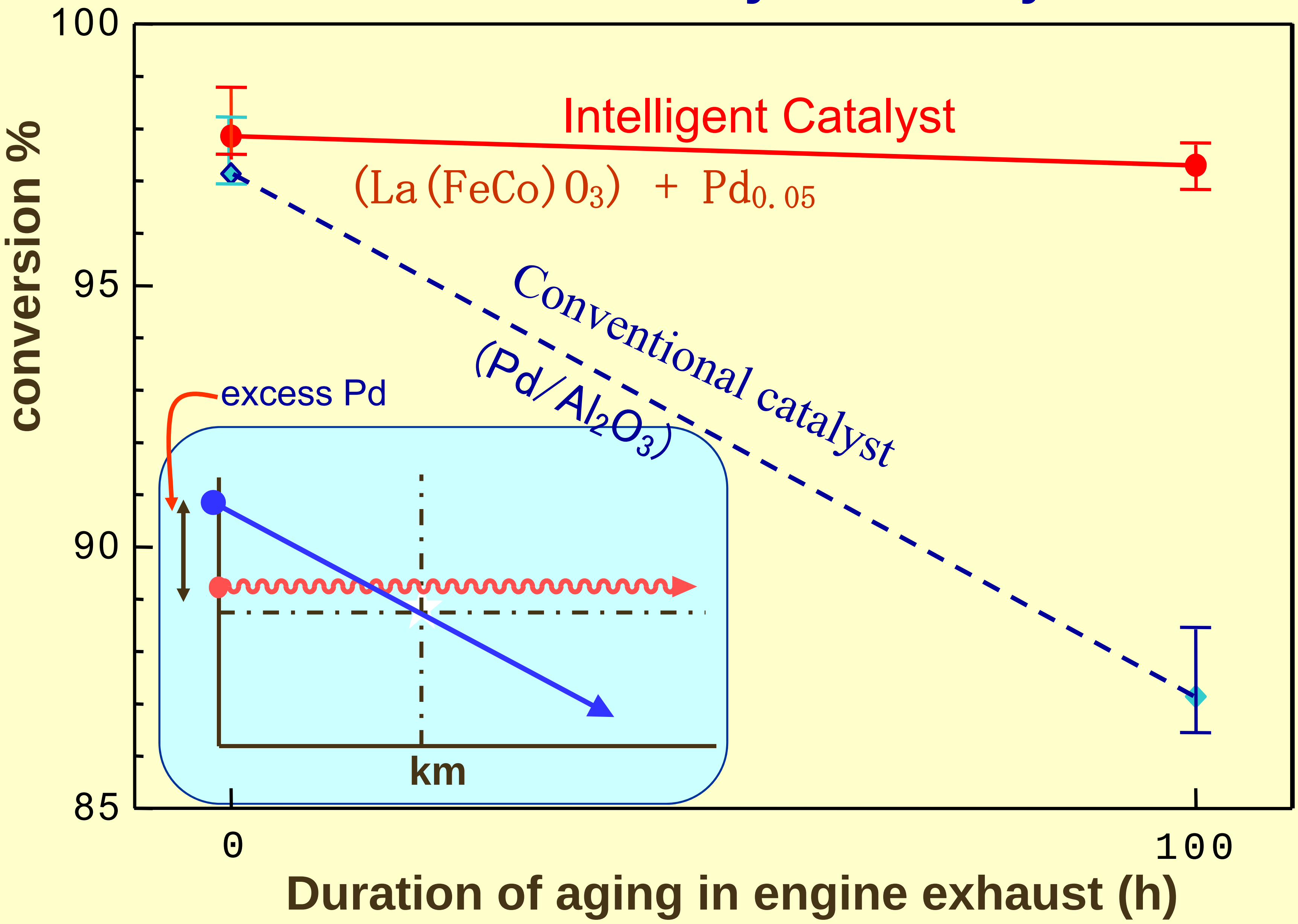


Feedback-controlled engine management causes

Reductive and Oxidative (Redox) Fluctuations

At 1~4Hz within ±4%

Life time of catalytic activity

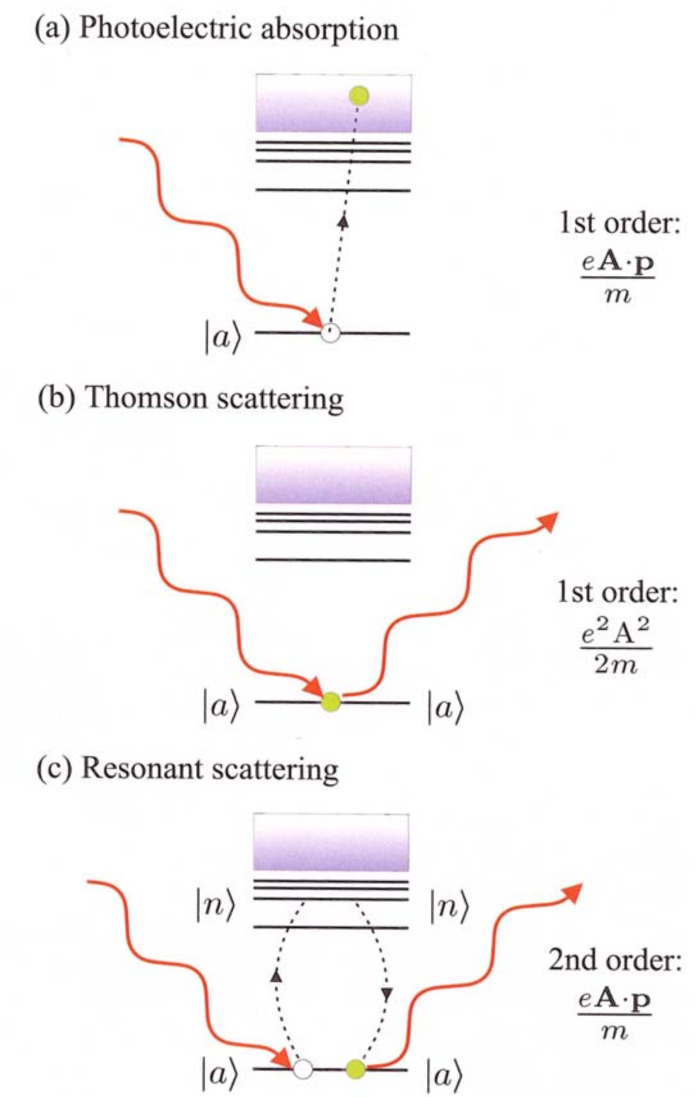


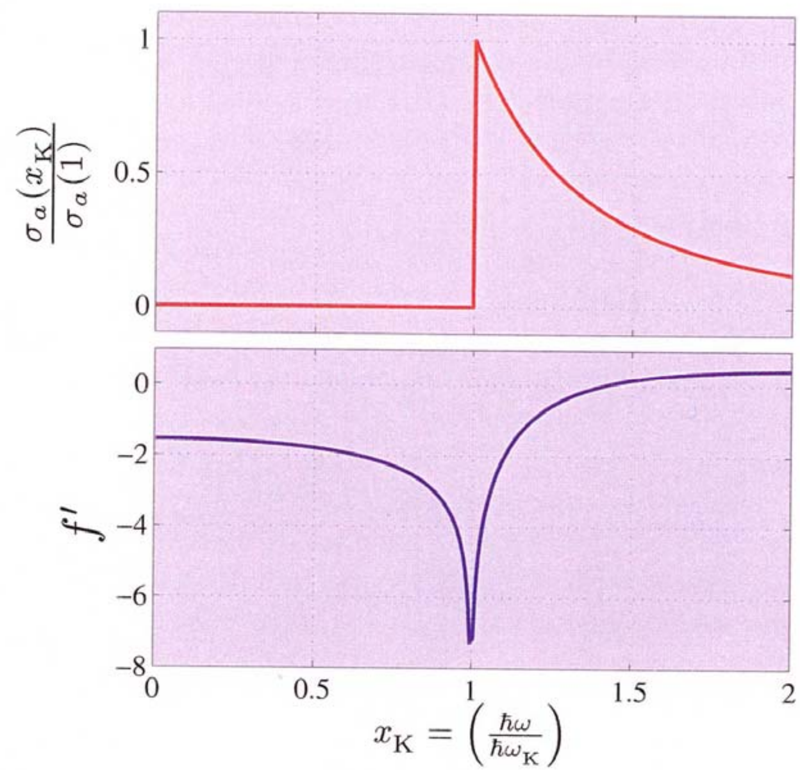
Energy tunability

↓

Resonance
Anomalous effect

Energy selectivity → Use of anomalous dispersion





$$f(\mathbf{Q},\omega)=f^0(\mathbf{Q})+f'(\omega)+if''(\omega)$$

K-K relation

From Elements of modern x-ray physics by J. Als-Nielsen and D. McMorrow

Quantum Mechanical Description

Free particle: $\Rightarrow$ $H = \dfrac{P^2}{2m}$

Interaction with an electromagnetic field:

$$H = \frac{\left(\vec{P} - e\vec{A}\right)^2}{2m} = \frac{P^2}{2m} + \frac{e^2}{2m}A^2 - \frac{e}{m}\vec{P} \bullet \vec{A}$$

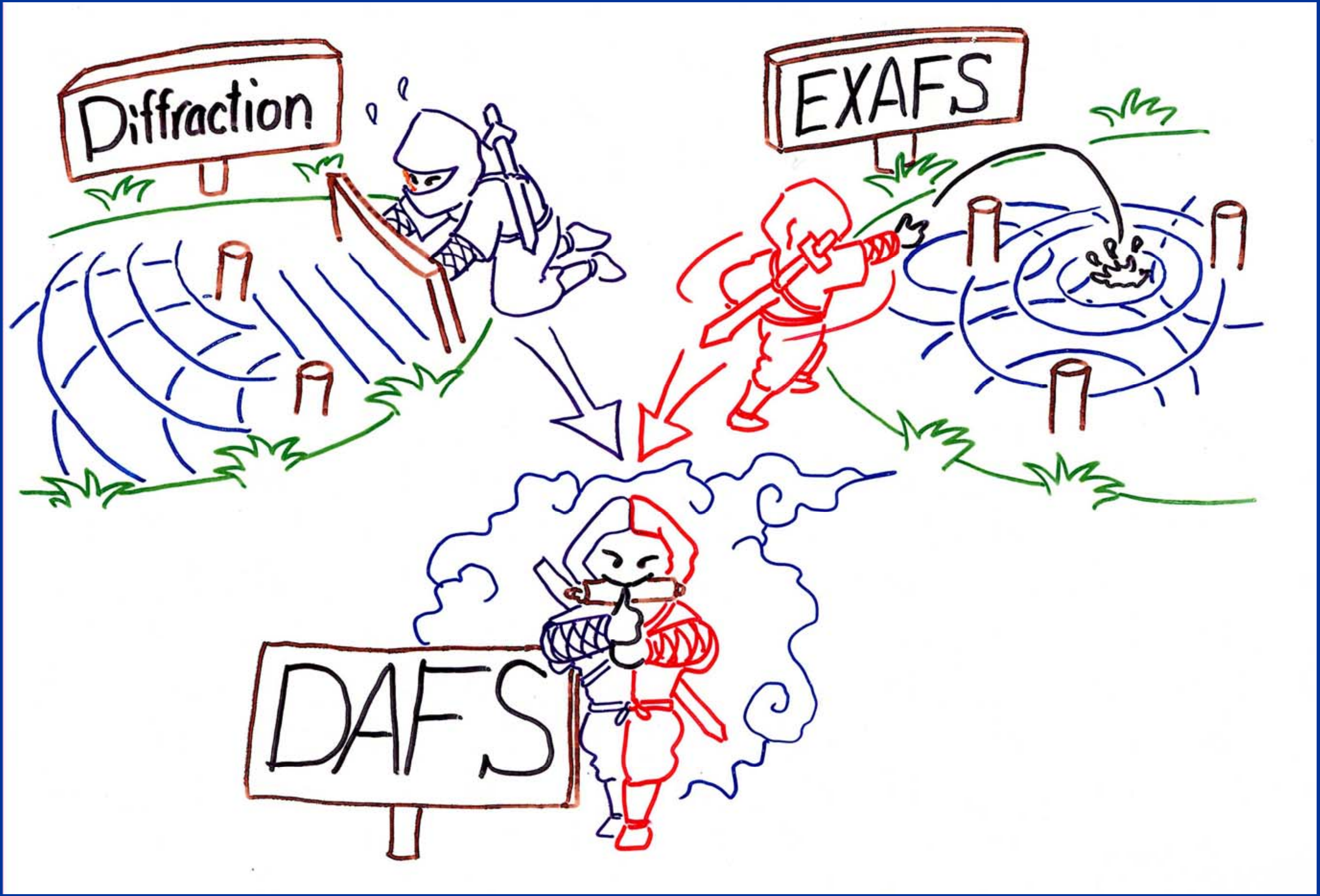
($\frac{e^2}{2m}A^2 \rightarrow H_1$, $\frac{e}{m}\vec{P} \bullet \vec{A} \rightarrow H_2$)

Transition probability W:

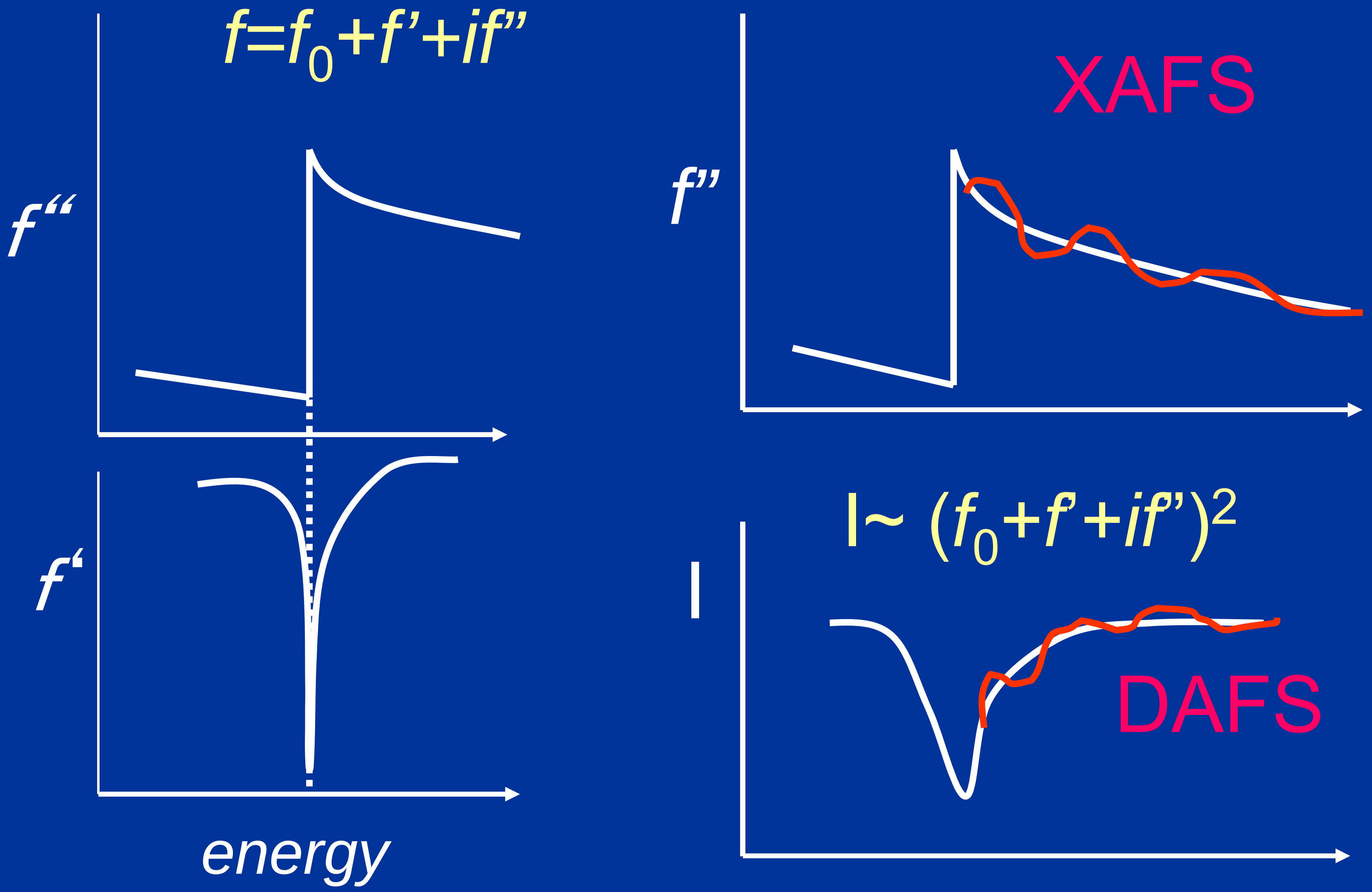
$$W = \frac{2\pi}{\hbar}\left|\langle f|H_1|i\rangle + \sum_{n=1}^{\infty} \frac{\langle f|H_2|n\rangle\langle n|H_2|i\rangle}{E_i - E_n}\right|^2 \times \rho\left(\varepsilon_f\right), \qquad E_i = \hbar\omega + E_a$$

($\langle f|H_1|i\rangle \rightarrow f_0$; $\sum_{n=1}^{\infty} \frac{\langle f|H_2|n\rangle\langle n|H_2|i\rangle}{E_i - E_n} \rightarrow f_1 + if_2$)

Marriage between XRD and XAFS



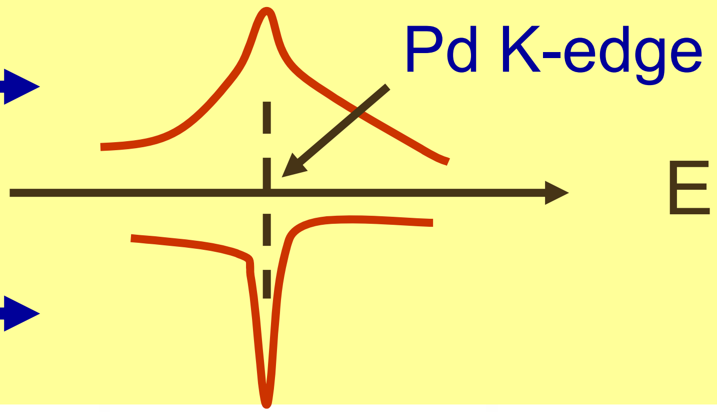
XAFS & DAFS

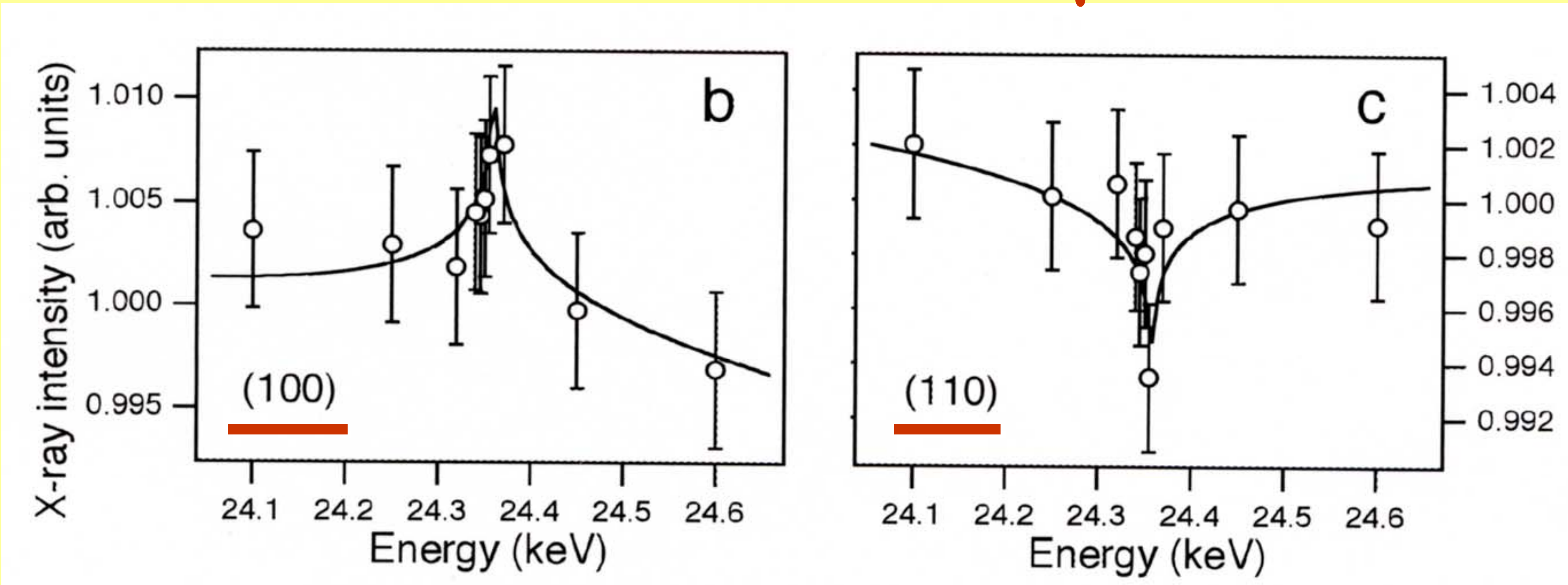


Anomalous Diffraction Intensity around Pd *k*-edge
Oxidized sample

$$F(100) \sim |f_A - \underline{f_B} - f_O|$$

$$F(110) \sim |f_A + \underline{f_B} - f_O|$$

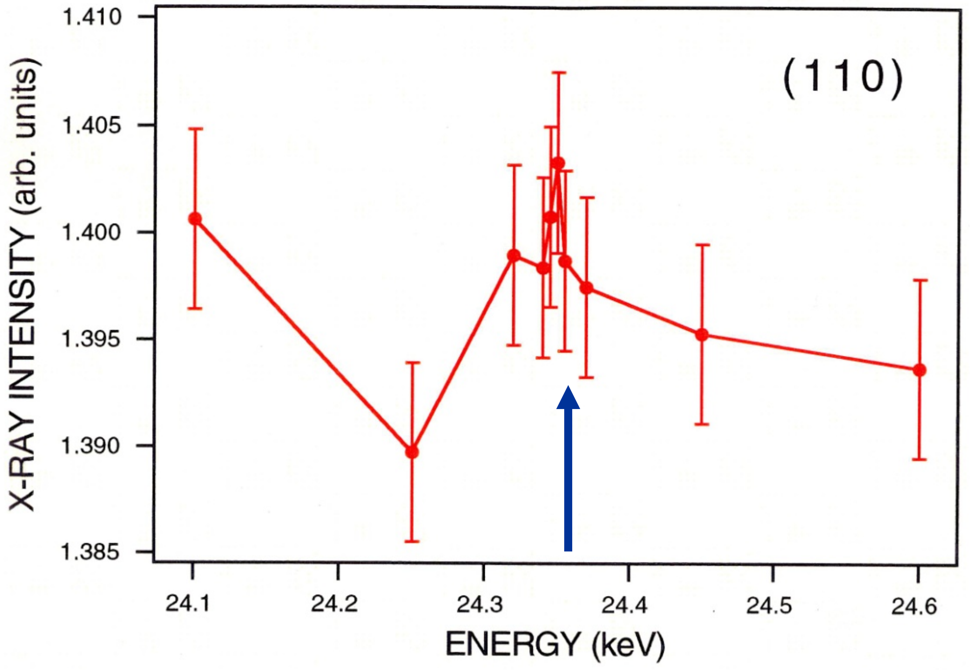


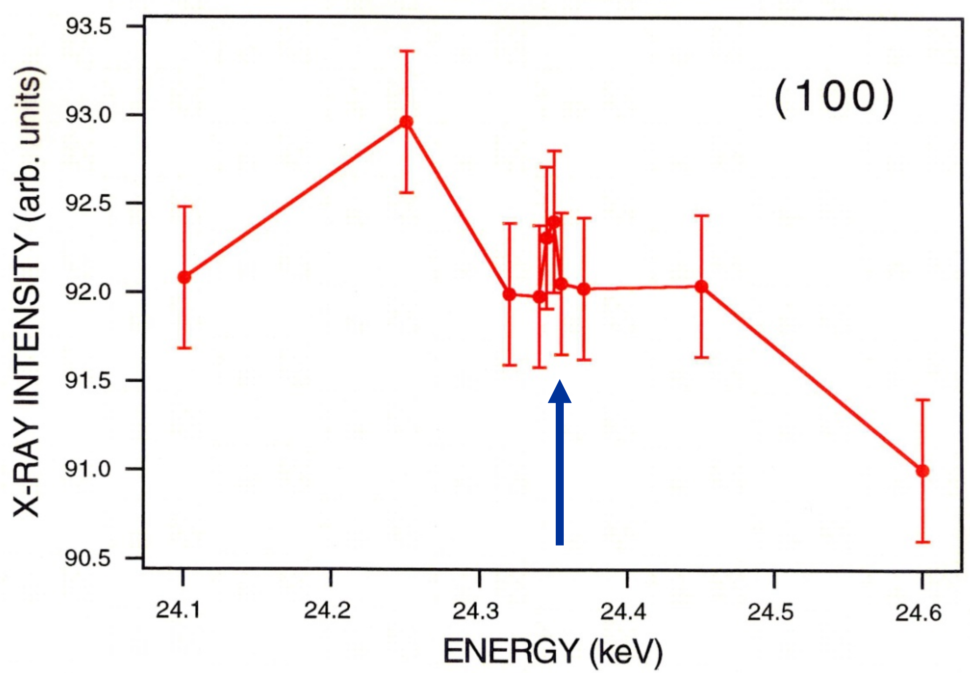


Anomalous Diffraction at (110), (100) of Reduced sample.

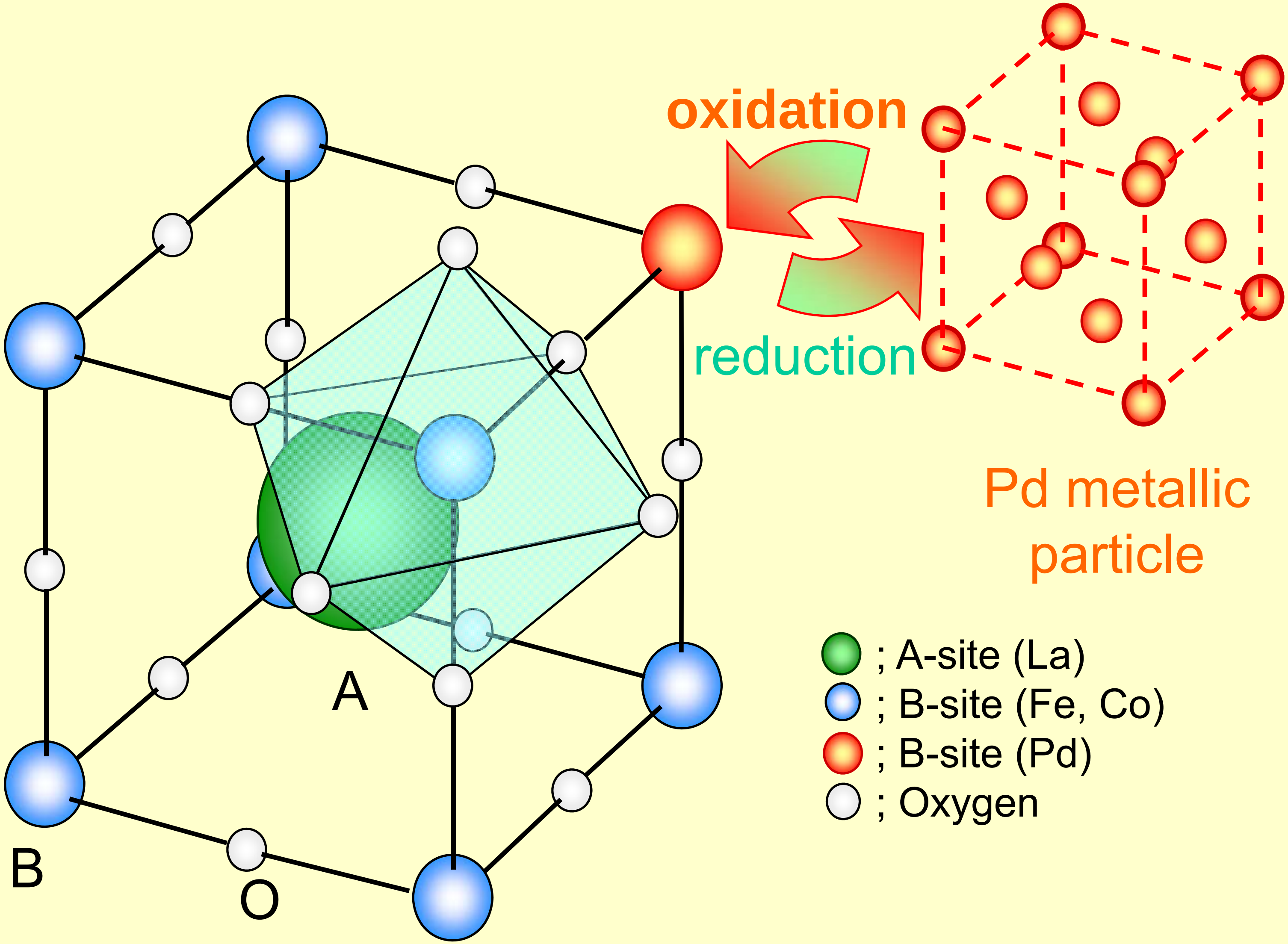
No change is observed !

Pd atom is out of the Perovskite lattice!?





Self-regeneration of Catalyst



Y. Nishihata, J. Mizuki, et al.,Nature 418 ('02) 164

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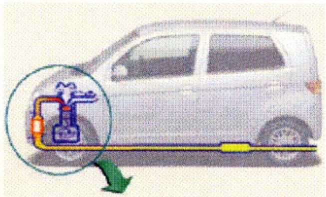
Cleaning up catalysts

Although the use of catalytic converters to reduce harmful automotive emissions has greatly improved the air quality in our cities, the metals required to achieve this are both expensive and rare. But by incorporating these metals into perovskite crystals, the longevity and metal content of these converters can be drastically reduced.

11 July 2002

Magdalena Helmer



Since its introduction more than 20 years ago, the catalytic converter has sharply reduced automotive emissions. It breaks down harmful carbon monoxide, nitrogen oxides and hydrocarbons before the exhaust leaves the car's tailpipe, by using catalysts containing palladium, platinum and rhodium. But these precious metals are expensive, and are produced through intensive and polluting chemical processing of sulphide ores extracted from often treacherous underground mines.

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nature 11 July 2002

highlights

Catalytic converter: Manifold delight

The catalytic converter in modern automobiles leads a hard — and hot — life. To counter the resultant loss in efficiency, comparatively large amounts of precious metals are packed into conventional converter systems to guarantee adequate performance over the 80,000 km range normally expected. A re-examination of a palladium-perovskite catalyst first considered as a catalytic converter in the 1970s reveals previously unrecognized properties that could significantly reduce wastage of precious metals and extend the life of converters. In an atmosphere alternating between oxidative and reductive, typical of the exhaust gas from modern engines, the palladium atom jumps in and out of the perovskite lattice, preventing the heat-induced growth of metal particles that can limit catalytic efficacy.

But, one referee still has doubts about the model because the experiments were done *ex-situ*

Questions:

- How fast does Pd move?
- What temperature does Pd start moving?

⇓

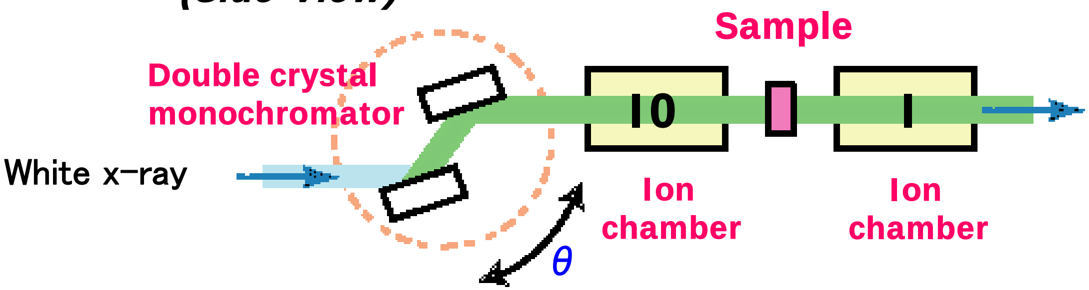
In-situ experiment

Y. Nishihata et al., nature 418, (2002) 164

DXAFS (Energy Dispersive XAFS)

■ Standard XAFS

(Side-View)

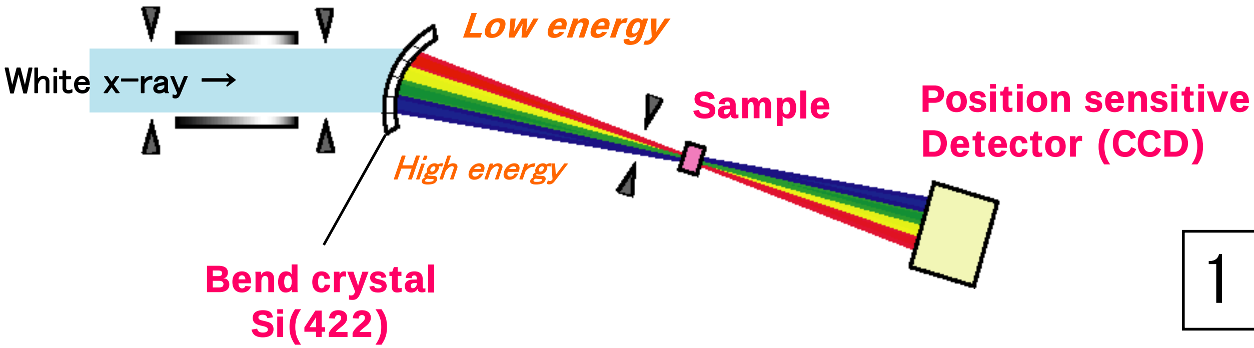


Data acquisition time

3 – 30 min

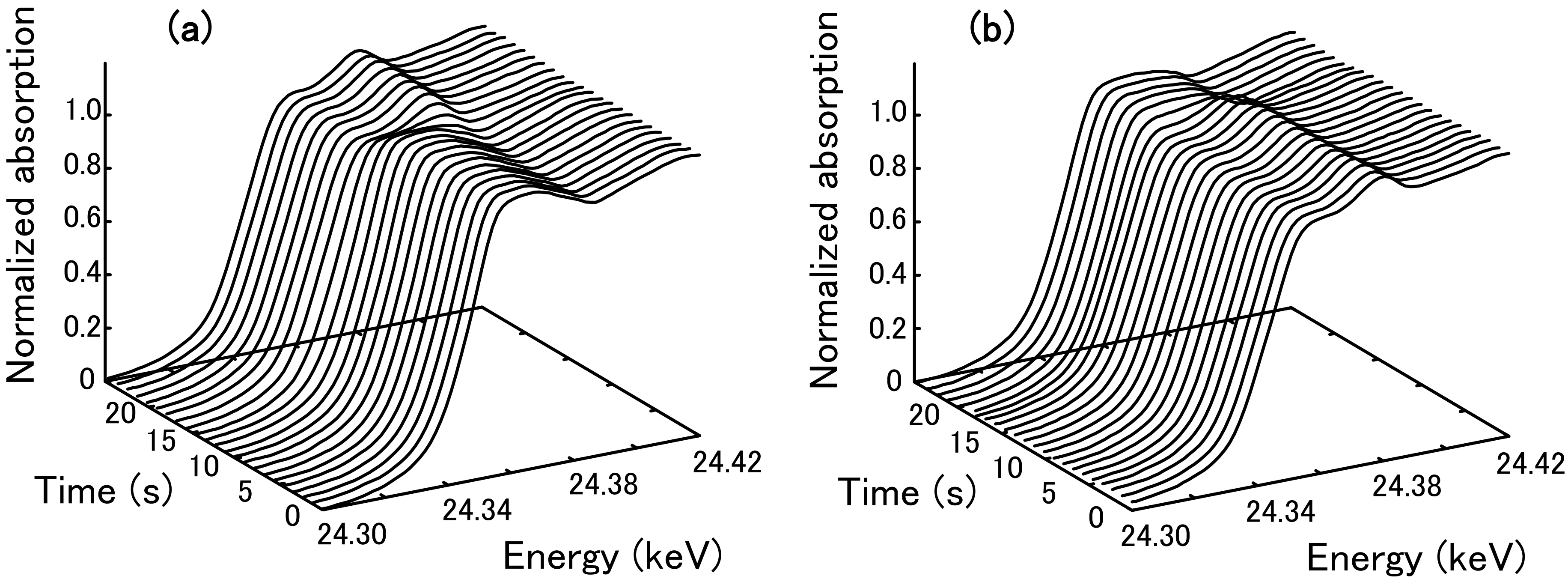
■ DXAFS

(Top-View)



1 – 100msec

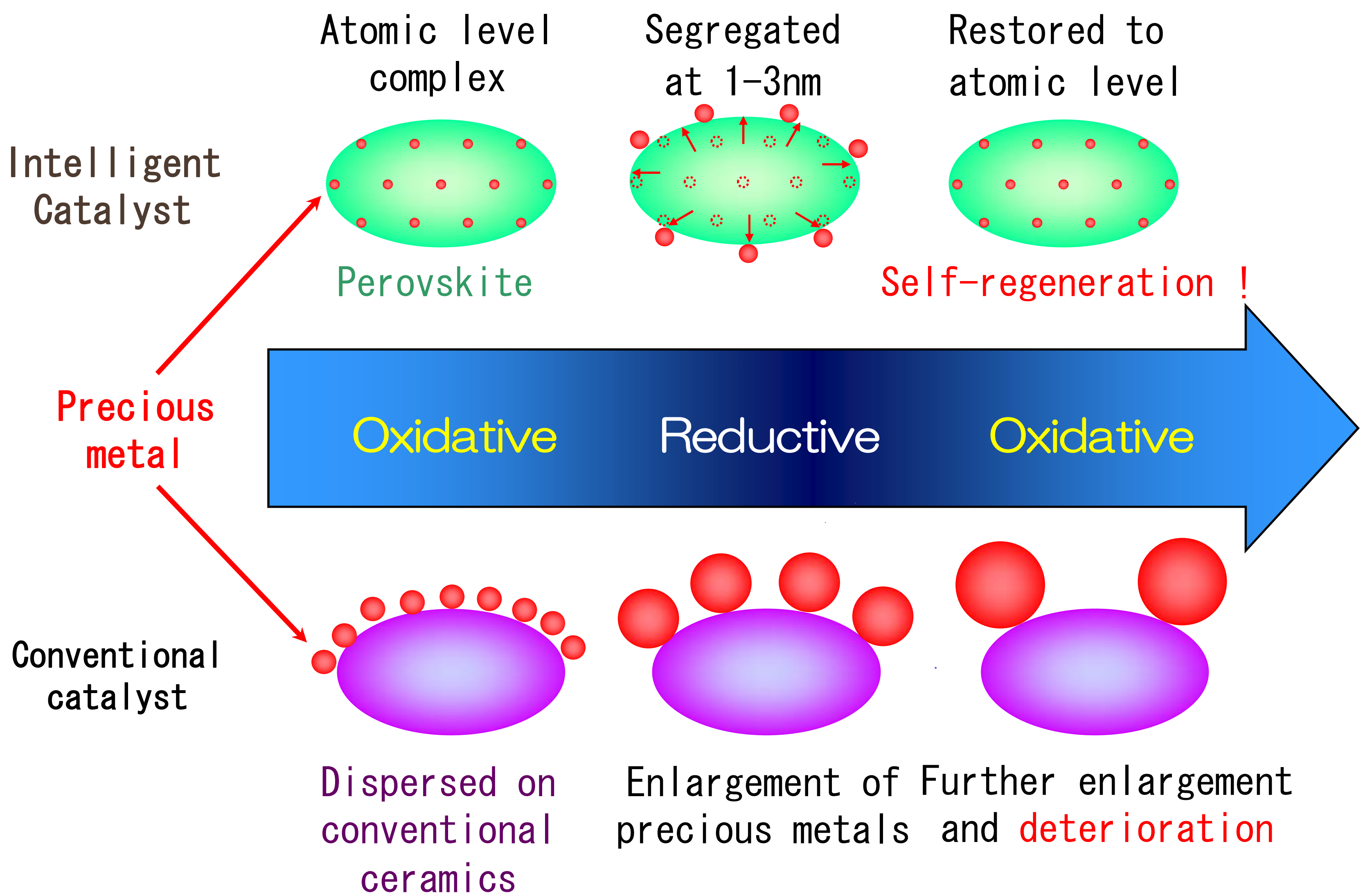
XANES(400℃)



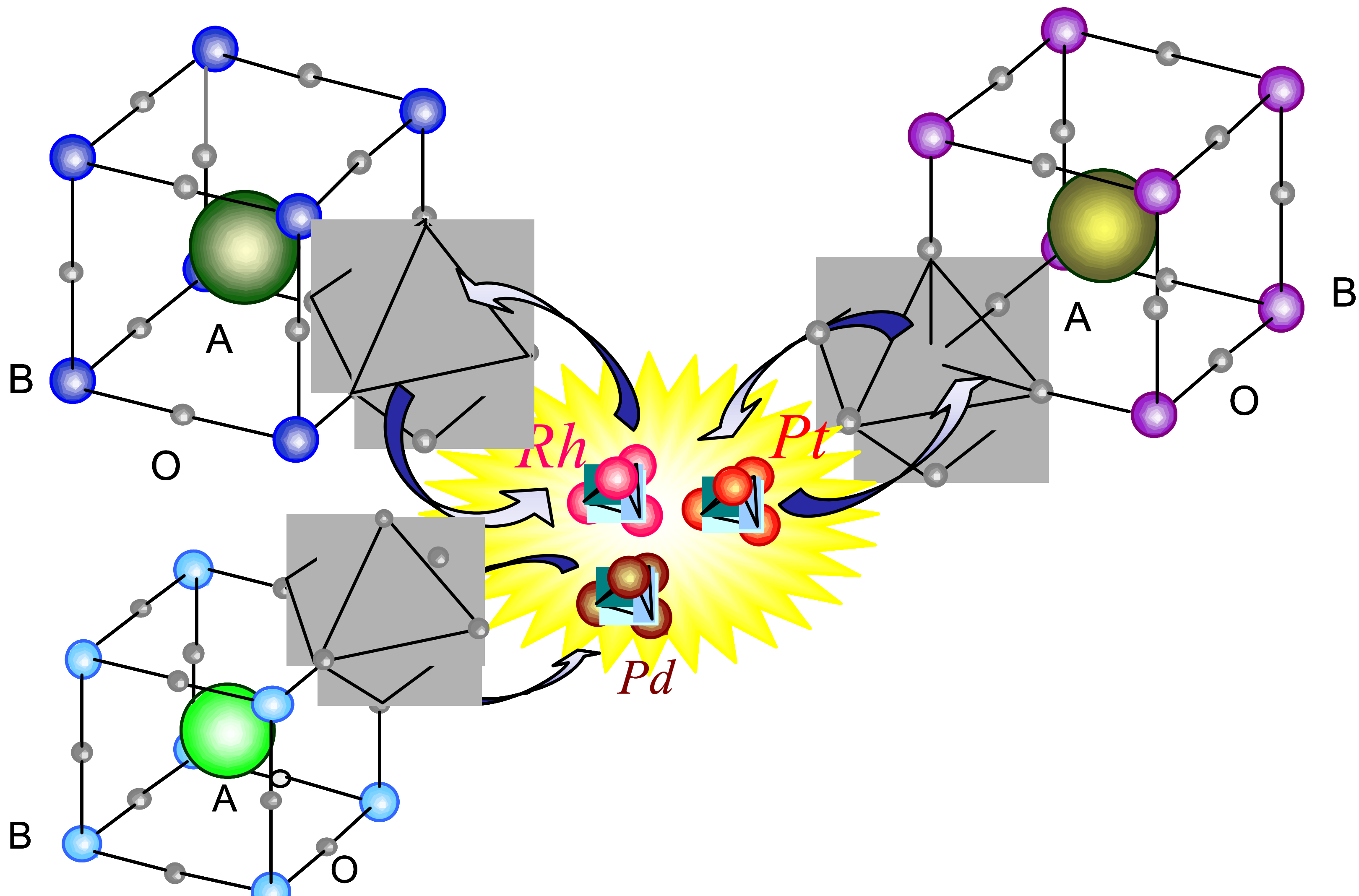
Reduction

Oxidation

Self-regeneration model



Super-intelligent catalysts !



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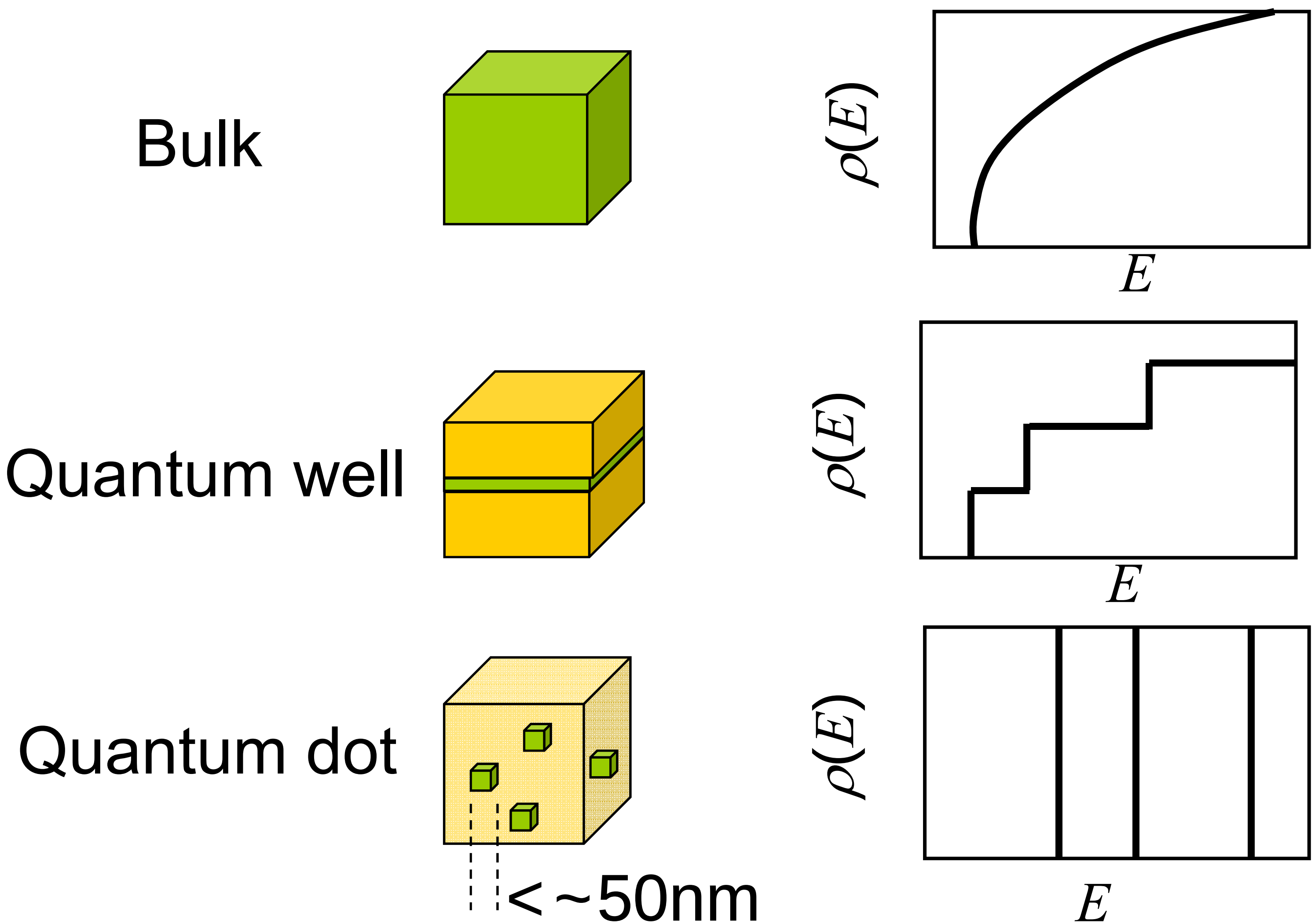
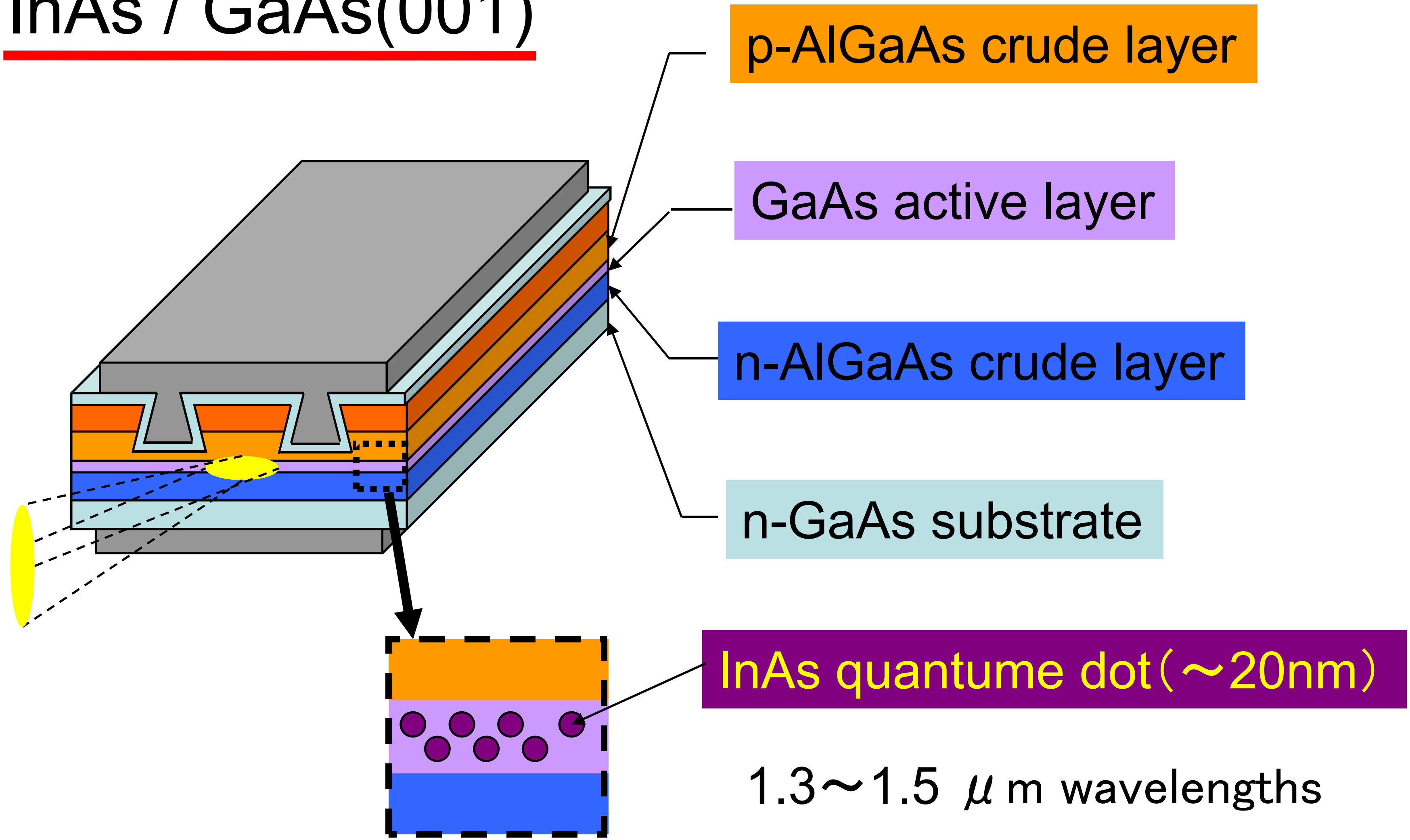
Semiconductor nano-structure



Semiconductor Laser

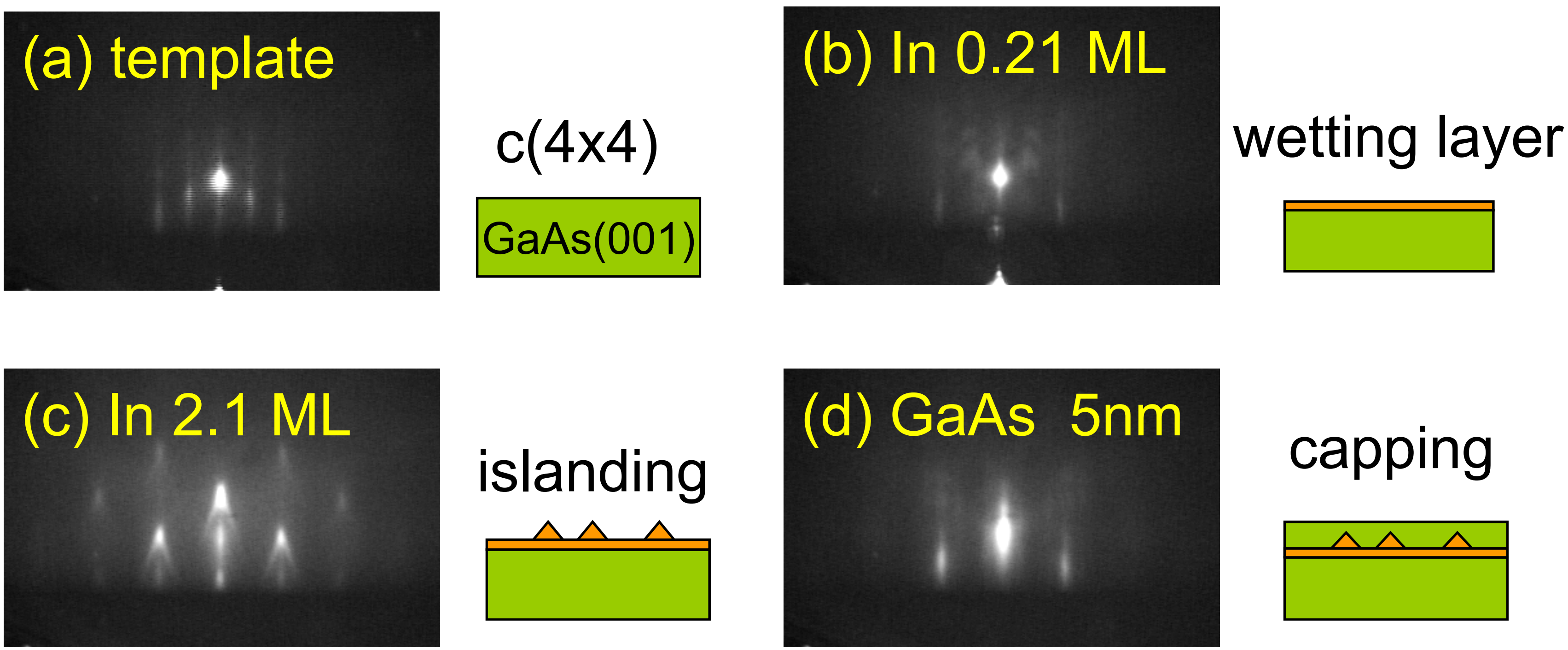
InAs / GaAs(001)



InAs/GaAs(001) self-assembled quantum dots

MBE・MOCVD（Stranski-Krastanow growth）

GaAs-InAs 7% mismatch



Problems to be overcome in QDs fabrication

- high uniformity in QDs size & shape
- control of chemical composition
- high QDs density

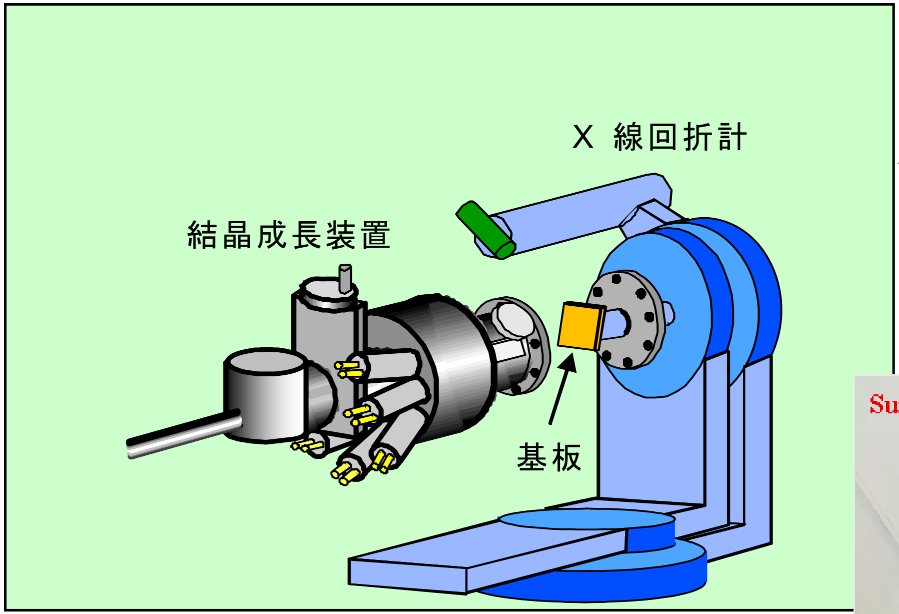
- Understanding the growth mechanism

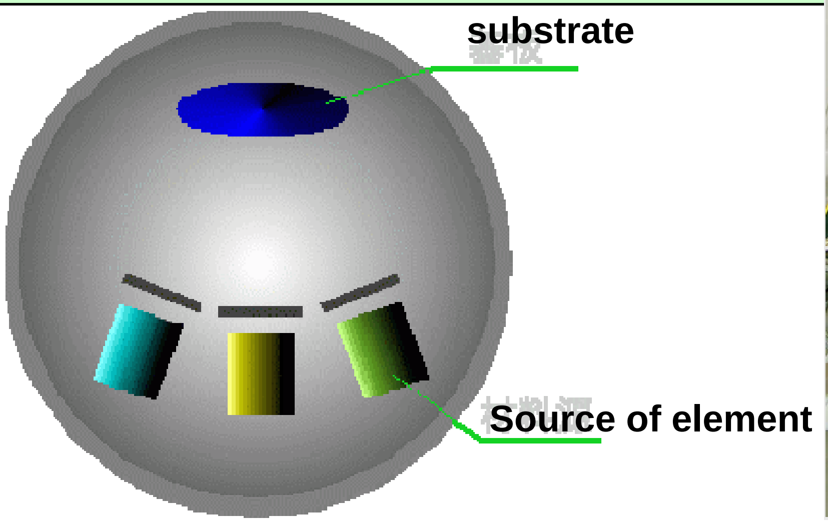
- Real time monitoring during the growth

Surface diffractometer + MBE

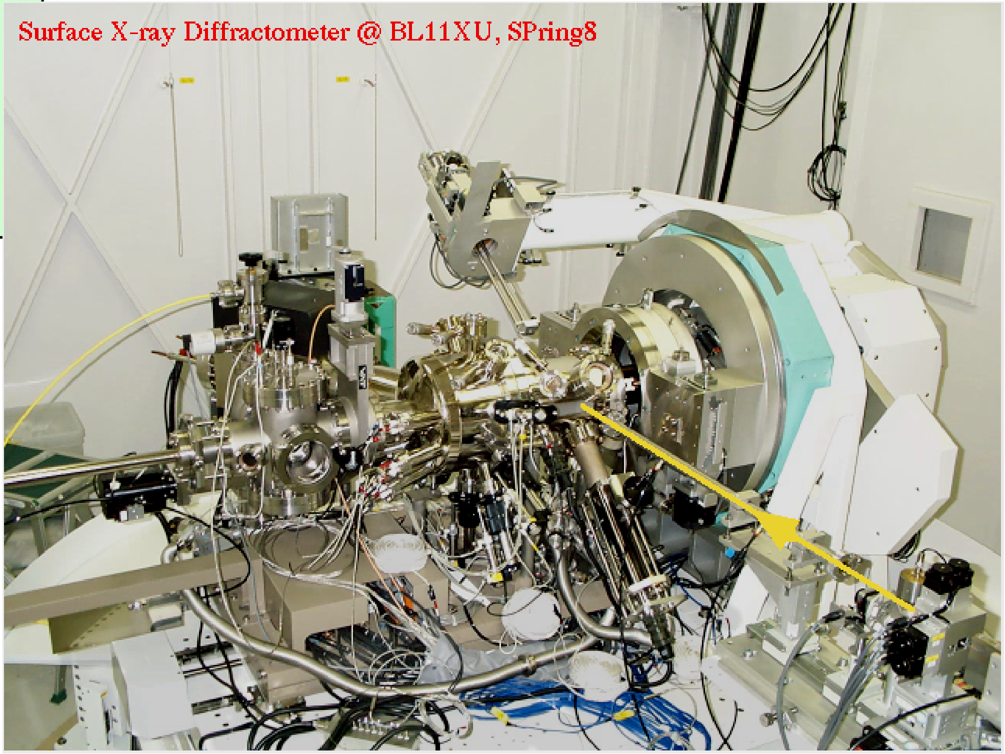
—study of reaction front—

Marriage between crystal growth and SR X-rays.



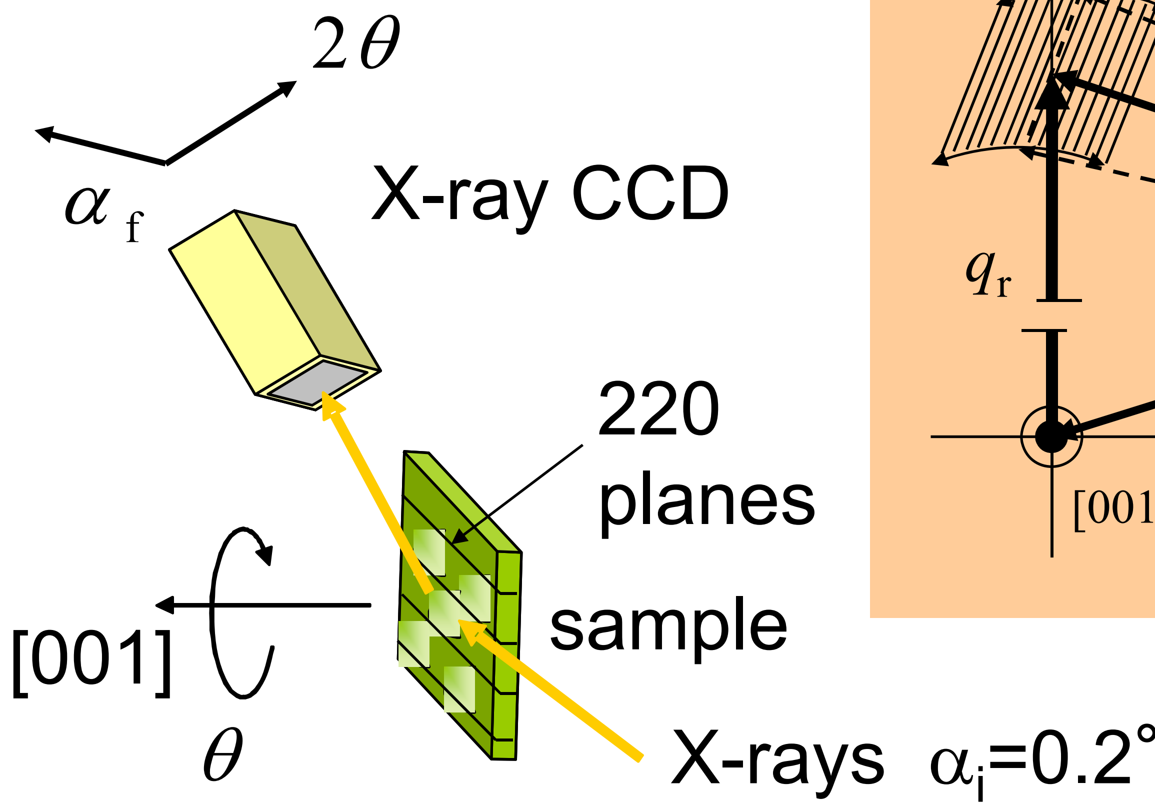


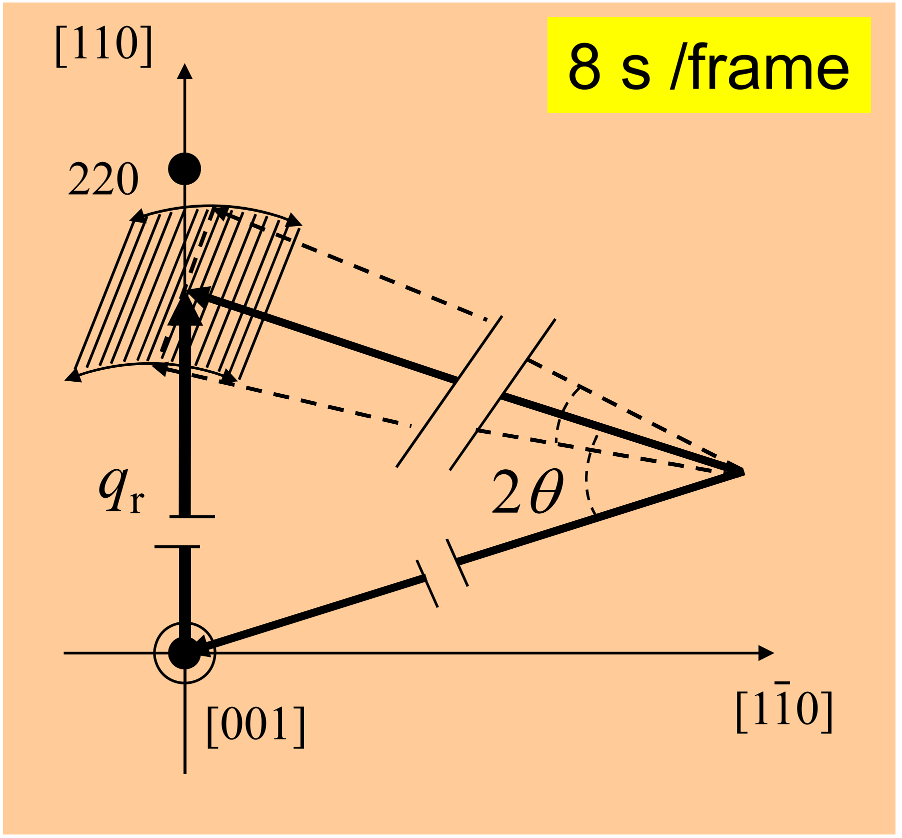
（from home page of Kishimoto Lab., Sophia Univ.）



M. Takahasi J. M. et al., Jpn. J. Appl. Phys. 41 ('02) 6247

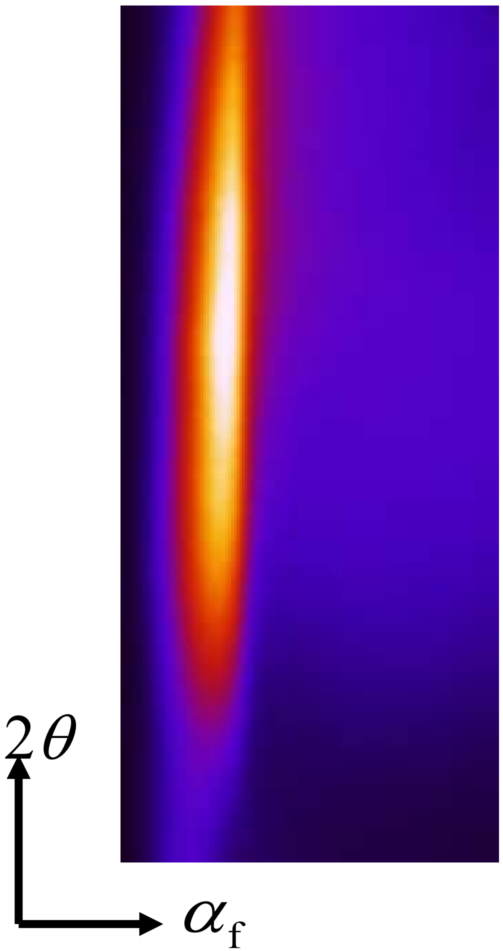
Experimental configuration





Interpretation of CCD images

4.9ML InAs
at 480°C



$$I(2\theta, \alpha_f) \propto T(\alpha_i, z) T(\alpha_f, z) S(2\theta)$$

$S(2\theta)$: kinematical θ–2θ spectrum

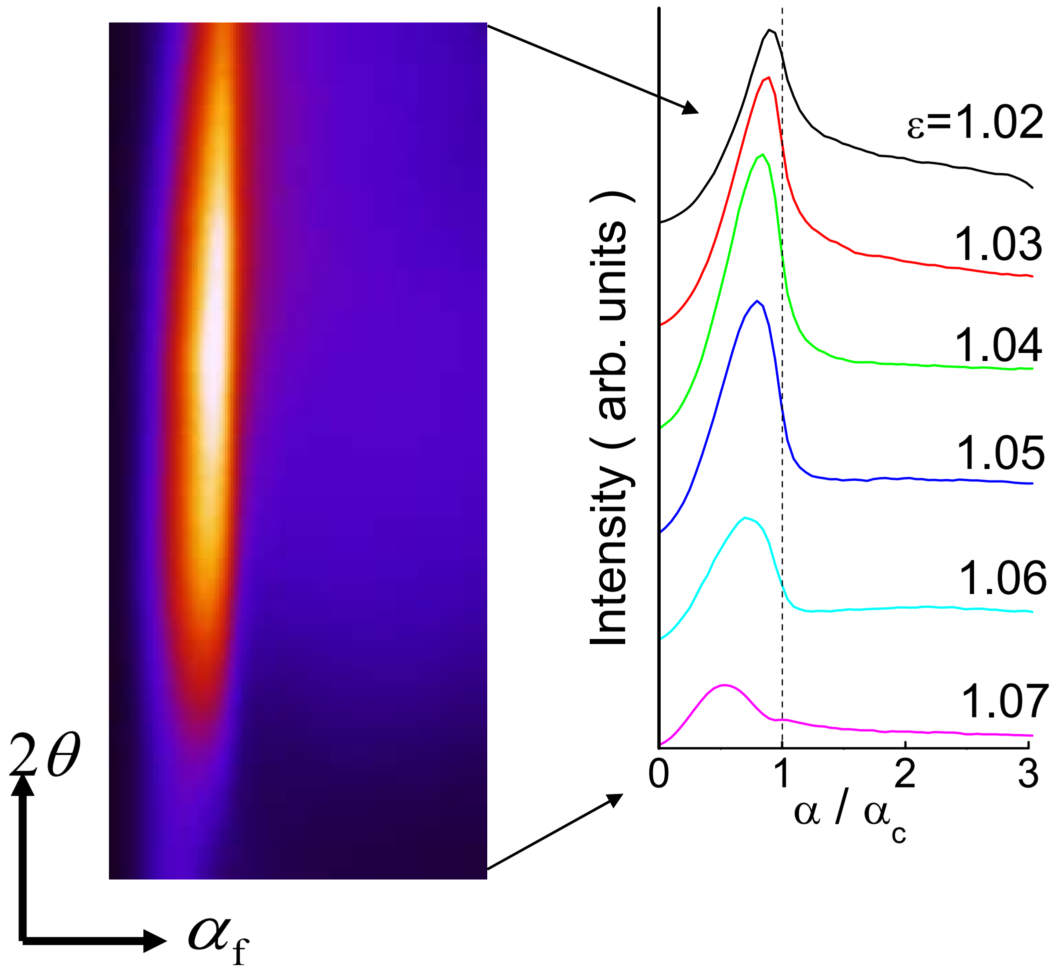
→ strain (reciprocal space)

$T(\alpha_{i,f}, z)$: multiple-diffraction effect

→ height (real space)

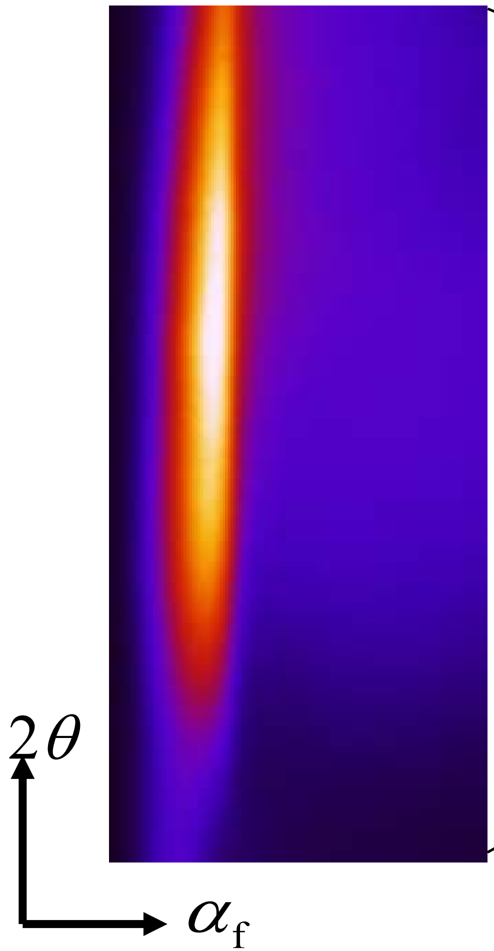
What is T(α,z)?

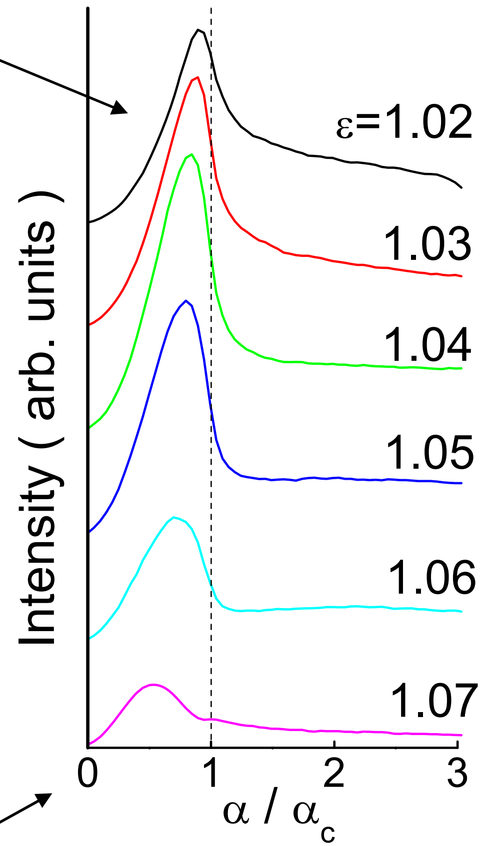
Experiment



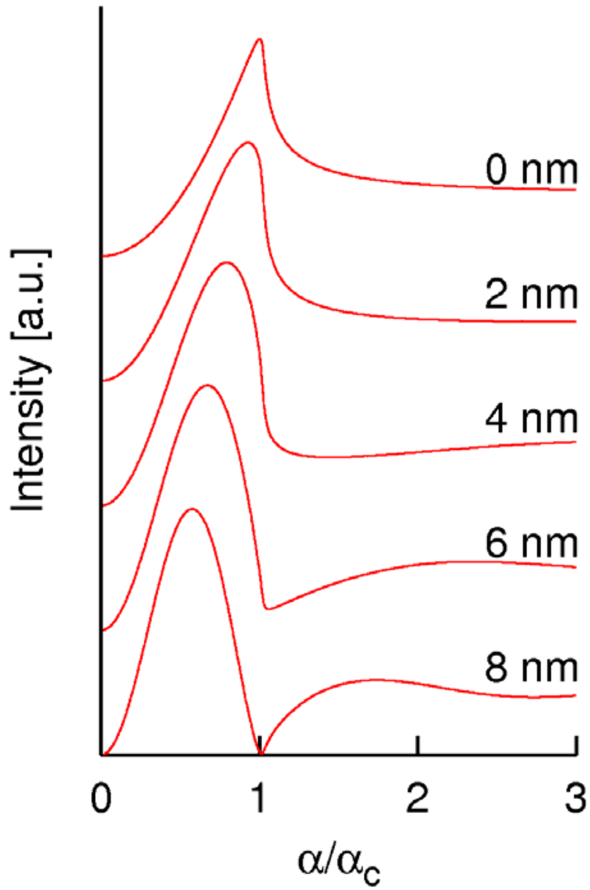
What is T(α,z)?

Experiment



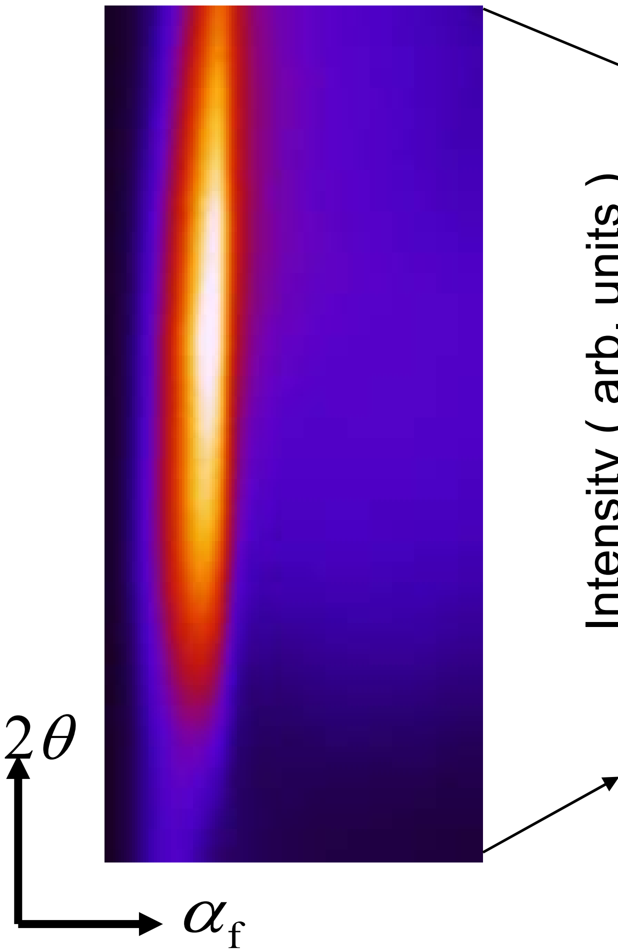


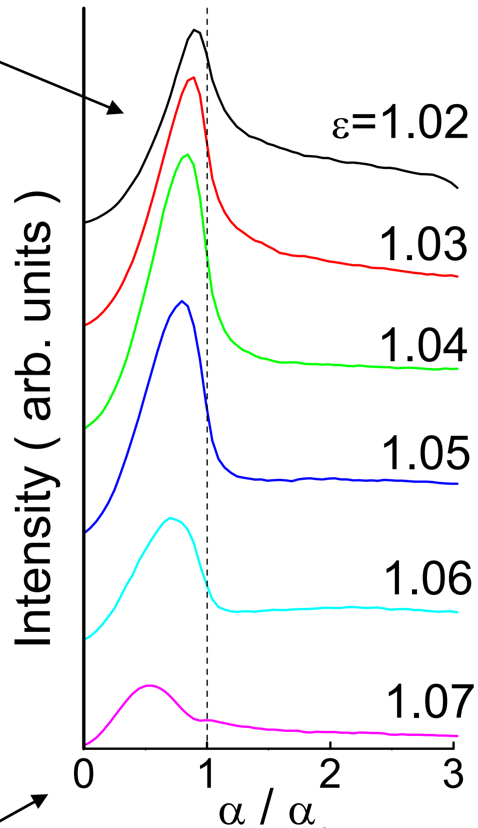
Calculation



What is T(α,z)?

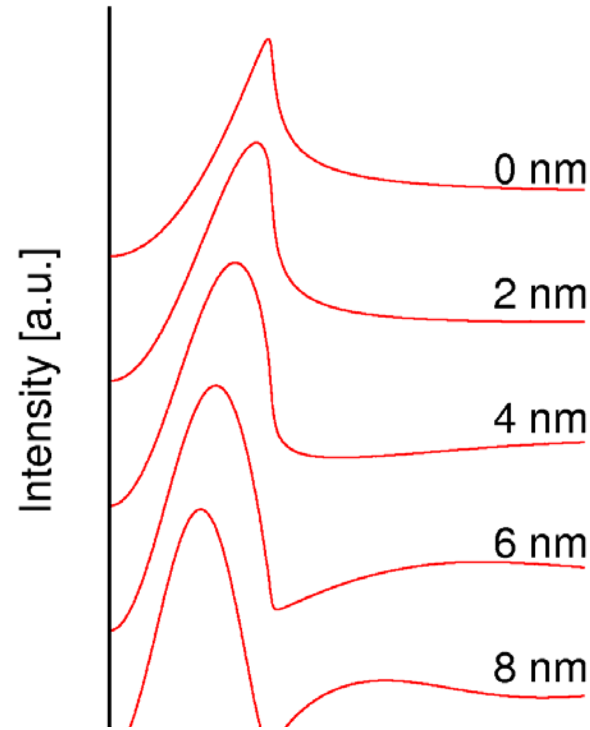
Experiment

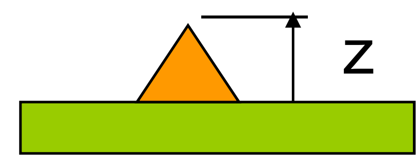




⇨ Height of QDs

Calculation

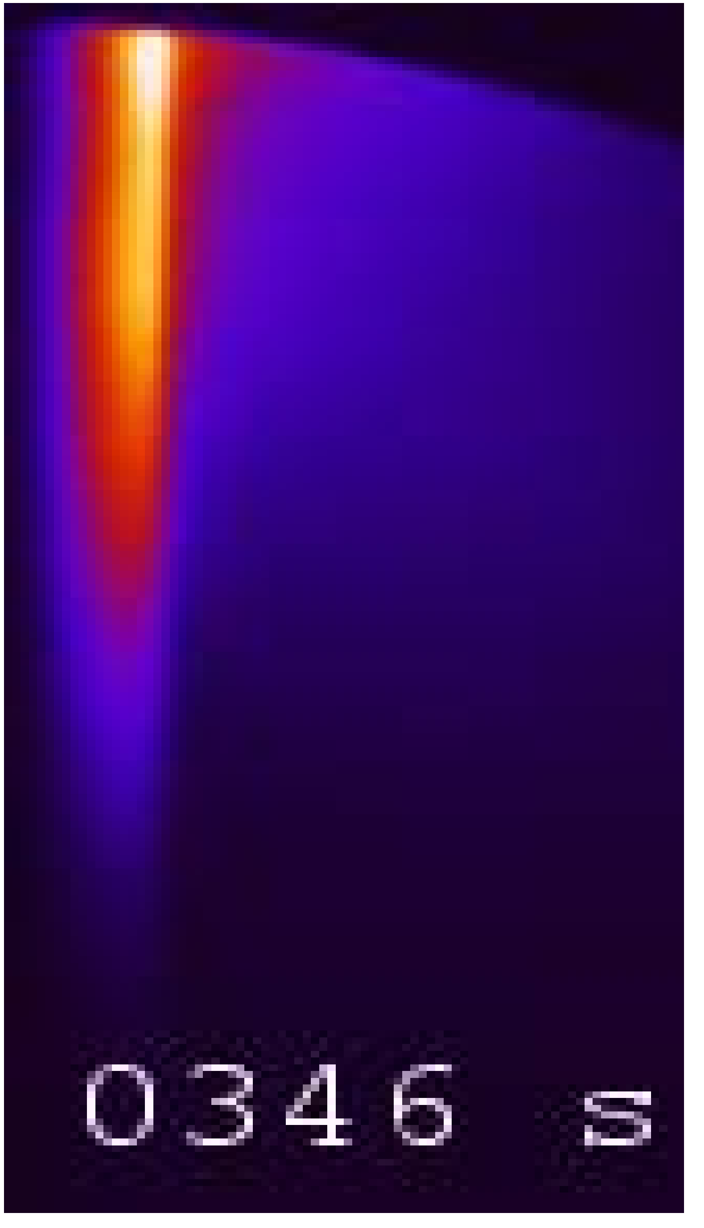




Results(1)

Stage 1: InAs growth

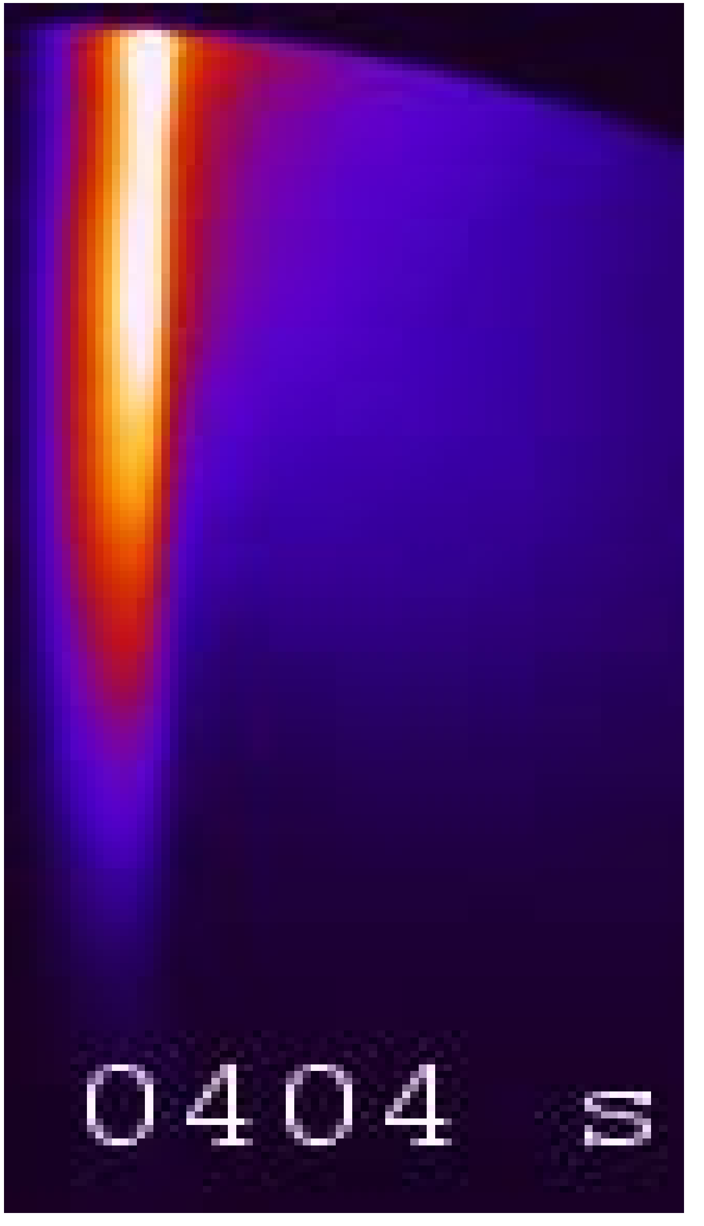
time	InAs thickness	height z
0 s	0 ML	
260 s	1.8 ML	
346 s	2.4 ML	5.1 nm



Results(2)

Stage 2: Annealing

time	height z
346 s	5.1 nm
404 s	5.5 nm



Results(3)

Stage 3: GaAs encapsulation

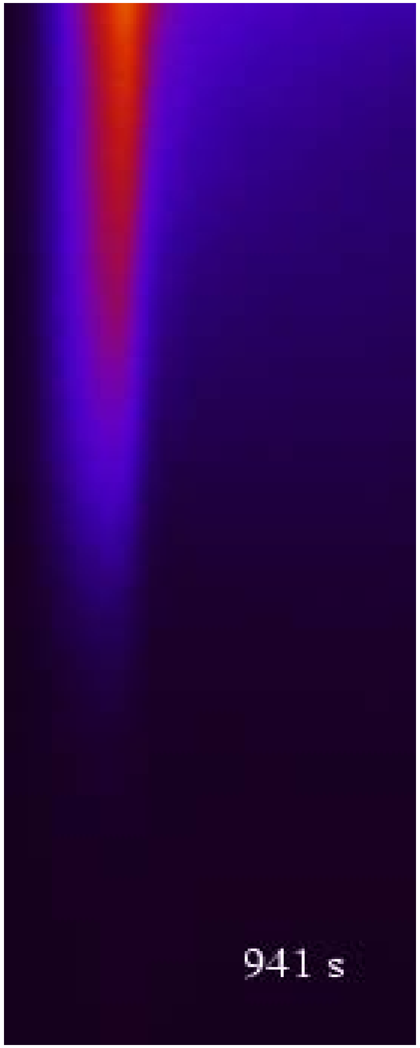
time	GaAs thickness
404 s	0 nm
452 s	0.4 nm
827 s	3.6 nm

Annealing of 3ML InAs dots

(1) $T=470^{o}C$
(2) $T=446^{o}C$

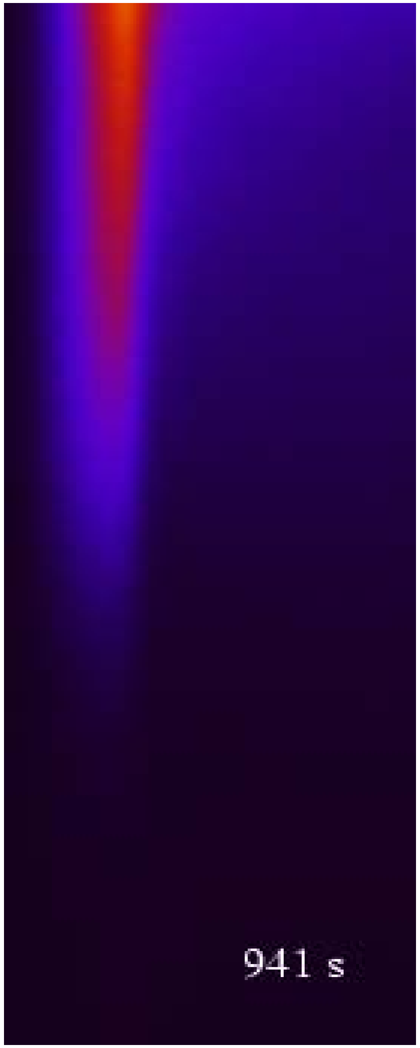
Evolution of 3ML-InAs/GaAs(001) during growth interruption

T=470^{o}C

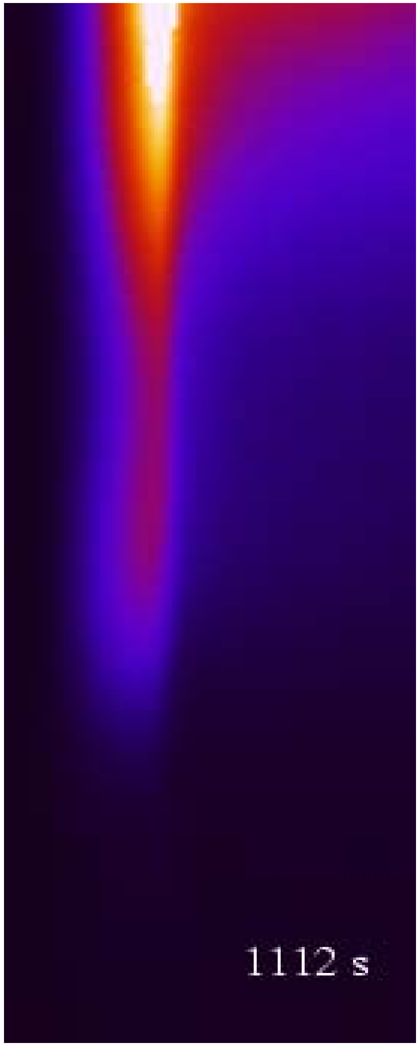


Evolution of 3ML-InAs/GaAs(001) during growth interruption

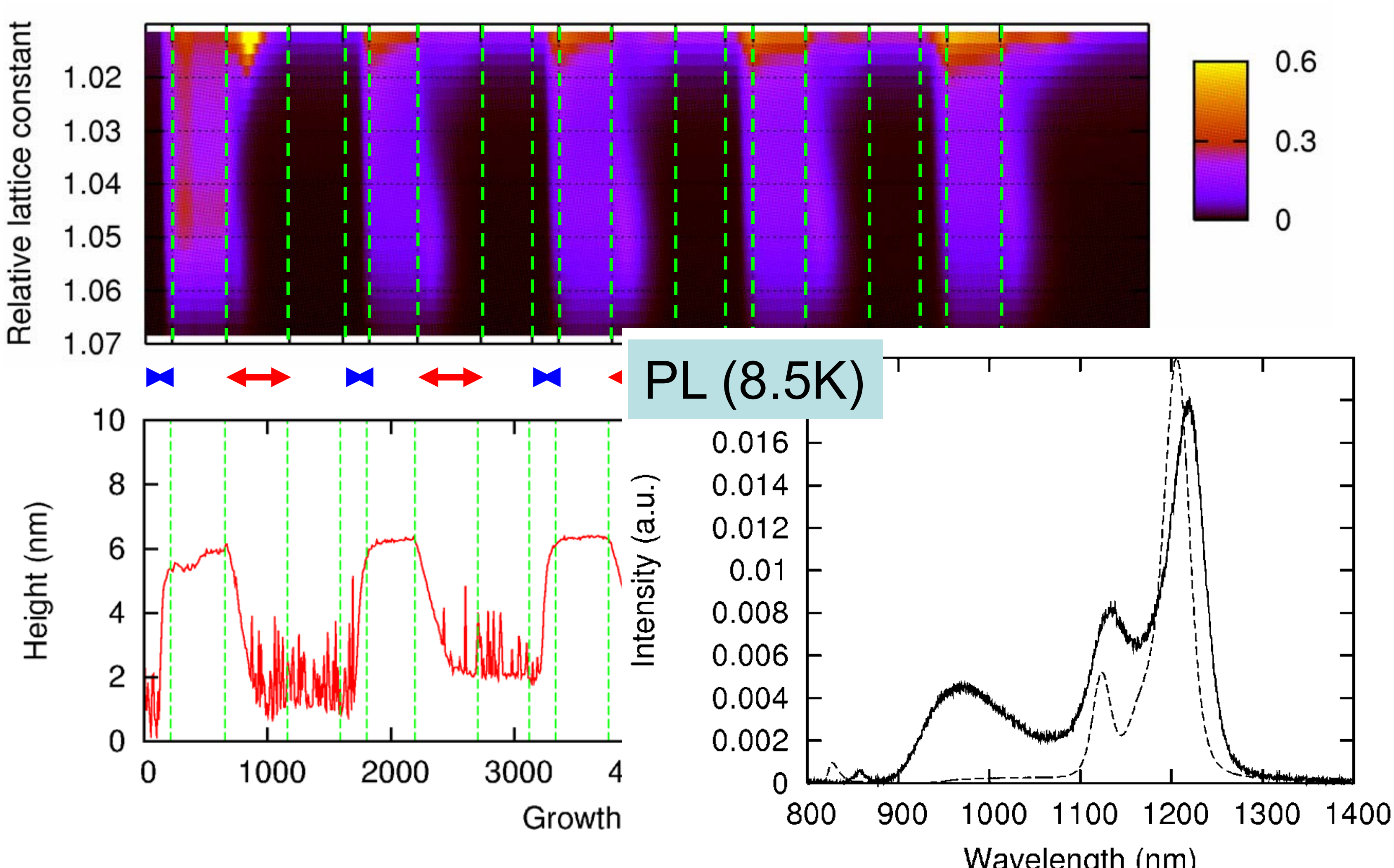
T=470^{o}C



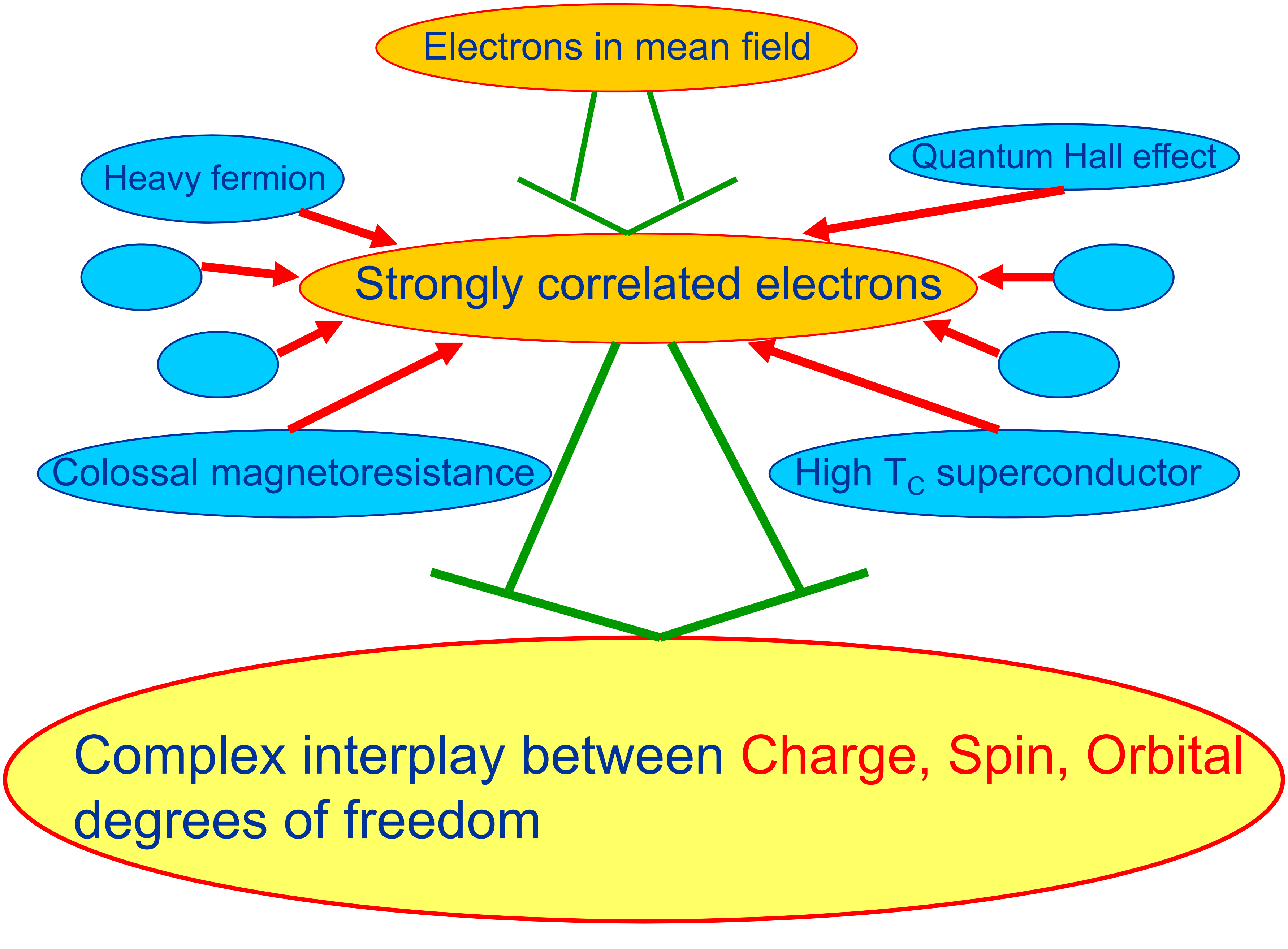
T=446^{o}C

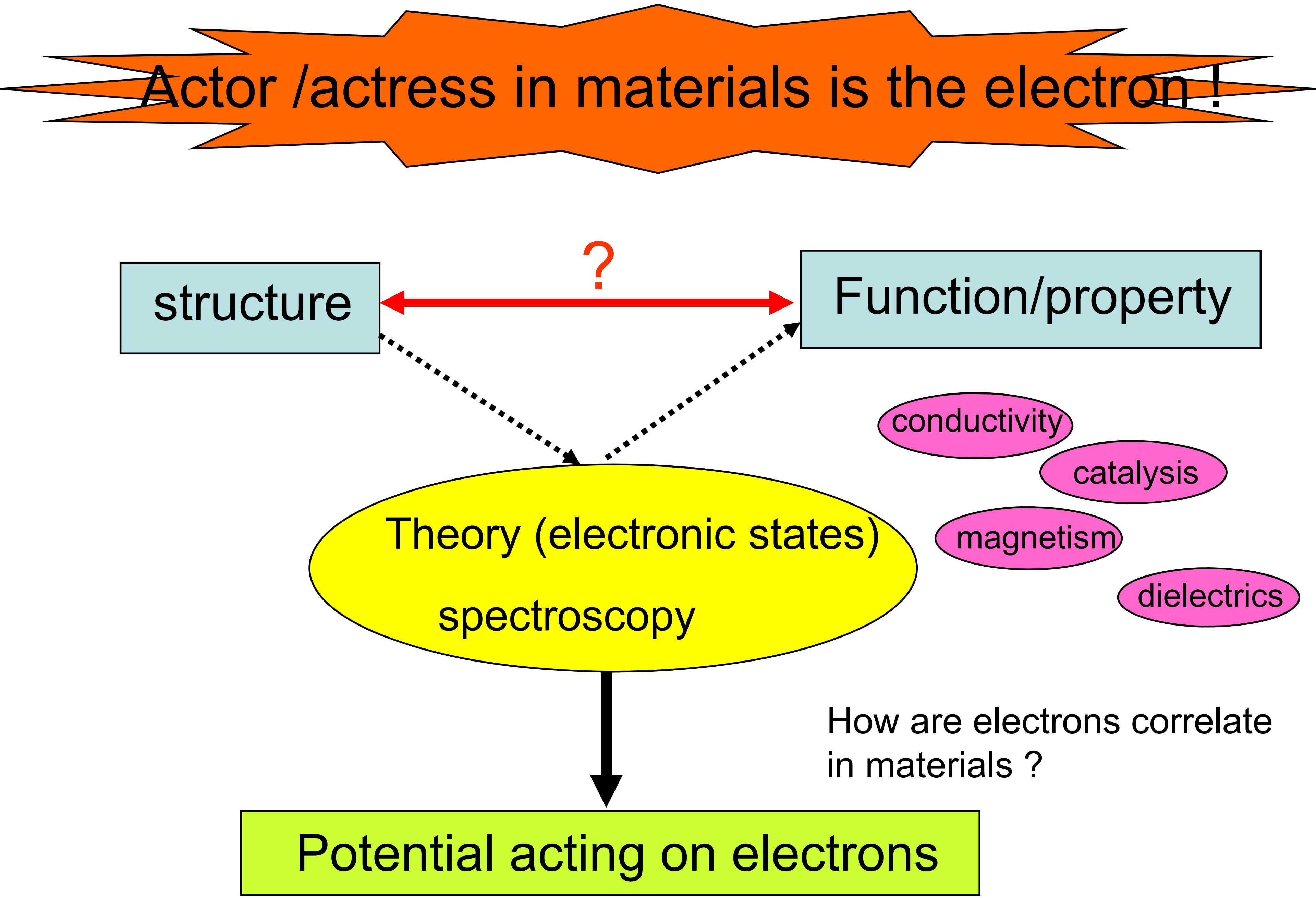


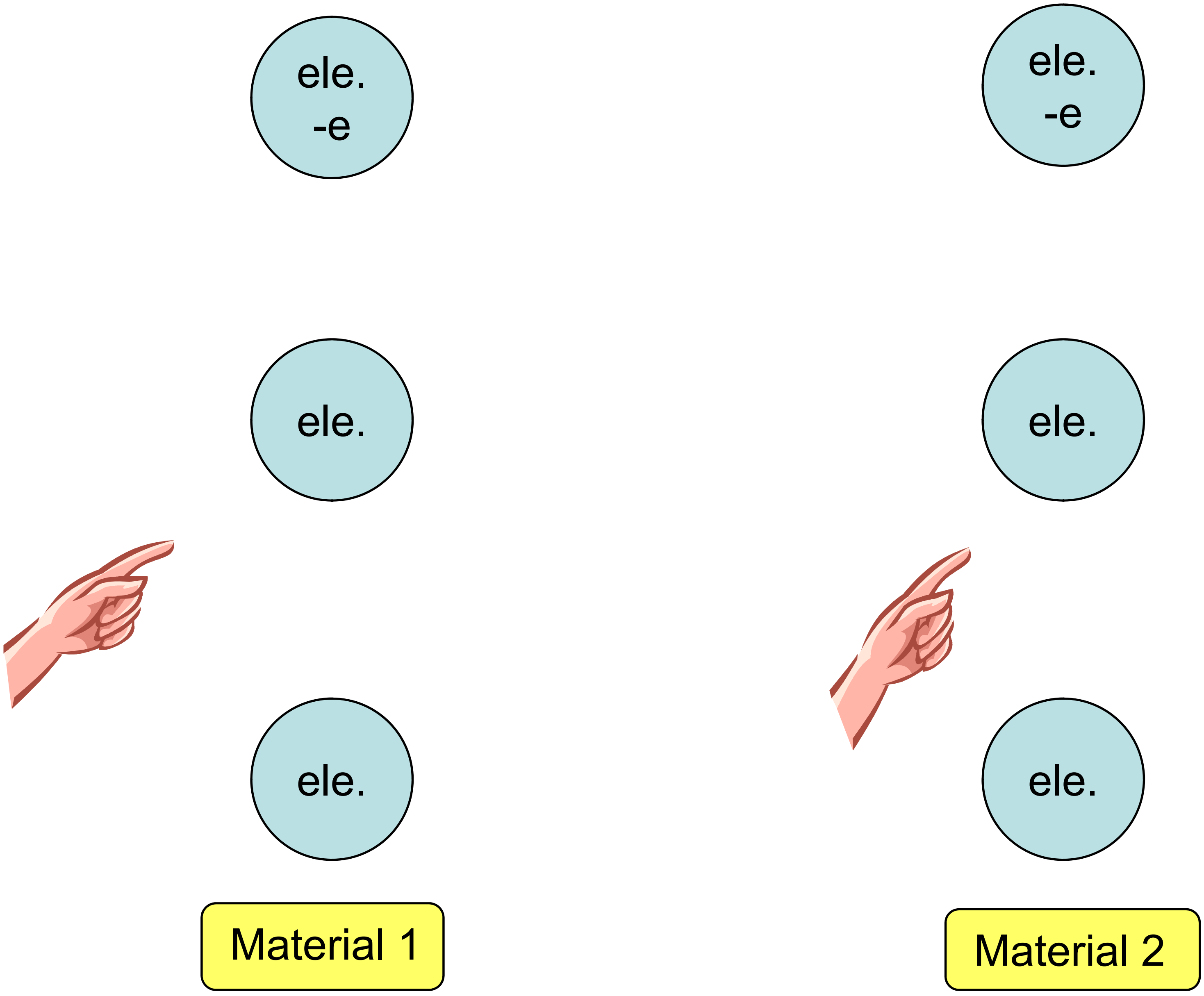
Stacking at Td=478^{o}C and Tc=450^{o}C



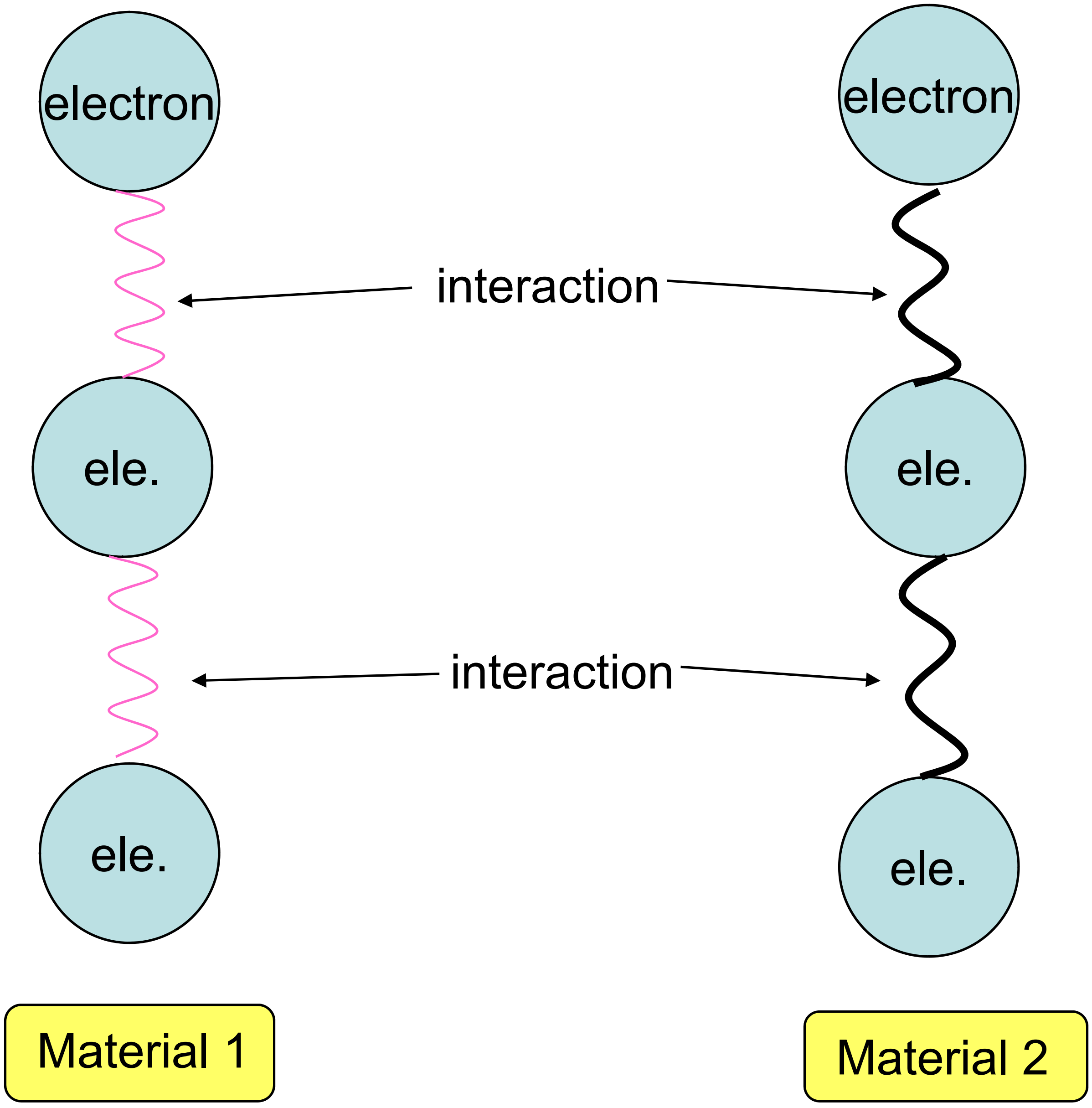
Discover new scientific phenomena
and invent new materials


Electrons in mean field
Heavy fermion
Quantum Hall effect
Strongly correlated electrons
Colossal magnetoresistance
High T_C superconductor
Complex interplay between Charge, Spin, Orbital degrees of freedom


Actor /actress in materials is the electron !
?
structure
Function/property
conductivity
catalysis
magnetism
dielectrics
Theory (electronic states)
spectroscopy
How are electrons correlate in materials ?
Potential acting on electrons



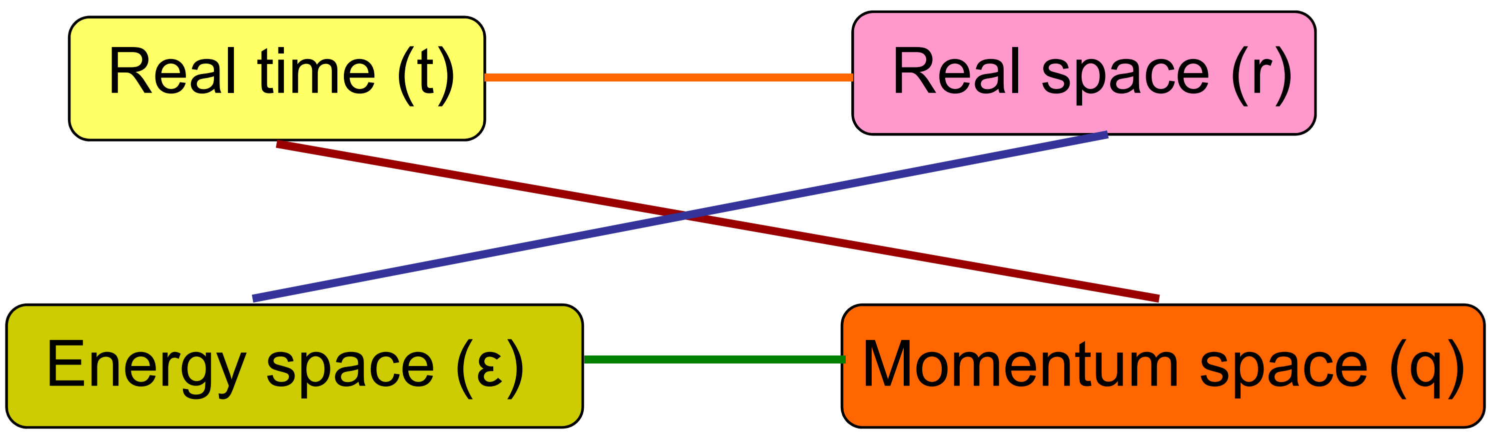
ele.
-e
ele.
-e
ele.
ele.
ele.
ele.
Material 1
Material 2


electron
ele.
ele.
interaction
interaction
electron
ele.
ele.
Material 1
Material 2

Dynamics

Observation space

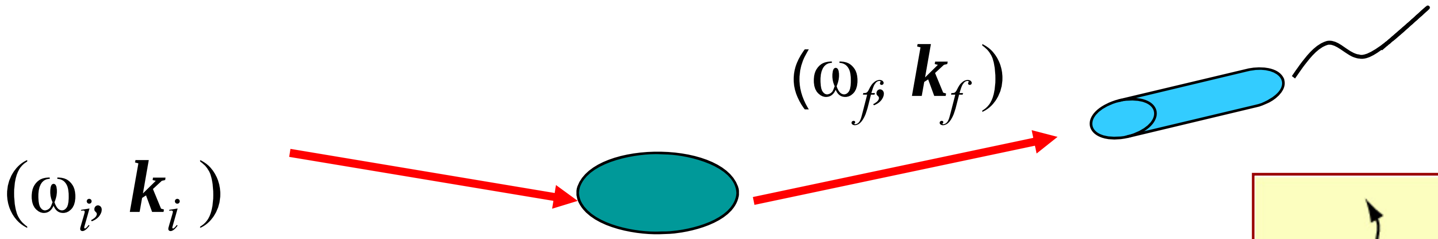
In what space should we measure physical properties?



How do we know the potential for electrons?

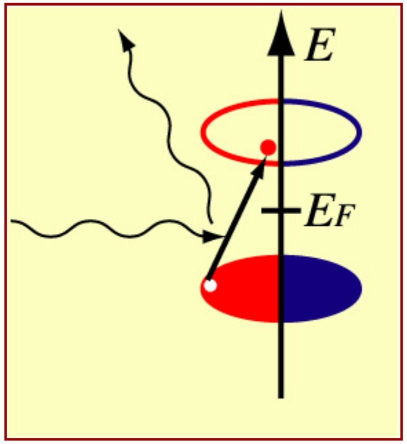
Dynamics!

Observation of dynamical properties of electrons and atoms



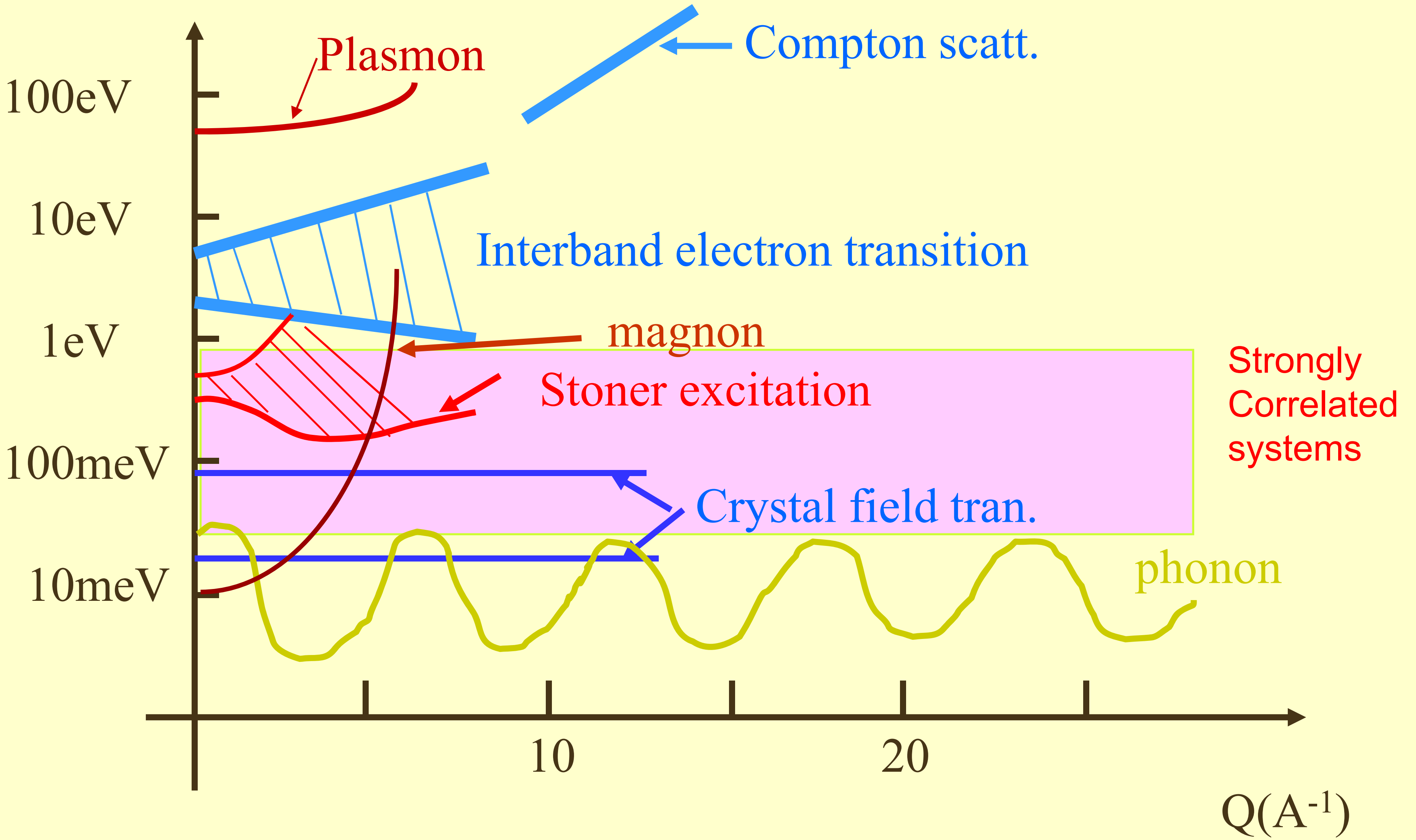
$$\mathbf{Q} = \boldsymbol{k}_i - \boldsymbol{k}_f$$

$$\Delta E = \omega_i - \omega_f \equiv \omega$$



inelastic scattering!

Elementary Excitations in Solids



Inelastic Scattering

$$I(Q,E) \sim [V(Q)]^2 [1 - e^{-\beta E}]^{-1} \bullet \operatorname{Im} \chi(Q,E)$$

Interaction of probe

Generalized susceptibility

- For neutrons → Spin susceptibility, Nuclear susceptibility
- For X-rays, For electrons → Charge susceptibility

⇒ $\chi(Q,E) = -(Q^2/4\pi^2 N)\, 1/\varepsilon(Q,E)$

Dynamical dielectric function

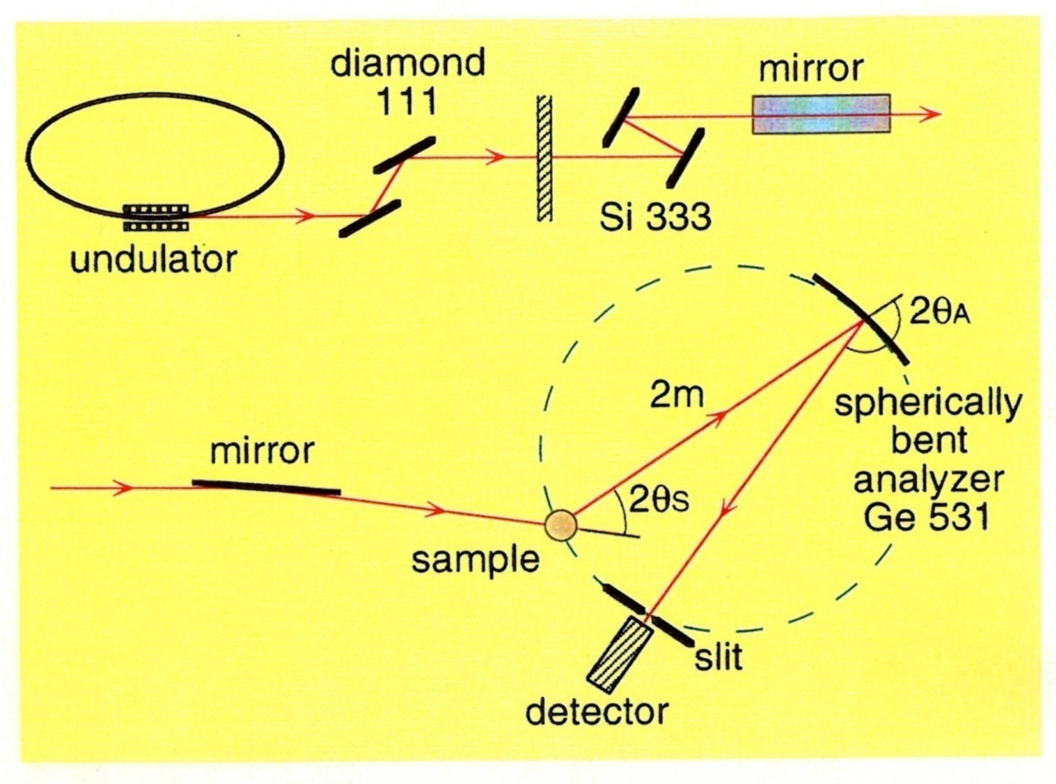
Inelastic X-ray scattering

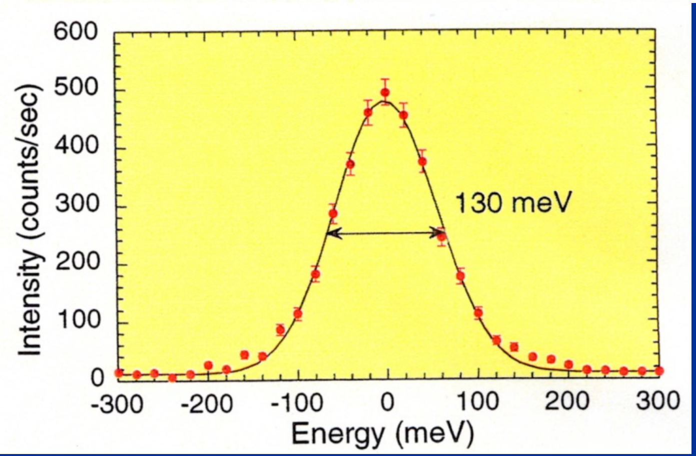
$$H=\sum_j \frac{1}{2m}\left(\mathbf{p}_j-\frac{e}{c}\mathbf{A}(\mathbf{r}_j)\right)^2=\sum_j\left(\frac{\mathbf{p}_j^2}{2m}-\frac{e}{mc}\mathbf{A}(\mathbf{r}_j)\cdot\mathbf{p}_j+\frac{e^2}{2mc^2}\mathbf{A}(\mathbf{r}_j)^2\right)$$

Fermi's golden rule $I\propto\frac{2\pi}{\hbar}\left|\langle f|\mathbf{A}^2|i\rangle+\frac{\langle f|\mathbf{A}\cdot\mathbf{p}|n\rangle\cdots\langle m|\mathbf{A}\cdot\mathbf{p}|i\rangle}{(E_i-E_m+\hbar\varpi-i\Gamma)}\right|^2$

- The first term: non-resonant inelastic scattering
  - All electrons (Ze) are contributed ⇒ phonon excitation
- The second term: resonant inelastic scattering (RIXS)
  - Electrons on the specific atom are contributed.
  - Resonance enhancement
  - Element specific ⇒ electronic excitation

Set-up of Inelastic Scattering Spectrometer at BL-11XU

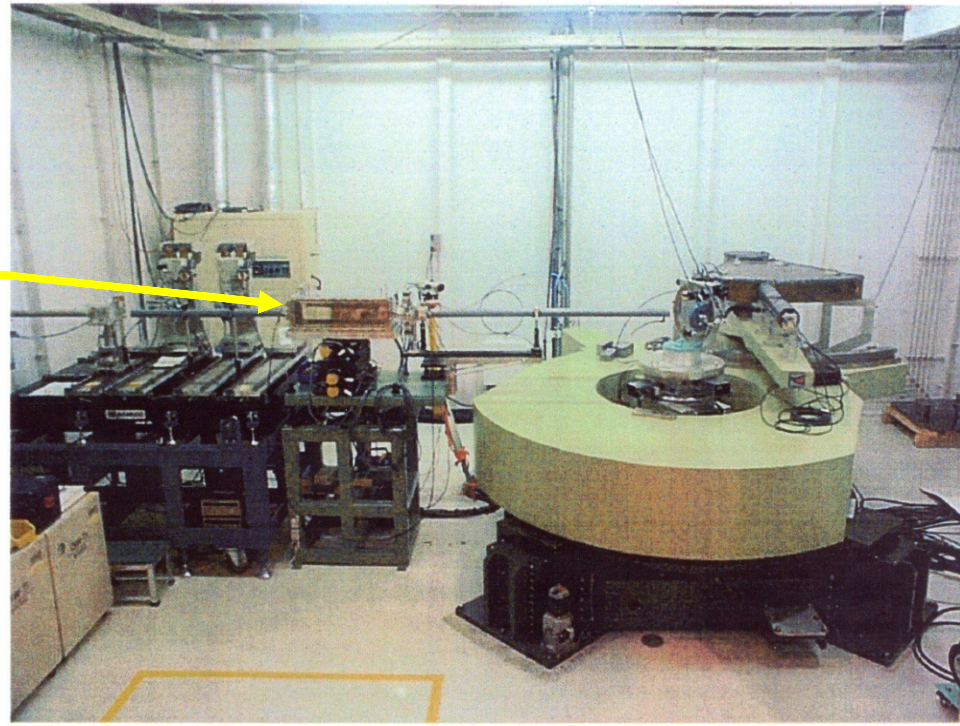


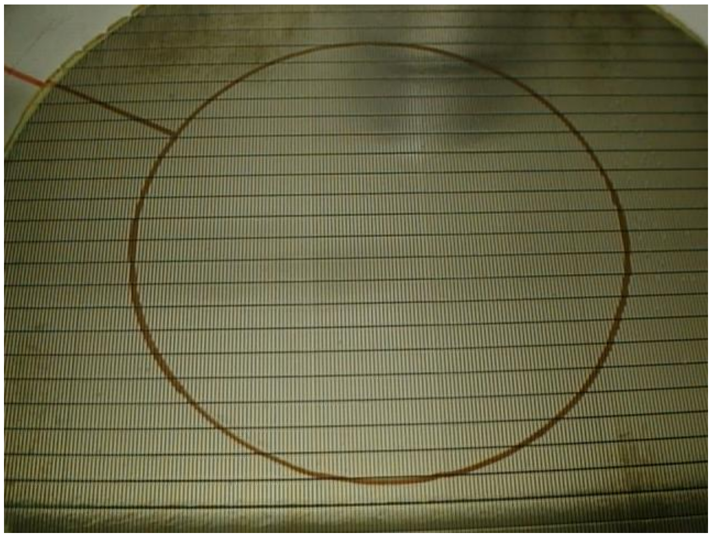


Observed energy Resolution at 6.5 keV

Picture of the spectrometer at BL-11 XU, SPring-8

Focusing mirror

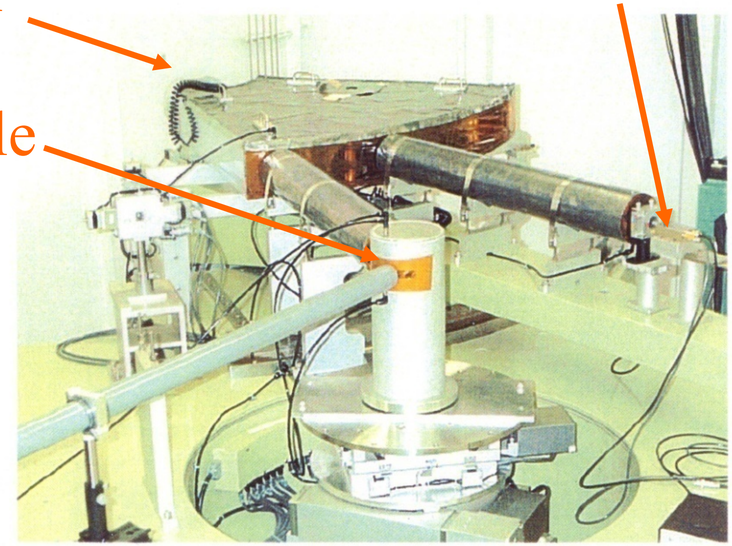


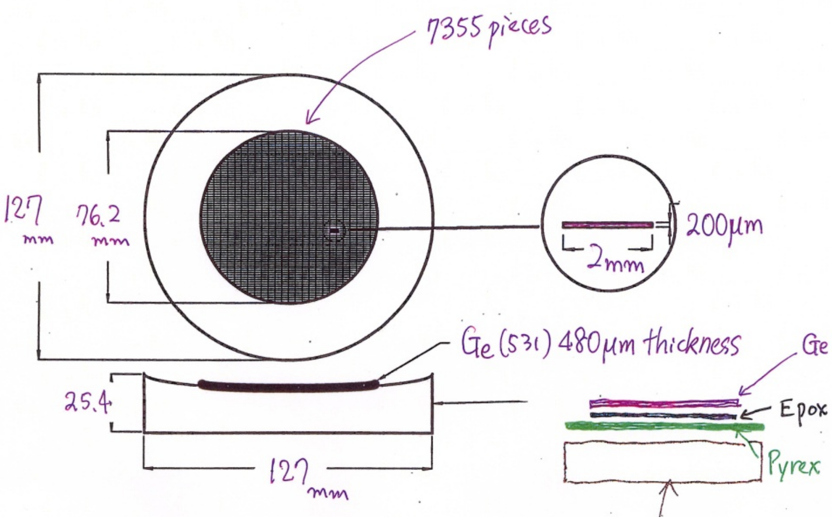


analyzer

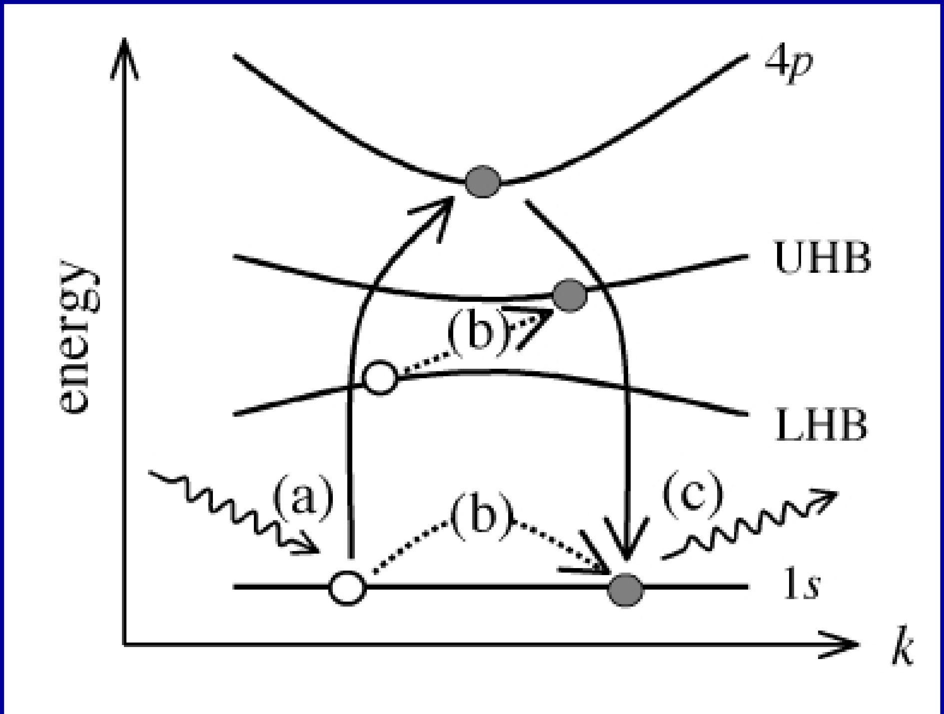
detector

sample





RIXS of 3d transition elements



K-edge （1s→4p、several keV）

(a) absorption

(b) interaction between

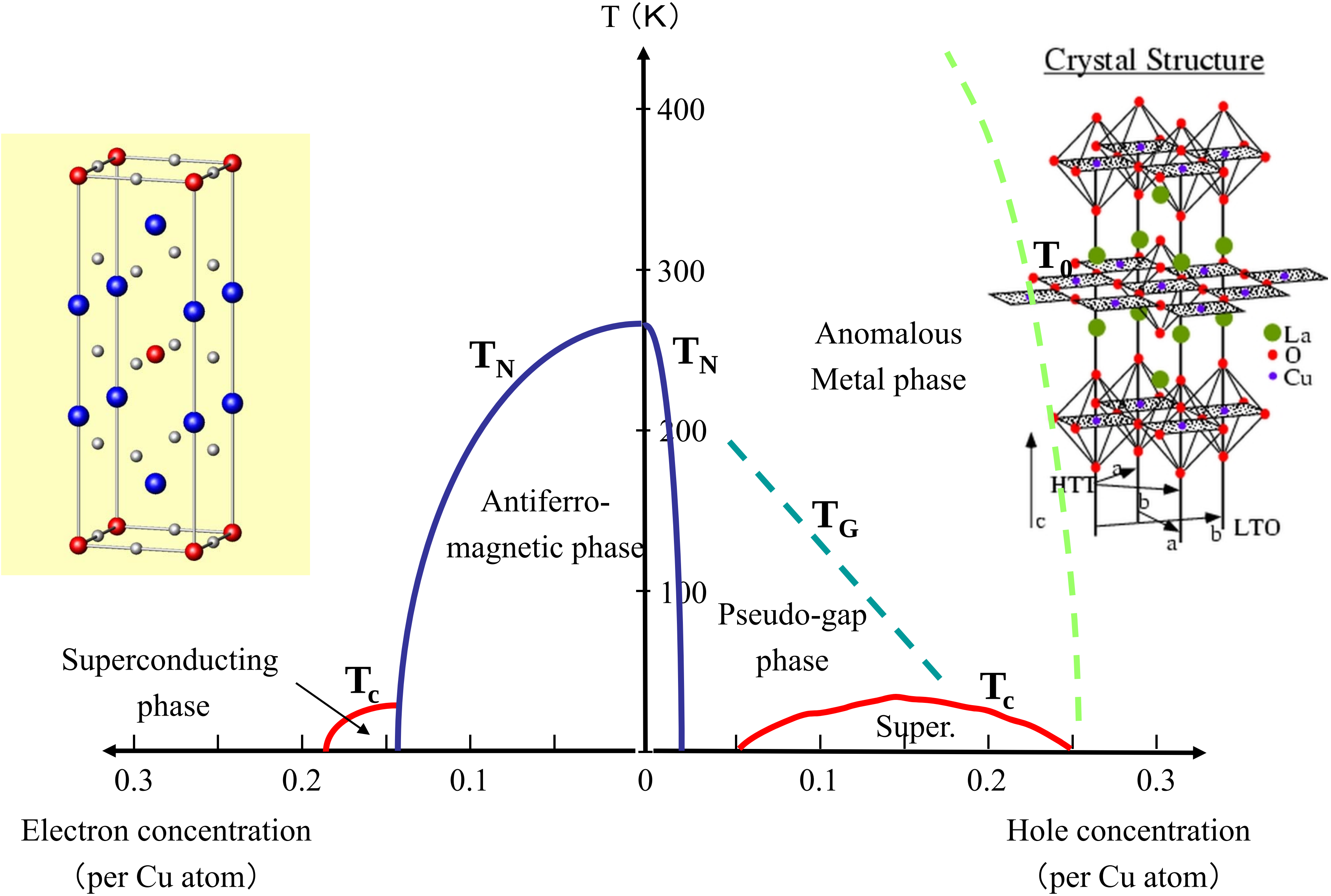
1s core-hole and 3d electron

(c) X-ray emission

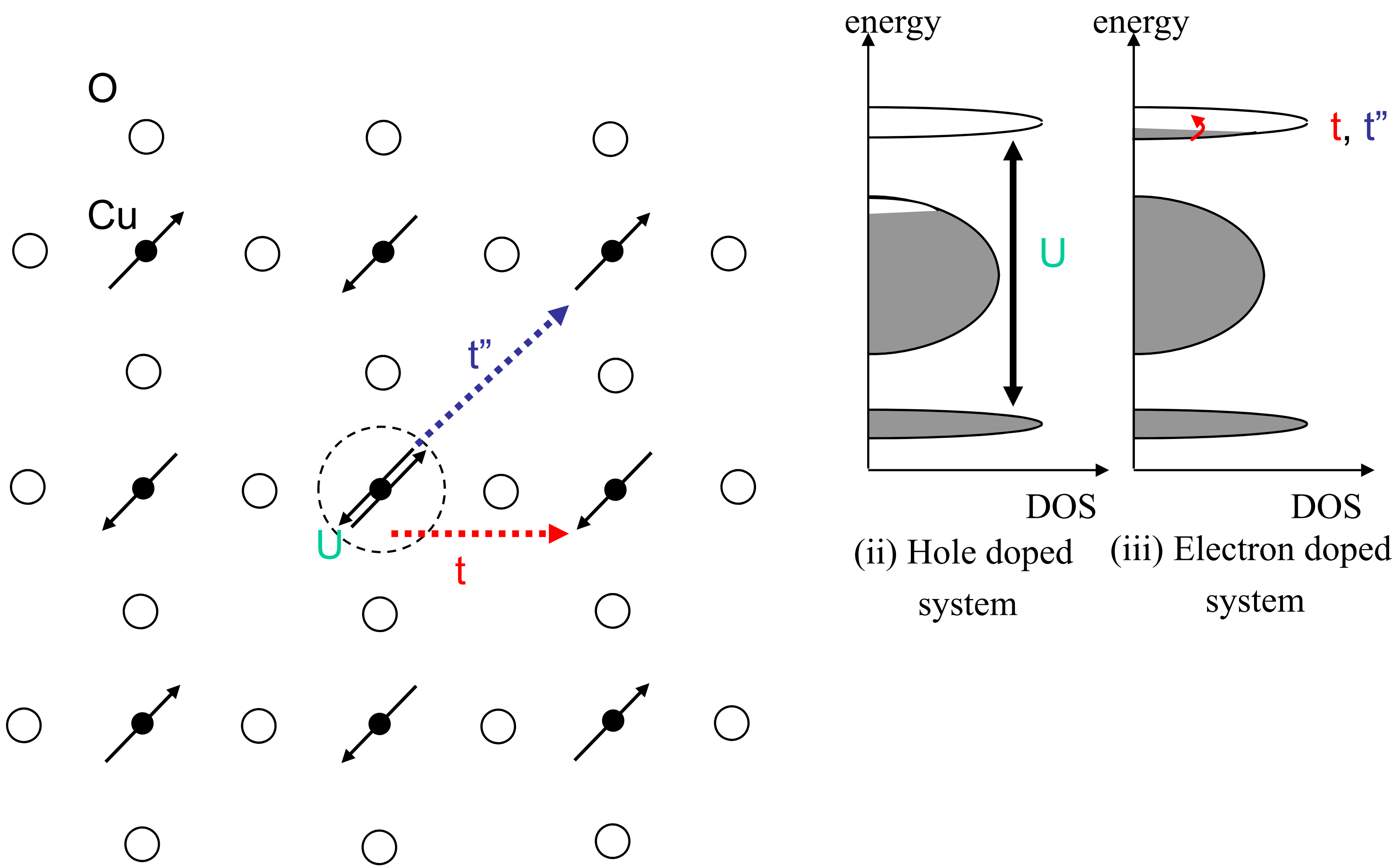
$$I \propto \left| \sum_{m,n} \frac{\langle f | \mathbf{A}\cdot\mathbf{p} | n \rangle \langle n | V_{1s-3d} | m \rangle \langle m | \mathbf{A}\cdot\mathbf{p} | i \rangle}{(E_f - E_n + \hbar\varpi_f - i\Gamma)(E_i - E_m + \hbar\varpi_i - i\Gamma)} \right|^2$$

Mechanism of High T_C superconductor ?

Symmetry of doping-phase diagram



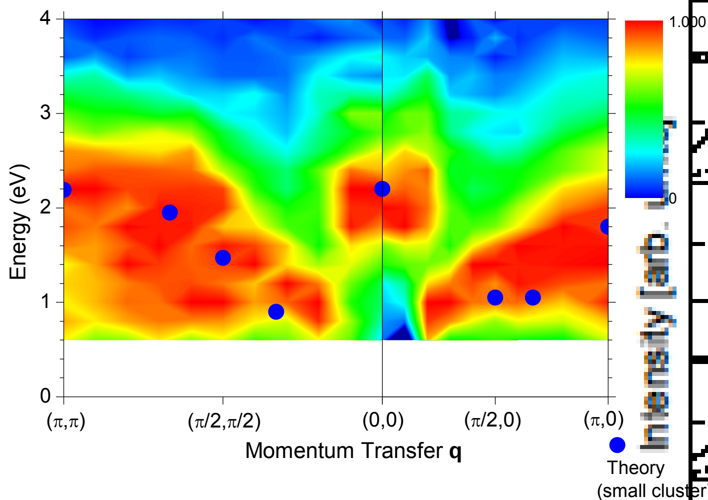
Schematic diagram of electronic states

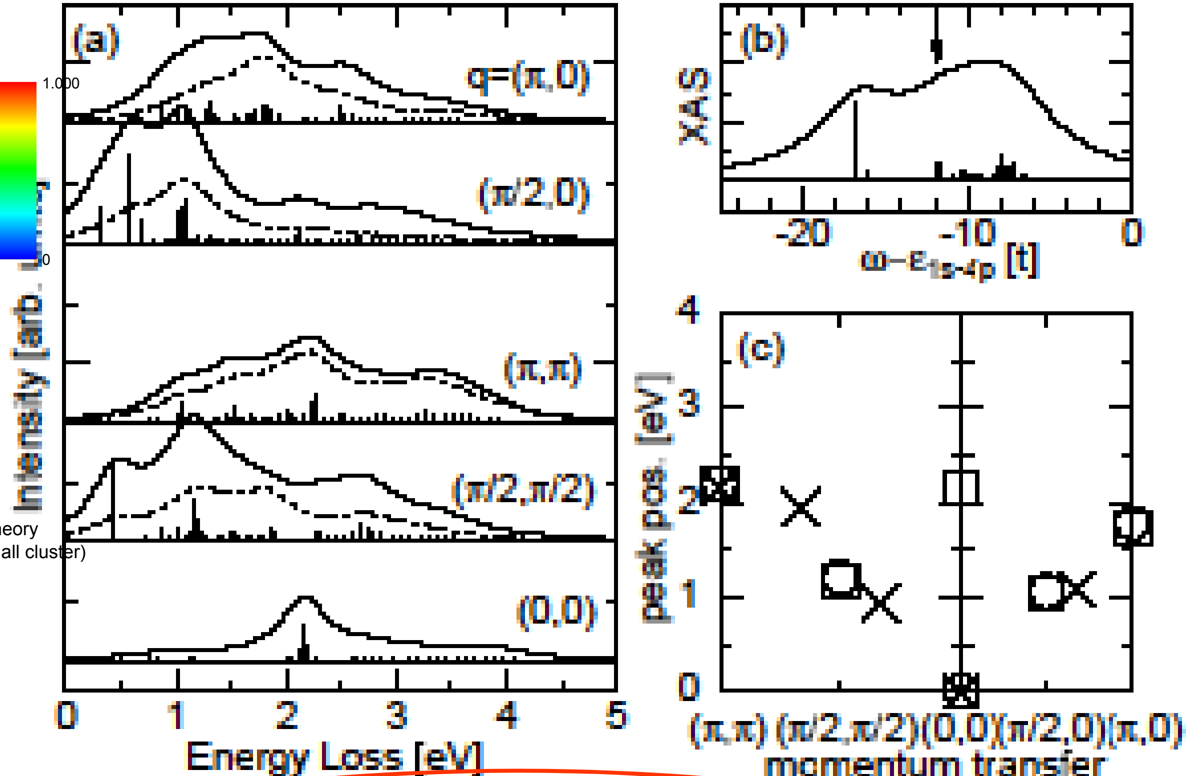


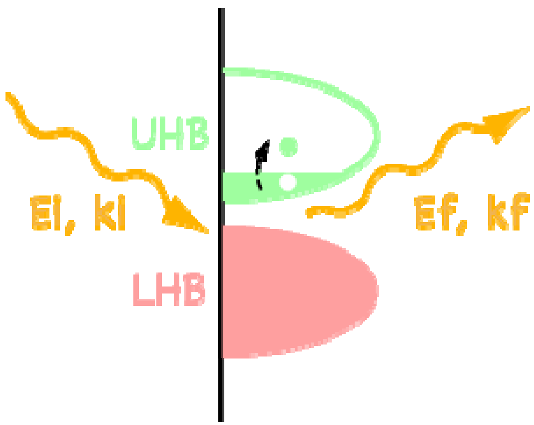
Electron doping

X=0.15

Calculated by K. Tsutsui







—— RIXS spectra

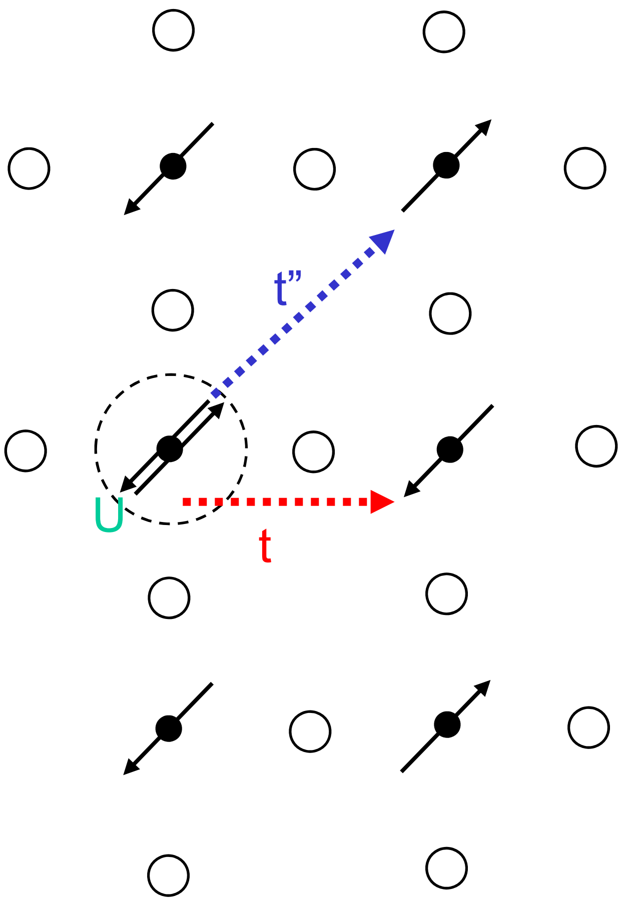
······· Dynamical density response function

The electron involved in dynamical density response function can be selected by RIXS !

K. Ishii, J. M. et al.,PRL. 94 ('05)207003

Future direction

Charge dynamics in strongly Correlated electron systems



-Excition across Mott/charge transfer gap

U: ΔE~0.5eV

-Excitation within bands across the Fermi level

t: ΔE~0.1eV

-Excitations related to the Spin degree of freedom

J: ΔE~0.05eV

Importance of the collaboration between Experiment and theory

Elastic ↔ Resonant

Elastic ↔ Non-resonant

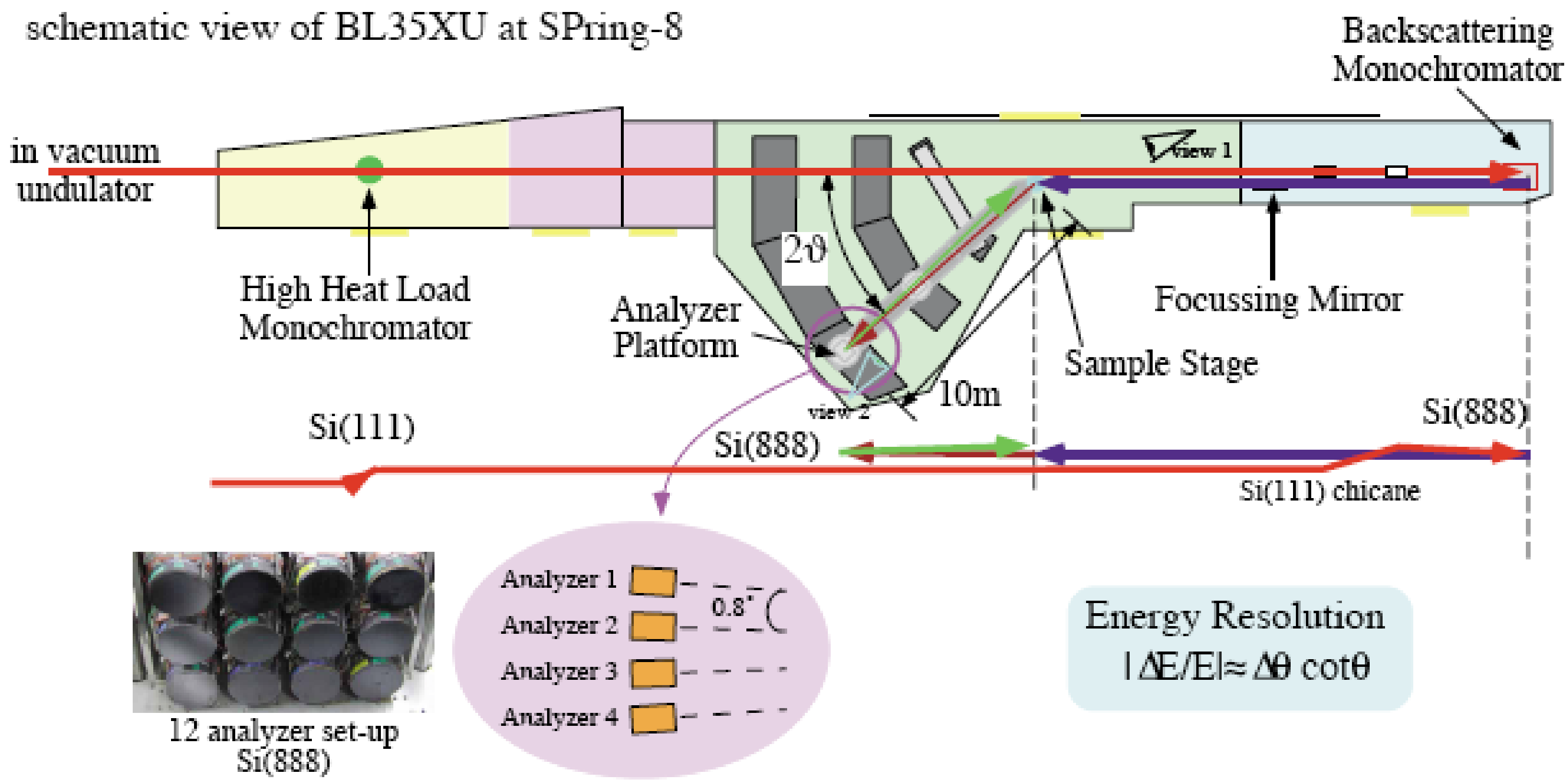
Inelastic ↔ Resonant

Inelastic ↔ Non-resonant

Actinide compounds

Transition metal compounds

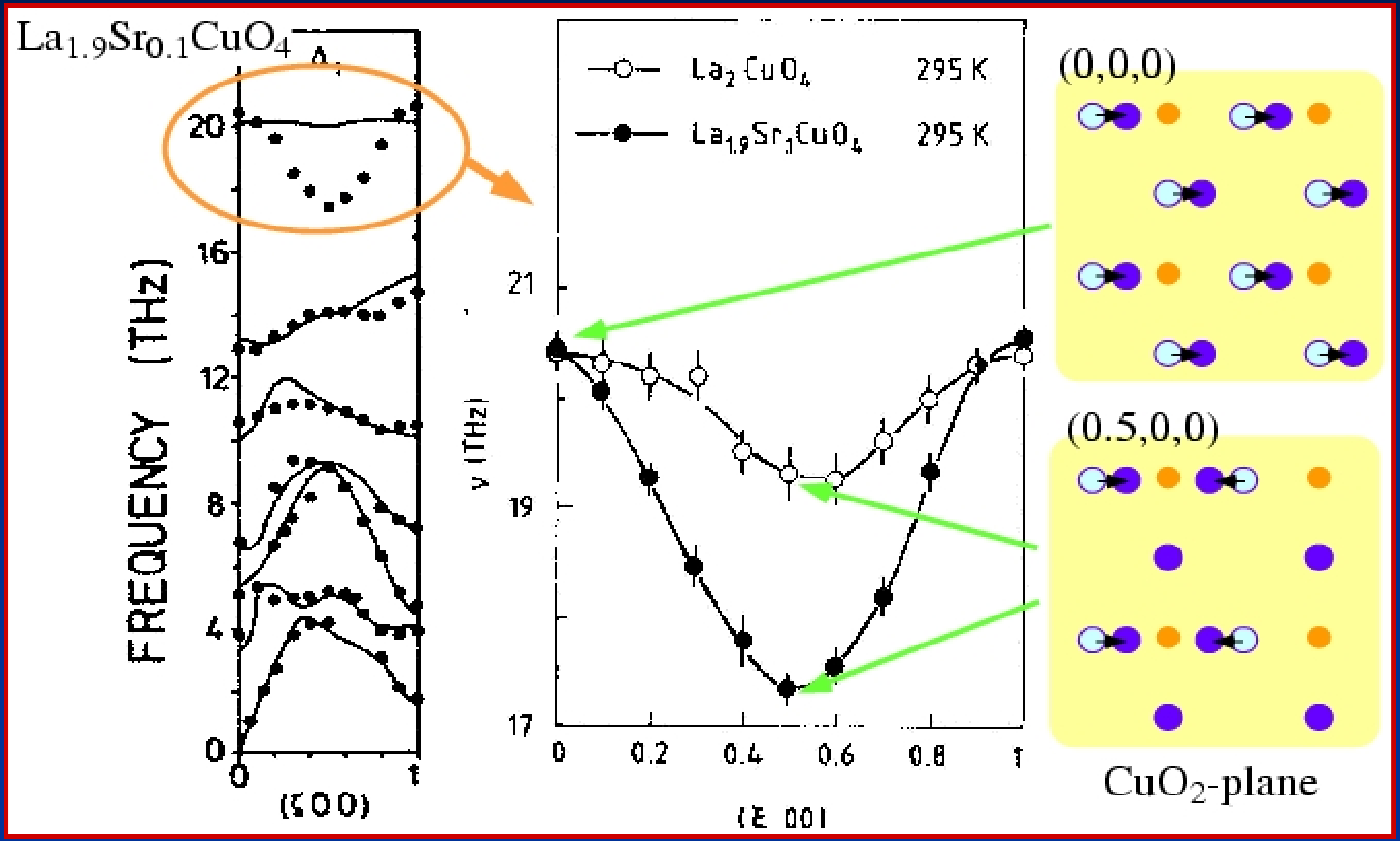
What does phonon play a role on superconducting?



Incident E(keV)	Resolution(meV)	Spot size(μm^2)
21.747	1.6	60 x 80
15.816	6.0	120 x 90

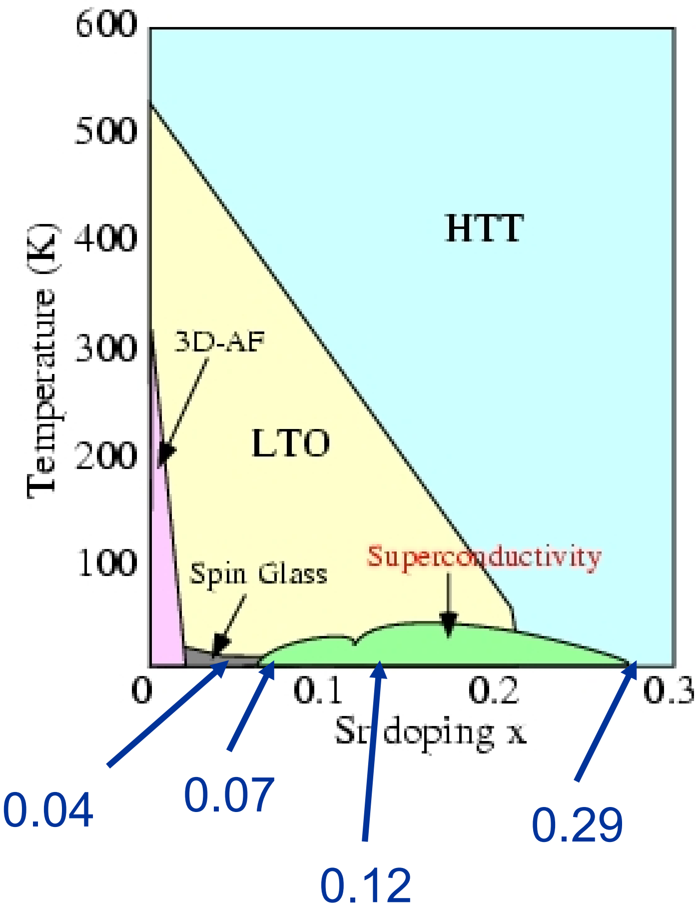
Anomalous dispersion of LO Cu-O bond stretching phonon modes observed by Neutron inelastic scattering

(Pintschovius et al., Physica B 174 (1991) 323)

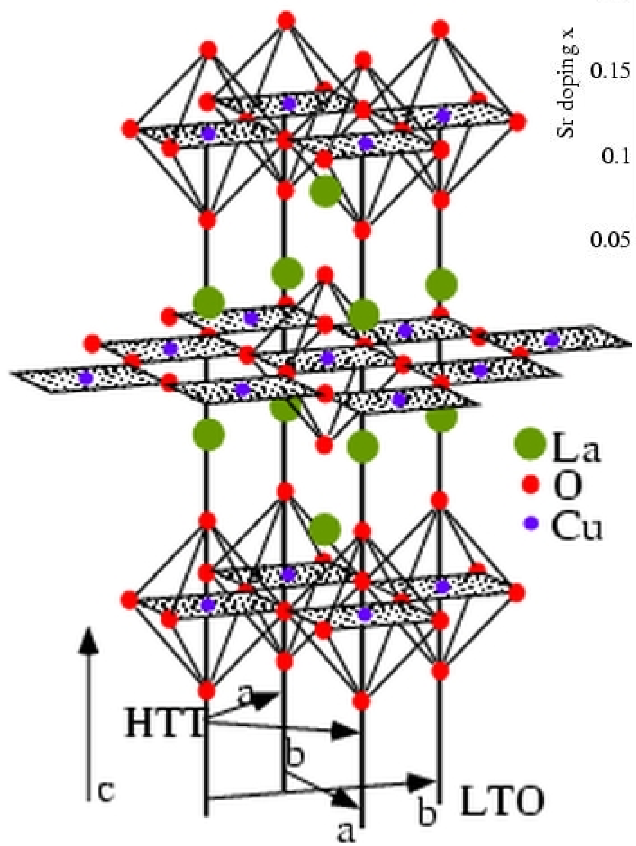


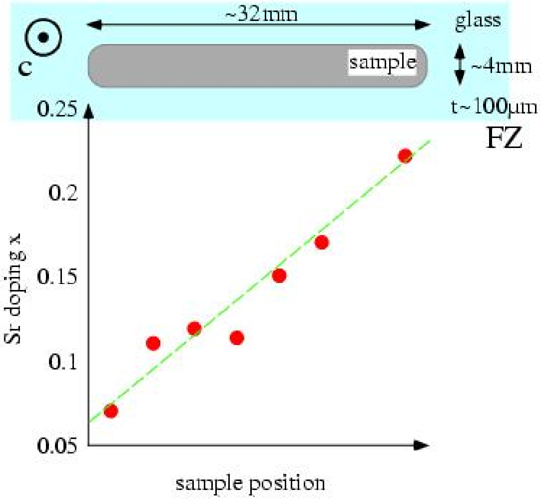
$La_{2-X}Sr_XCuO_4$

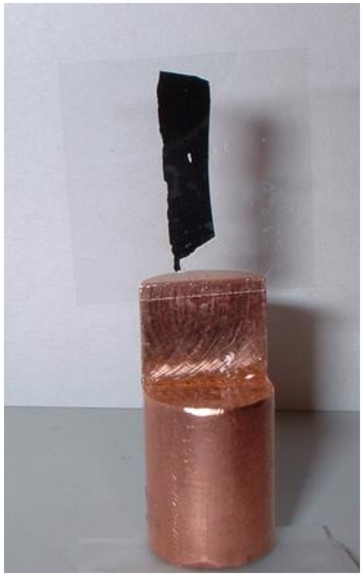
Phase Diagram

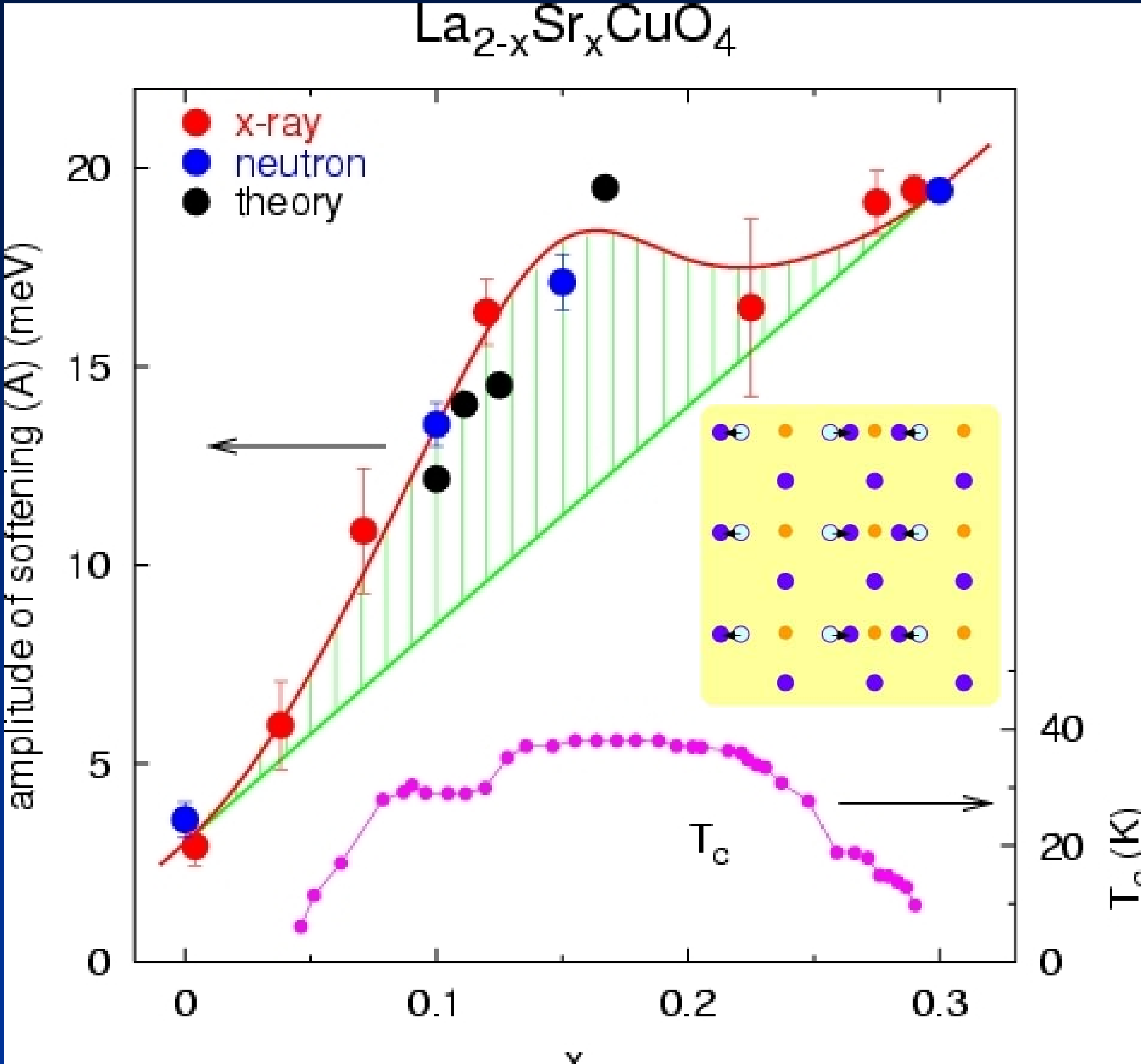


Crystal Structure









T. Fukuda, J. Mizuki, et al., P. R. B. in press

Future plan

Study in Dynamics of Materials to investigate Physical Properties, Chemical Reactions, Crystal Growth, etc.

Real time (t)

Real space (r)

Energy space (ε)

Momentum space (q)

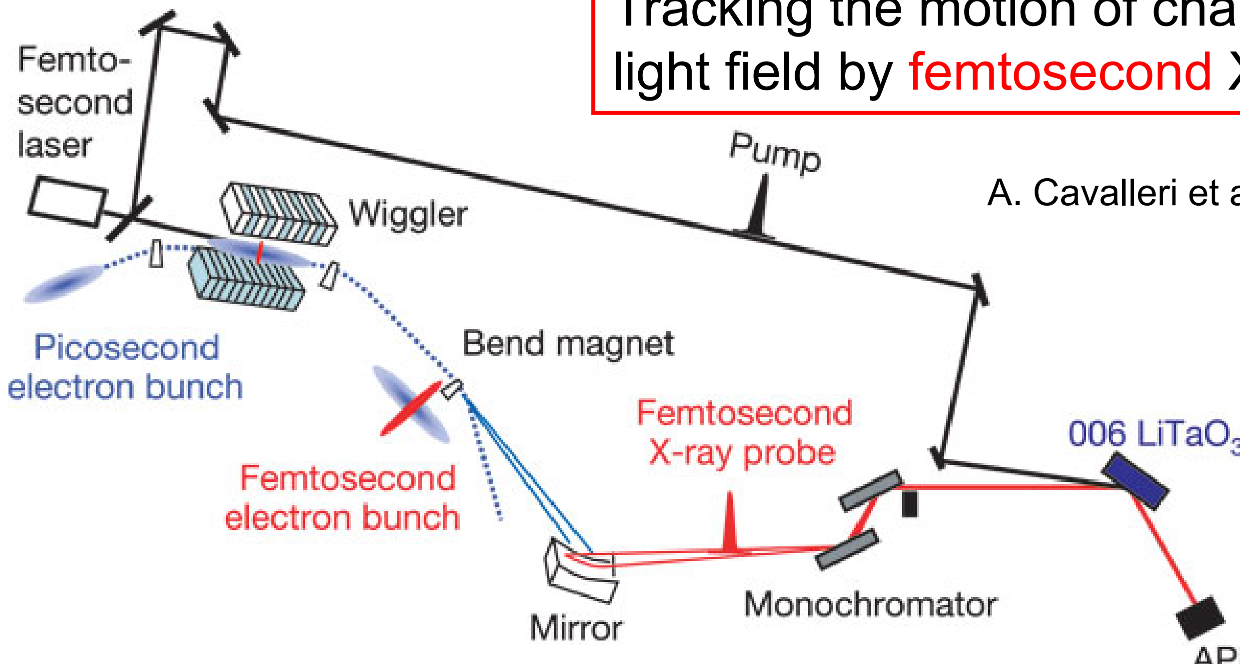
complementary

Room temperature superconductor

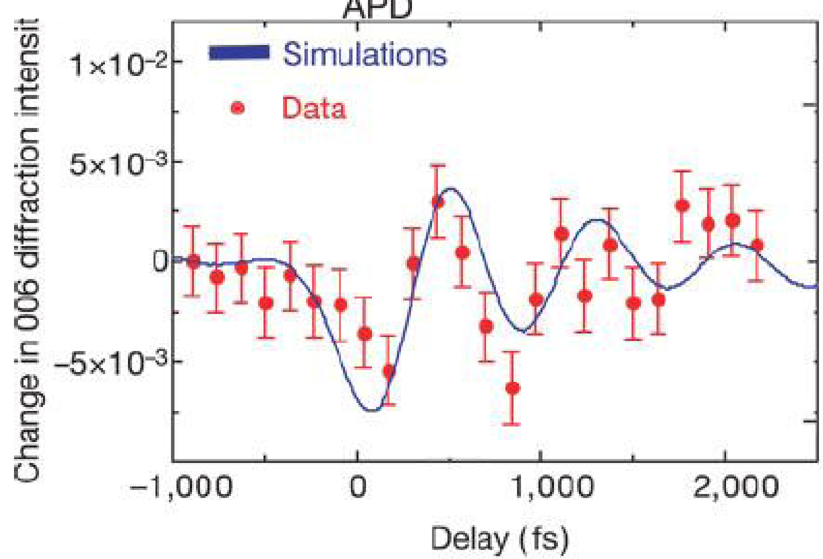
Dynamics in time domain

Tracking the motion of charges in a terahertz light field by femtosecond X-ray diffraction

A. Cavalleri et al., Nature 442 ('06) 664

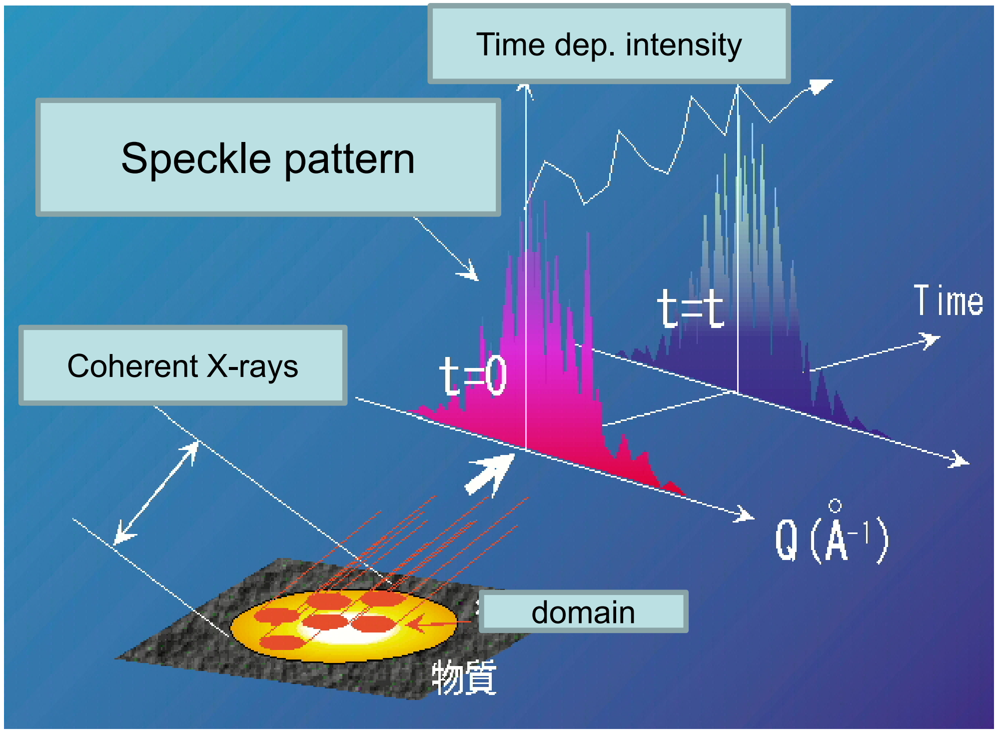


Time-dependent
Structure factor

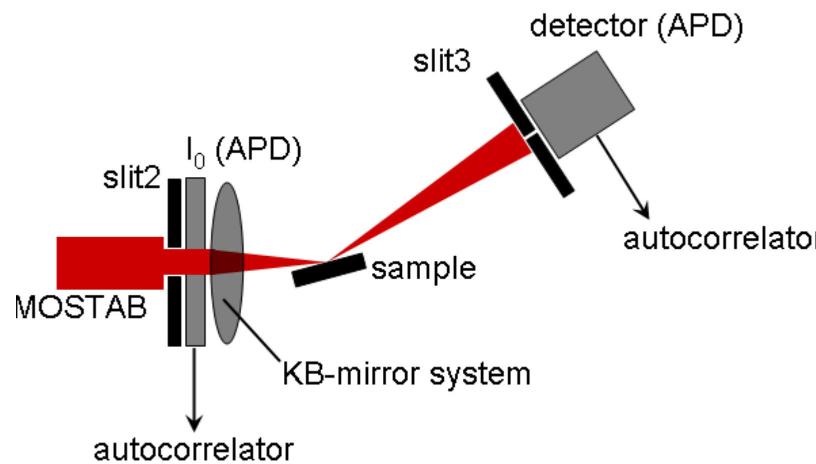


Excitation of phonon polaritons in LiTaO3

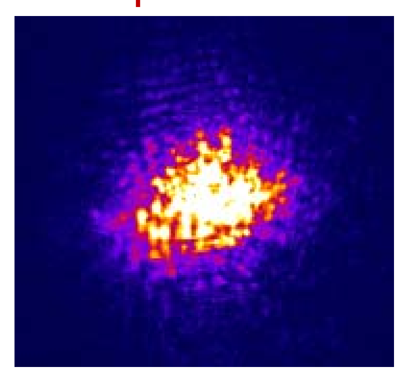
Use of coherence for slow dynamics



BL-22XU



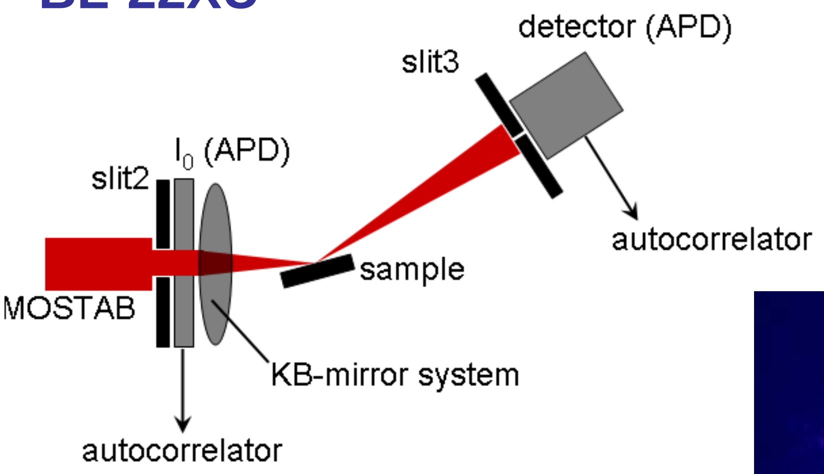
speckle



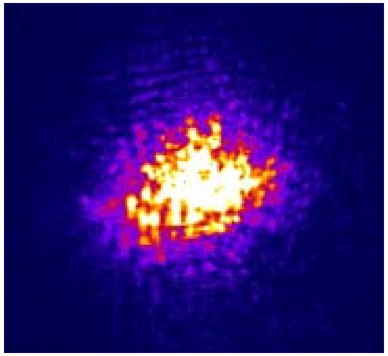
Use of coherence for slow dynamics

Domain motion of relaxor by coherent X-ray diffraction: (t, Q)

BL-22XU

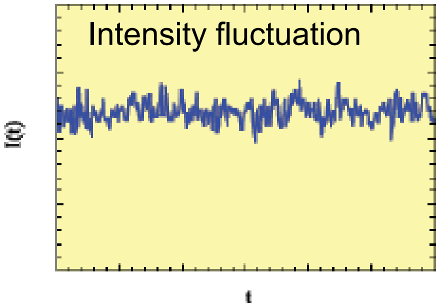


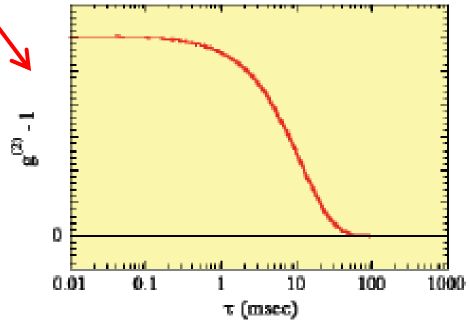
speckle

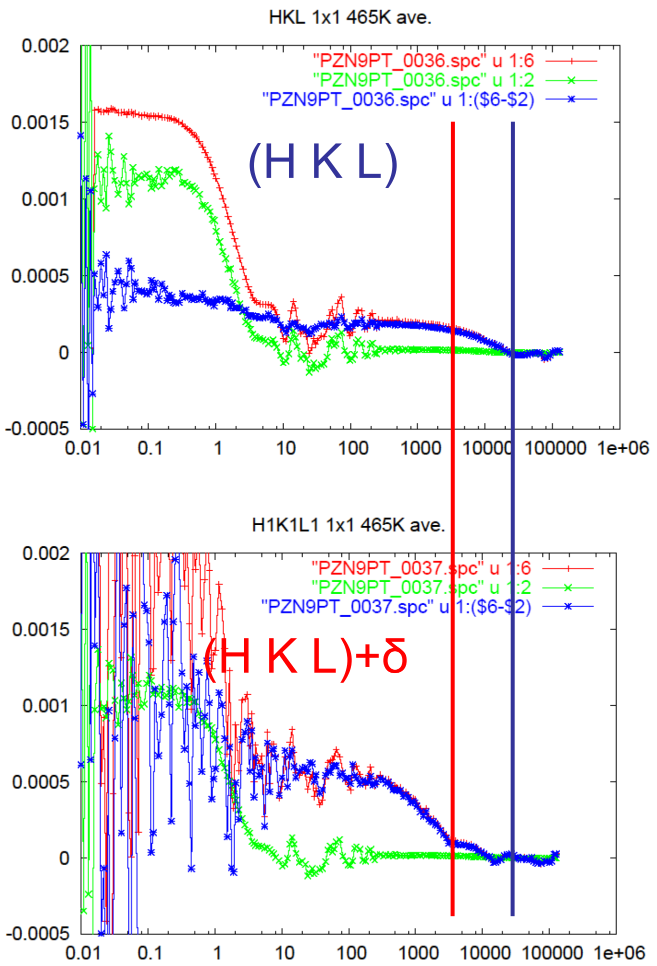


Auto-correlation function

$$g_t^{(2)}(\mathbf{q},\tau) \equiv \frac{\langle I(\mathbf{q},t) I(\mathbf{q},t+\tau)\rangle_t}{\langle I(\mathbf{q},t)\rangle_t \langle I(\mathbf{q},t+\tau)\rangle_t}$$







K. Ohwada, et al., preparation

Future direction for SR performance:

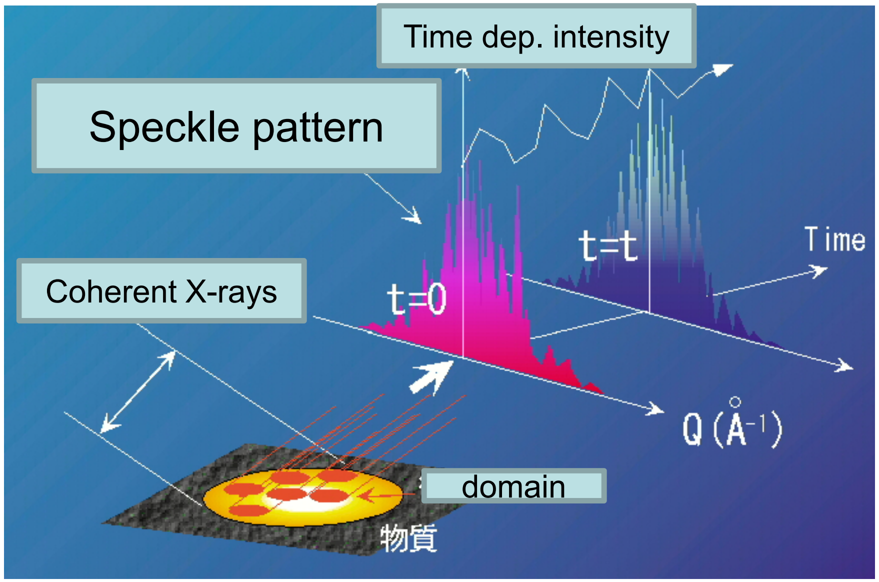
more lower emittance → better spatial coherence

more shorter pulse duration → better time resolution

↓

XFEL

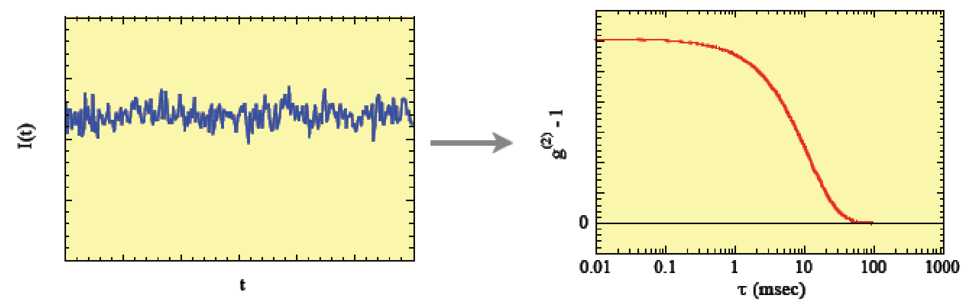
Domain Dynamics by Coherent X-ray Diffraction

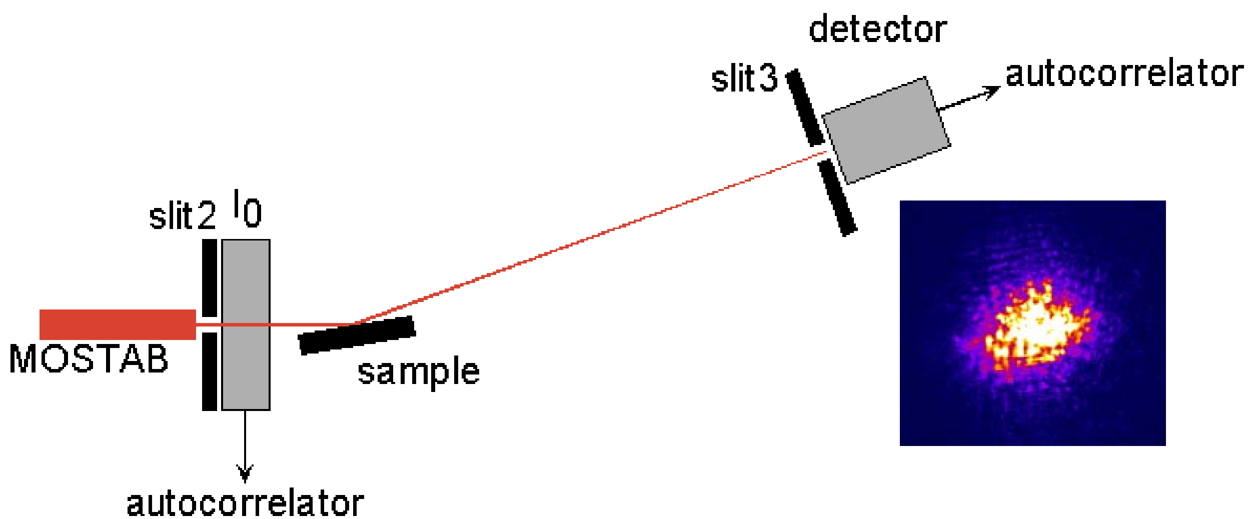


Intensity fluctuation by time

Self-correlation

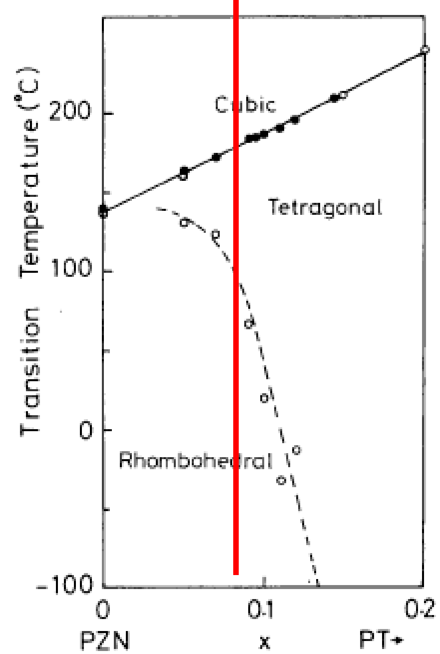
$$g^{(2)}(\tau) = \frac{\langle I(t+\tau)I(t)\rangle}{\langle I(t)\rangle^2}$$





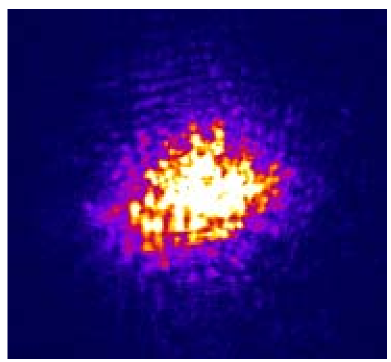
Domain fluctuation of Relaxor PZT-9%PT

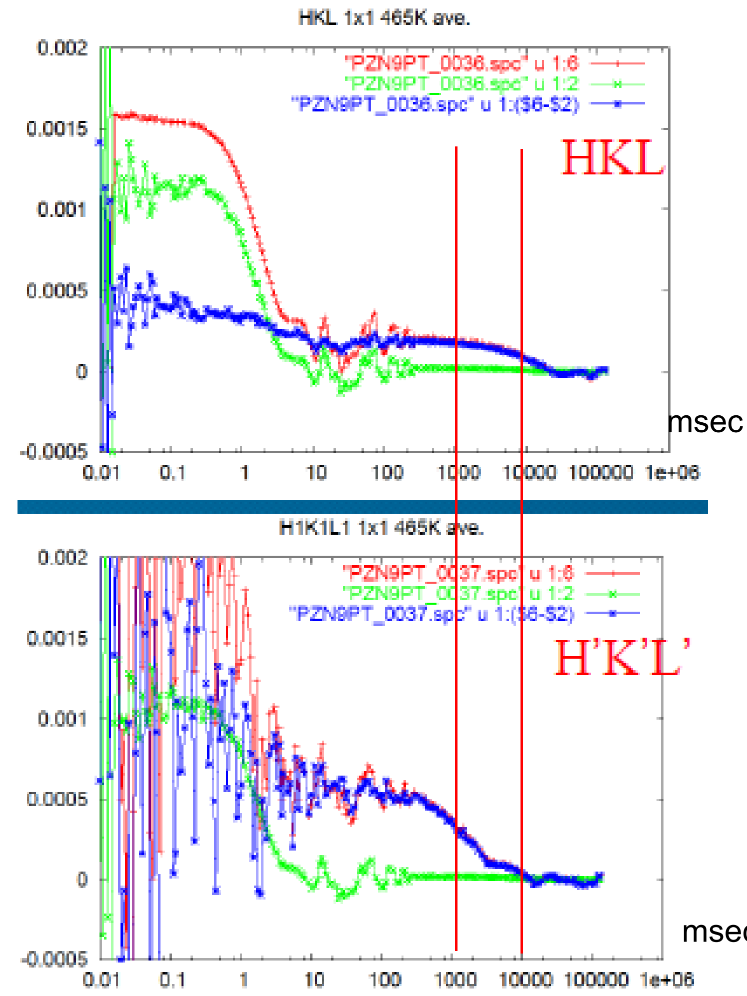
$91\%Pb(Zn_{1/2}Nb_{1/2})O_3+9\%PbTiO_3$



Kuwata *et al.*, Jpn. J. Appl. Phys. Vol. 21 (1982) 1298.

Speckle around (200)





K. Ohwada, private comm.

Coherence：Bose condensation

Photon number in a coherent volume

Longitudinal (temporal) coherence: $\sigma_t \sim 2h/\Delta\omega$

Transverse (spatial) coherence: $\sigma_{x,y} \sim \lambda \cdot L/2\pi S_{X,Y}$

Coherent volume: $V_C = \sigma_X \cdot \sigma_Y \cdot \sigma_t = \lambda^2 \cdot L^2 \cdot 2h/(4\pi^2 \cdot S^2 \cdot \Delta\omega)$

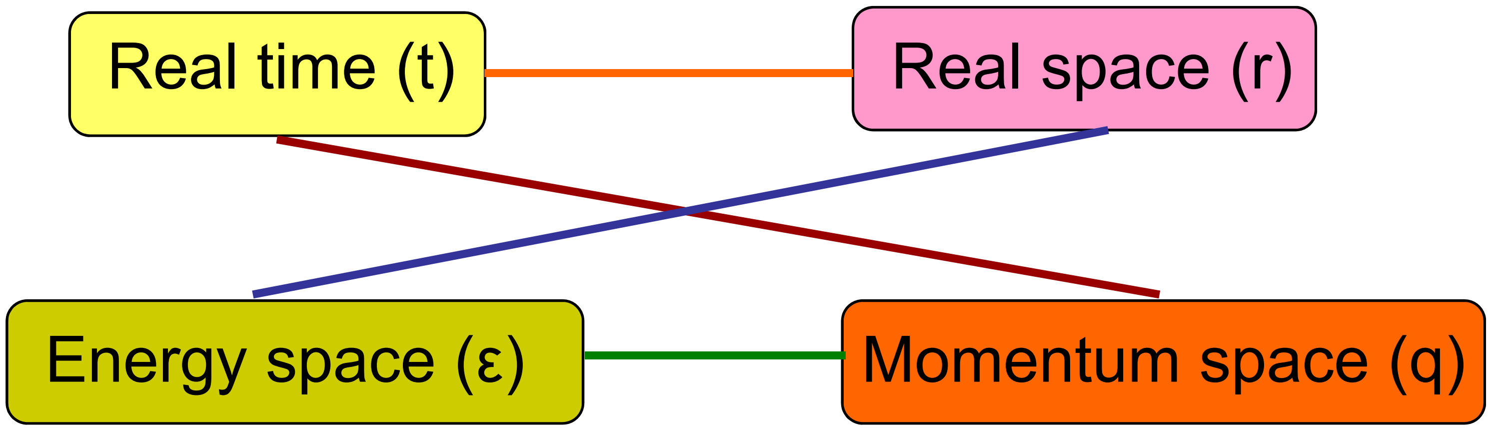
Beam Volume: $V = \Delta X \cdot \Delta Y \cdot \Delta t$

Bose degeneracy: $\delta = n \cdot V_C/V \sim 0.1$ for SPring-8

for XFEL(SASE-mode): $\delta \sim 10^{10}$ **!!**

non-linear optical phenomena

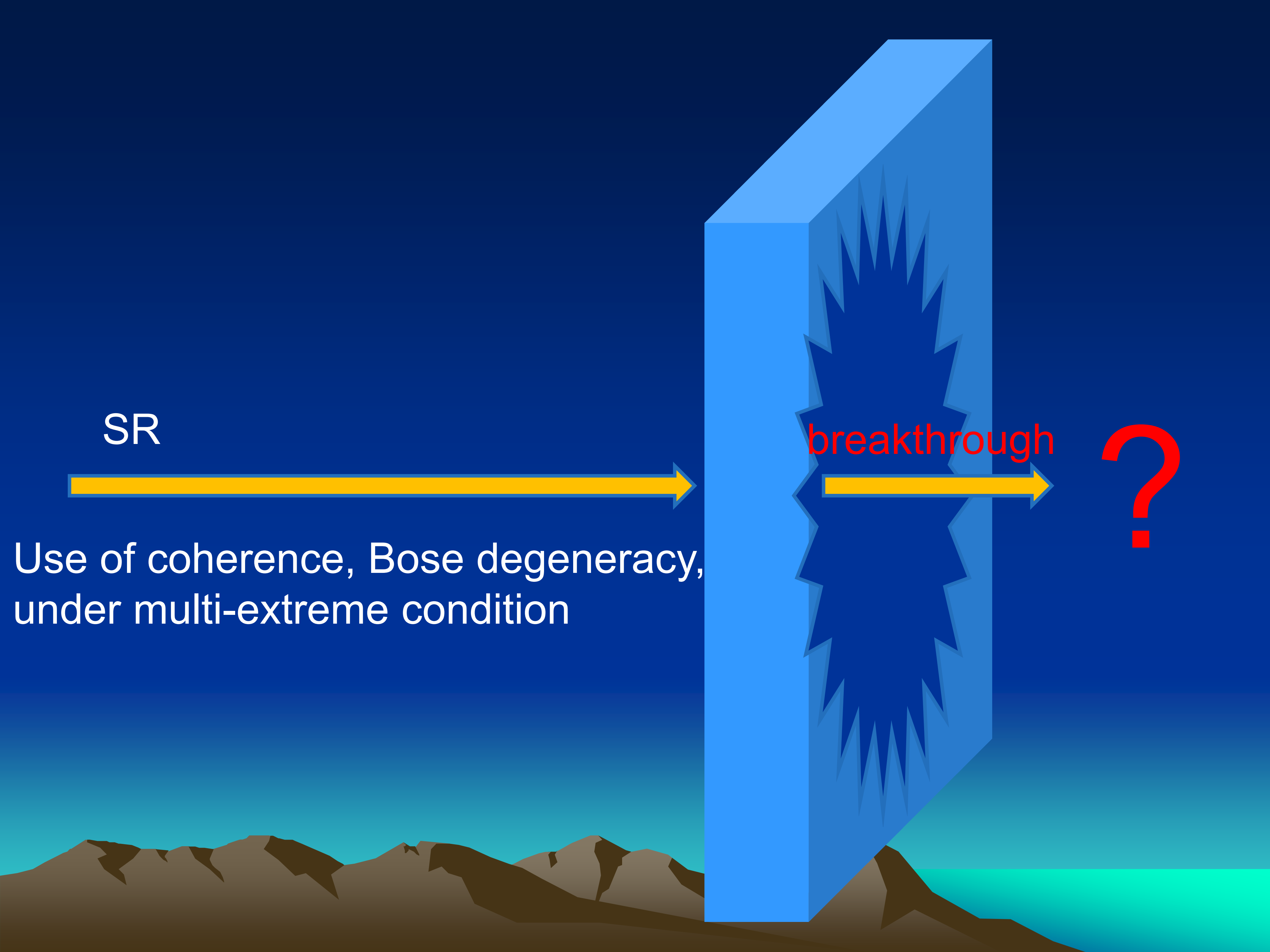
Dynamics



from Observation of $|E(t)|^2$ toward $E(t)$

→ Phase information of electron

→ Manipulation of electron wavefuction


SR
Use of coherence, Bose degeneracy,
under multi-extreme condition
breakthrough
?