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

Diffuse Scattering
- Concepts of rough surfaces
- Correlation functions
- Scattering Born-approximation
- DWBA
- Examples

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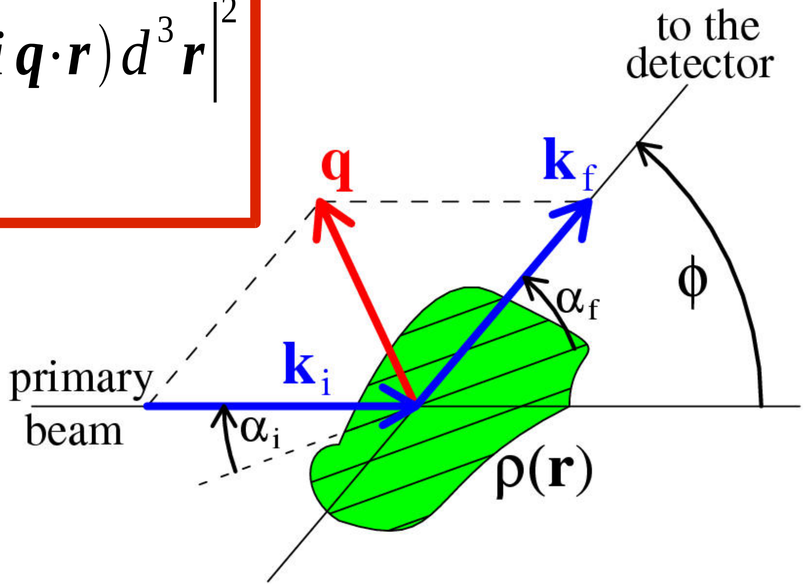
Introduction

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.

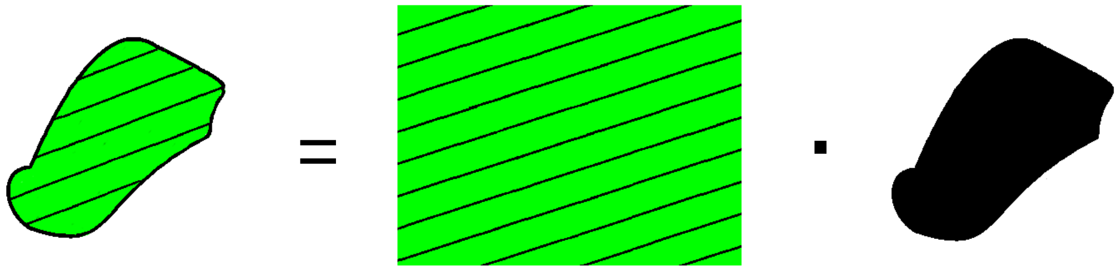
$$I(\boldsymbol{q}) \propto \left| \int \rho(\boldsymbol{r}) \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\, d^3\boldsymbol{r} \right|^2$$
$$= |\mathcal{F}\{\rho(\boldsymbol{r})\}|^2$$

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



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

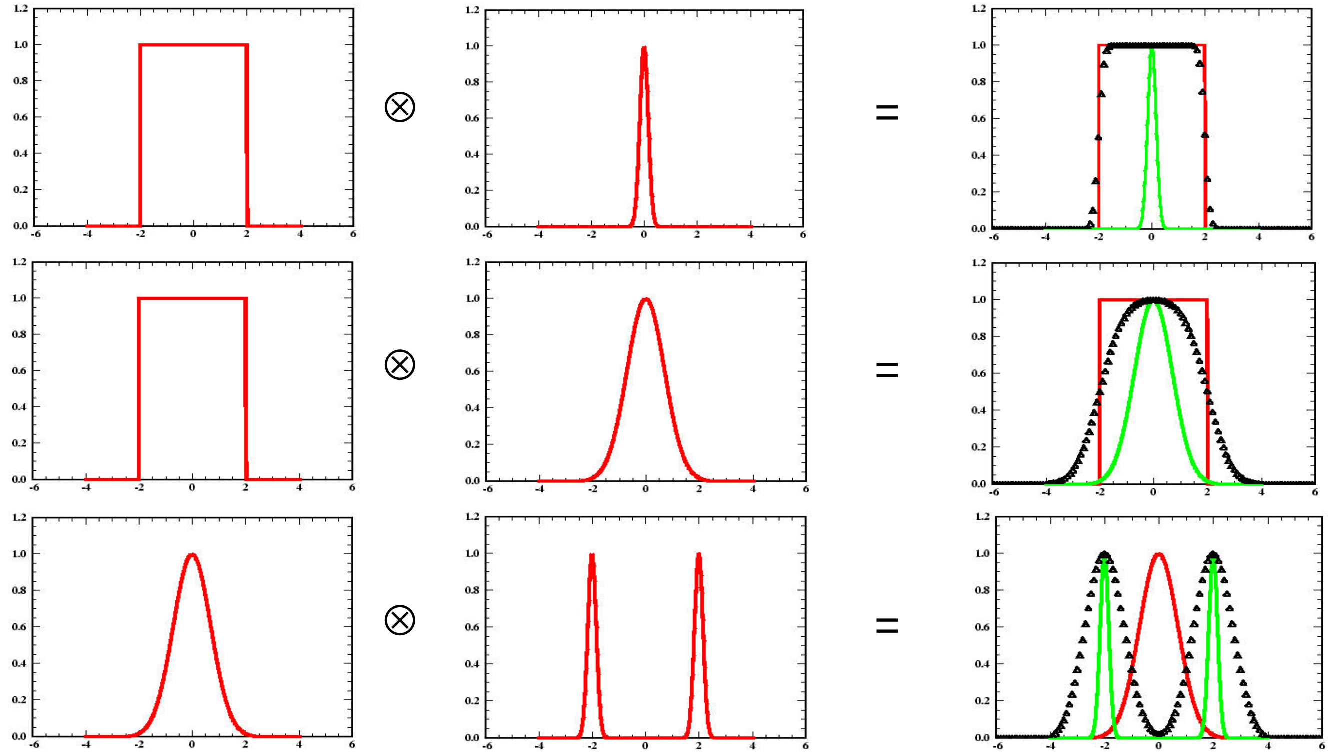
$$I(\boldsymbol{q}) = |\mathcal{F}\{\rho(\boldsymbol{r})\}(\boldsymbol{q})|^2 = |\mathcal{F}\{\rho_\infty(\boldsymbol{r})S(\boldsymbol{r})\}(\boldsymbol{q})|^2$$

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:

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

$$= \iint f_1(y)\, f_2(x-y)\mathrm{d}y\, \exp(iqx)\mathrm{d}x \qquad \text{substitute : } x-y = w$$

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

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

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

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:

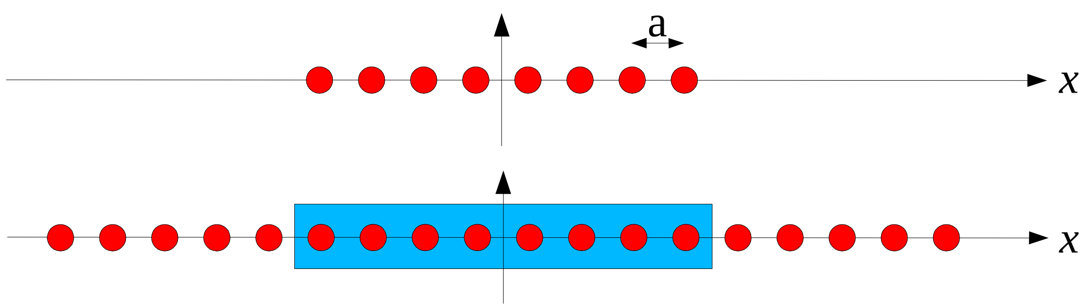
$$\begin{aligned}\mathcal{F}^{-1}\{f_1 \cdot f_2\} &= \mathcal{F}^{-1}\{\mathcal{F}\{\mathcal{F}^{-1}\{f_1\}\} \cdot \{\mathcal{F}\{\mathcal{F}^{-1}\{f_2\}\}\} \\ &= \mathcal{F}^{-1}\{\mathcal{F}\{F_1\} \cdot \mathcal{F}\{F_2\}\} \quad \text{with } F = \mathcal{F}^{-1}\{f\} \\ &= \mathcal{F}^{-1}\{\mathcal{F}\{F_1 \otimes F_2\}\} = F_1 \otimes F_2 \\ &= \mathcal{F}^{-1}\{f_1\} \otimes \mathcal{F}^{-1}\{f_2\}\end{aligned}$$

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

Thus:

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

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

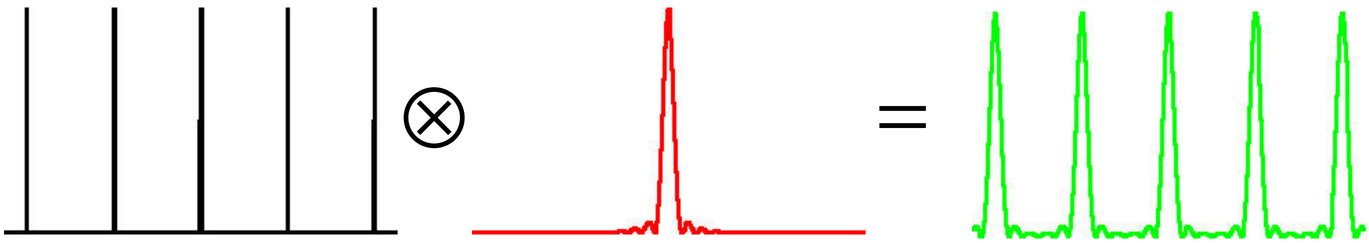
$$I(q) = \left| \mathcal{F}\left\{ S(x) \cdot \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \right\}(q) \right|^2 = \left| \mathcal{F}\{S(x)\} \otimes \mathcal{F}\left\{ \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \right\} \right|^2$$

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 :

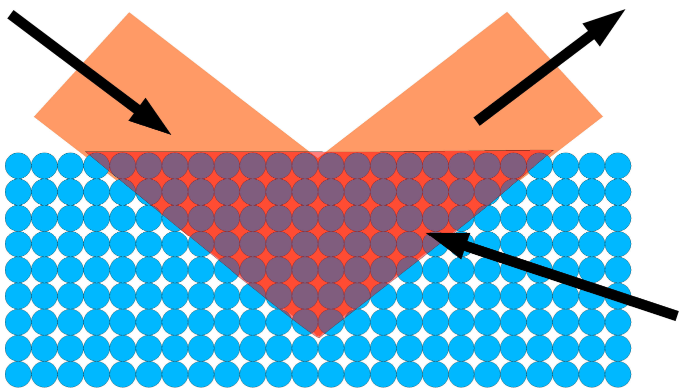
$$\mathcal{F}\{S(x)\}(q) \sim \frac{2}{q} \sin\left(\frac{Naq}{2} \right)$$



Bragg peaks are modified: Laue oscillations

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

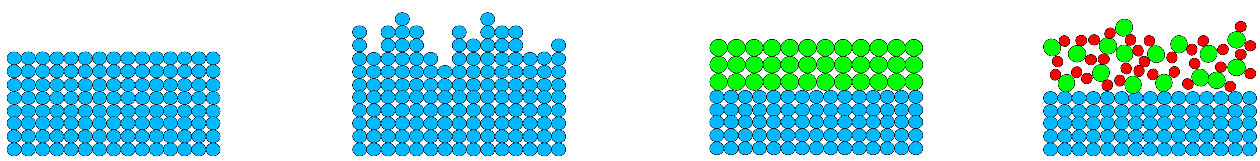
e.g.:



(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)

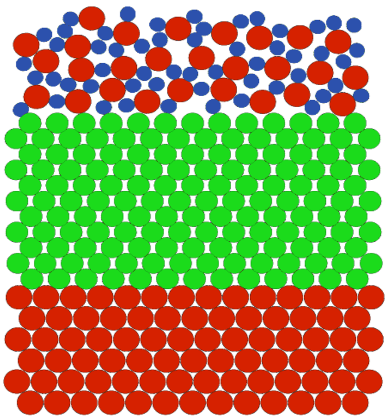
(2) Non-crystalline samples $\Rightarrow$ no real Bragg-peaks, but the zero order Bragg-peak at (0,0,0) (the primary beam) is modified $\Rightarrow$ Reflectivity
(Is also used for crystalline samples, if the crystallinity is of no interest).

(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)

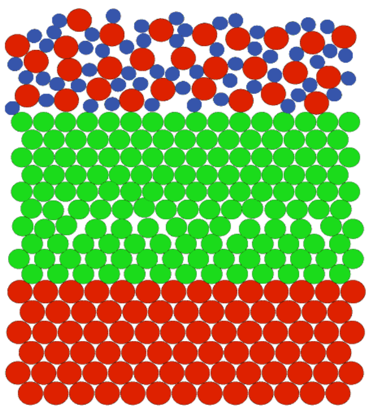
With Crystal Truncation Rod measurements (CTR) structural properties of surfaces and thin film systems at CRYSTALLINE samples can be investigated on a nanoscale.



CTR insensitive

CTR sensitive

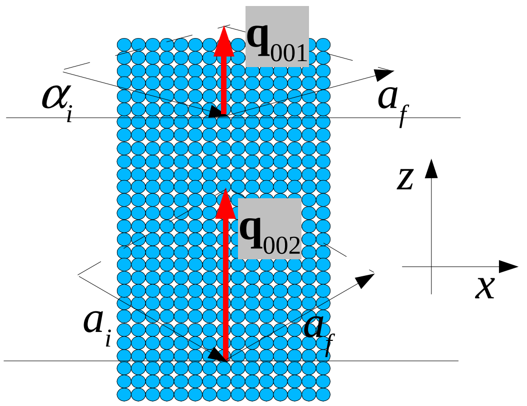
CTR sensitive

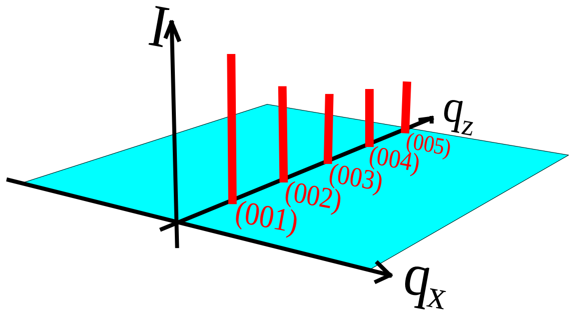


An infinite crystal lattice has δ-like Bragg-peaks: At a particular $\boldsymbol{q}$-vectors (depending on the incident and exit angles) scattered intensity can be found. In Born approximation ($I_{scatt} << I_0$):

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

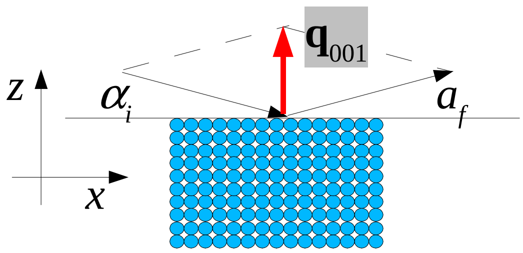
e.g.: [001]-orientation of the crystal
scan-mode : incident angle = exit angle
(001), (002) ... -reflections will appear during the scan

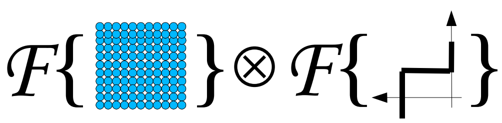


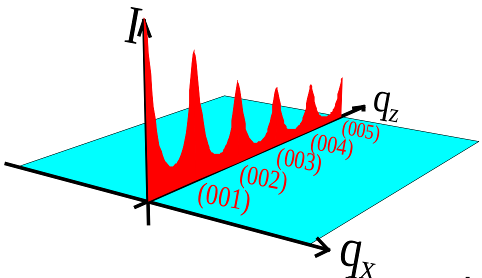


(00n) Bragg-peaks
in $\boldsymbol{q}$-space

Considering a simple surface

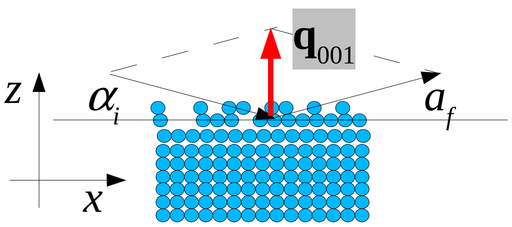


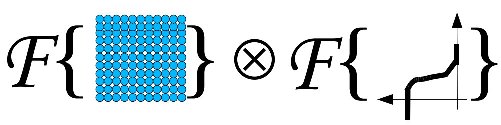


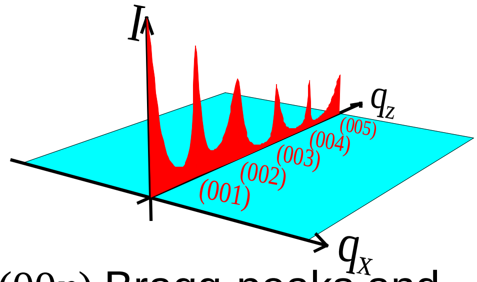


(00n) Bragg-peaks and
crystal truncation rods
along q_z

Considering a more complicate surface



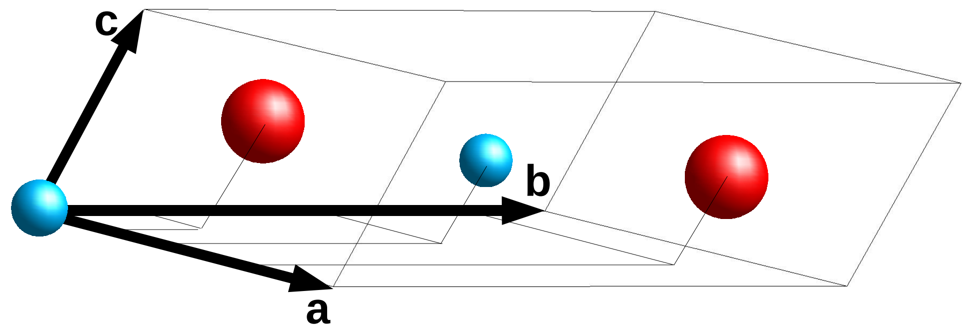




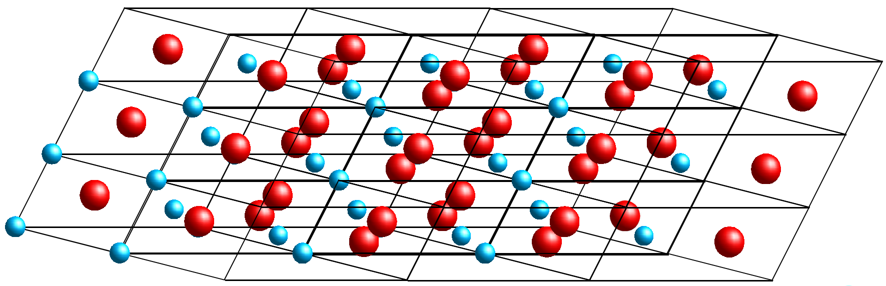
(00n) Bragg-peaks and
asymmetric
crystal truncation rods

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 $n_1, n_2, n_3 \in \mathbb{N}$



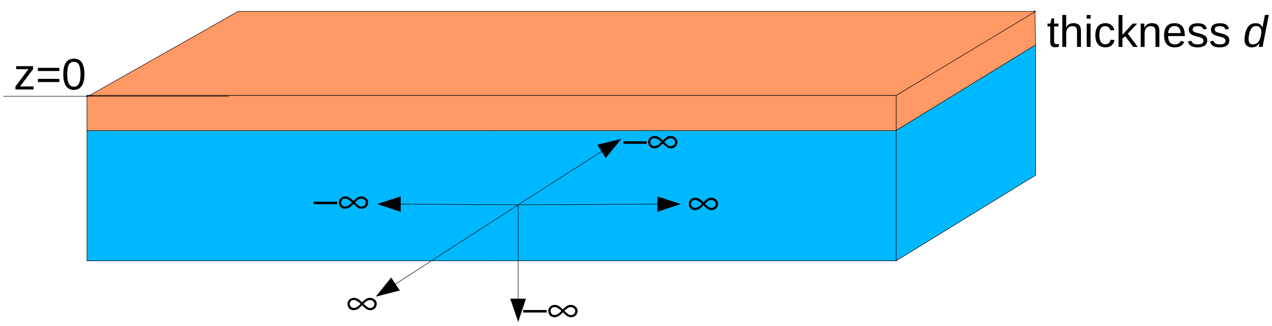
electron density of the crystal:

$$\rho(\boldsymbol{r})=\sum_{n_1=1}^{N_1}\sum_{n_2=1}^{N_2}\sum_{n_3=1}^{N_3}\sum_{j=1}^{M}\rho_j(\boldsymbol{r}+n_1\boldsymbol{a}+n_2\boldsymbol{b}+n_3\boldsymbol{c}+\boldsymbol{R_j})$$
$$=\sum_{n_1,n_2,n_3}\sum_j\int\rho_j(\boldsymbol{u})\,\delta(\boldsymbol{u}-\boldsymbol{r}-n_1\boldsymbol{a}-n_2\boldsymbol{b}-n_3\boldsymbol{c}-\boldsymbol{R_j})\,d\boldsymbol{u}$$

scattering amplitude A(**q**) :

$$A(\boldsymbol{q})=\int\rho(\boldsymbol{r})e^{i\boldsymbol{q}\cdot\boldsymbol{r}}d\boldsymbol{r}=\int\int\sum_{n_{1,2,3}}\sum_j\rho_j(\boldsymbol{u})\,\delta(\boldsymbol{u}-\boldsymbol{r}-n_1\boldsymbol{a}-n_2\boldsymbol{b}-n_3\boldsymbol{c}-\boldsymbol{R_j})e^{i\boldsymbol{q}\cdot\boldsymbol{r}}d\boldsymbol{u}\,d\boldsymbol{r}$$
$$=\int\sum_{n_{1,2,3}}\sum_j\rho_j(\boldsymbol{u})\int e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\delta(\boldsymbol{u}-\boldsymbol{r}-n_1\boldsymbol{a}-n_2\boldsymbol{b}-n_3\boldsymbol{c}-\boldsymbol{R_j})\,d\boldsymbol{r}\,d\boldsymbol{u}$$
$$=\sum_{n_{1,2,3}}\sum_j\int\rho(\boldsymbol{u})e^{i\boldsymbol{q}\cdot(-\boldsymbol{u}+n_1\boldsymbol{a}+n_2\boldsymbol{b}+n_3\boldsymbol{c}+\boldsymbol{R}_j)}d\boldsymbol{u}=\sum_{n_{1,2,3}}e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a}+n_2\boldsymbol{b}+n_3\boldsymbol{c})}\sum_j e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j}\underbrace{\left[\int\rho_j(\boldsymbol{u})e^{-i\boldsymbol{q}\cdot\boldsymbol{u}}d\boldsymbol{u}\right]}_{f_j(q)\text{ form factor}}$$
$$=\sum_{n_{1,2,3}}e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a}+n_2\boldsymbol{b}+n_3\boldsymbol{c})}\underbrace{\sum_j f_j(\boldsymbol{q})e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j}}_{S_j(q)\text{ structure factor}}=S_f(\boldsymbol{q})\sum_{n_{1,2,3}}e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a}+n_2\boldsymbol{b}+n_3\boldsymbol{c})}$$

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)

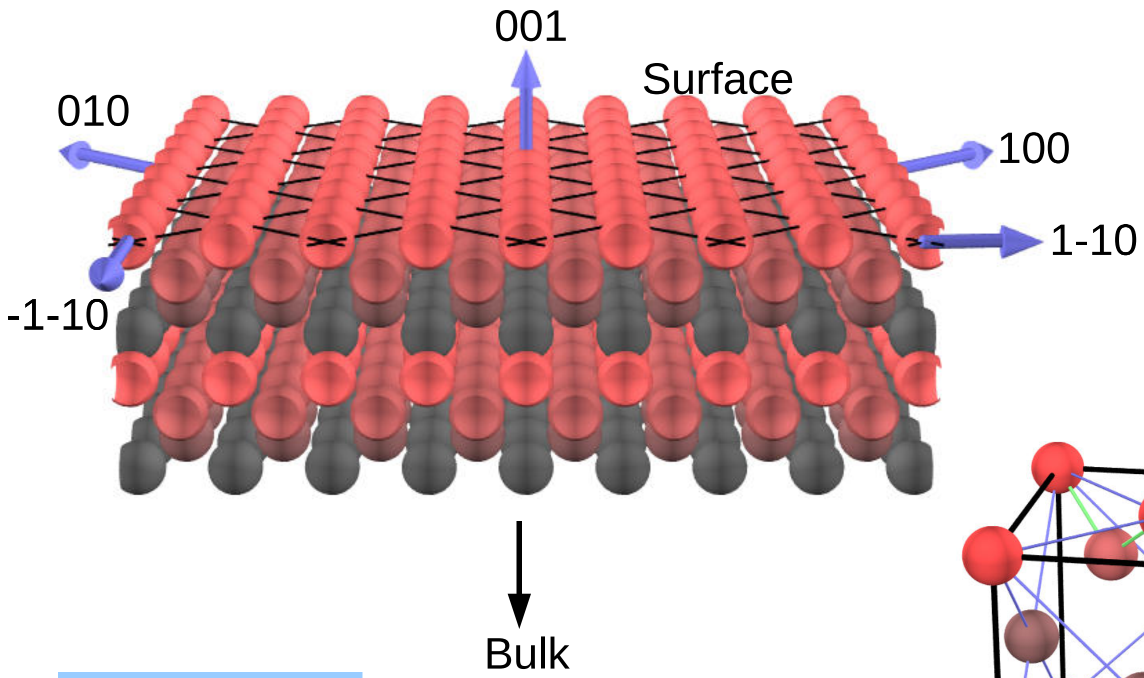
$$A_{bulk}(\boldsymbol{q}) = e^{-i q_z d} S_{f,bulk}(\boldsymbol{q}) \sum_{n_x=-\infty}^{n_x=\infty} \sum_{n_y=-\infty}^{n_y=\infty} \sum_{n_z=-\infty}^{n_z=0} e^{i\boldsymbol{q}\cdot(n_x \boldsymbol{a}_{bulk} + n_y \boldsymbol{b}_{bulk} + n_z \boldsymbol{c}_{bulk})}$$

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

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

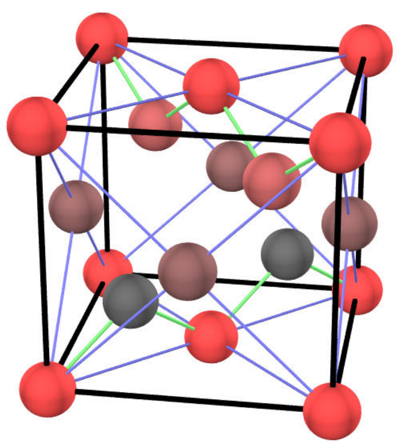
Scattered Intensity $\quad I(\boldsymbol{q}) = |A_{film}(\boldsymbol{q}) + A_{bulk}(\boldsymbol{q})|^2$

Example: Reconstruction of Si-(001)Surface

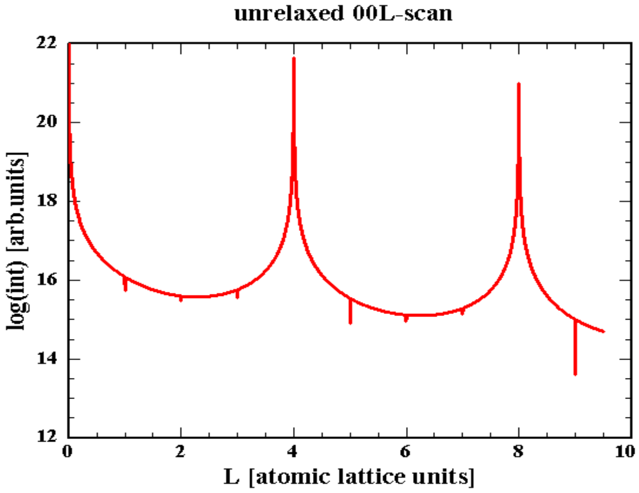


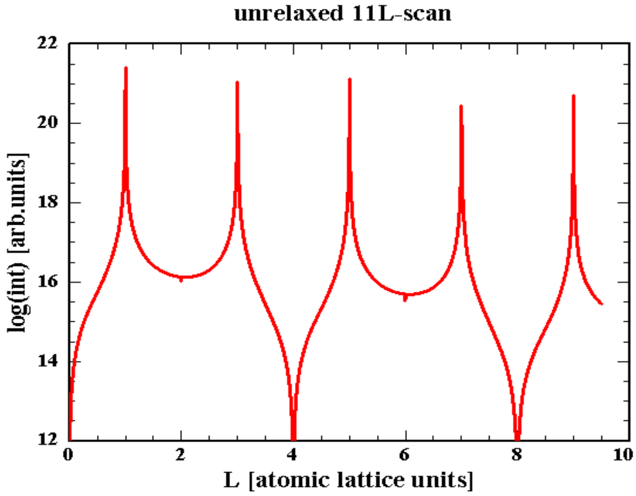
Cut of crystal results into unterminated bonds (orbitals)

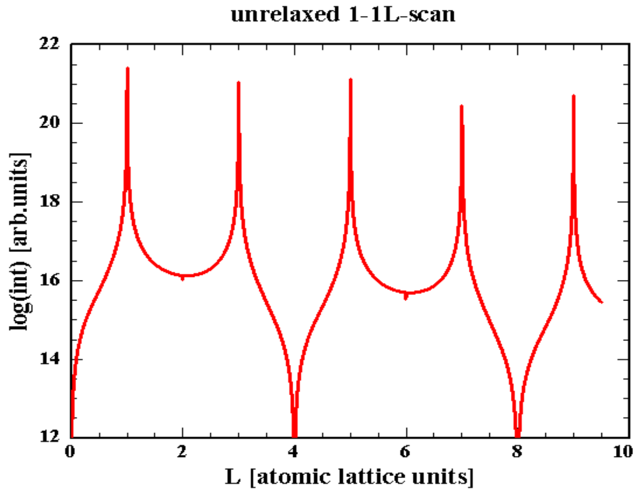
Silicon unit cell (diamond structure with a = 5.431Å)



CTRs of un-reconstructed Si-(001)Surface

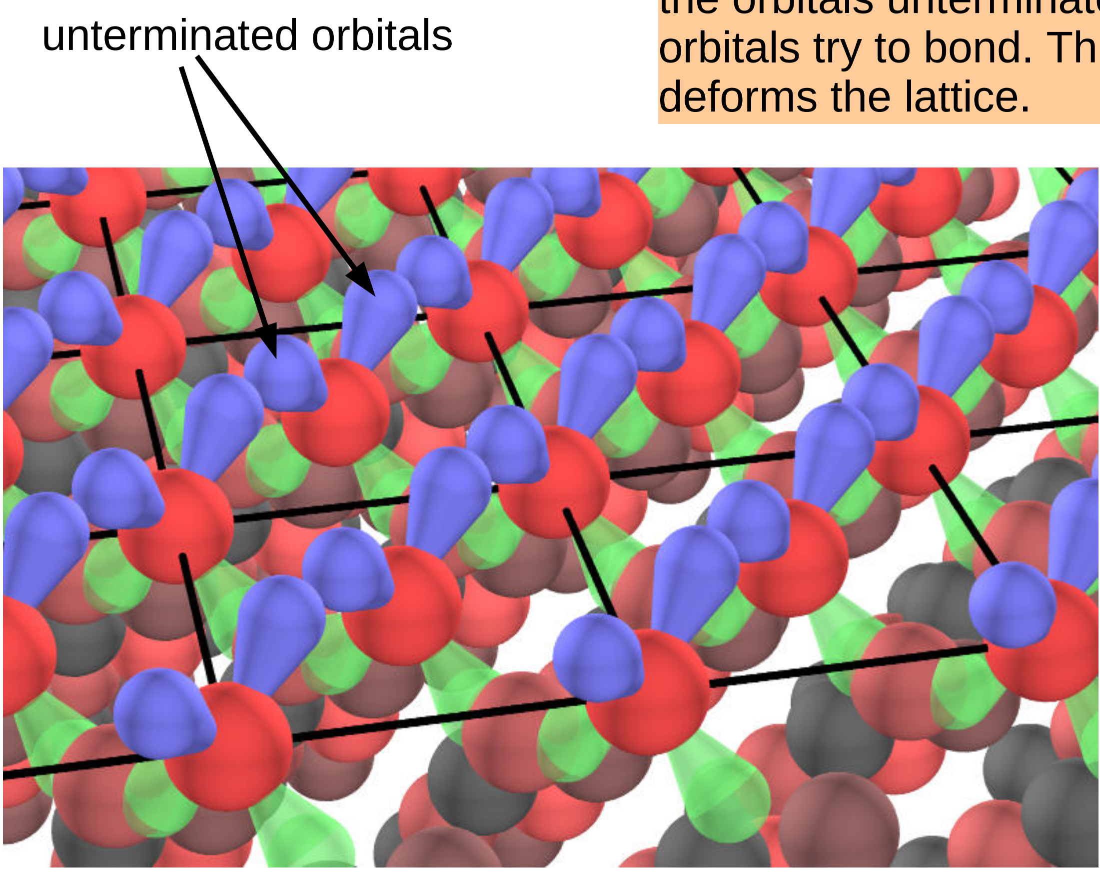




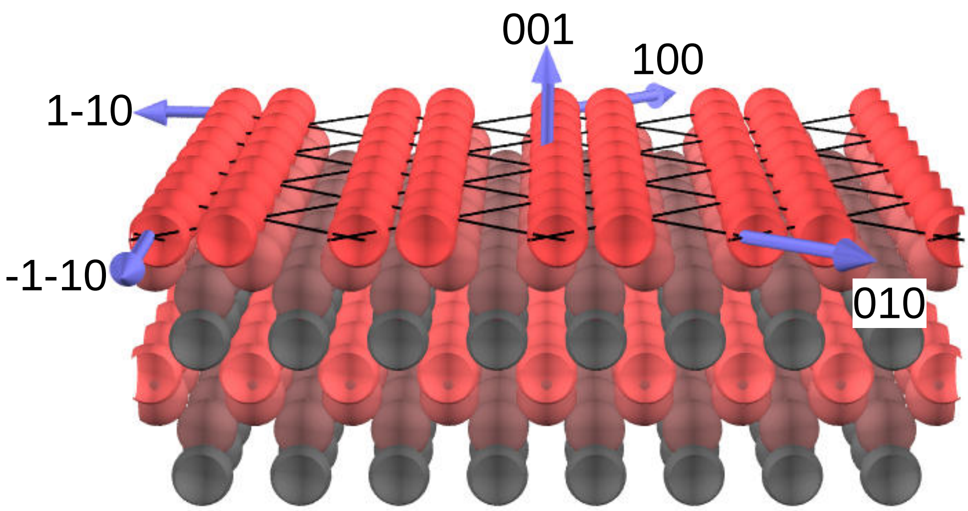


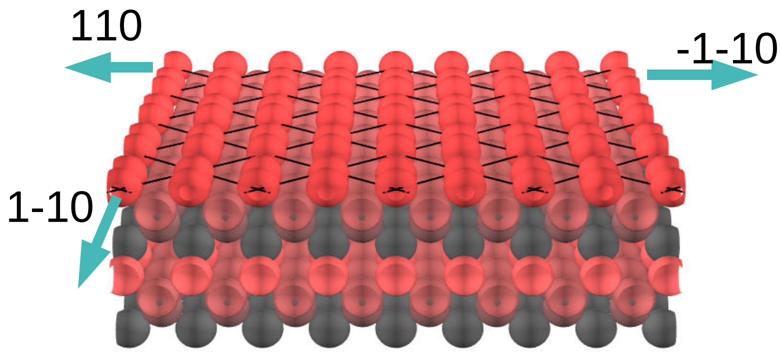
1) 00L scan looks easy (the dips mark the position of forbidden reflections and are caused by numerical problems)
2) 11L and 1-1L scans are identical

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



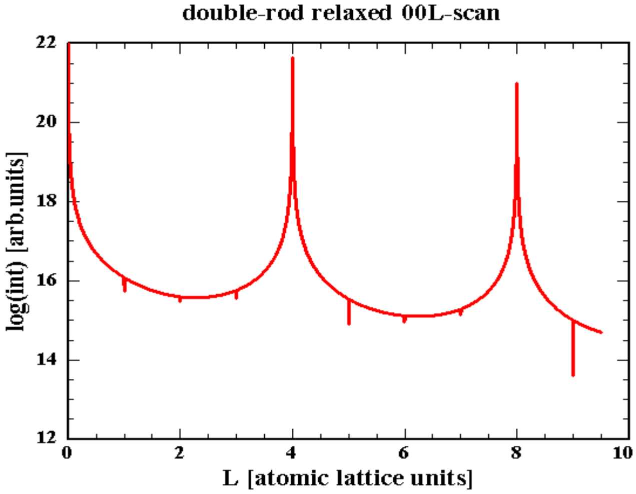
Possible relaxation: Forming "double rods" along 110-direction

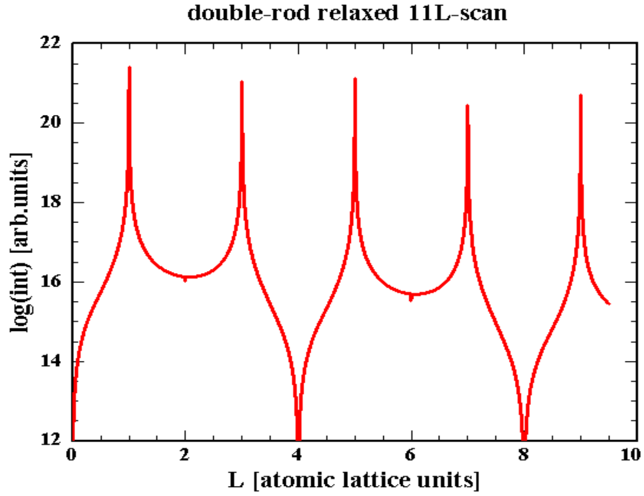


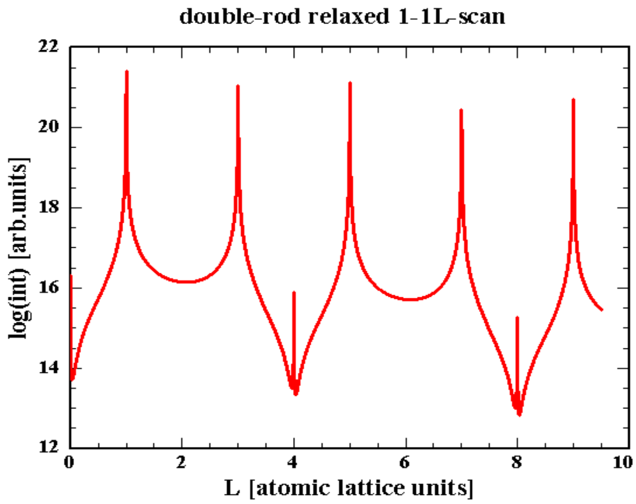


90° turn looks pretty much like unrelaxed surface

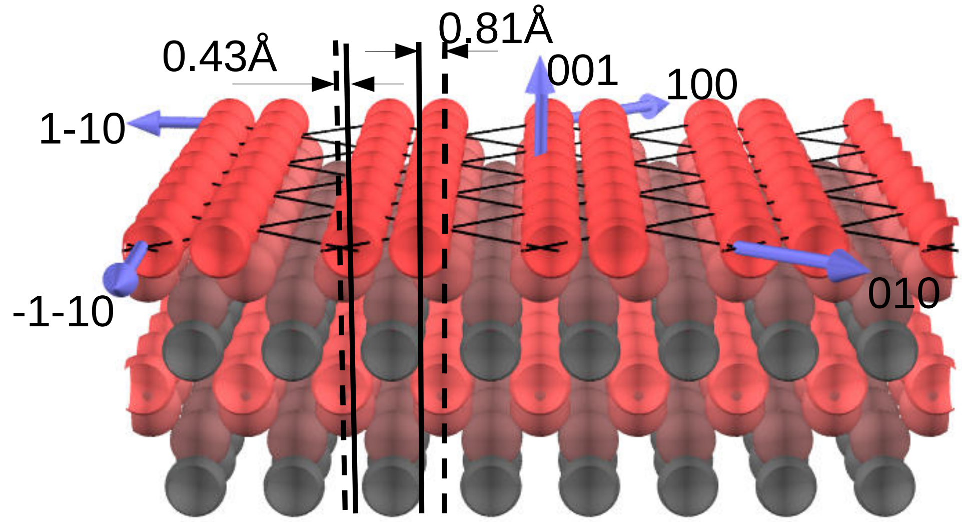
CTRs of simple "dimer rod" reconstructed Si-(001)Surface



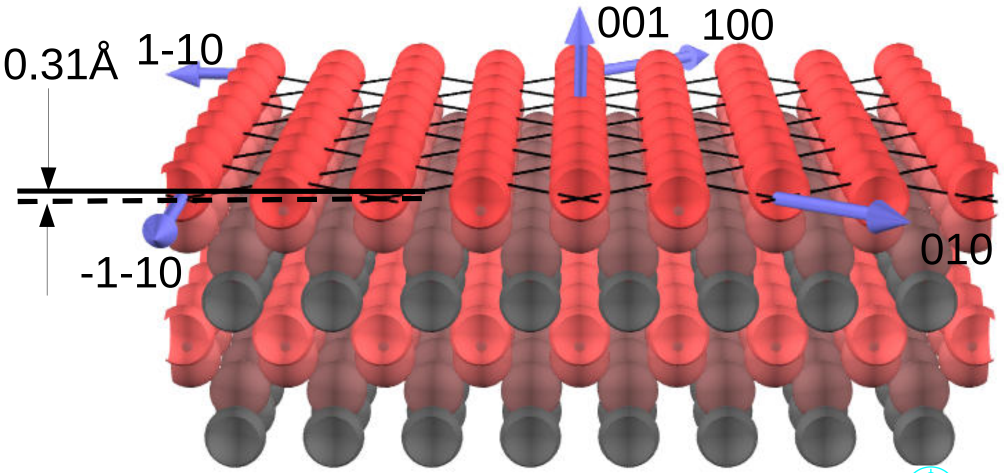




1) 00L scan has not changed (no change in z-direction)
2) 11L has not changed (in this direction identical to unrelaxed lattice)
3) slight changes is 1-1L : breaking of symmetry -> additional small peaks

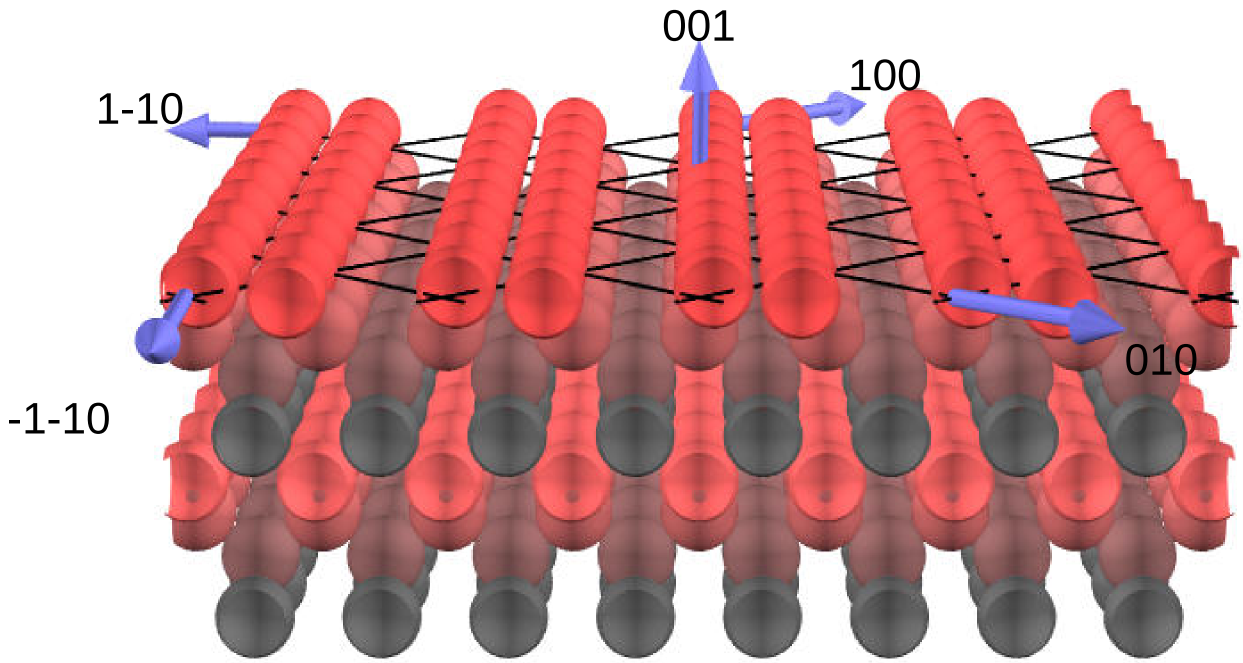


actual
situation:

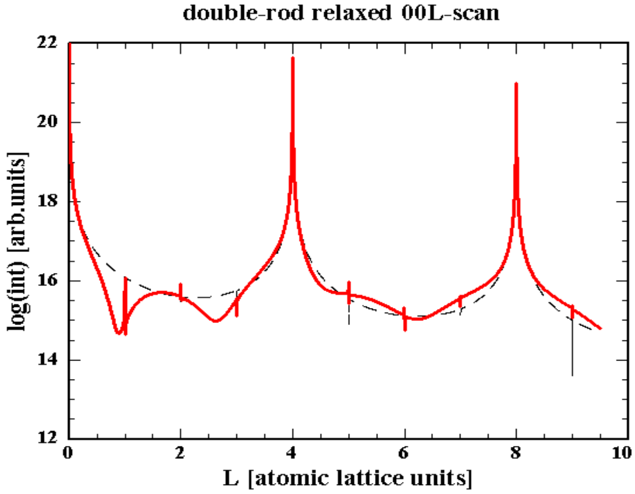


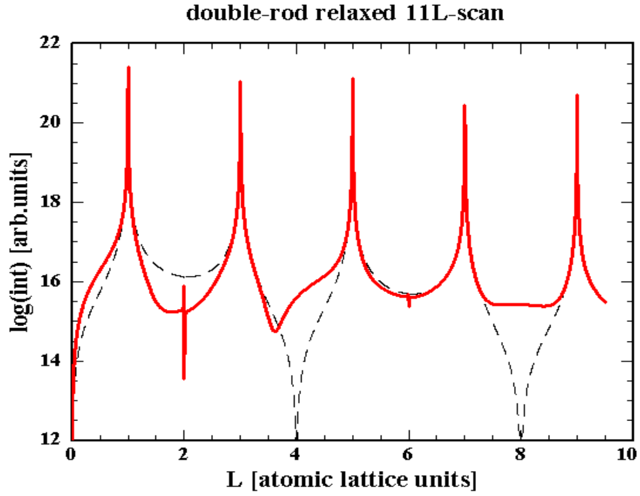
strained
“dimer rod”

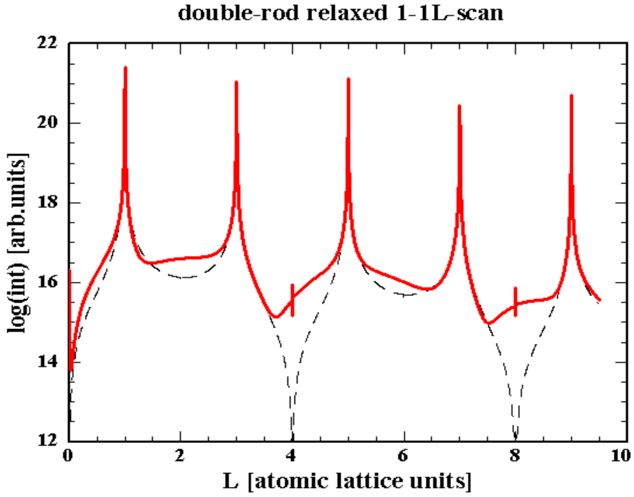
Resulting 2x1 lattice reconstruction
the of 001 Silicon surface



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 ($I_{scatt} << I_0$)

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

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