Surface Sensitive X-ray Scattering

Oliver H. Seeck

Hasylab, DESY

Introduction

- Concepts of surfaces
- Scattering (Born approximation)

Crystal Truncation Rods

- The basic idea
- How to calculate
- Examples

Reflectivity

- In Born approximation
- Exact formalism (Fresnel)
- Examples

Grazing Incidence Diffraction

- The basic idea
- Penetration depth
- Example

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Introduction

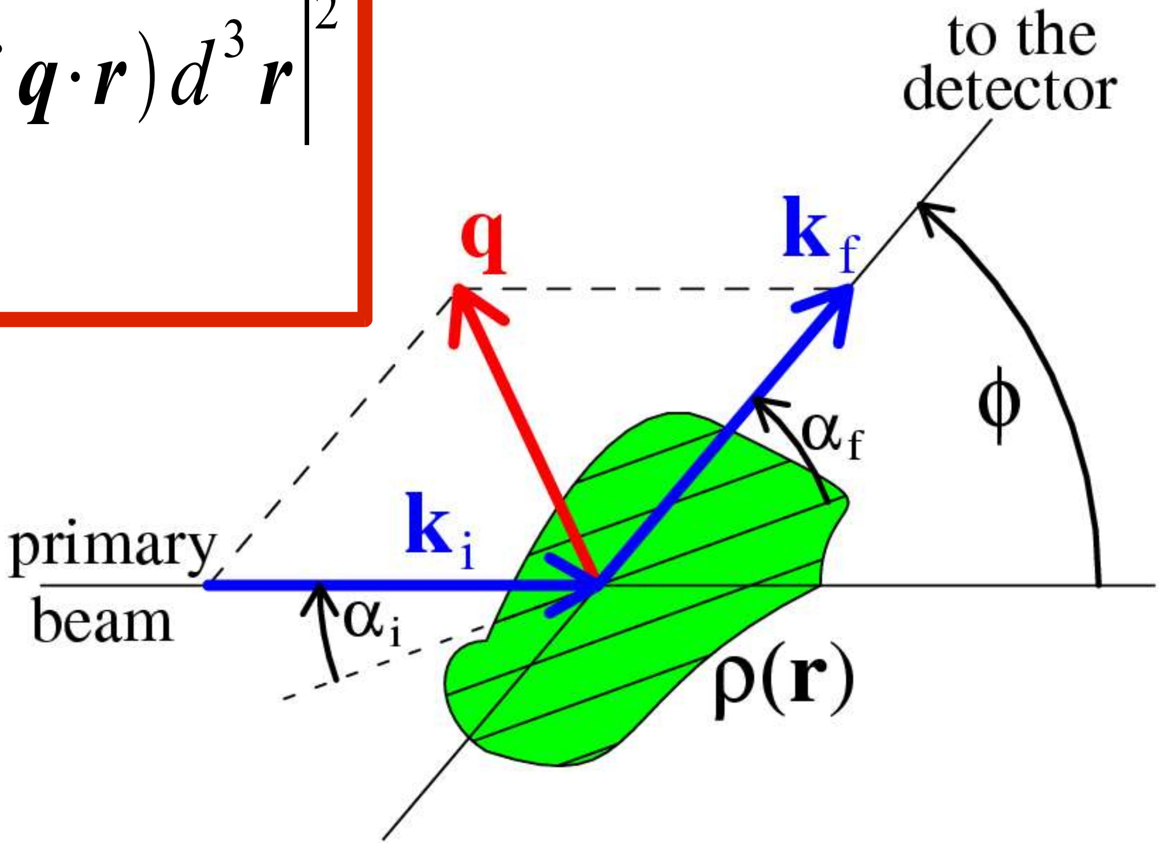
No samples are infinite. A surface always exist!

In simplest approximation (Born approximation) the scattered intensity is given by the Fourier Transformation of the electron density.

$$I(\boldsymbol{q}) \propto \left| \int \rho(\boldsymbol{r}) \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\, d^3\boldsymbol{r} \right|^2$$

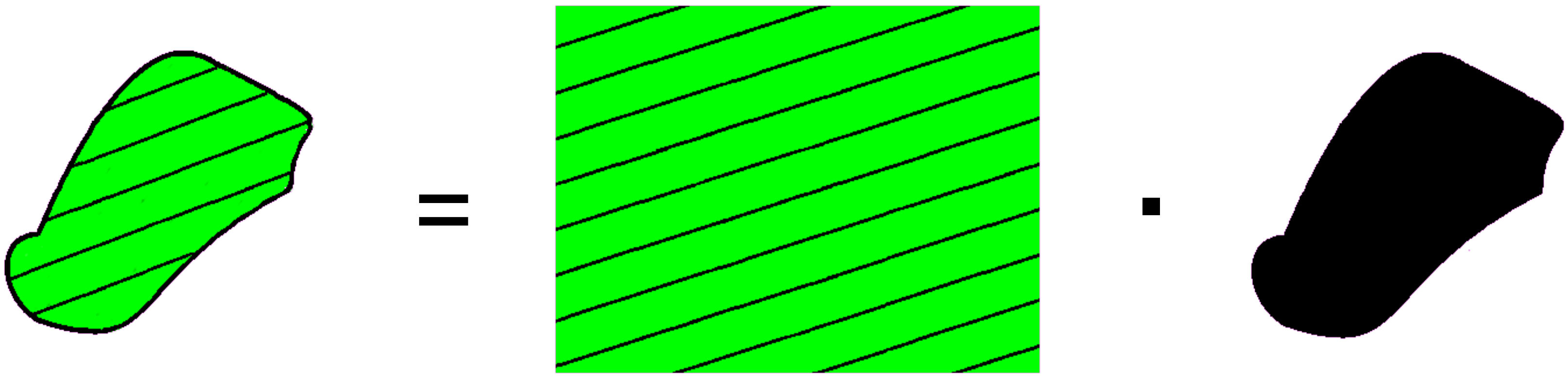
$$= |\mathcal{F}\{\rho(\boldsymbol{r})\}|^2$$

How does the presence of a surface effects the scattered signal?



Estimate of the surface effects on the scattering

real sample = infinite sample · shape function



$$\rho(\boldsymbol{r}) = \rho_\infty(\boldsymbol{r}) \cdot S(\boldsymbol{r})$$

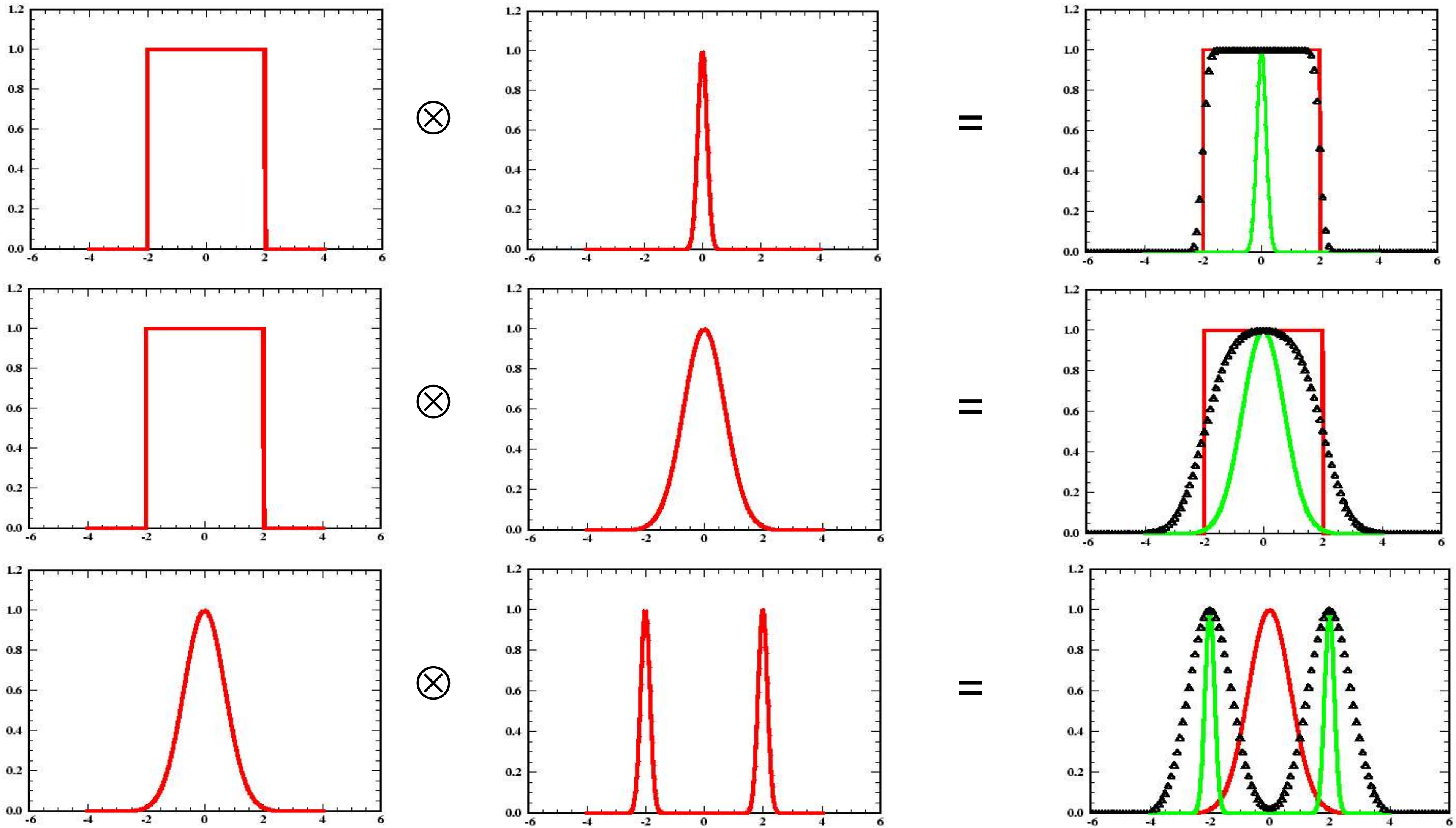
$$I(\boldsymbol{q}) = |\mathcal{F}\{\rho(\boldsymbol{r})\}(\boldsymbol{q})|^2 = |\mathcal{F}\{\rho_\infty(\boldsymbol{r})S(\boldsymbol{r})\}(\boldsymbol{q})|^2$$

The infinite sample density could be a crystal lattice (→ Bragg peaks)

The shape function could be a cube (for a cube shaped sample)

In the following the so called convolution $f_1(y) \otimes f_2(y)$ of two functions $f_1(y), f_2(y)$ is important

Definition : $\{f_1(y) \otimes f_2(y)\}(x) = \int f_1(y) f_2(y-x) \mathrm{d}y$



In Born approximation the scattered intensity is given by:

$$I(\boldsymbol{q}) = |\mathcal{F}\{\rho(\boldsymbol{r})\}(\boldsymbol{q})|^2 = |\mathcal{F}\{\rho_\infty(\boldsymbol{r})S(\boldsymbol{r})\}(\boldsymbol{q})|^2$$

Extremely important: **The Convolution Theorem**

$$\mathcal{F}\{f_1 \otimes f_2\}(\boldsymbol{q}) = \mathcal{F}\{f_1\}(\boldsymbol{q}) \cdot \mathcal{F}\{f_2\}(\boldsymbol{q})$$

Proof of the Convolution Theorem:

$$\mathcal{F}\{f_1 \otimes f_2\}(q) = \mathcal{F}\left\{\int f_1(y) f_2(x\text{-}y)\mathrm{d}y\right\}(q)$$

$$= \iint f_1(y) f_2(x\text{-}y)\mathrm{d}y \exp(iqx)\mathrm{d}x$$

substitute : $x\text{-}y = w$

$$= \iint f_1(y) f_2(w) \exp(iq[w+y])\mathrm{d}w\mathrm{d}y$$

$$= \int f_1(y) \exp(iqy)\mathrm{d}y \int f_2(w) \exp(iqw)\mathrm{d}w$$

$$= \mathcal{F}\{f_1\}(q)\mathcal{F}\{f_2\}(q)$$

From the Convolution Theorem follows :

$$\mathcal{F}\{f_1 \cdot f_2\}(\boldsymbol{q}) = \{\mathcal{F}\{f_1\} \otimes \mathcal{F}\{f_2\}\}(\boldsymbol{q})$$

Proof:

$$\mathcal{F}^{-1}\{f_1 \cdot f_2\} = \mathcal{F}^{-1}\{\mathcal{F}\{\mathcal{F}^{-1}\{f_1\}\} \cdot \{\mathcal{F}\{\mathcal{F}^{-1}\{f_2\}\}\}$$

$$= \mathcal{F}^{-1}\{\mathcal{F}\{\mathrm{F}_1\} \cdot \mathcal{F}\{\mathrm{F}_2\}\} \quad \text{with } \mathrm{F} = \mathcal{F}^{-1}\{f\}$$

$$= \mathcal{F}^{-1}\{\mathcal{F}\{\mathrm{F}_1 \otimes \mathrm{F}_2\}\} = \mathrm{F}_1 \otimes \mathrm{F}_2$$

$$= \mathcal{F}^{-1}\{f_1\} \otimes \mathcal{F}^{-1}\{f_2\}$$

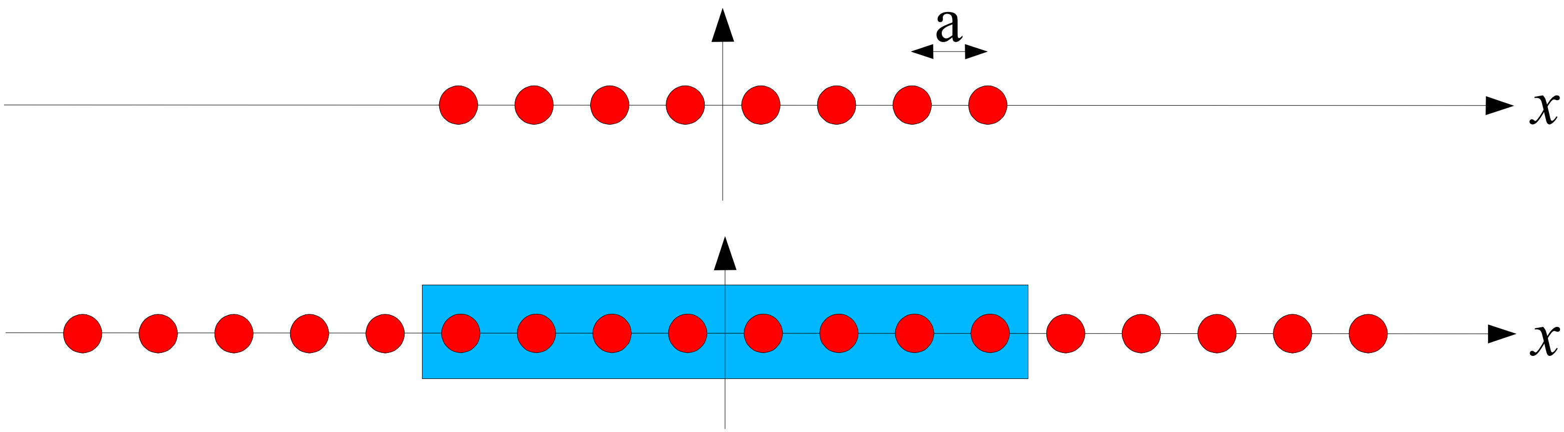
The Inverse Fourier Transformation Operator $\mathcal{F}^{-1}$ can be replaced by the Fourier Transformation $\mathcal{F}$ without violating the proof.

Thus:

$$I(\boldsymbol{q}) = |\mathcal{F}\{\rho(\boldsymbol{r})\}(\boldsymbol{q})|^2 = |\mathcal{F}\{\rho_\infty(\boldsymbol{r}) S(\boldsymbol{r})\}(\boldsymbol{q})|^2$$

$$= |\{\mathcal{F}\{\rho_\infty(\boldsymbol{r})\} \otimes \mathcal{F}\{S(\boldsymbol{r})\}\}(\boldsymbol{q})|^2 = |\mathcal{F}\{\rho_\infty\} \otimes \mathcal{F}\{S\}|^2$$

1. Example: N atoms on a 1-dimensional crystal lattice, lattice distance is a



$$I(q) = \left| \int S(x) \cdot \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \exp(iqx) \mathrm{d}x \right|^2 = \left| \mathcal{F}\left\{ S(x) \cdot \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \right\}(q) \right|^2$$

With the delta-function $\delta(x-x_0) = \begin{cases} \infty & : \; x = x_0 \\ 0 & : \; x \neq x_0 \end{cases}$ and $\int \delta(x-x_0)\mathrm{d}x = 1$

and the shape function $S(x) = \begin{cases} 1 & : \; -Na/2 < x < +Na/2 \\ 0 & : \; \text{otherwise} \end{cases}$

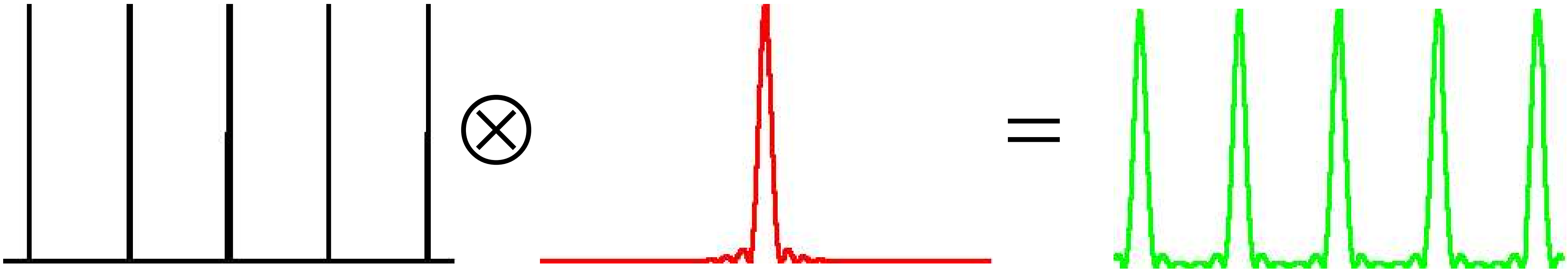
$$I(q) = \left| \mathcal{F}\left\{ S(x)\cdot\sum_{n=-\infty}^{\infty}\rho_0\delta(x-na+a/2) \right\}(q) \right|^2 = \left| \mathcal{F}\{S(x)\}\otimes\mathcal{F}\left\{\sum_{n=-\infty}^{\infty}\rho_0\delta(x-na+a/2)\right\} \right|^2$$

Fourier transformation of an infinite lattice:

$$\mathcal{F}\left\{\sum_{n=-\infty}^{\infty}\rho_0\delta(x-na+a/2)\right\} \sim \sum_{n=-\infty}^{\infty}\delta(q-2\pi n/a)$$

Fourier transformation of the shape function :

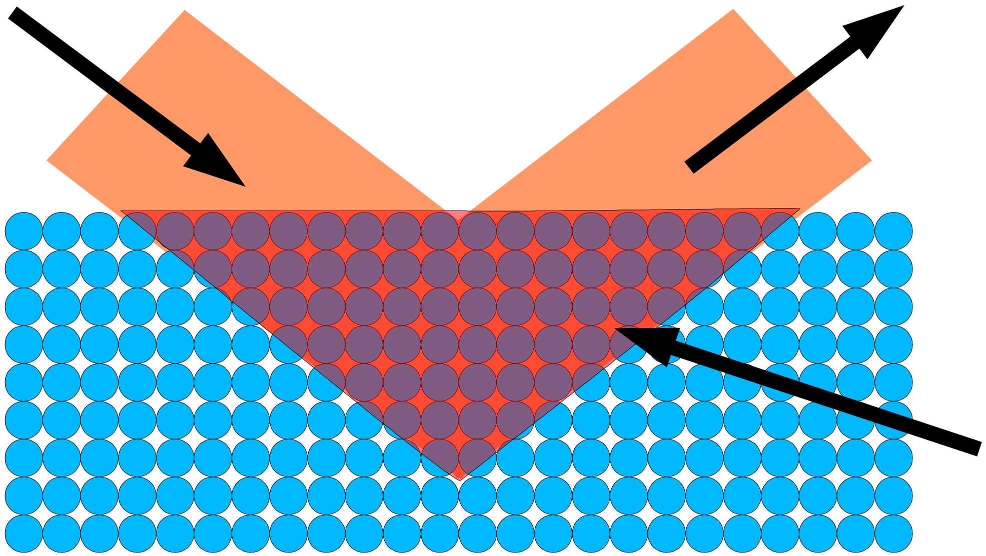
$$\mathcal{F}\{S(x)\}(q) \sim \frac{2}{q}\sin\left(\frac{Naq}{2}\right)$$



Bragg peaks are modified: Laue oscillations

Result: Due to the convolution with the shape function the scattered signal from the sample is modified.

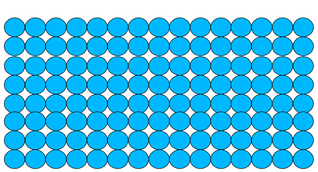
e.g.:



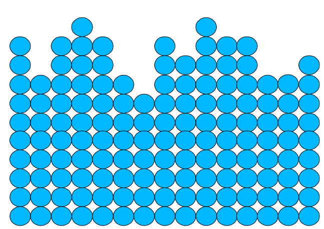
(1) Limited beam size
(2) Limited penetration
(3) Beam size >> penetration

Illuminated part contains only one surface

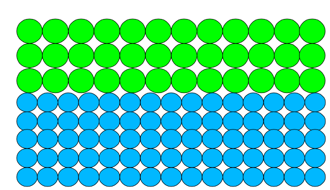
Scattering becomes sensitive to all properties of the illuminated surface via the special shape function $S(\mathbf{r})$.



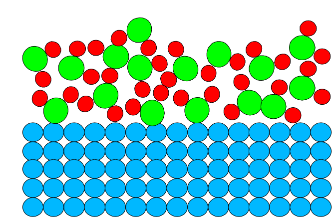
Single surface



Rough surface



Layer system



Amorphous

Scattering methods:

(1) If the samples are crystalline: The shape of the Bragg-peaks are modified $\Rightarrow$ Crystal Truncation Rods (CTR)

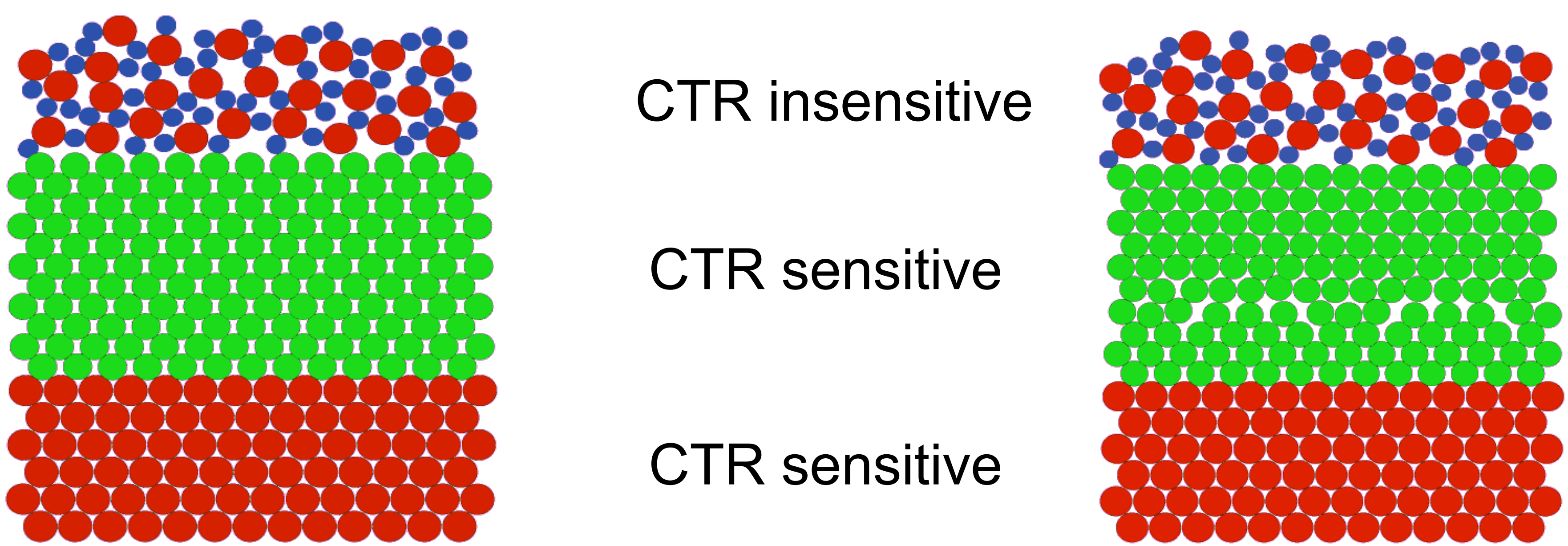
(2) Non-crystalline samples $\Rightarrow$ no real Bragg-peaks, but the zero order Bragg-peak at (0,0,0) (the primary beam) is modified $\Rightarrow$ Reflectivity
(Is also used for crystalline samples, if the crystallinity is of no interest).

(3) Grazing Incidence Diffraction (GID) to analyze crystalline in-plane properties (also depth dependent).

(4) Diffuse scattering around the CTR or the reflectivity to learn about non-crystalline in-plane properties.

Crystal Truncation Rods (CTR)

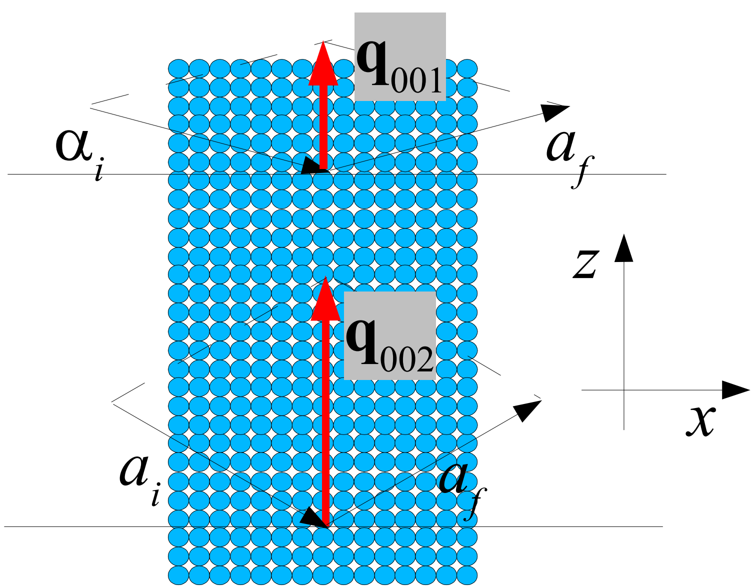
With Crystal Truncation Rod measurements (CTR)
structural properties of surfaces
and thin film systems at CRYSTALLINE samples
can be investigated on a nanoscale.

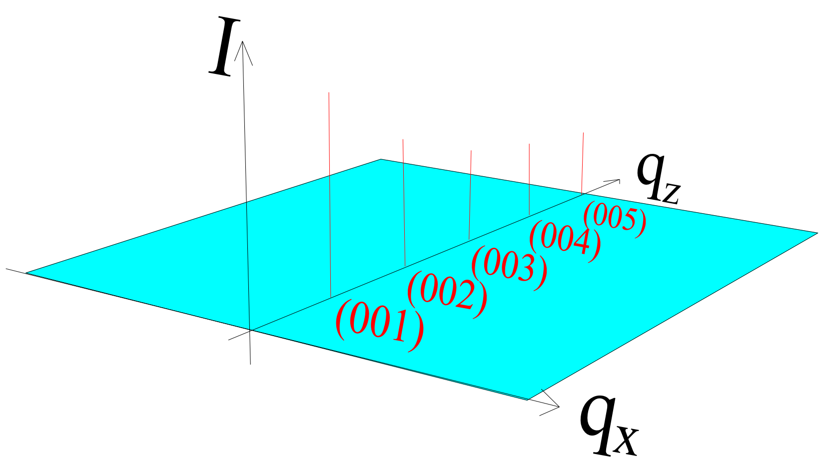


An infinite crystal lattice has δ-like Bragg-peaks: At a particular $\boldsymbol{q}$-vectors (depending on the incident and exit angles) scattered intensity can be found. In Born approximation ($I_{scatt} << I_0$):

$$I(\boldsymbol{q}) = |\mathcal{F}\{\rho(\boldsymbol{r})\}(\boldsymbol{q})|^2 = |\mathcal{F}\{\rho_\infty(\boldsymbol{r})S(\boldsymbol{r})\}(\boldsymbol{q})|^2$$

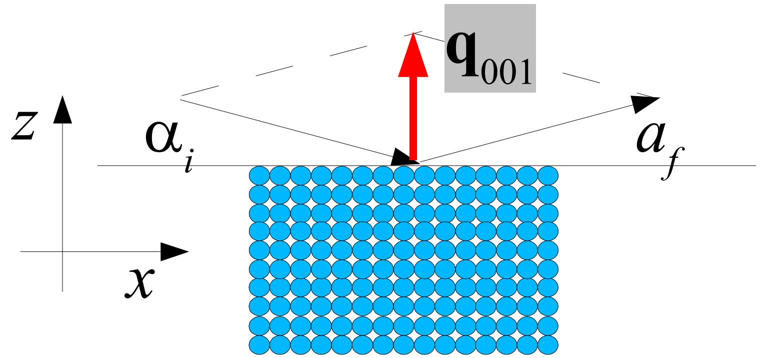
e.g.: [001]-orientation of the crystal
scan-mode : incident angle = exit angle
(001), (002) ... -reflections will appear during the scan

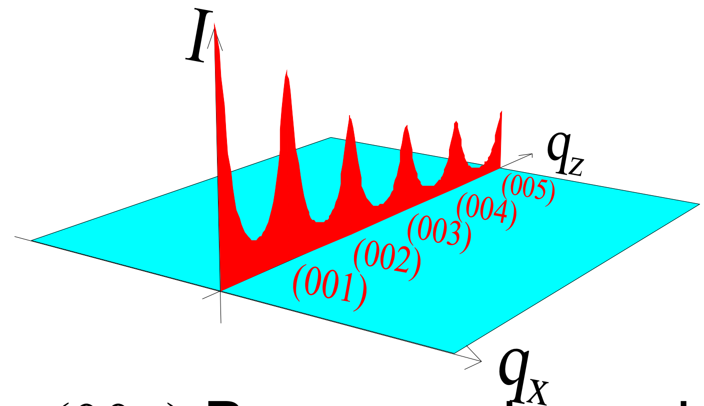


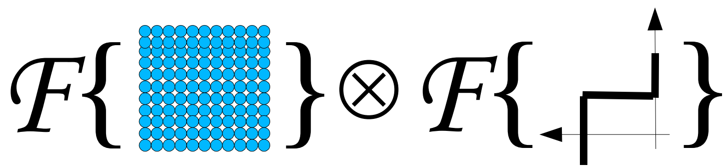


(00n) Bragg-peaks in $\boldsymbol{q}$-space

Considering a simple surface

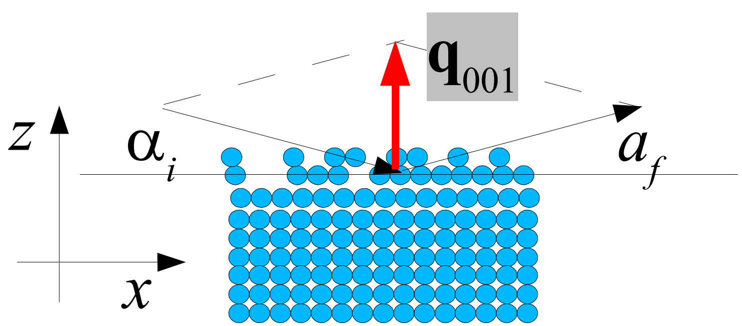


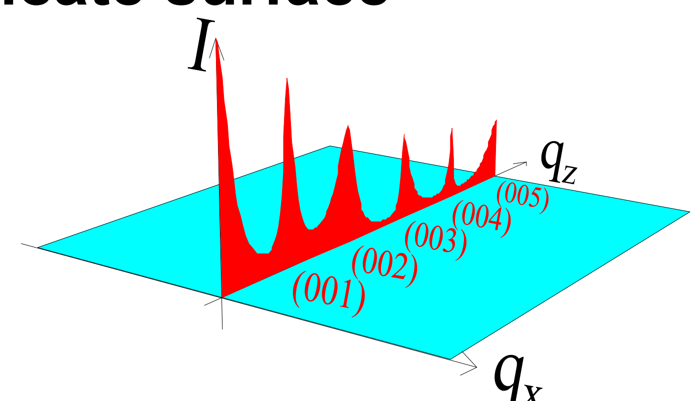


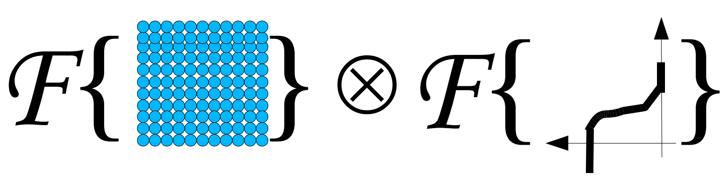


$(00n)$ Bragg-peaks and crystal truncation rods along q_z

Considering a more complicate surface



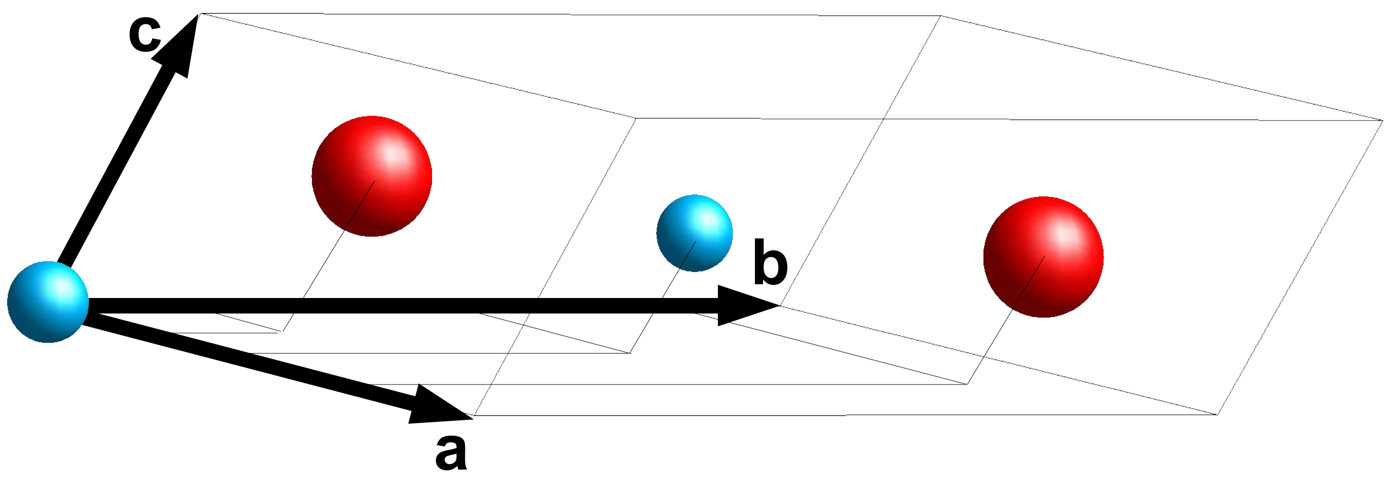




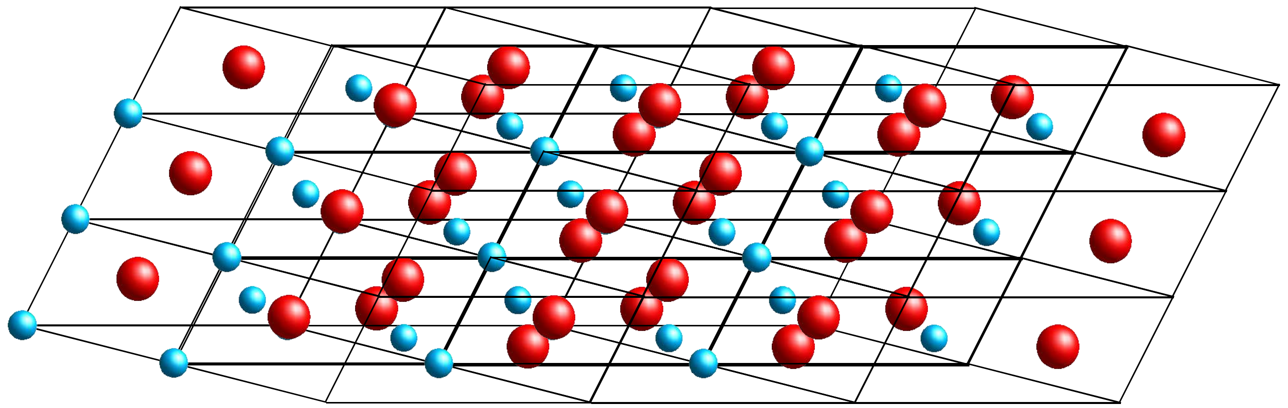
$(00n)$ Bragg-peaks and asymmetric crystal truncation rods

Calculation of CTRs

Crystals are made from unit cells with base vectors **a**, **b**, **c** [volume $\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})$] containing M atoms with density $\rho_j(\mathbf{r})$ at the positions $\mathbf{R}_j = \mu_j\mathbf{a}+\nu_j\mathbf{b}+\phi_j\mathbf{c}$ with $\mu_j, \nu_j, \phi_j < 1$



each unit cell repeats at $n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c}$ with $n_1, n_2, n_3 \in \mathbb{N}$



electron density of the crystal:

$$\rho(\boldsymbol{r}) = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} \sum_{j=1}^{M} \rho_j(\boldsymbol{r} + n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c} + \boldsymbol{R_j})$$

$$= \sum_{n_1, n_2, n_3} \sum_{j} \int \rho_j(\boldsymbol{u})\, \delta(\boldsymbol{u} - \boldsymbol{r} - n_1\boldsymbol{a} - n_2\boldsymbol{b} - n_3\boldsymbol{c} - \boldsymbol{R_j})\, d\boldsymbol{u}$$

scattering amplitude A(**q**) :

$$A(\boldsymbol{q}) = \int \rho(\boldsymbol{r}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r} = \int\int \sum_{n_{1,2,3}} \sum_j \rho_j(\boldsymbol{u})\, \delta(\boldsymbol{u} - \boldsymbol{r} - n_1\boldsymbol{a} - n_2\boldsymbol{b} - n_3\boldsymbol{c} - \boldsymbol{R}_j) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{u}\, d\boldsymbol{r}$$

$$= \int \sum_{n_{1,2,3}} \sum_j \rho_j(\boldsymbol{u}) \int e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \delta(\boldsymbol{u} - \boldsymbol{r} - n_1\boldsymbol{a} - n_2\boldsymbol{b} - n_3\boldsymbol{c} - \boldsymbol{R}_j)\, d\boldsymbol{r}\, d\boldsymbol{u}$$

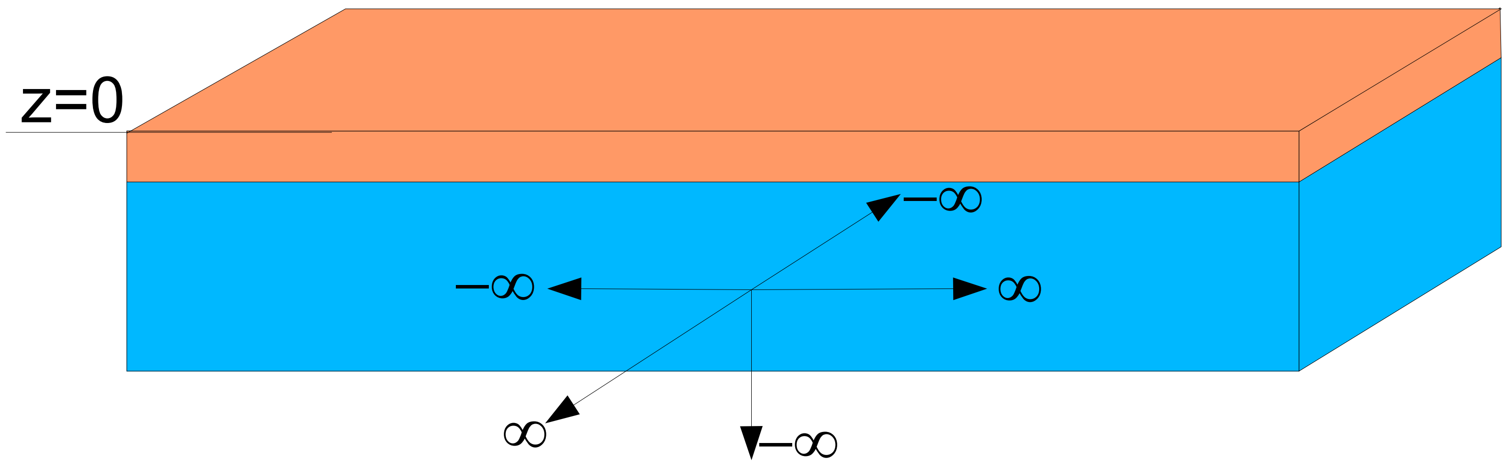
$$= \sum_{n_{1,2,3}} \sum_j \int \rho(\boldsymbol{u}) e^{i\boldsymbol{q}\cdot(-\boldsymbol{u} + n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c} + \boldsymbol{R}_j)} d\boldsymbol{u} = \sum_{n_{1,2,3}} e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c})} \sum_j e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j} \left[\int \rho_j(\boldsymbol{u}) e^{-i\boldsymbol{q}\cdot\boldsymbol{u}} d\boldsymbol{u}\right]$$

$$= \sum_{n_{1,2,3}} e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c})} \sum_j f_j(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j} = S_f(\boldsymbol{q}) \sum_{n_{1,2,3}} e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c})}$$

$f_j(q)$
form factor

$S_j(q)$ structure factor

e.g. Bulk crystal and a thin film crystal, infinity in x and y and -z



Bulk scattering amplitude (truncated a z=0 and shifted by -d)

$$A_{bulk}(\boldsymbol{q}) = e^{-i q_z d} S_{f,bulk}(\boldsymbol{q}) \sum_{n_x=-\infty}^{n_x=\infty} \sum_{n_y=-\infty}^{n_y=\infty} \sum_{n_z=-\infty}^{n_z=0} e^{i\boldsymbol{q}\cdot(n_x \boldsymbol{a}_{bulk} + n_y \boldsymbol{b}_{bulk} + n_z \boldsymbol{c}_{bulk})}$$

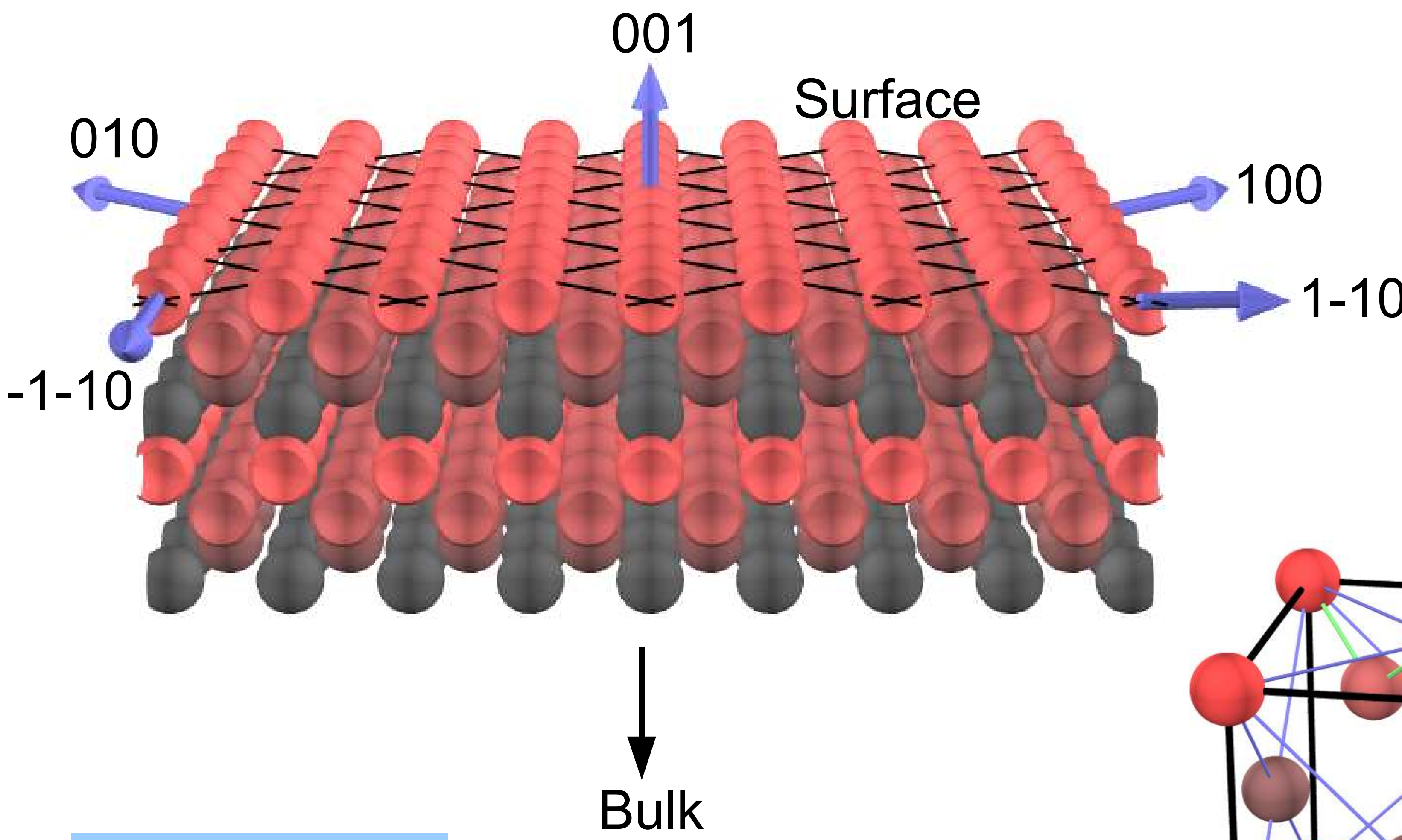
Film scattering amplitude (truncated a z=0 and z = -N unit cells)

$$A_{film}(\boldsymbol{q}) = S_{f,film}(\boldsymbol{q}) \sum_{n_x=-\infty}^{n_x=\infty} \sum_{n_y=-\infty}^{n_y=\infty} \sum_{n_z=-N}^{n_z=0} e^{i\boldsymbol{q}\cdot(n_x \boldsymbol{a}_{film} + n_y \boldsymbol{b}_{film} + n_z \boldsymbol{c}_{film})}$$

Scattered Intensity

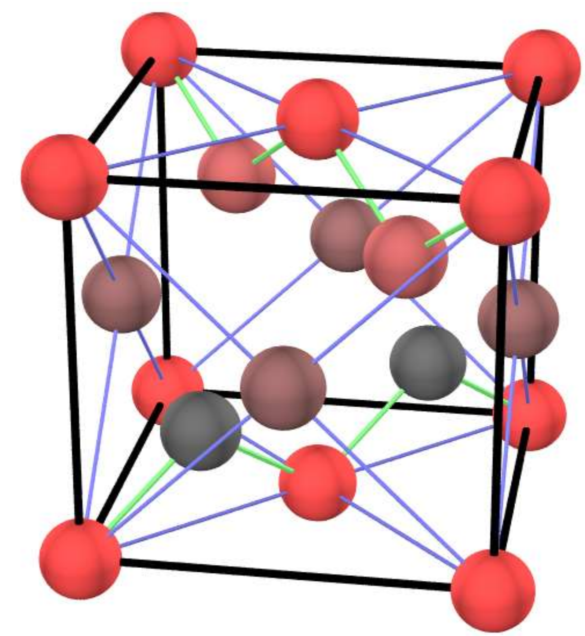
$$I(\boldsymbol{q}) = |A_{film}(\boldsymbol{q}) + A_{bulk}(\boldsymbol{q})|^2$$

Example: Reconstruction of Si-(001)Surface

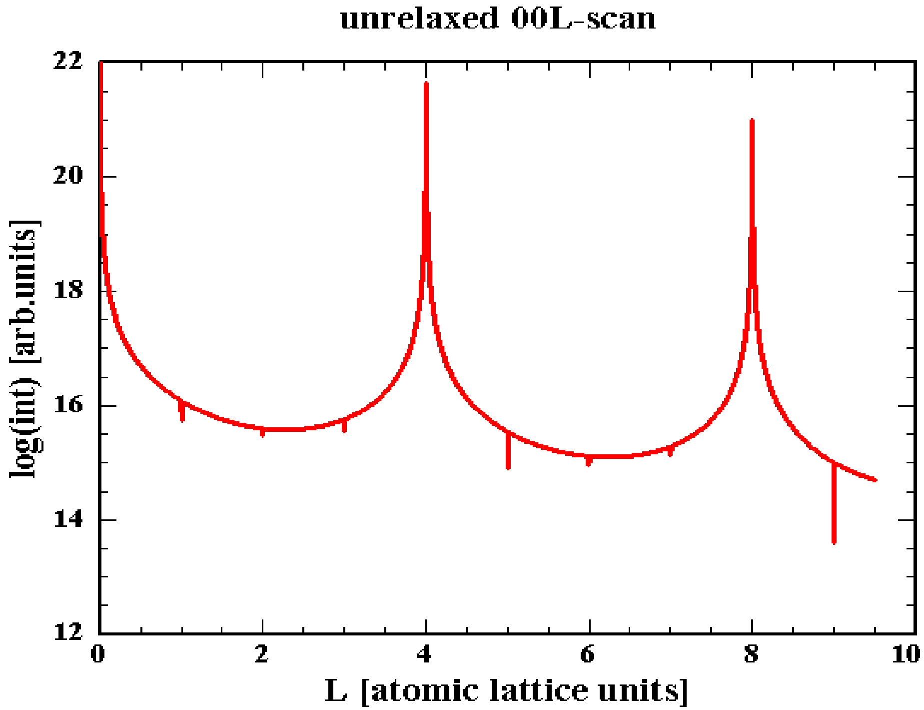


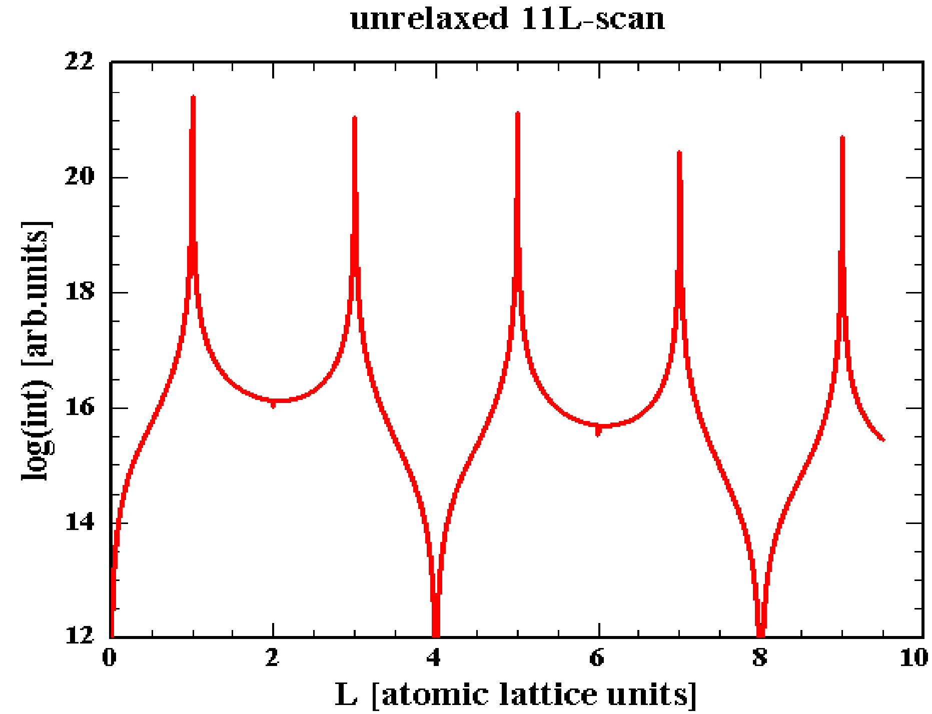
Cut of crystal results into unterminated bonds (orbitals)

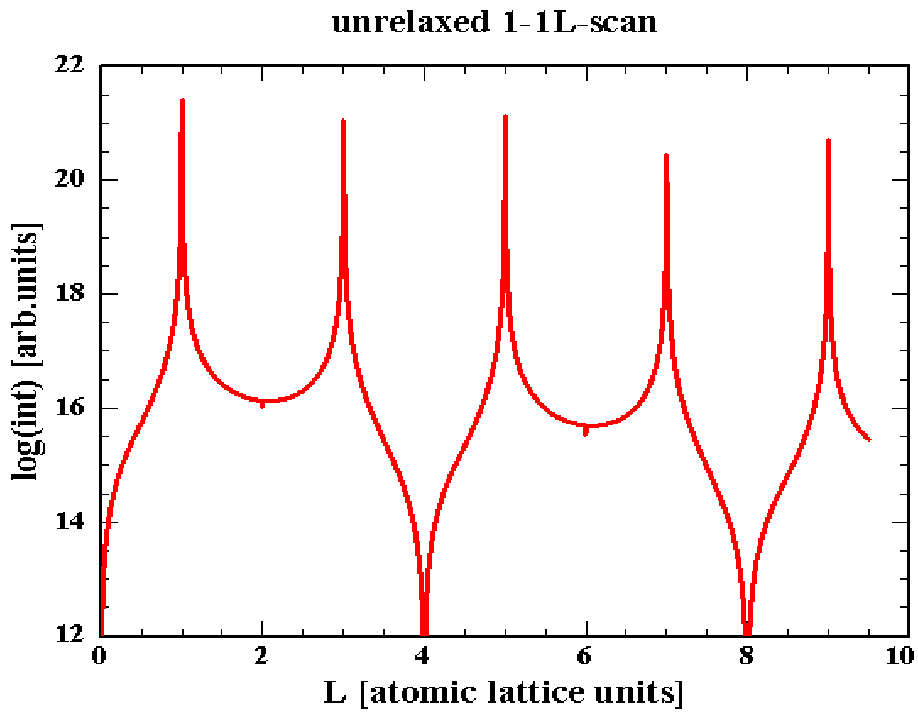
Silicon unit cell (diamond structure with a = 5.431Å)



CTRs of un-reconstructed Si-(001)Surface

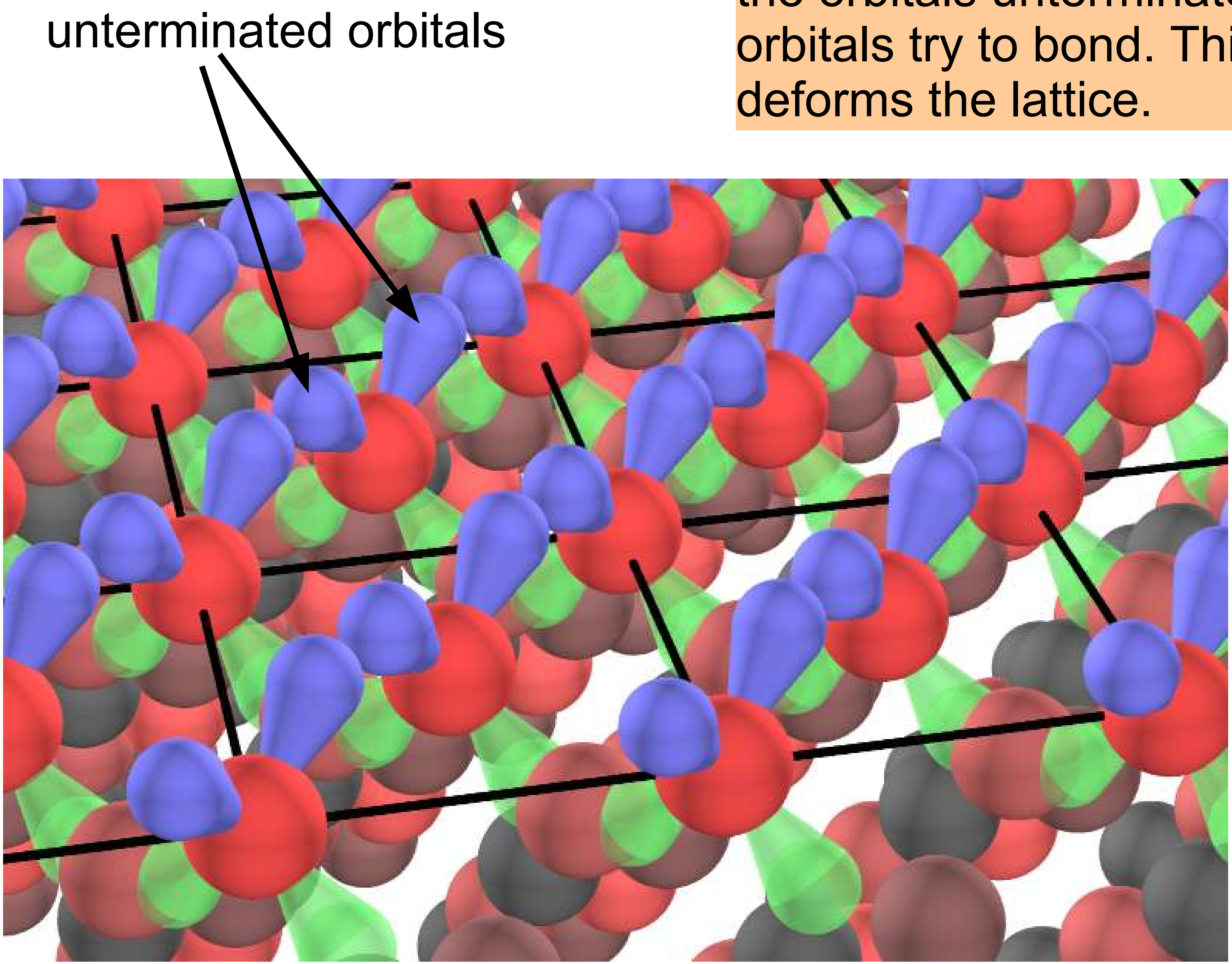




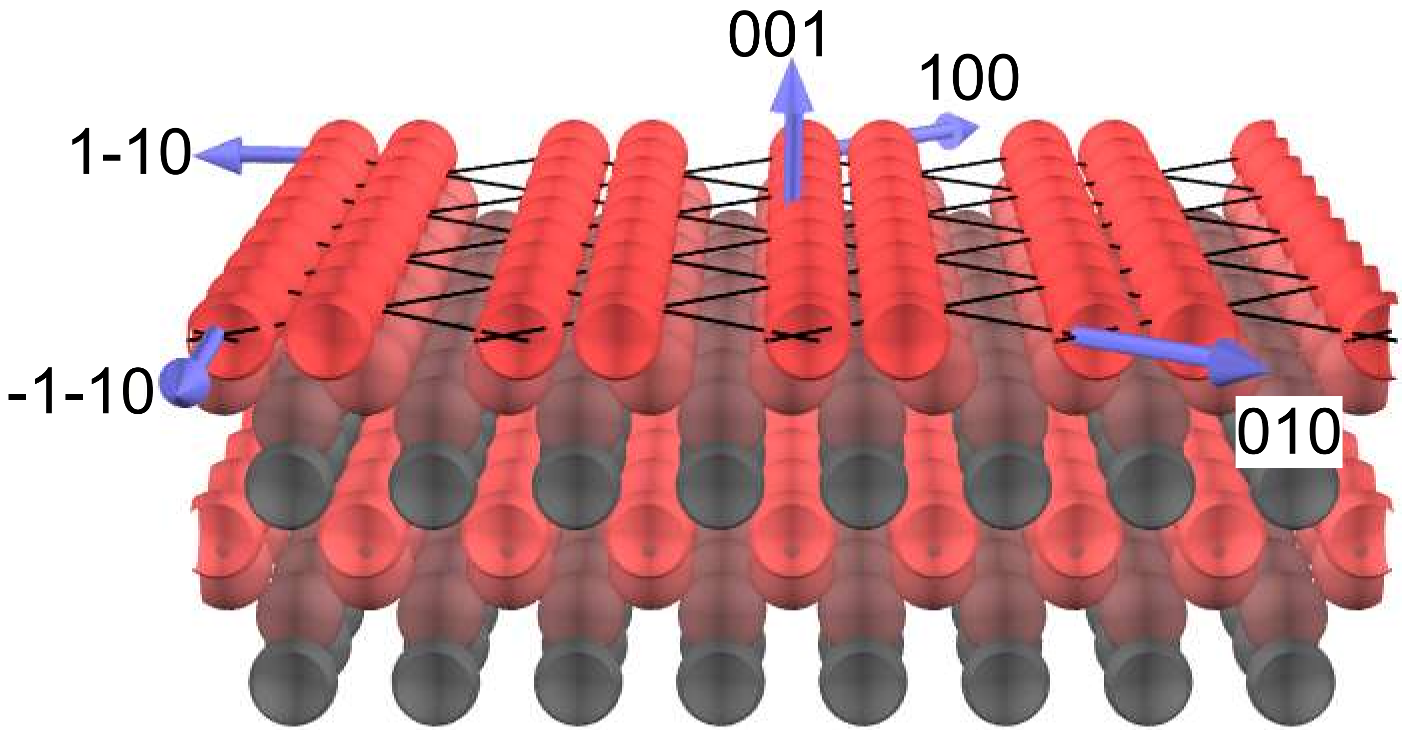


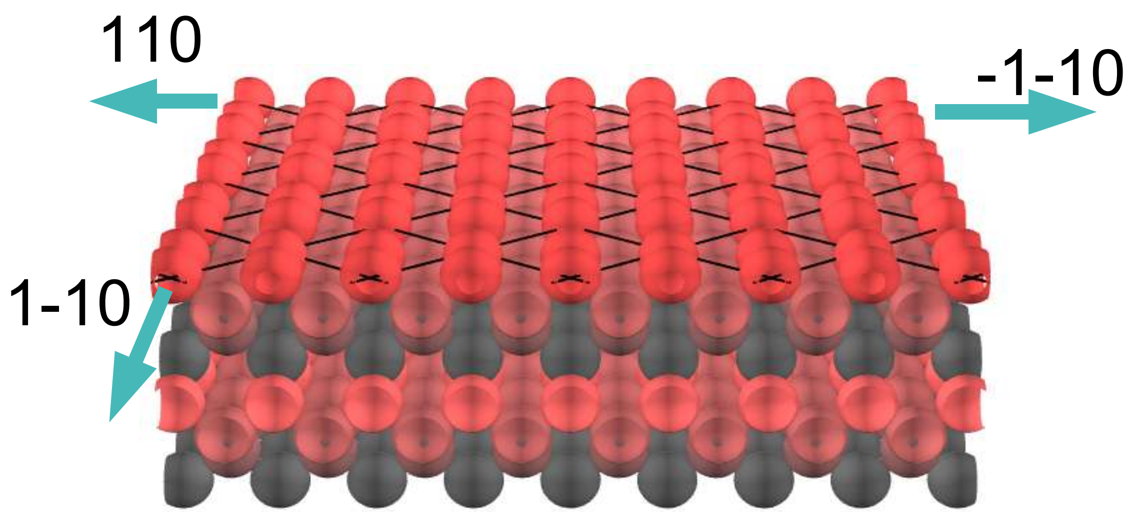
1) 00L scan looks easy (the dips mark the position of forbidden reflections and are caused by numerical problems)
2) 11L and 1-1L scans are identical

To lower the free engery the orbitals unterminated orbitals try to bond. This deforms the lattice.



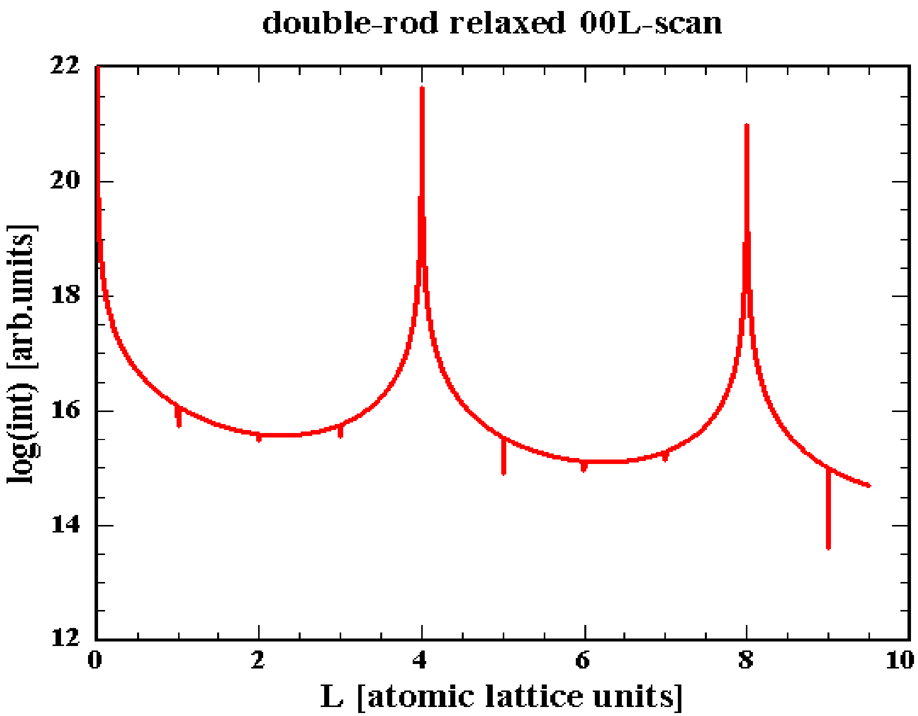
Possible relaxation: Forming “double rods” along 110-direction

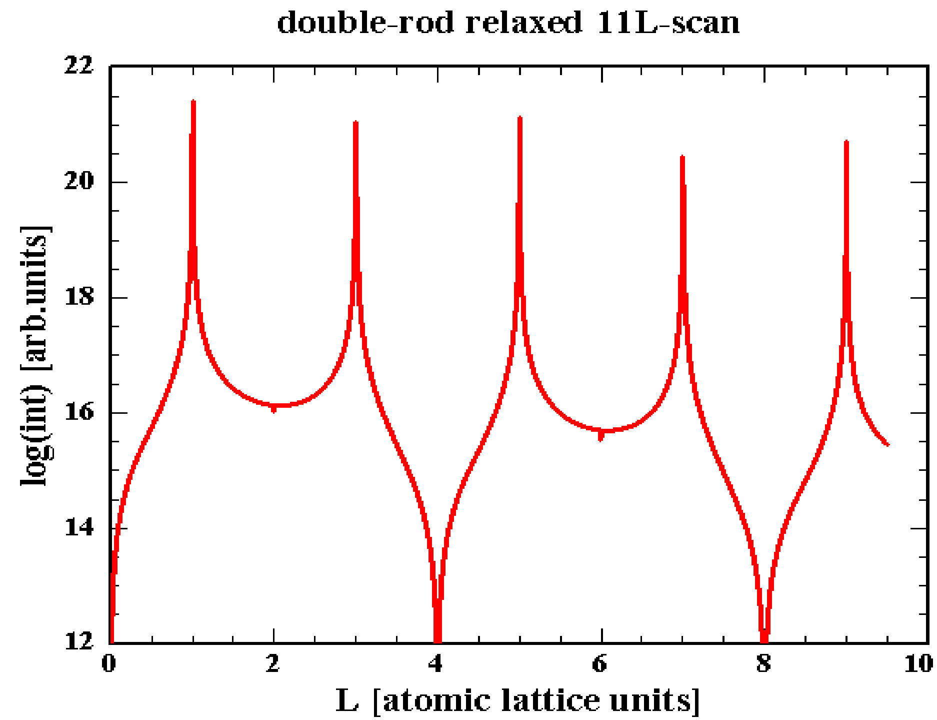


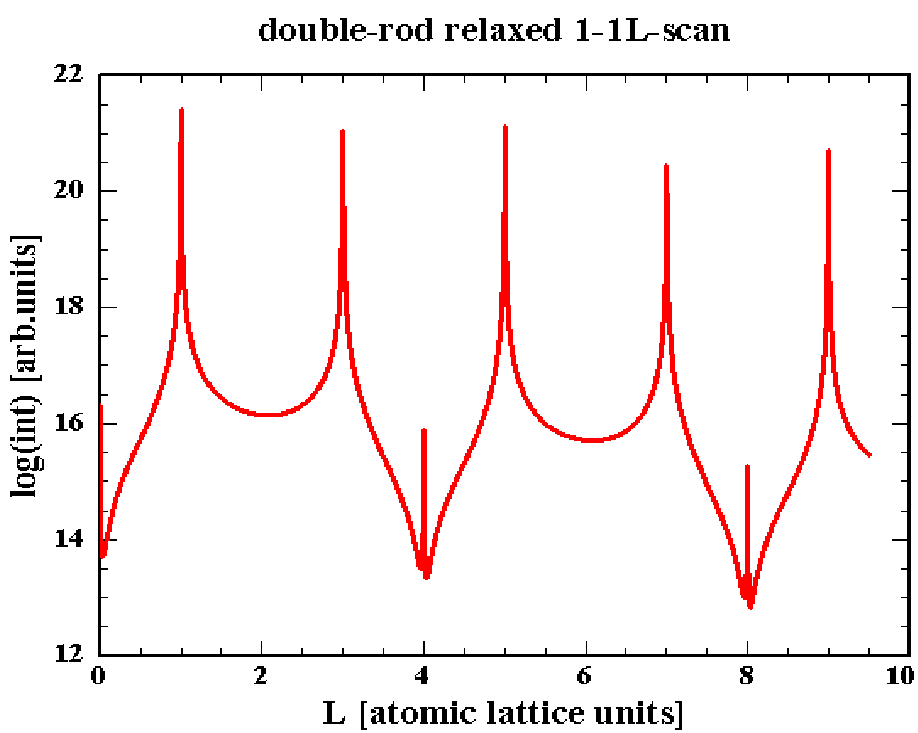


90° turn looks pretty much like unrelaxed surface

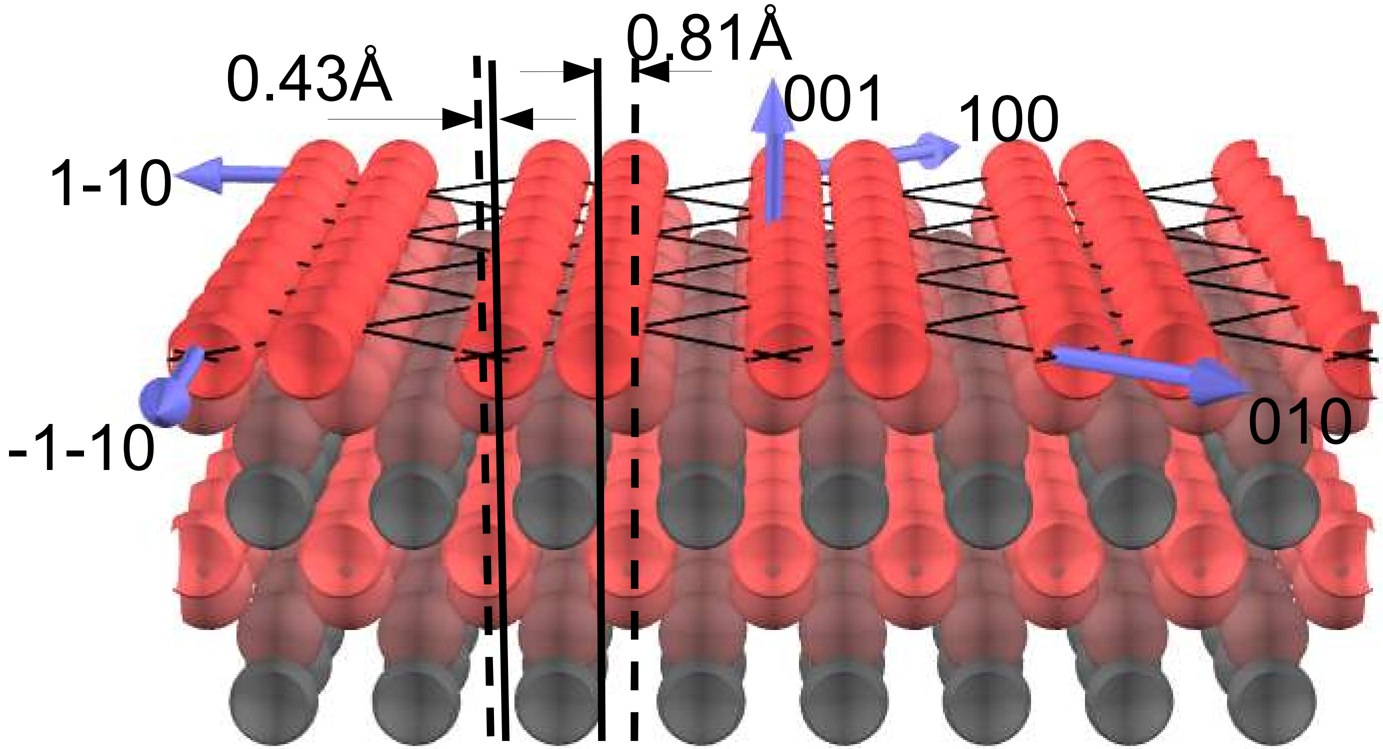
CTRs of simple "dimer rod" reconstructed Si-(001)Surface



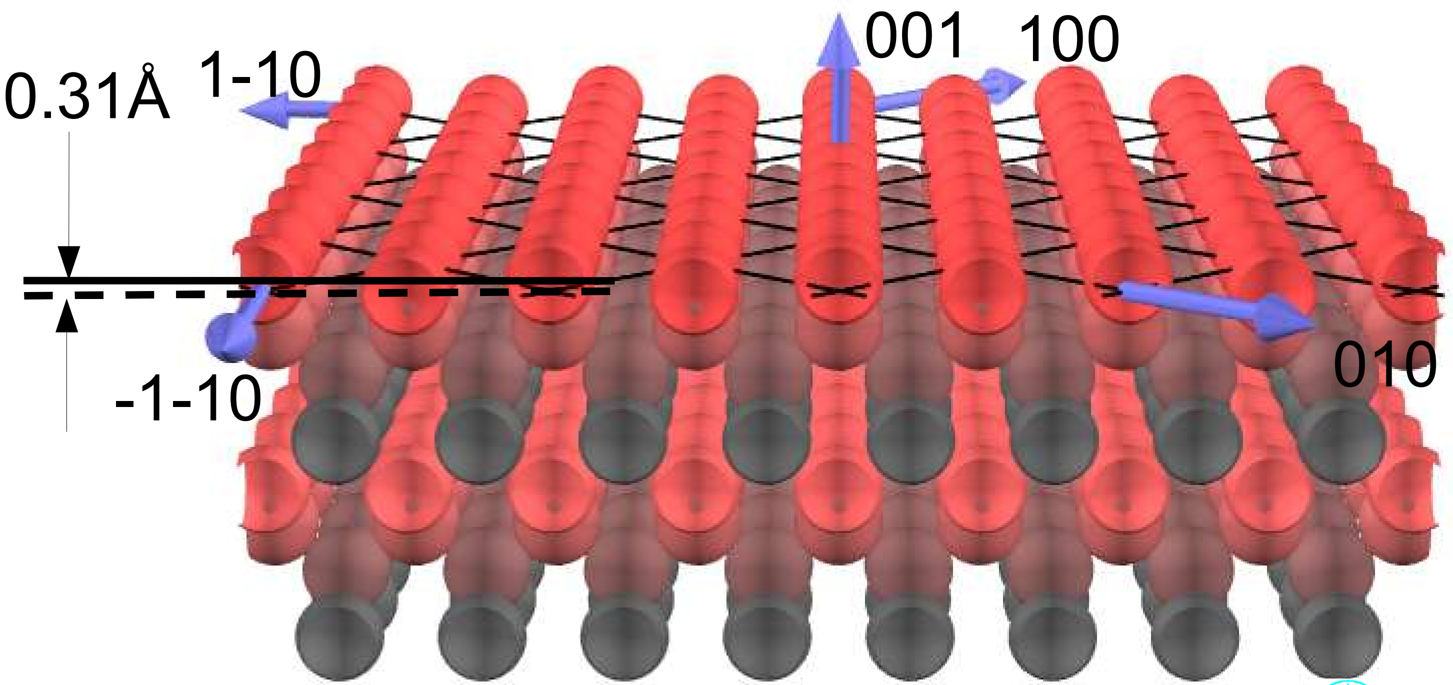




1) 00L scan has not changed
   (no change in z-direction)
2) 11L has not changed
   (in this direction identical to unrelaxed lattice)
3) slight changes is 1-1L : breaking of symmetry -> additional small peaks

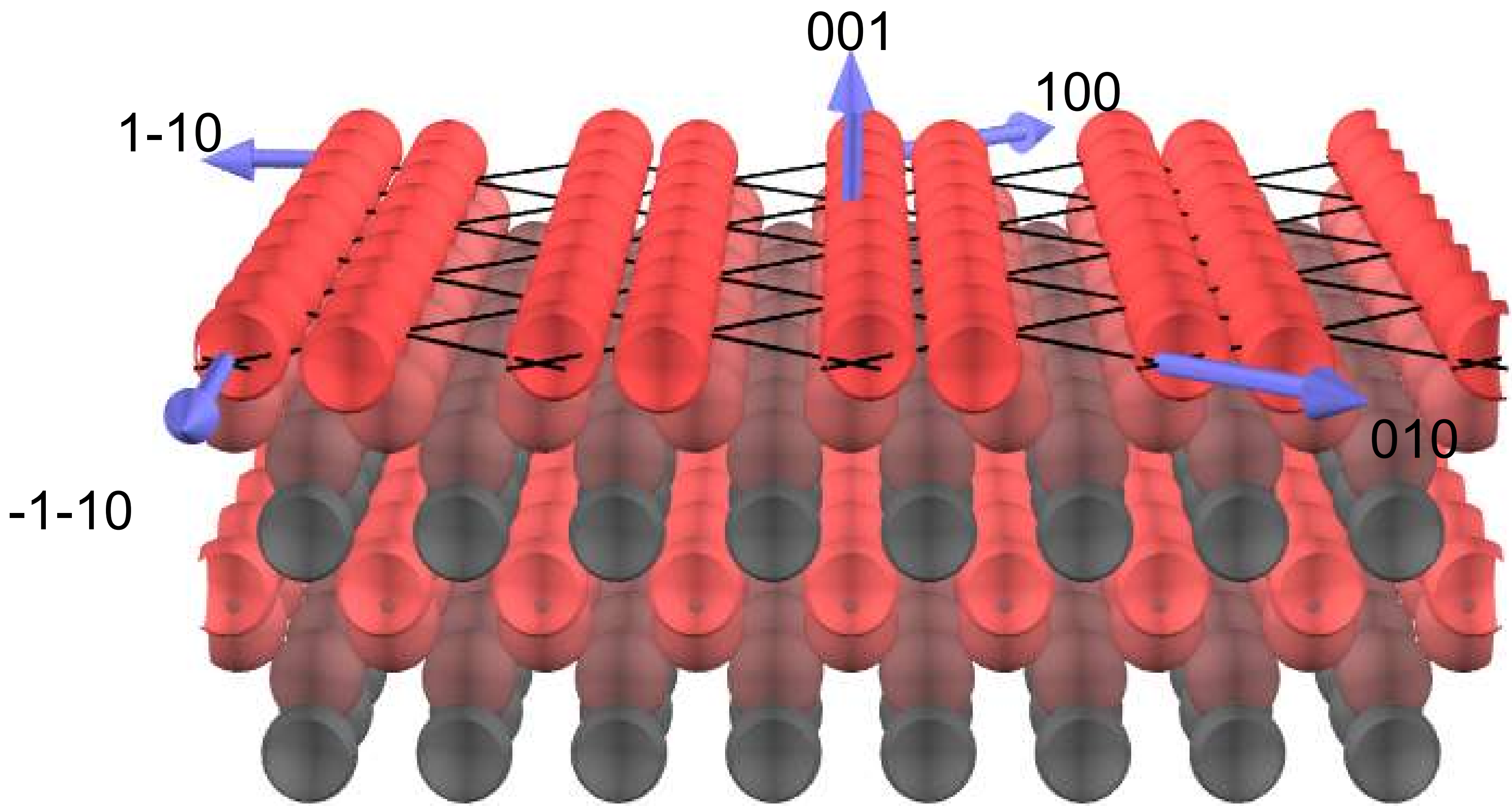


actual situation:

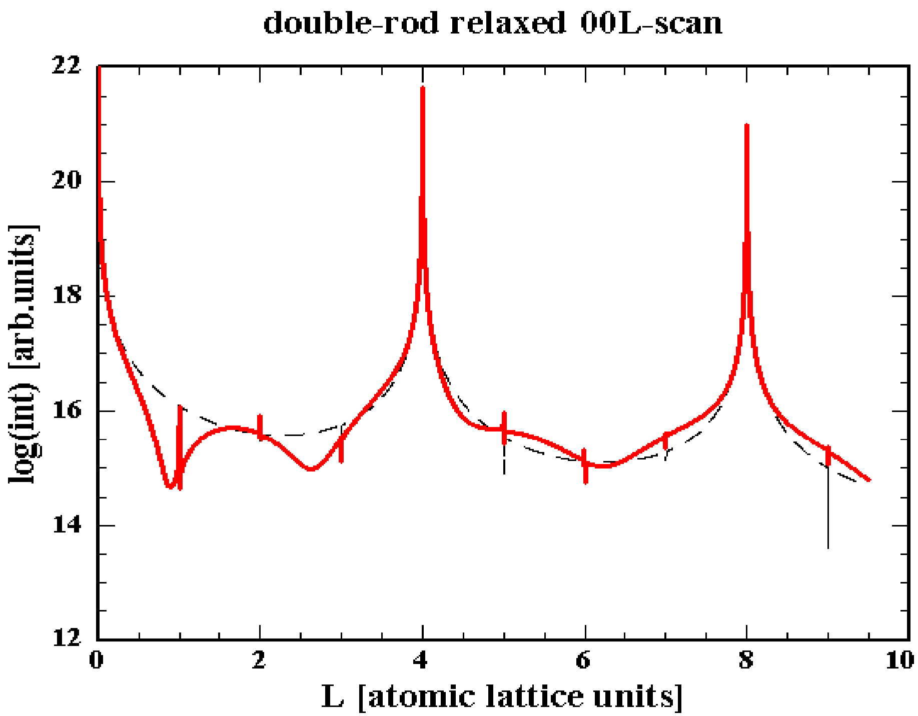


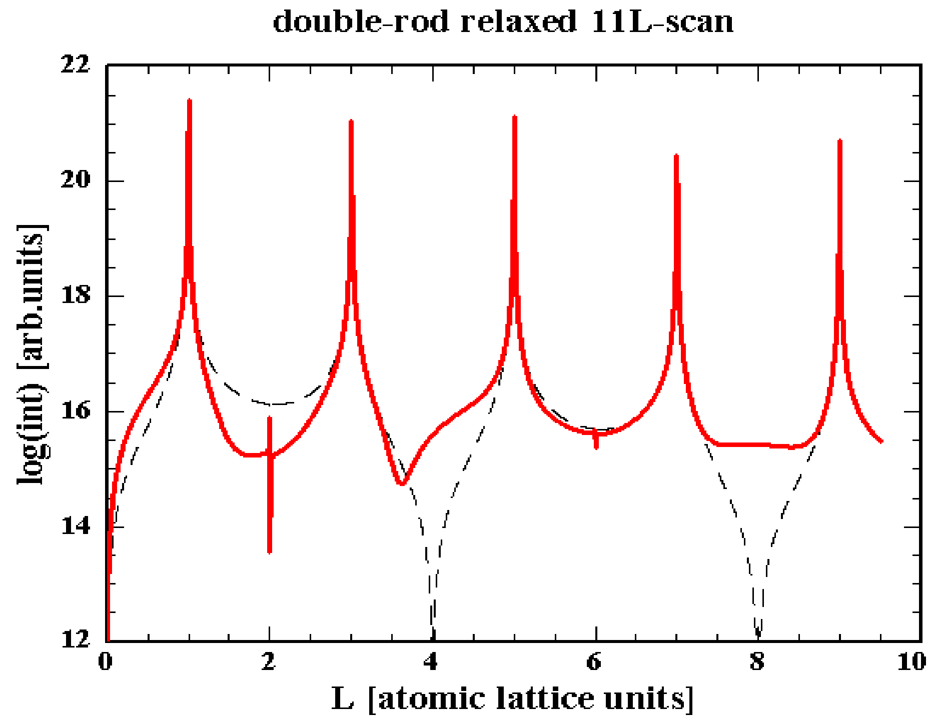
strained “dimer rod”

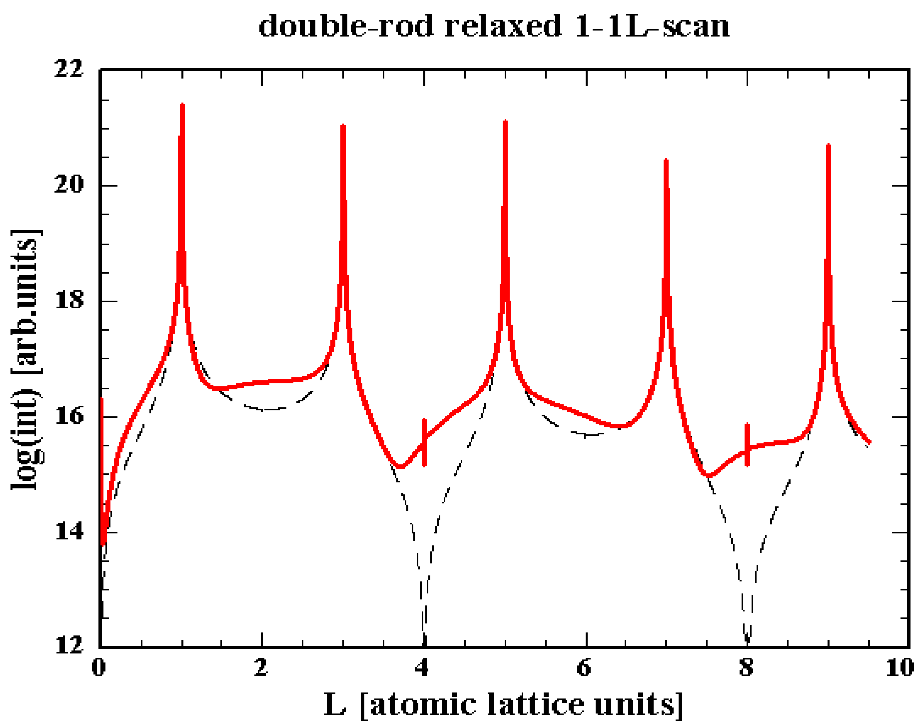
Resulting 2x1 lattice reconstruction the of 001 Silicon surface



CTRs of “strained dimer rod” reconstructed Si-(001)Surface







1) 00L has changed (atoms lifted)
2) the additional break in symmetry causes the 11L and 1-1L to be different.

Crystal Truncation Rods

- CTR measuremtents are applicable for crystalline samples ONLY

- They are sensitive to very small displacements of atoms near the surface

- For full information about the sample, three or more linear independent CTRs are necessary

- In Born approximation ($I_{scatt} << I_0$)

$$I(\boldsymbol{q}) = |\mathcal{F}\{\rho(\boldsymbol{r})\}(\boldsymbol{q})|^2 = |\mathcal{F}\{\rho_\infty(\boldsymbol{r})S(\boldsymbol{r})\}(\boldsymbol{q})|^2$$

with $\rho_\infty(r)$ the periodic infinit electron density
and $S(r)$ the shape function.