National Synchrotron Radiation Research Center

03/05/2014

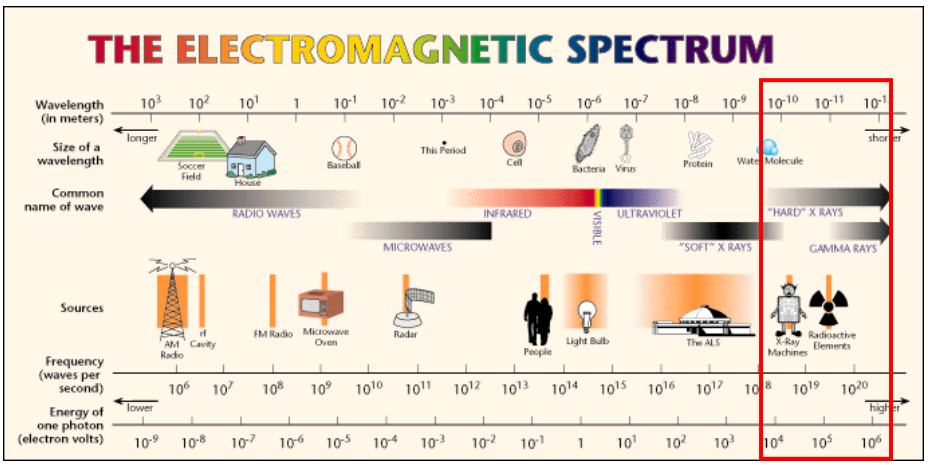
# Special Topic on Nanophysics - Structural investigation of nanomaterials by synchrotron x-ray scattering

徐嘉鴻

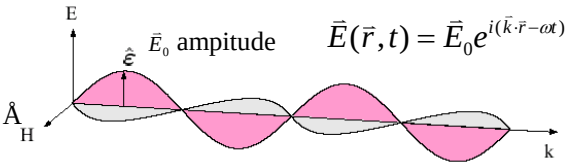
國家同步輻射研究中心 科學研究組

X-rays, wave, and interference
Crystal and Bragg Law
Applications -
- fiber diffraction
- epitaxial growth
- quantum dots
- phase transformation

## X-ray - electromagnetic wave

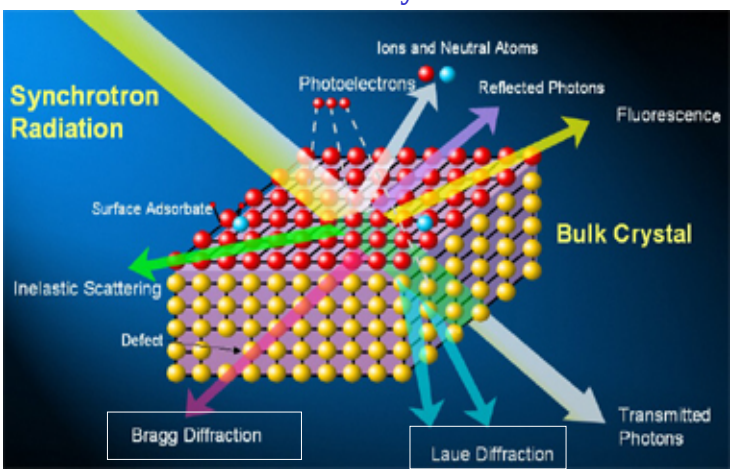



Hard X-rays
E: a few keV ~ a few MeV
λ: a few Å ~ 0.01 Å
Typical λ for structure study : 1 Å




$$\vec{E}(\vec{r},t) = \vec{E}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

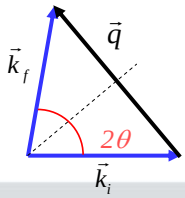
## The Interaction of X-rays with Materials




Diffraction & Elastic scattering

$\boldsymbol{E}_i = \boldsymbol{E}_f$ i.e. $\lambda_i = \lambda_f$ (elastic process)

$|k_i| = |k_f|$, $i$ : incoming, $f$ : outgoing



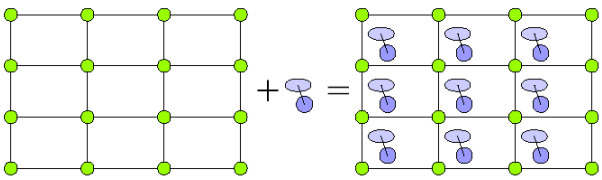

scattering vector

$$\vec{q} = \vec{k}_f - \vec{k}_i$$

$2\theta$: scattering angle

## Crystal: a repeated (periodic) array of atoms

**Crystal structure = Lattice + Basis of the Lattice Point**




A crystal structure consists of identical copies of the same physical unit (a group of atoms), called the **basis**, attached to all the points of a **lattice**.

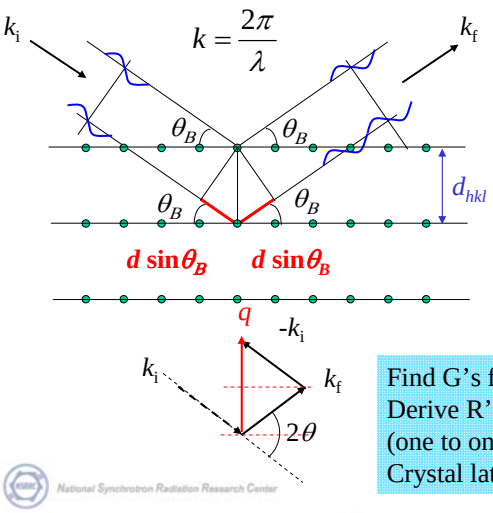
A lattice is defined as an array of equivalent points in 1, 2 or 3 dimensions. The environment of an atom placed on any one of these lattice points would be identical to that placed on any other lattice point. Therefore the lattice locates equivalent positions and shows the **translational symmetry**. The actual positions of atoms or molecules, however, is not provided.

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

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

Path Difference $L = 2d_{hkl}\, sin(2\theta/2)$

Constructive interference: $L = n\lambda$




Bragg Law: $2d_{hkl}\, sin(2\theta/2) = n\lambda$

$$2\pi \frac{2}{\lambda}\sin(2\theta/2) = 2\pi \frac{1}{d_{hkl}}$$

$$\vec{q} = \frac{4\pi}{\lambda}\sin(2\theta/2)\,\hat{q} = \frac{2\pi}{d_{hkl}}\hat{n} = \vec{G}_{hkl}$$

condition for diffraction to occur

Find G's from measurements,
Derive R's from G's
(one to one correspondence between G's and R's)
Crystal lattice is determined

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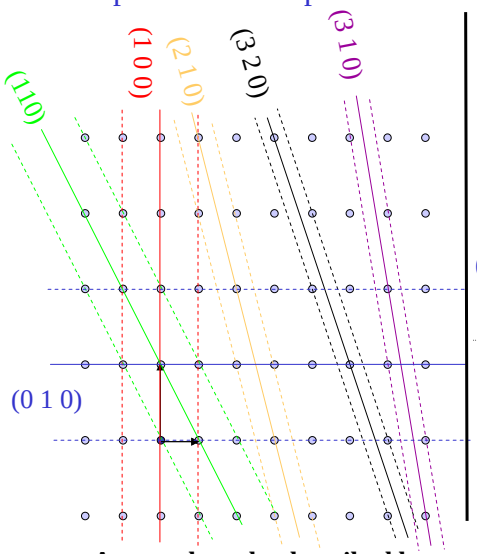
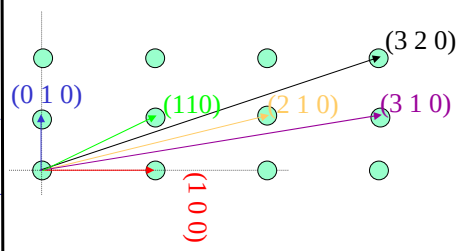
## lattice planes in real space




## lattice points in reciprocal space




**A crystal can be described by sets of evenly spaced parallel planes.**
**Represent each set of planes by its $\hat{n}$ and $1/d_{hkl}$, a vector (point) in reciprocal space**

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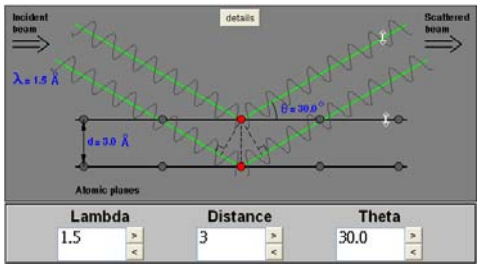
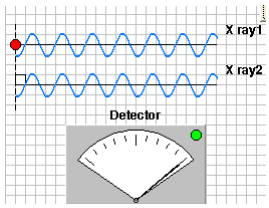
## Bragg Law: x-rays reflected from crystalline planes

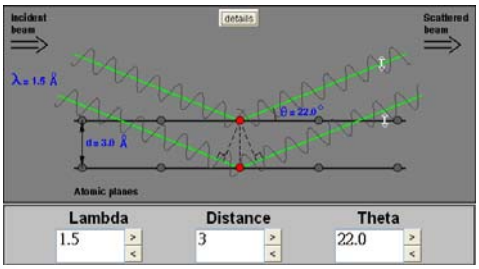
$\lambda = 1.5$Å

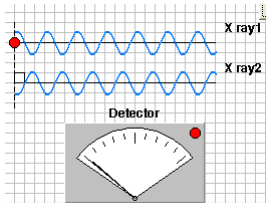



$2*3.0*\sin(30^\circ) = 3 = 2\lambda$

Bragg law holds => strong signal




$2*3.0*\sin(22^\circ) = 2.25 \neq n\lambda$

Bragg law fails => no signal

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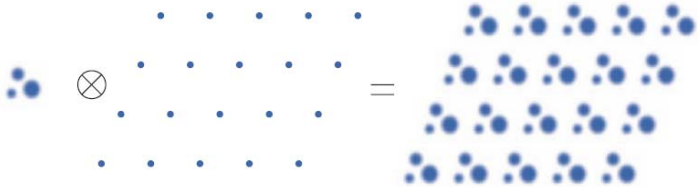
http://www.eserc.stonybrook.edu/ProjectJava/Bragg/

**Real space**

basis ⊗ lattice = crystal ($e^-$ density)

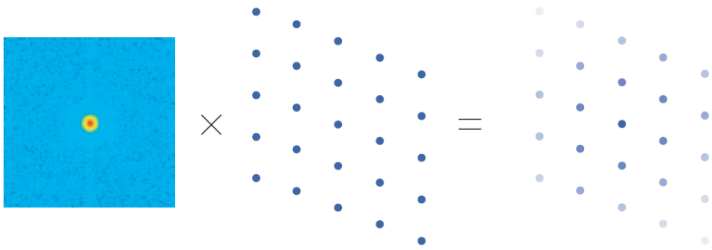


The electronic distribution of the crystal can be described as the convolution of the Bravais lattice with the electronic distribution of the basis.

Fourier transform

**Reciprocal space**

structure factor × reciprocal lattice = diffraction pattern

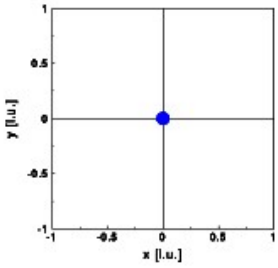


Reproduced from An Introduction to Synchrotron Radiation by Philip Willmont

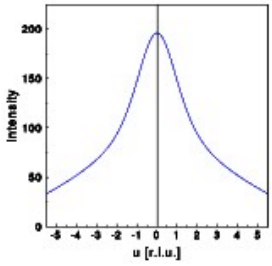
## Diffraction Pattern of A Single Atom

Assume a spherical charge distribution

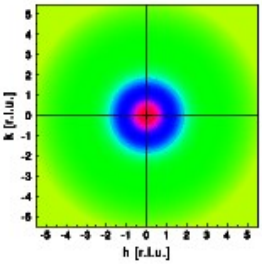
Real space




A cut in reciprocal space




2D in reciprocal space

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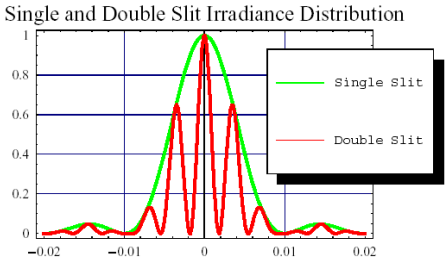
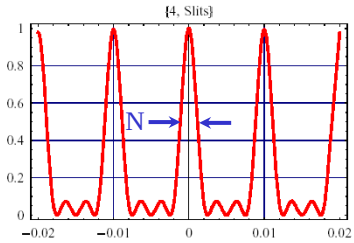
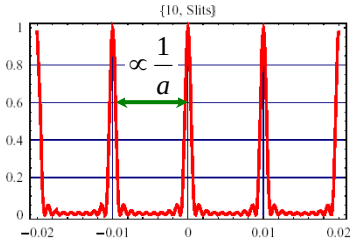
## 狹縫繞射




繞射峰間距 ⟷ 狹縫間距 a
繞射峰峰寬 ⟷ 狹縫數目 N

$$I = I_0 \left( \frac{\sin(Nka\sin(2\theta)/2)}{N\sin(ka\sin(2\theta)/2)} \right)^2$$

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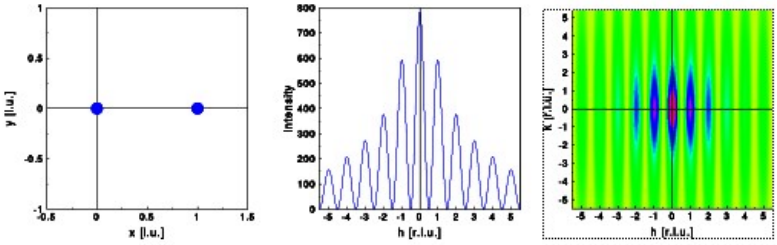
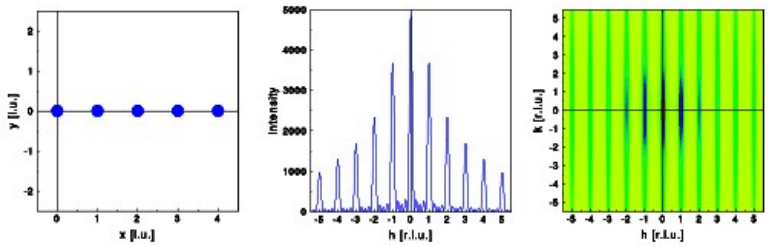
## Size Effect - Diffraction Pattern of A Row of Atoms

2 atoms




1 l.u.= a Å
1 r.l.u. = $2\pi/a$ Å$^{-1}$

5 atoms




Scherrer's equation $L \approx \dfrac{2\pi}{FWHM(q)}$ $L \approx \dfrac{0.9\lambda}{FWHM(2\theta)\cos\theta_B}$

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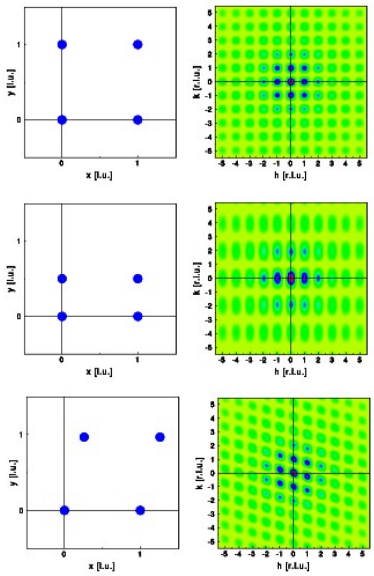
Pictures reproduced from Interactive Tutorial about Diffraction
(http://www.lks.physik.uni-erlangen.de/diffraction/teaching.html)

## Diffraction Patterns of Various Lattices

Real space




Reciprocal space

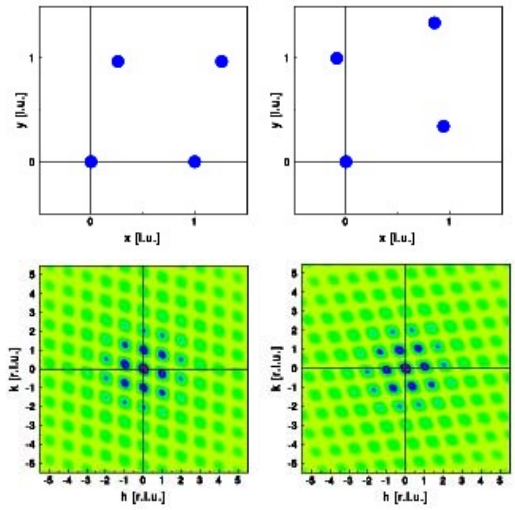
a square lattice

an orthorhombic lattice

an oblique lattice

The inverse relationship between real and reciprocal space

## Rotation of Crystal




Rotation of atomic arrangement in real space

Rotation of diffraction pattern in reciprocal space

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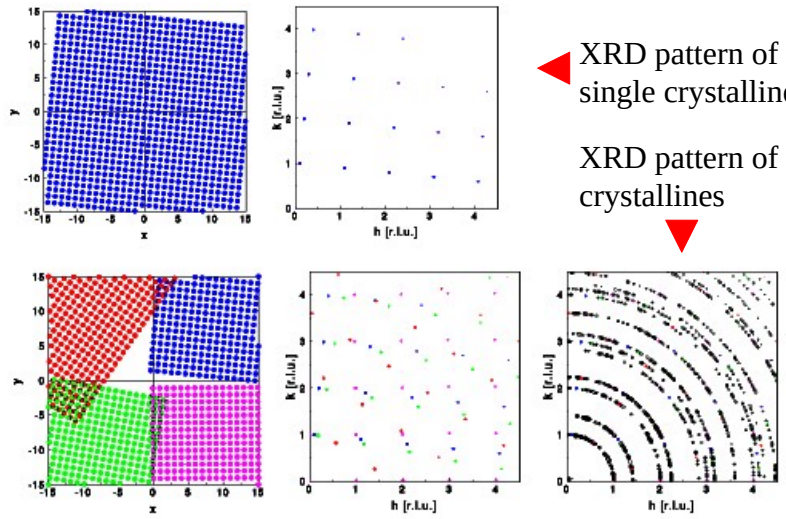
## X-ray Powder Diffraction (XRD)




XRD pattern of a single crystalline

XRD pattern of many crystallines

Powder rings

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**Lattice** → **diffraction peak position**

**Basis** → **intensity profile**

**Diffraction peak position** → **crystal symmetry**
**lattice constant**

**Intensity profile** → **structure factor**
**charge distribution**

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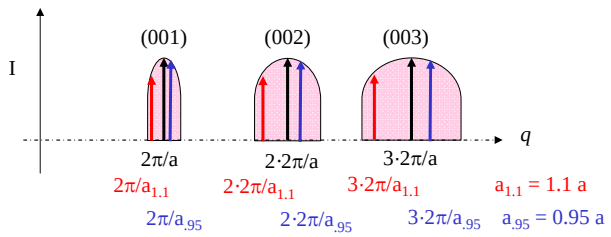
## Peak broadening – strain

$$q = \frac{2\pi}{d} \qquad |\Delta q| = \frac{2\pi}{d^2}\Delta d = \frac{2\pi}{d}\varepsilon = q\varepsilon$$

$\Delta q = q\varepsilon$ **proportional to *q***

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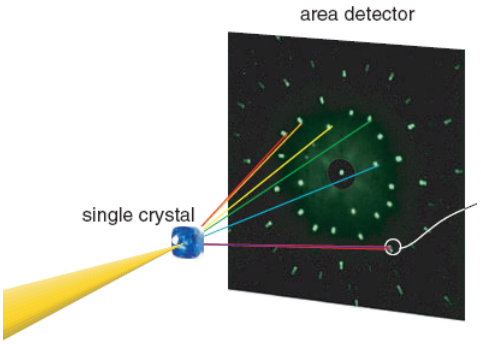
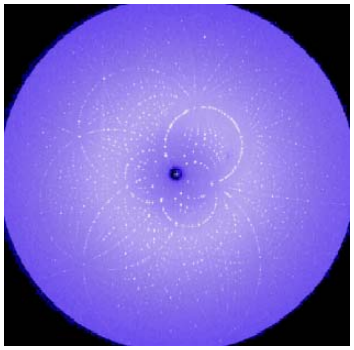
Diffraction Patter of Single Crystals

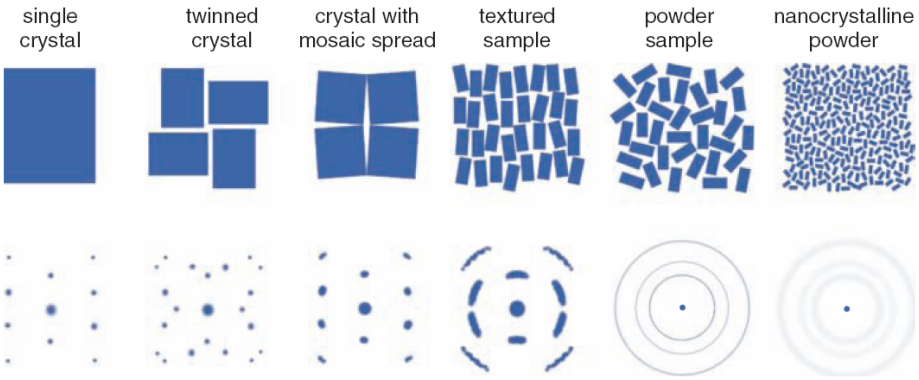
Diffraction patter of a protein crystal



Lattice: symmetry, lattice parameters
Intensity distribution: atomic arrangement within a unit cell

## Types of Crystalline Samples and Their Diffraction Patterns

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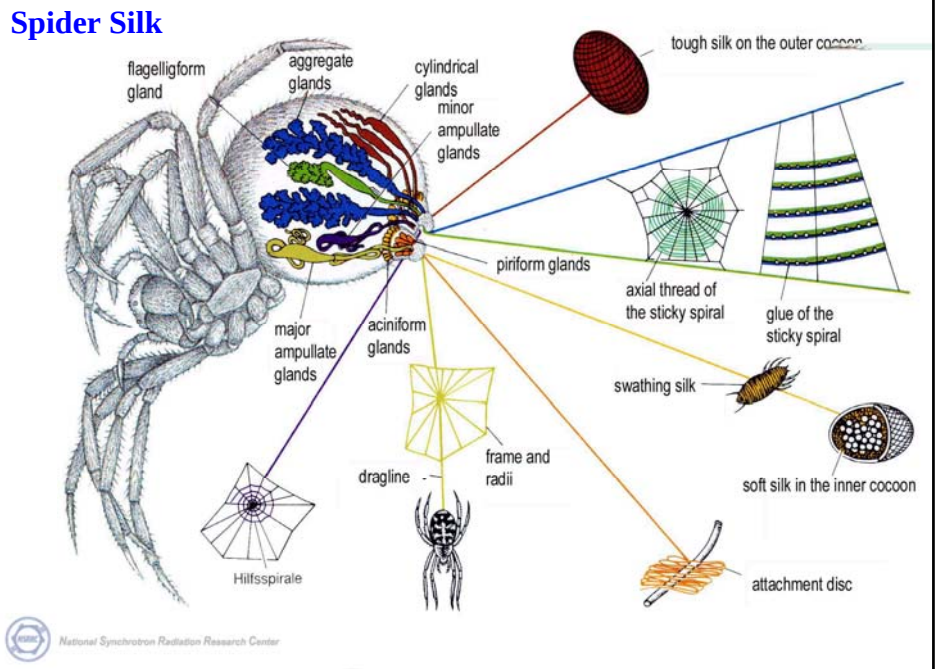
## Spider Silk



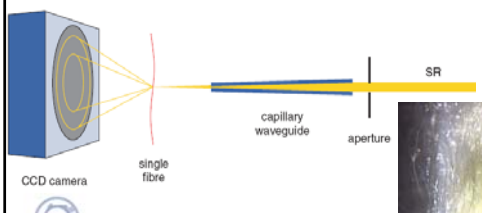

## Fiber Diffraction

Two types of nano-crystallines exist in spider silk

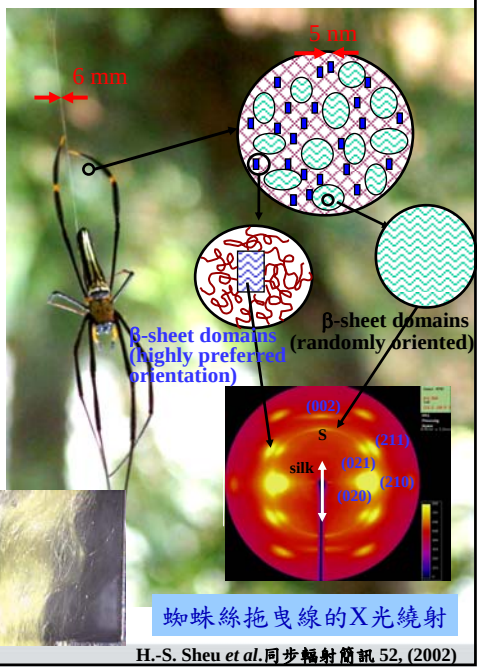
從二維X光繞射圖譜發現 蜘蛛絲裡含兩種奈米晶體

**The most basic & stable (secondary) structural units found in proteins**

**α-helix** **β-sheets** **turns**




Spider Silk (Nephila 人面蜘蛛 drag line )

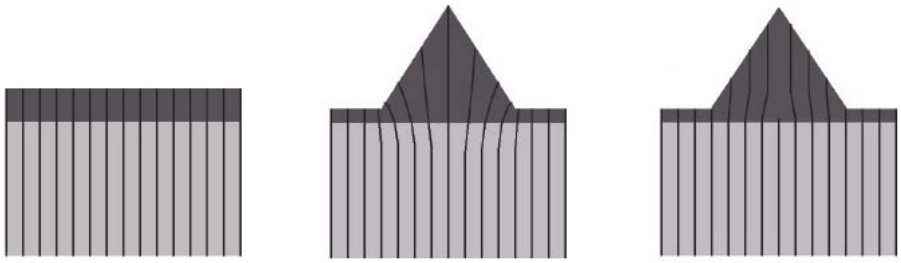



蜘蛛絲拖曳線的X光繞射

H.-S. Sheu *et al.* 同步輻射簡訊 52, (2002)

## Elastic Strain Relaxation during the S-K Growth
(2-D followed by 3-D)

**Uniformly Strained Layer** | **Coherently Strained Islands** | **Dislocation Relaxed Islands**



increasing coverage

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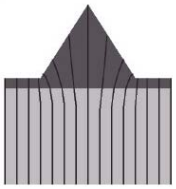
## "Coherently Strained" Quantum Materials Fabricated by Heteroepitaxial Growth



coherent (dislocation free) dots/wires
grown via the S-K mode

narrow size distribution
preferred shape
correlated spatial distribution

sensitive to the details of growth condition

### Issues of Interest

Application: uniform size, high density, regular arrangement

Fundamental: to understand and control the formation of quantum dots

Nucleation phase (growth kinetics)
Growth of islands (energetic balance)
Ostwald ripening

strain relaxation, chemical intermixing, inter-dot interaction, surface energy

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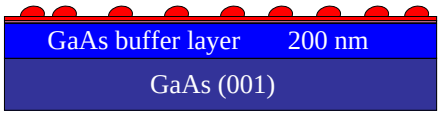
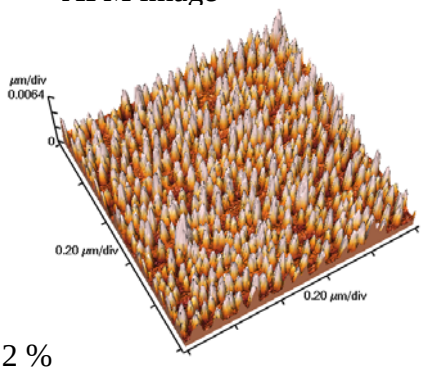
## Uncapped $In_{0.5}Ga_{0.5}As$ Quantum Dots

Grown by MEE

$In_{0.5}Ga_{0.5}As$ 5ML/ Ga (4x2)
grown @ 520°C 0.1ML/s.




AFM image




$a_{InAs}$ = 6.0583Å
$a_{GaAs}$ = 5.65325Å

mismatch = 7.2 %

n ~ $5.3 \times 10^{10}$ $cm^{-2}$

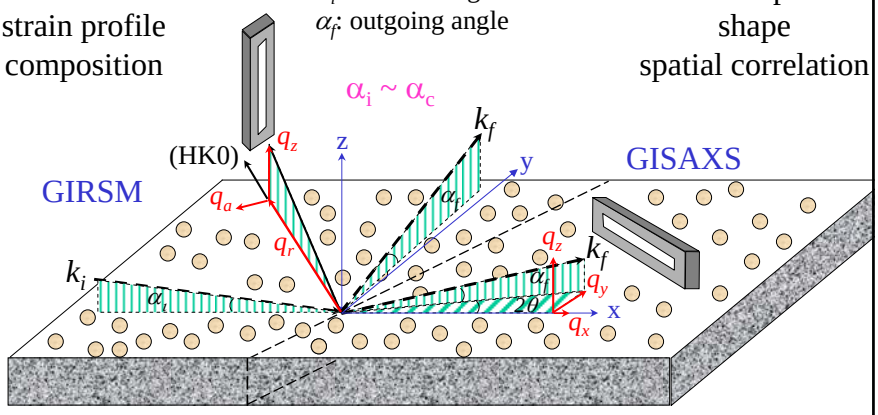
J. Cryst. Growth, 175/176, 777 (1997).

## Scattering geometry of Grazing Incidence X-ray Scattering

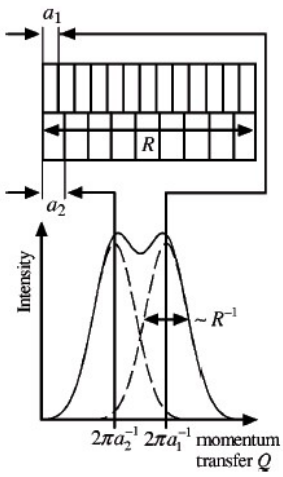
GIRSM
q ~ (H K 0)
Strain sensitive
strain profile
composition

$\boldsymbol{k}_i$: incident wave vector.
$\boldsymbol{k}_f$: scattered wave vector.
$\boldsymbol{q}$ : scattering vector.
$\alpha_i$: incident angle
$\alpha_f$: outgoing angle

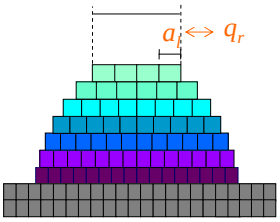
GISAXS
q ~ 0
Strain independent
shape
spatial correlation



## Reconstruct Quantum Dots Structure from Reciprocal Space Map (RSM)




$2\pi(a_2^{-1} - a_1^{-1}) \geq R^{-1}$




**Iso-strain slab**:
region of constant lateral lattice parameter $a_l$

For given $\boldsymbol{G}$ = (HK0), x-ray scattered by a slab with $a_l$ distributes around $q_r = \frac{2\pi}{a_l}\sqrt{H^2 + K^2}$ .

large $a_l \Leftrightarrow$ small $q_r$

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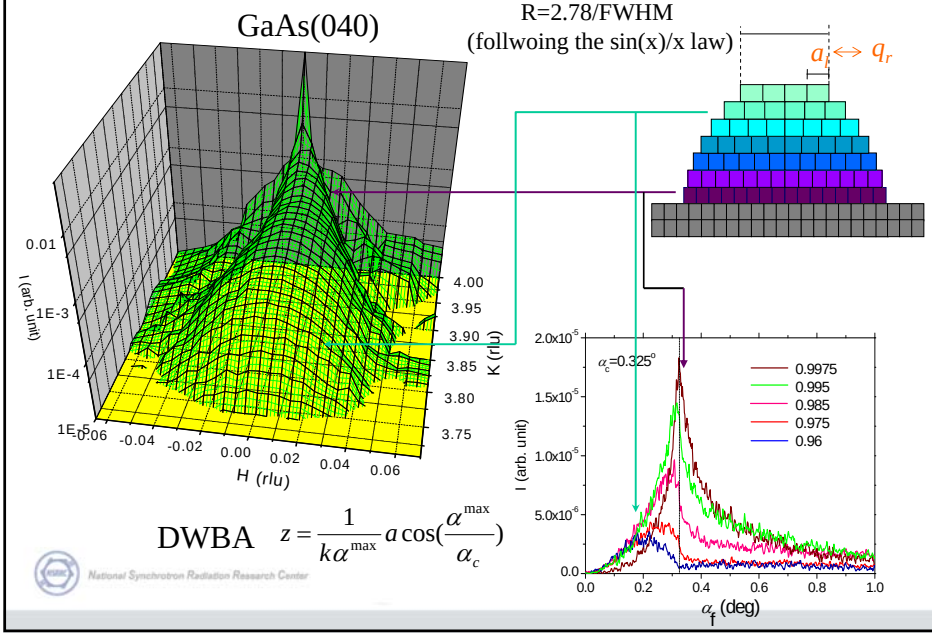
PRB 63, 35318 (2001) by I. Kegel *et al.*

## Shape and Strain Distribution of $In_{0.5}Ga_{0.5}As$ QDs

GaAs(040)

R=2.78/FWHM
(follwoing the sin(x)/x law)




DWBA $z = \frac{1}{k\alpha^{\max}} a \cos(\frac{\alpha^{\max}}{\alpha_c})$

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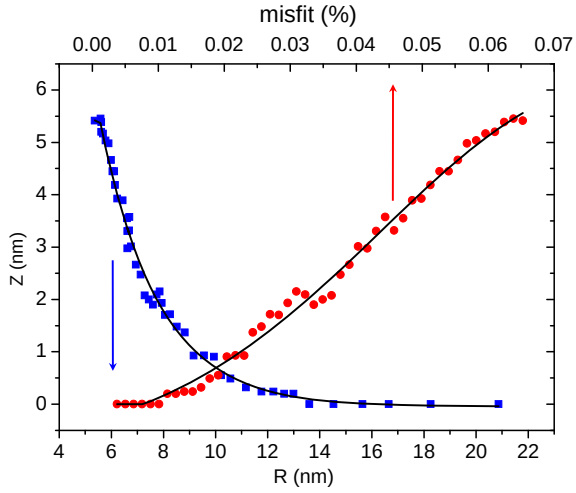
## Shape and Strain Distribution of $In_{0.5}Ga_{0.5}As$ QDs




(■) height *Z* and (●) misfit vs. radius *R* measured along [040]

misfit = $(a_{exp} - a_{GaAs})/a_{GaAs}$, where $a_{GaAs}$ denotes the lattice parameter of bulk GaAs

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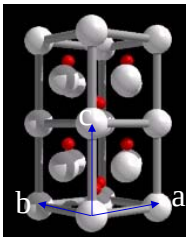
## Composition of Iso-Strain Region

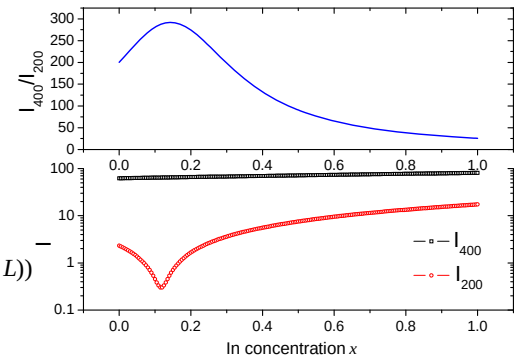
Structure factor is a simple linear combination of atomic scattering factors and atomic percentage of consisting elements

$In_xGa_{1-x}As$: FCC structure
Ga, In: (0,0,0), As: (1/4,1/4,1/4)

$$\frac{I^{400}}{I^{200}}(q_r) = \left| \frac{x(q_r) f_{In} + (1 - x(q_r)) f_{Ga} + f_{As}}{x(q_r) f_{In} + (1 - x(q_r)) f_{Ga} - f_{As}} \right|^2$$




$$F_{HKL} = x f_{In} + (1-x) f_{Ga} + f_{As} \exp(i \frac{\pi}{2}(H+K+L))$$

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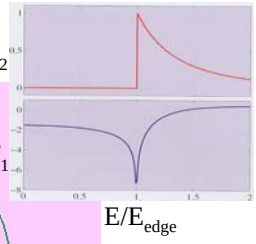
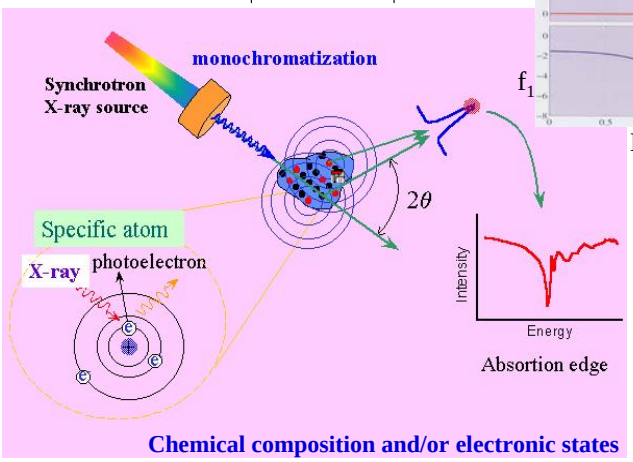
## Anomalous X-ray Scattering

Atomic scattering factor $f(q,E) = f_0(q) + f'(E) + i\,f''(E) = f_1 + i\,f_2$

Intensity $I \approx |F_{HKL}|^2 = \left|\sum_i f_i \cdot e^{i\vec{q}_{HKL}\cdot\vec{r}_i}\right|^2$

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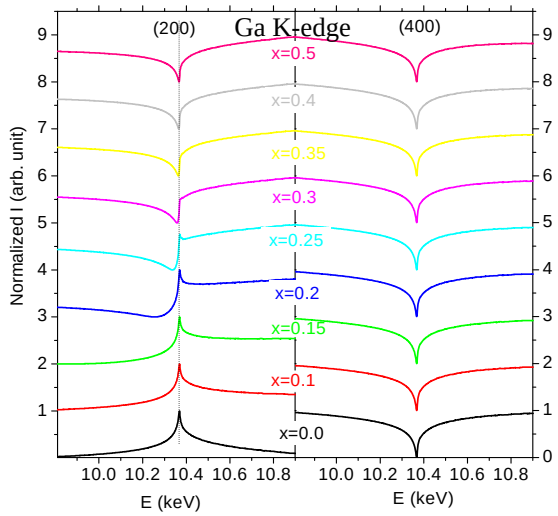
## Simulated Spectra of the (200) and (400) Reflections of the InGaAs

narrower dip
shift to larger E

dip

peak




weak reflection: H + K + L = 4n +2 strong reflection: H + K + L = 4n

$F_{200} = x\,f_{In} + (1-x)\,f_{Ga} - f_{As}$ $F_{400} = x\,f_{In} + (1-x)\,f_{Ga} + f_{As}$

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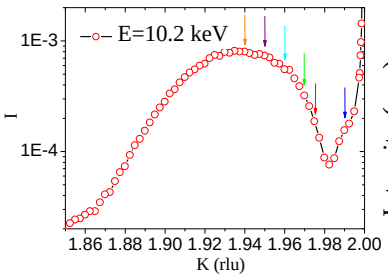
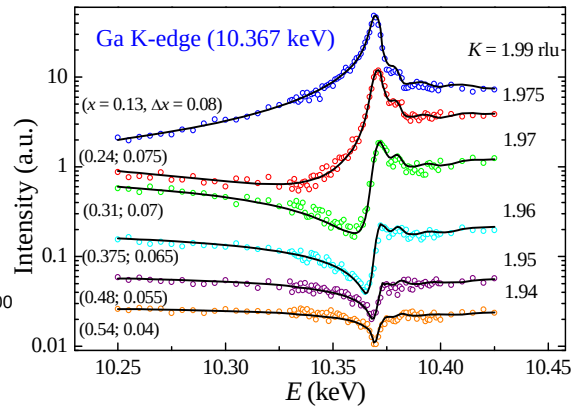
## Resonant X-ray Scattering around GaAs(020)

$$I(\mathbf{Q},E,x) = |F(\mathbf{Q},E,x)|^2 \,\mathrm{LP}(\mathbf{Q},E)A(\mathbf{Q},E)$$

$$|F(Q,E,x)|^2 = \int |F(\mathbf{Q},E,x')|^2 \exp[-(x-x')^2/\Delta x^2]\mathrm{d}x'$$

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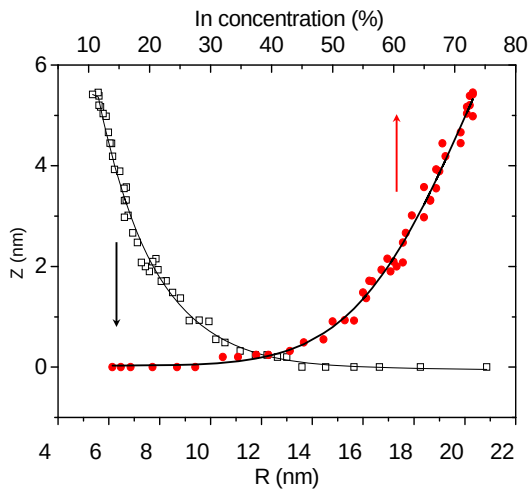
## Compositional Distribution




$x$ increases monotonically with $Z$

$x$ << 0.5 at the base
$x$ > 0.5 near the top

(●) In concentration and (□) radius $R$ vs. height $Z$

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**Presentation No.**