Applications of XAFS and COBRA methods.

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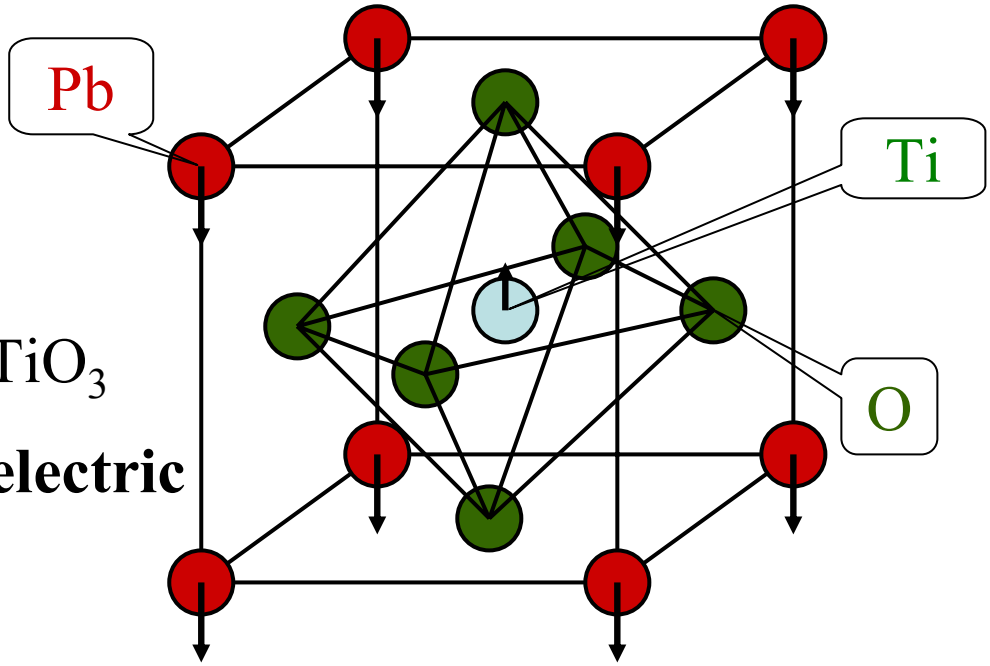
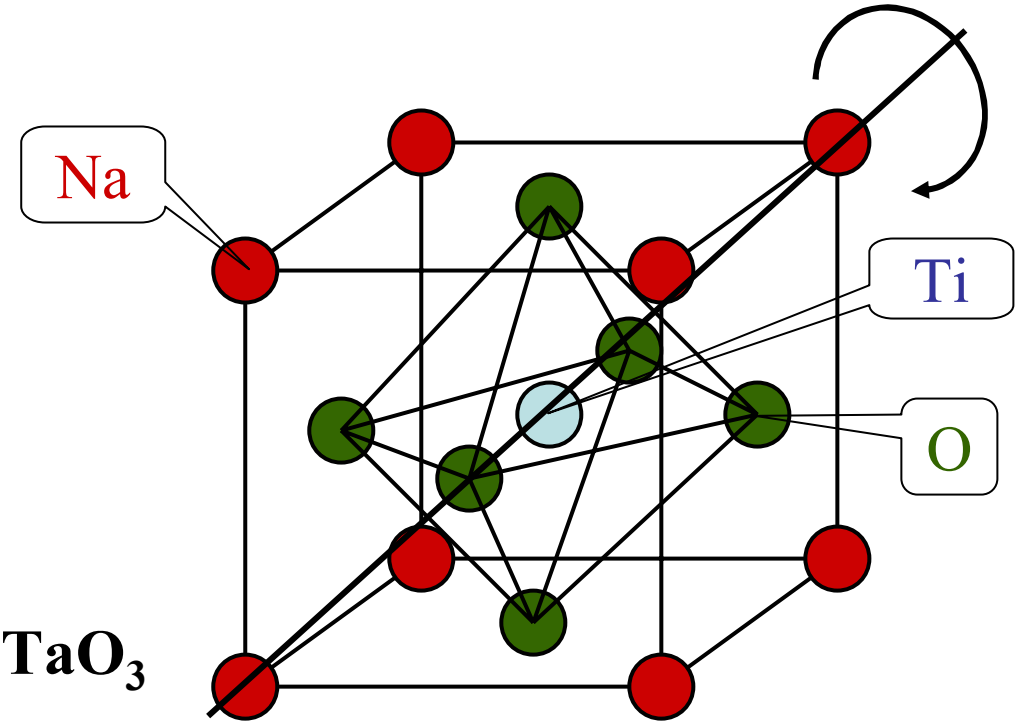
Perovskite crystals ABO_3



$PbTiO_3$

Ferroelectric

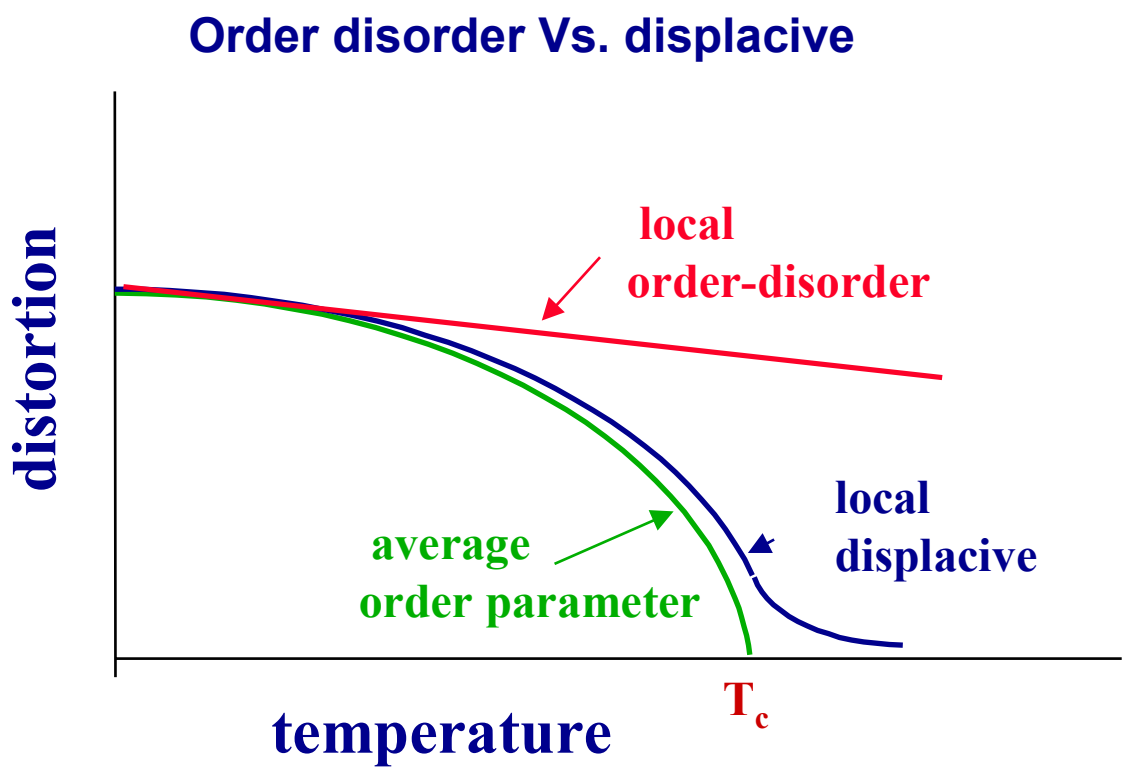


$NaTaO_3$

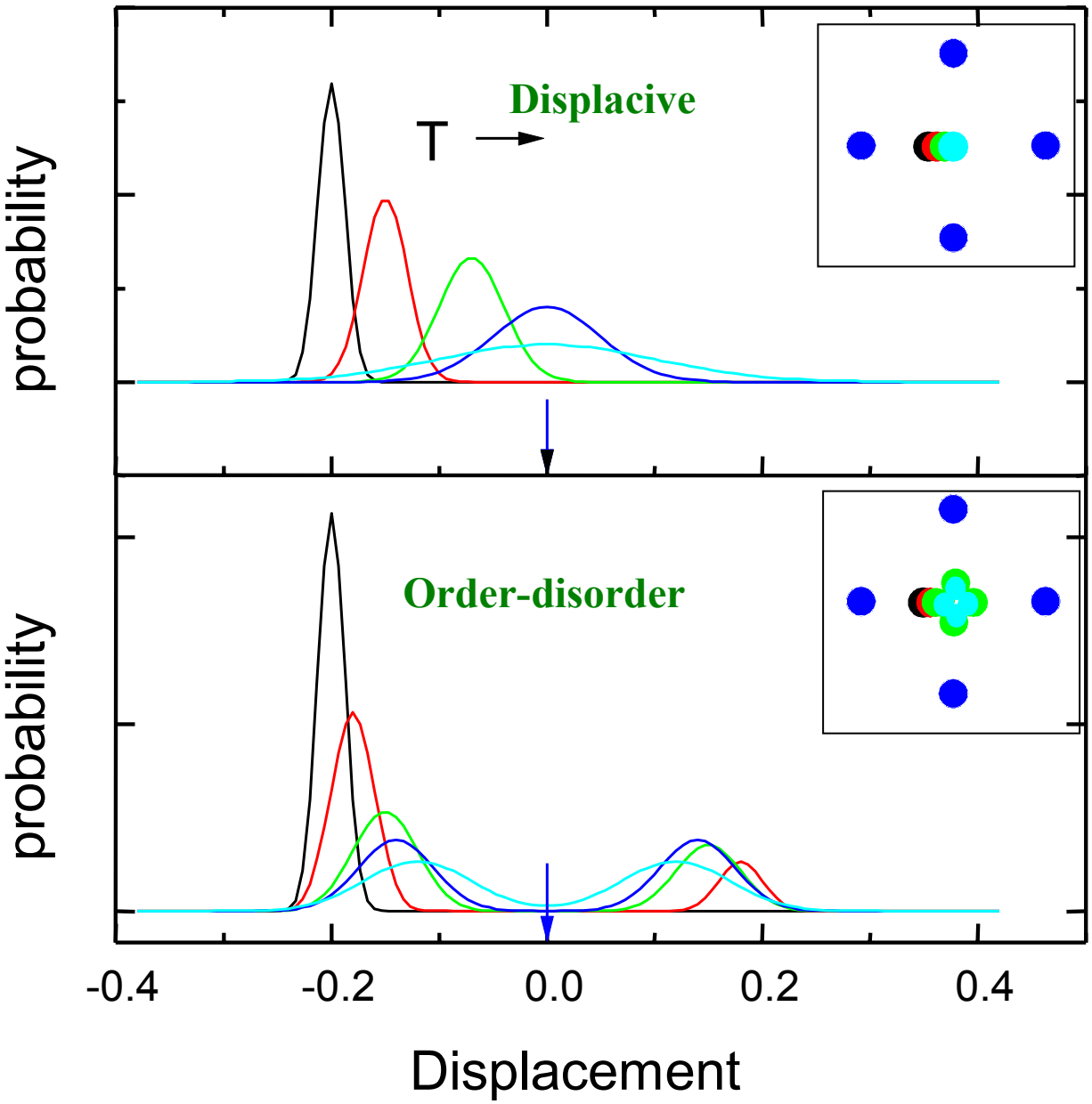
Antiferrodistortive

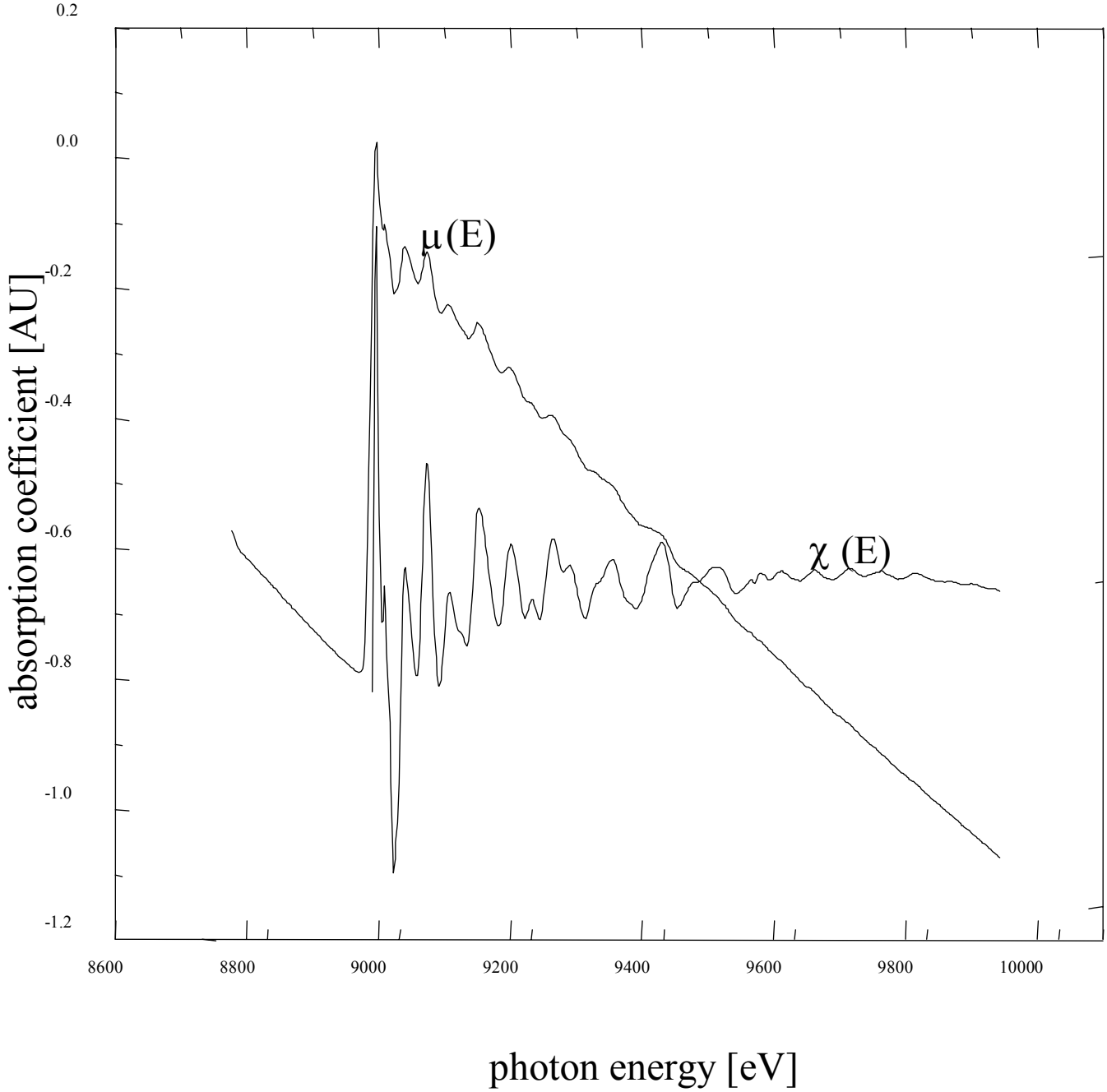
Local structure in crystals undergoing structural phase transitions.

Classical theory: Displacive transitions driven by Soft mode.



Position probability distribution function

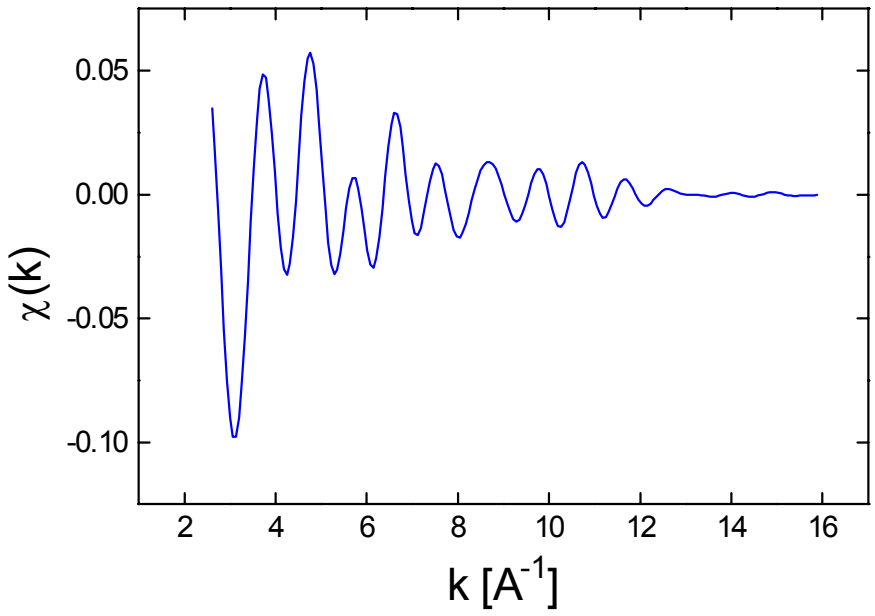



0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
absorption coefficient [AU]
μ(E)
χ (E)
8600
8800
9000
9200
9400
9600
9800
10000
photon energy [eV]

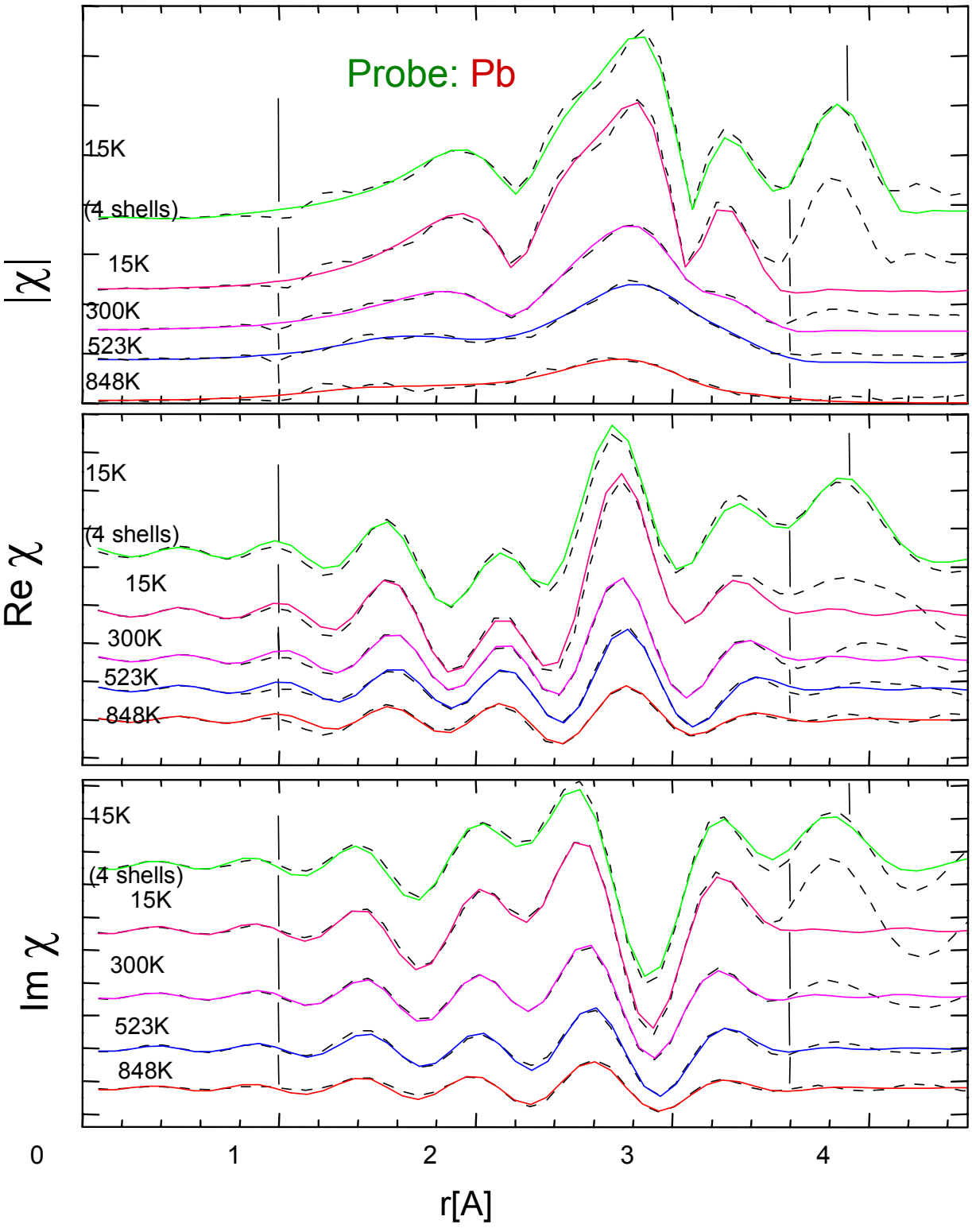
XAFS Formula:

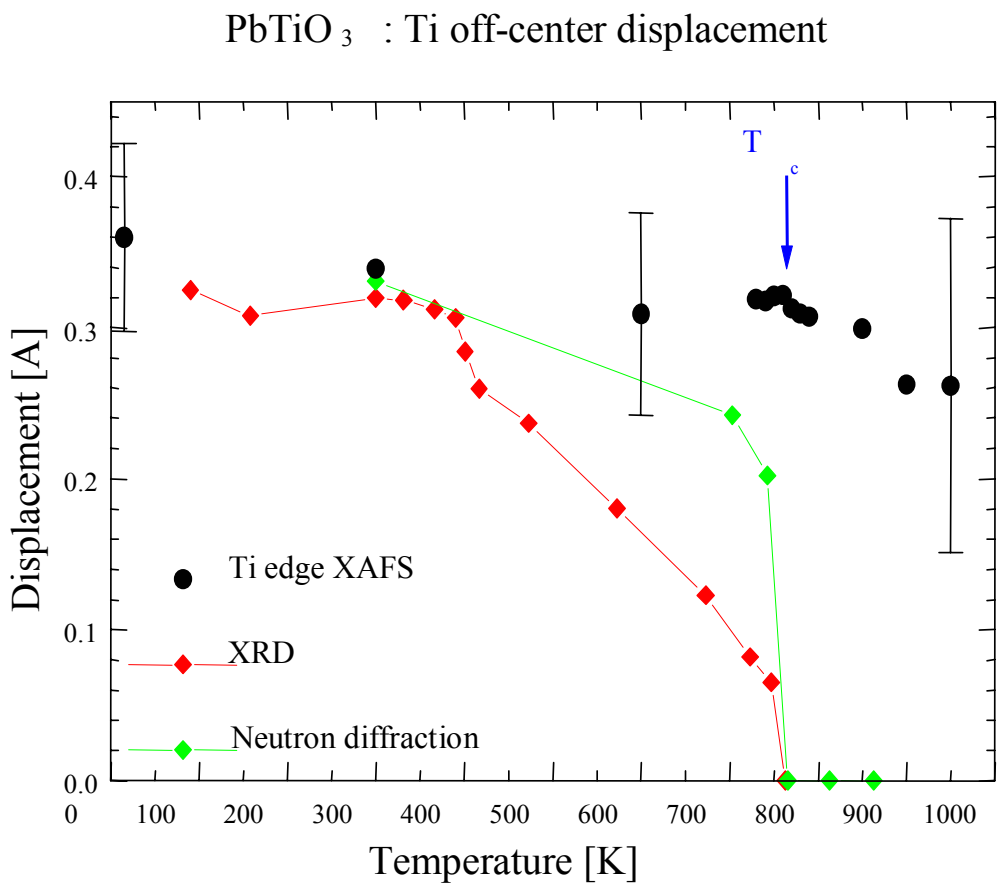
$$\chi(k) = \sum_{\Gamma} \frac{S_0^2}{k\, R_\Gamma{}^2} |f_{eff}^{\Gamma}(k)| \sin[2kR_\Gamma + \phi^{\Gamma}(k) + 2\delta_c(k)]$$
$$\times e^{-2\sigma_\Gamma^2 k^2} e^{-2R_\Gamma/\lambda(k)}.$$

$$k = \sqrt{2m(E - E_0)}$$

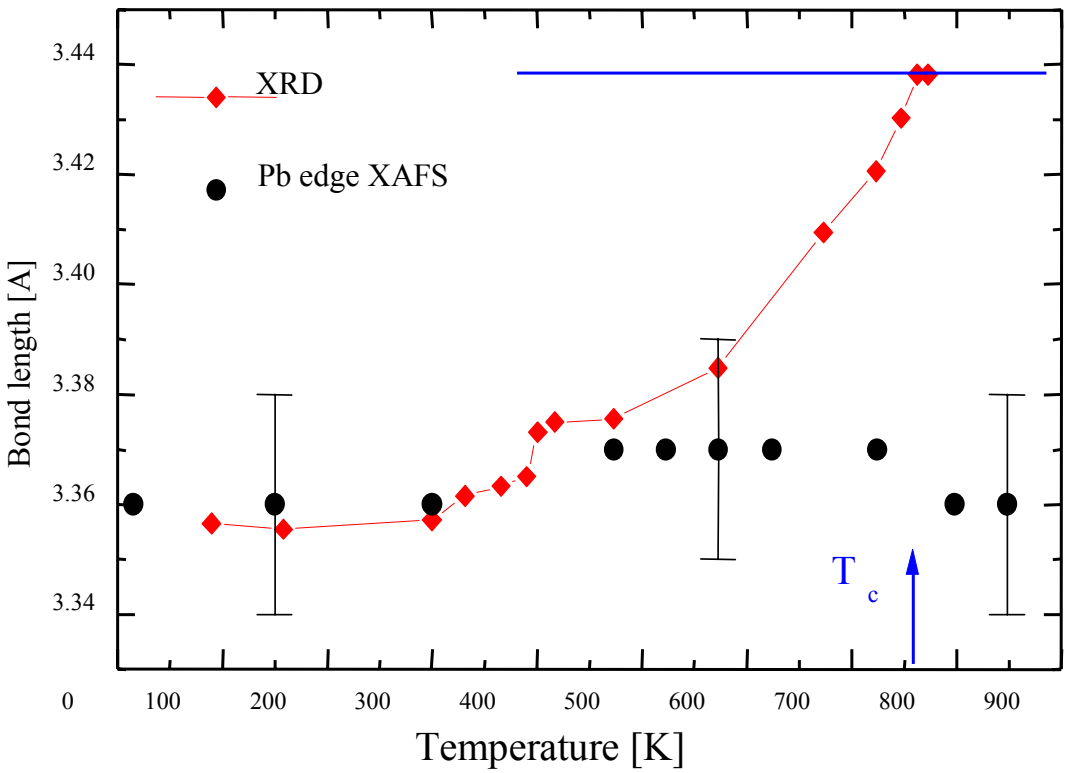


$PbTiO_3$: Fit of theory (solid line)
to experiment (dashed line).

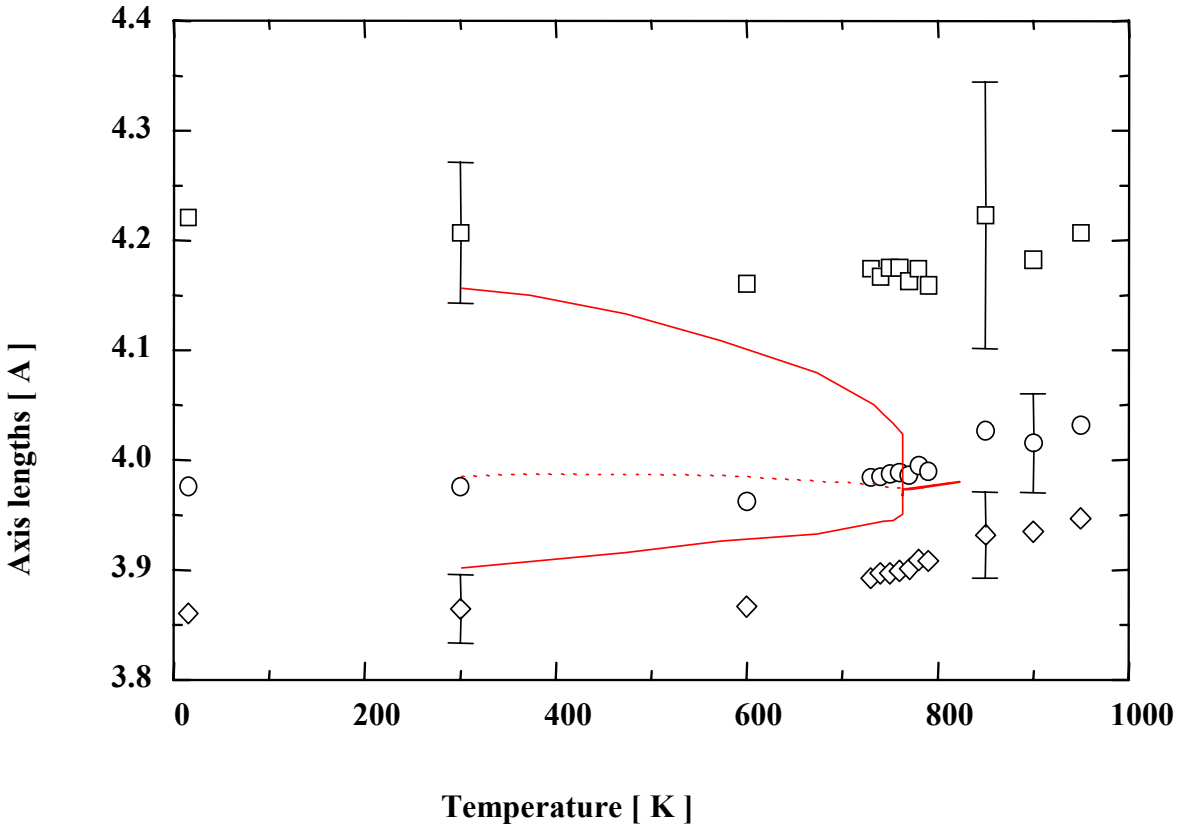



PbTiO 3 : Ti off-center displacement
T
c
Displacement [A]
Temperature [K]
Ti edge XAFS
XRD
Neutron diffraction
0.0
0.1
0.2
0.3
0.4
0
100
200
300
400
500
600
700
800
900
1000

$PbTiO_3$: Pb to close Ti bond length



$PbTiO_3$: Temperature dependence of unit-cell parameters



a and c X-ray diffraction (Glazer et al.)

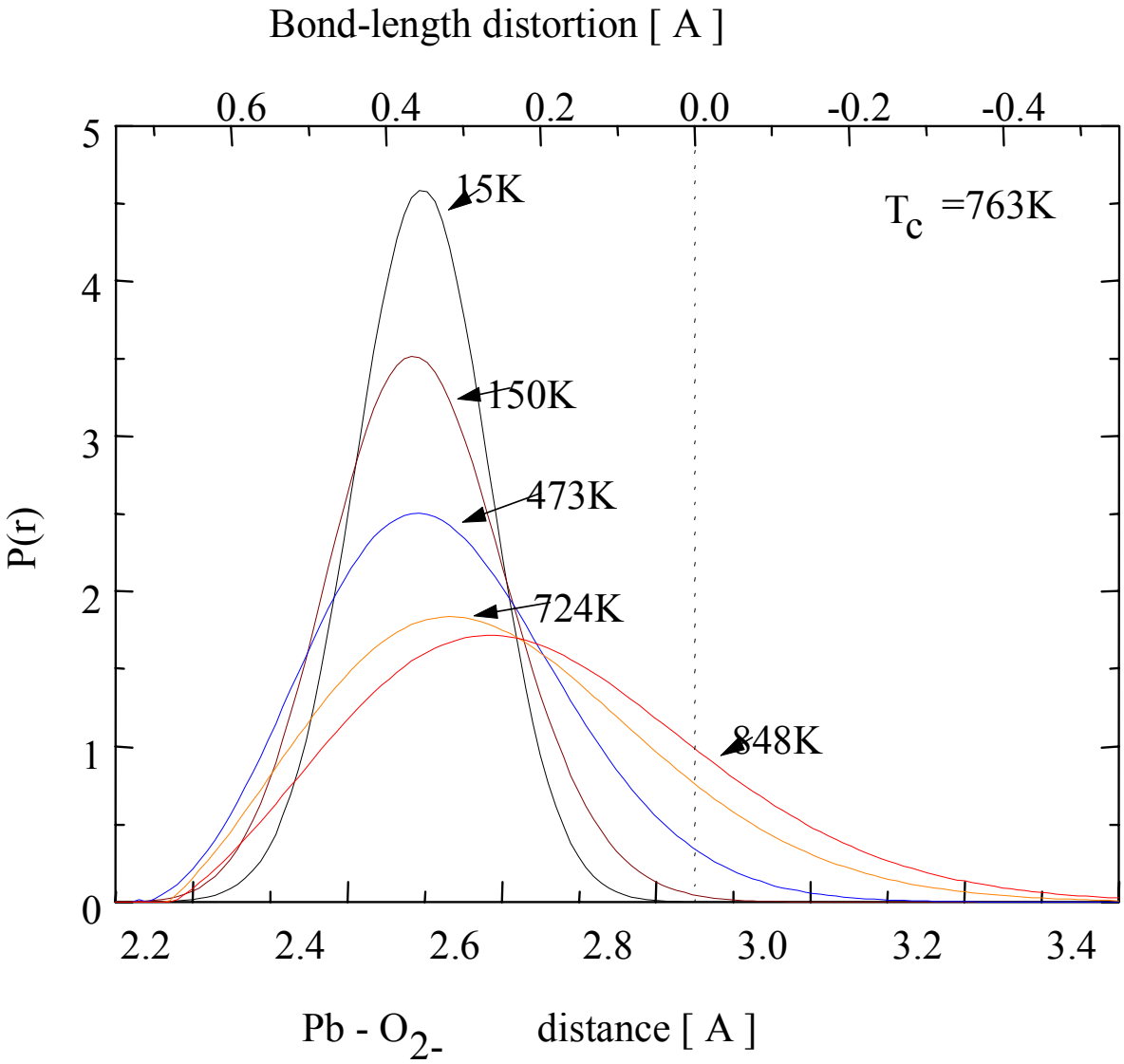
$(a^2 c)^{1/3}$ X-ray diffraction (Glazer et al.)

◇ a XAFS (Ti edge)

□ c XAFS (Ti edge)

○ $(a^2 c)^{1/3}$ XAFS (Ti edge)

Probability Distribution Function (PDF) of the Pb - O_{2-} distance



Local off-center displacements are present in the high symmetry phase of:

- **Ferroelectric**
- **antiferroelectric**
- **antiferrodistortive**
- **other crystal families**

In all these materials:

- **Distortions present far above T_c**
- **The distortions are large**

New theory of ferroelectricity:

The local off-center displacements interact with the soft mode and drive the phase transition.

The theory explains quantitatively:

- Why the soft mode frequency does not vanish at T_c
- Why is the Currie-Weiss coefficient large in these material.
- What is the origin of the central peak
- Why do these materials display diffuse x-ray scattering
- Why do these materials display first order Raman scattering.
- All the properties of mixed crystals such as $KTaO_3$:Nb.

Thin films.

Structural information is essential in understanding the

- Dynamical properties
- Phase transitions
- Electronic properties

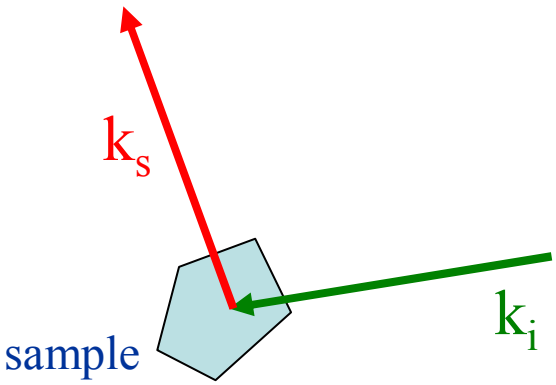
Difficulties:

- The structure changes with the distance from the interface

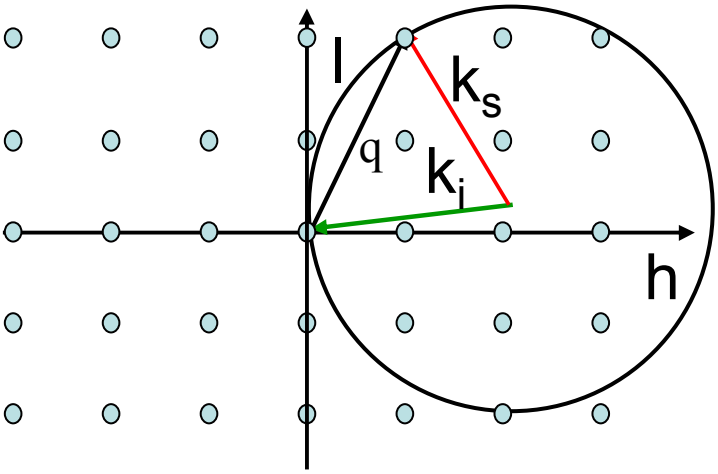
Coherent Bragg Rod Analysis (COBRA).

X-ray diffraction with phase determination.

X-ray diffraction



Reciprocal space



$$|K_i| = |K_s|;$$
$$\vec{K}_i + \vec{q} = \vec{K}_s.$$

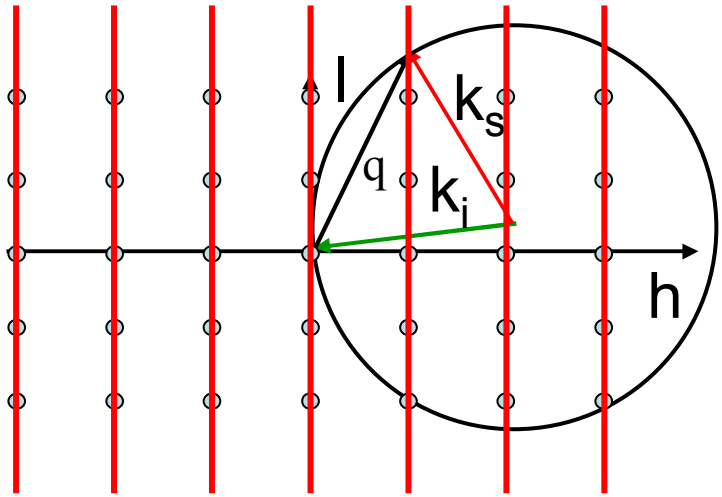
The Phase problem

Scattering factor $S = \frac{E_s}{E_i} = A(\bar{q})FT(\rho(\bar{r}));$

X-ray diffraction from a 2D system

$$S = \frac{E_s}{E_i} = A(\vec{q})FT(\rho(\vec{r}));$$

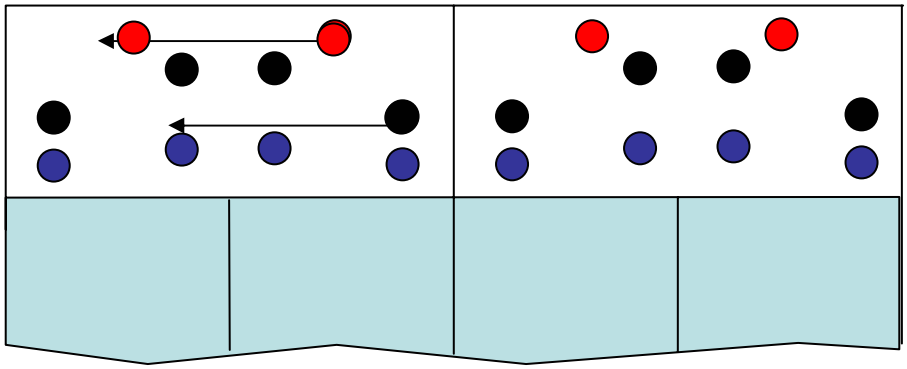
Reciprocal space



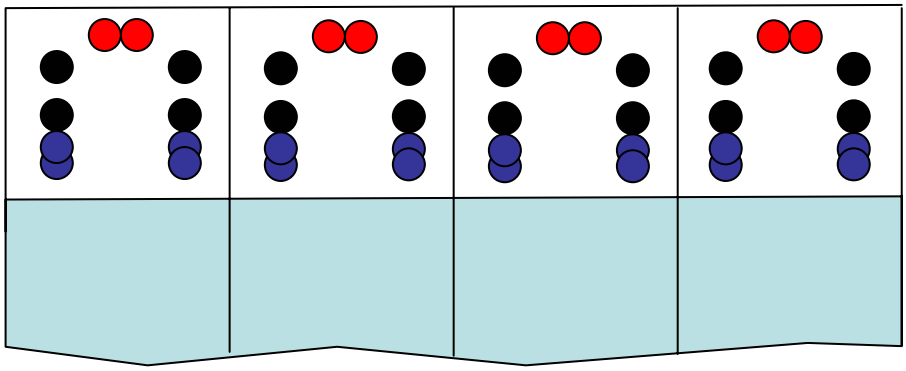
Partially periodic structure

- Different periods
- Strains
- Local incommensurability

Different periods



The folded structure

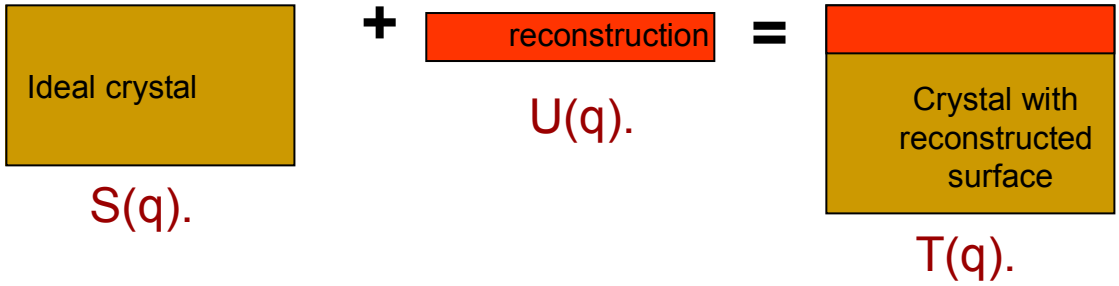


Determination of the complex scattering factor

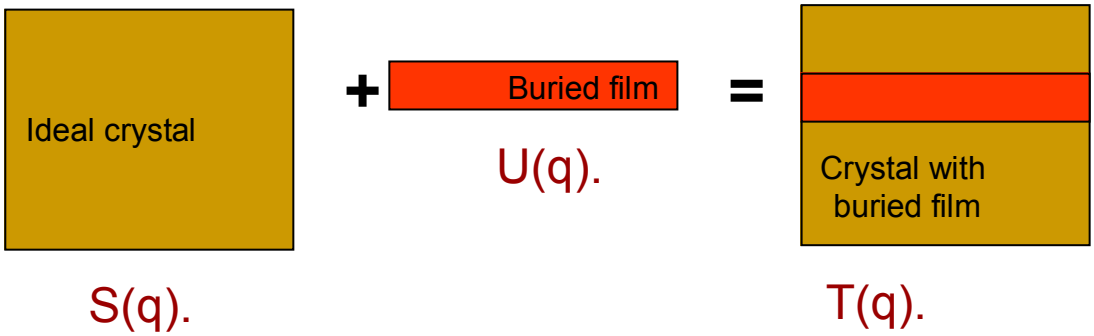
We assume knowledge of the structure of a fraction of the system. The corresponding complex scattering factor is S(q).

- Examples:

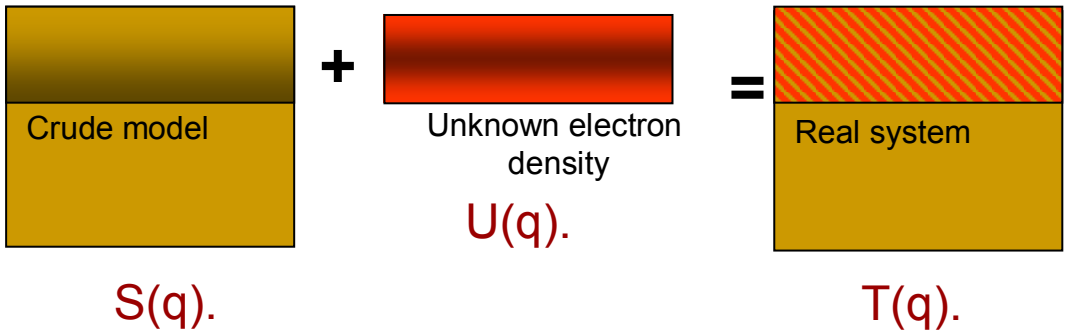
•A crystal undergoing surface reconstruction.



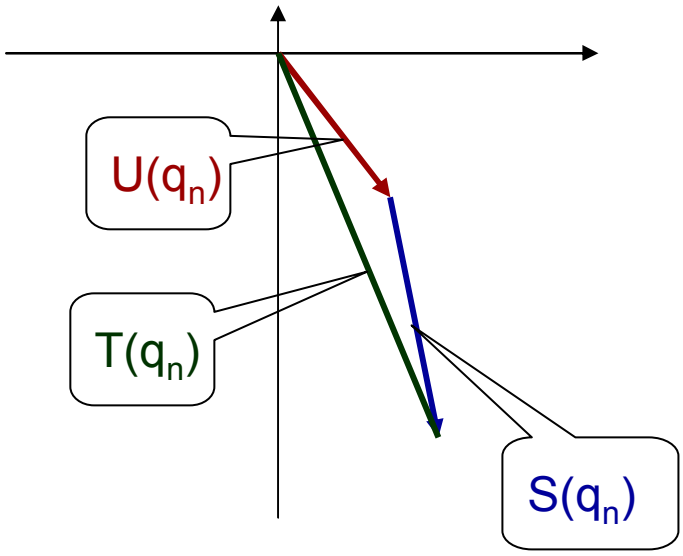
•A crystal containing layers of another material GaAs-AlAs



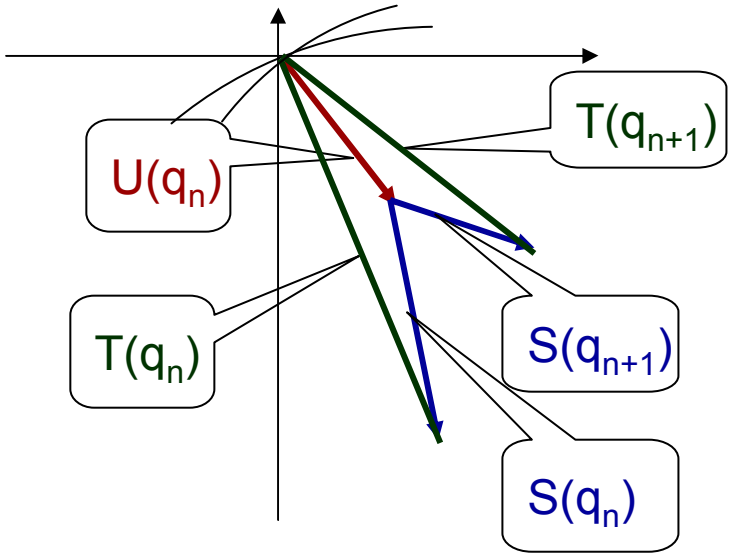
•A crystalline film epitaxially grown on a crystalline substrate.



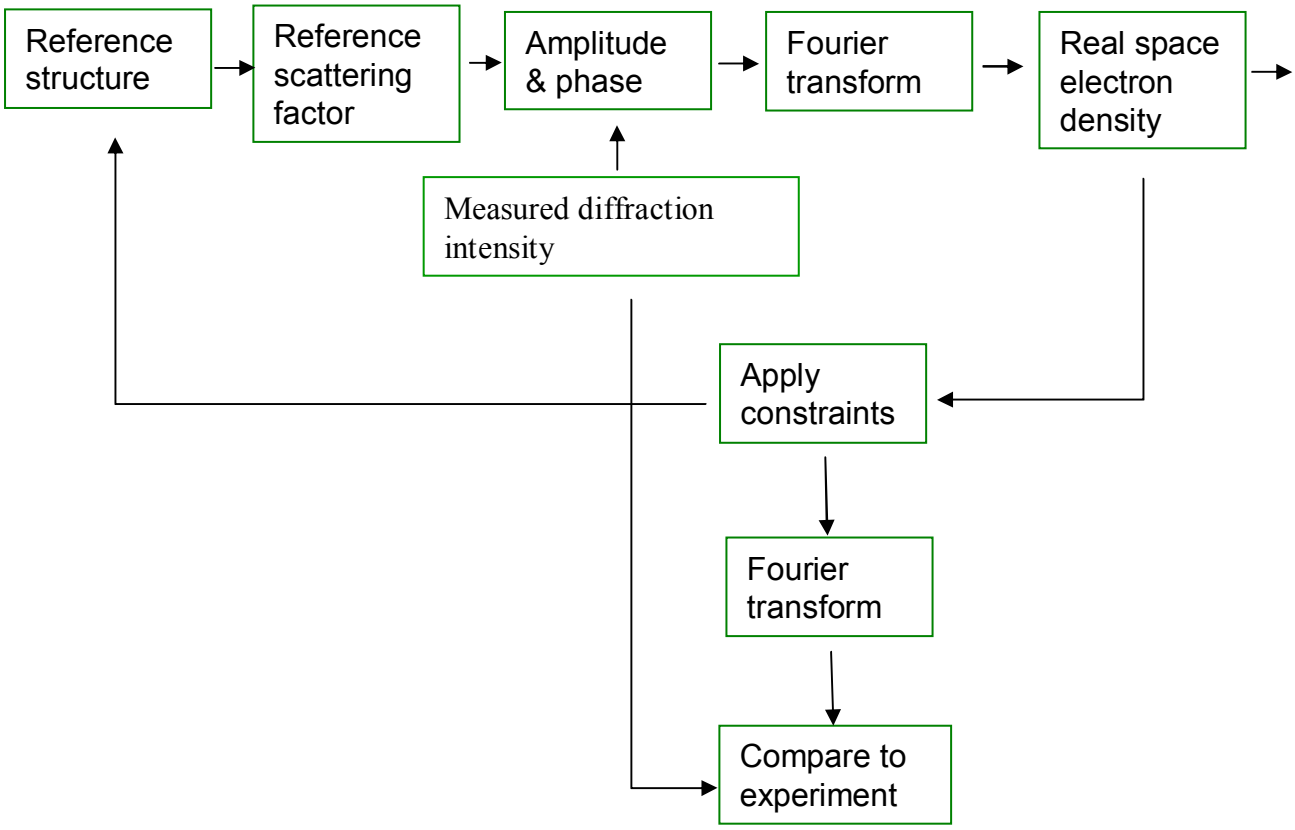
In the complex plane



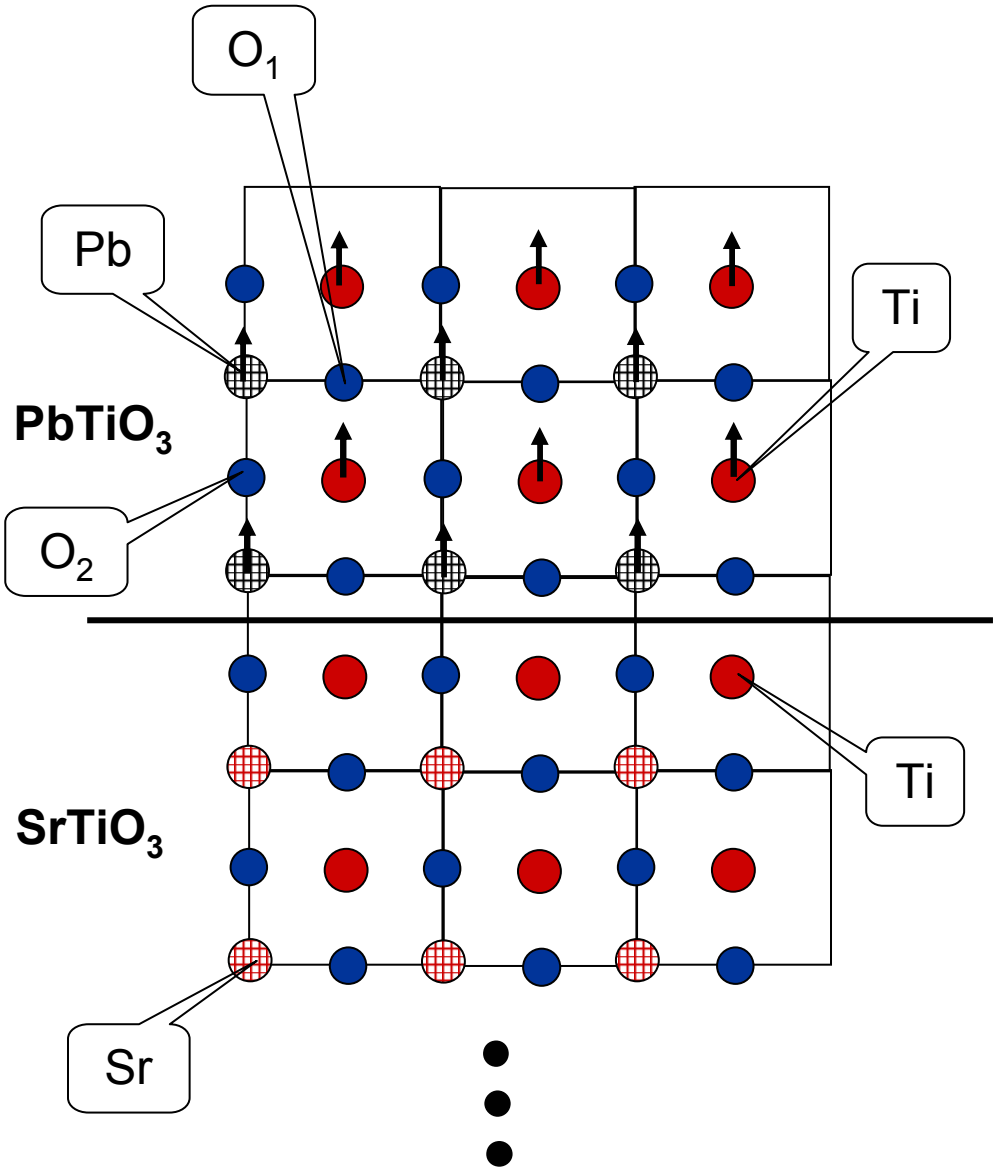
Approximation: $U(q_n) = U(q_{n+1})$

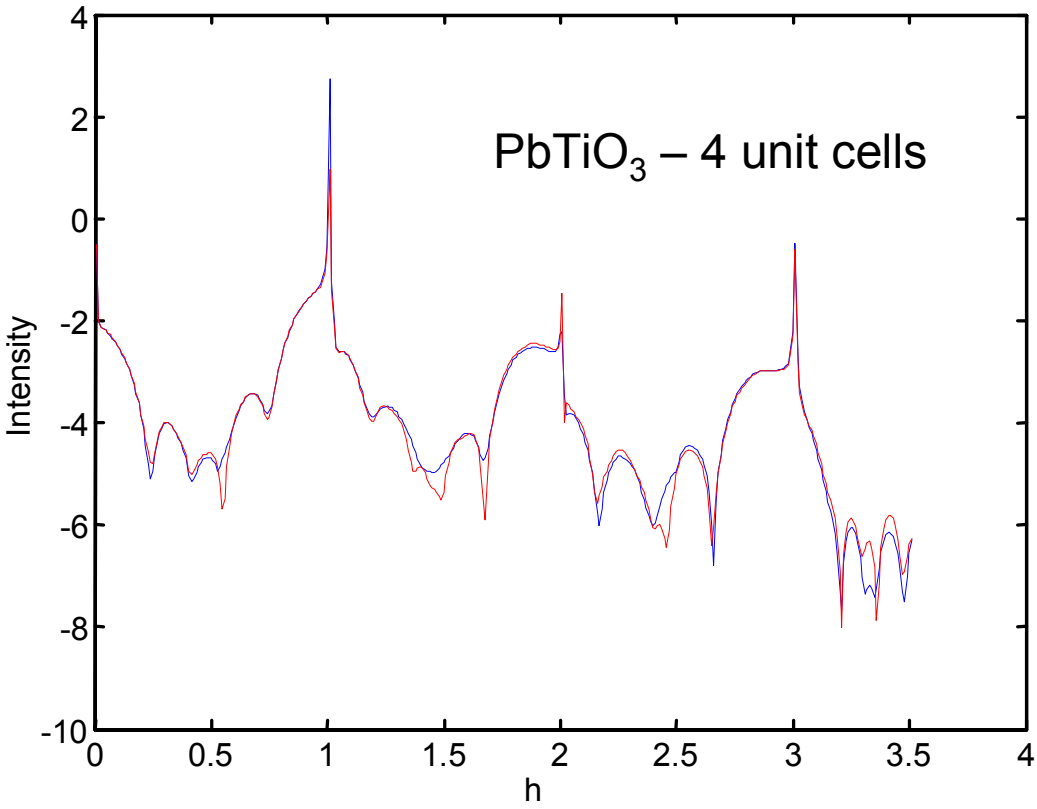


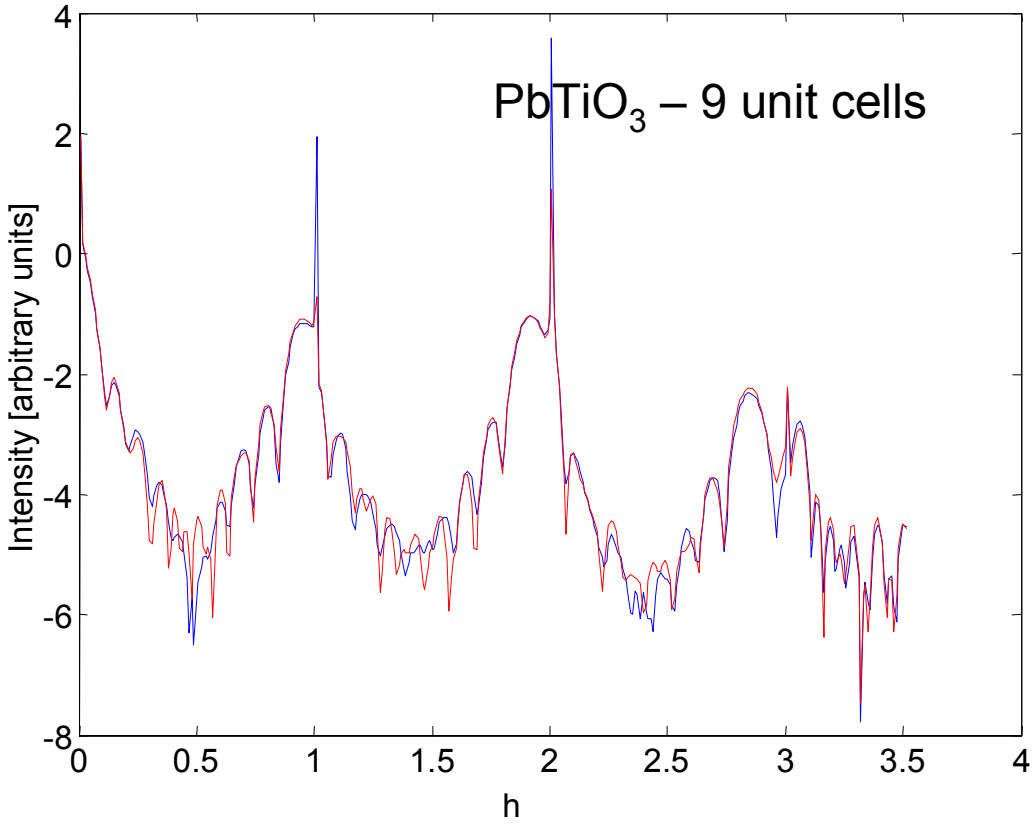
COBRA data analysis



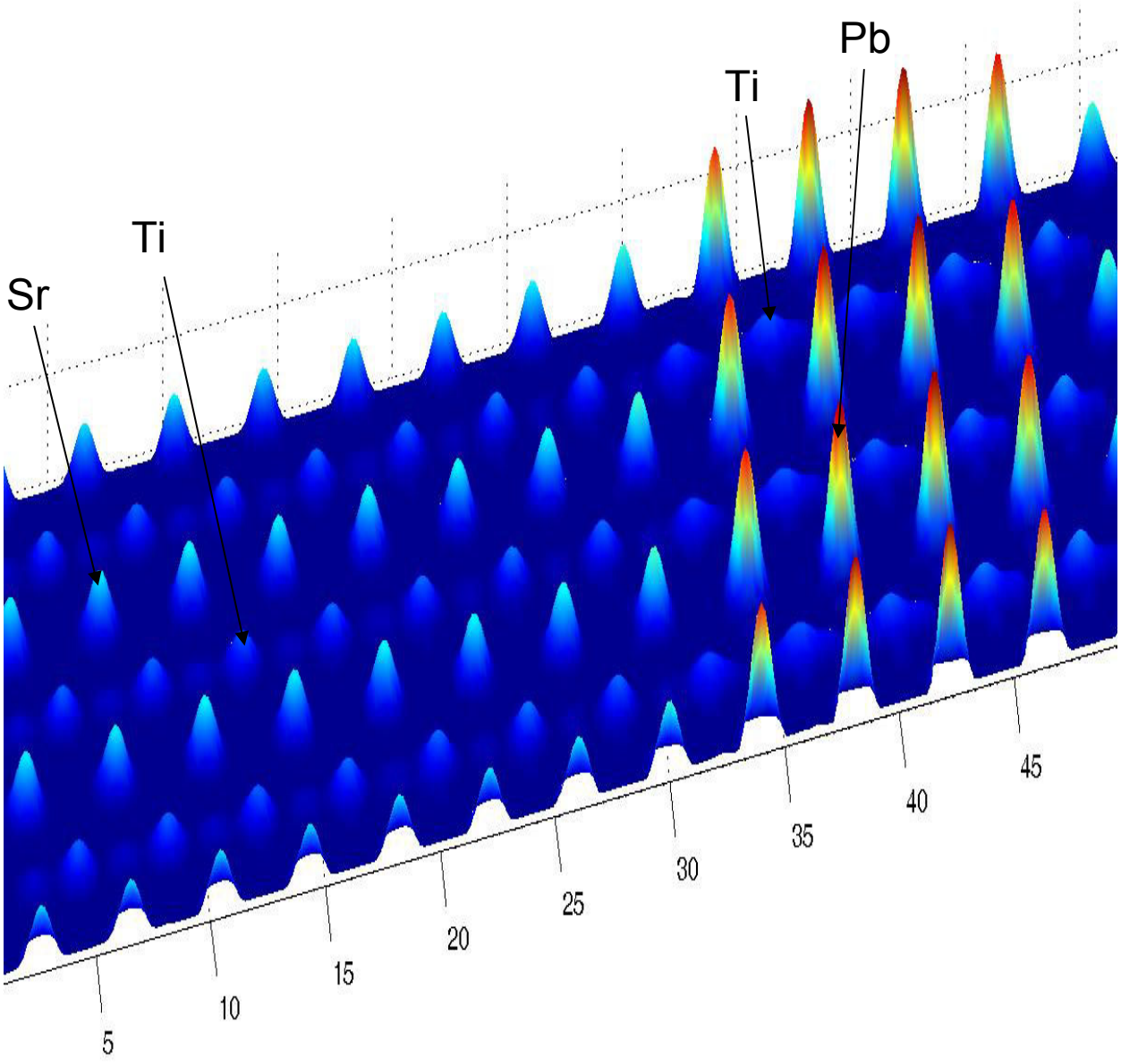
Epitaxially grown $PbTiO_3$ on $SrTiO_3$

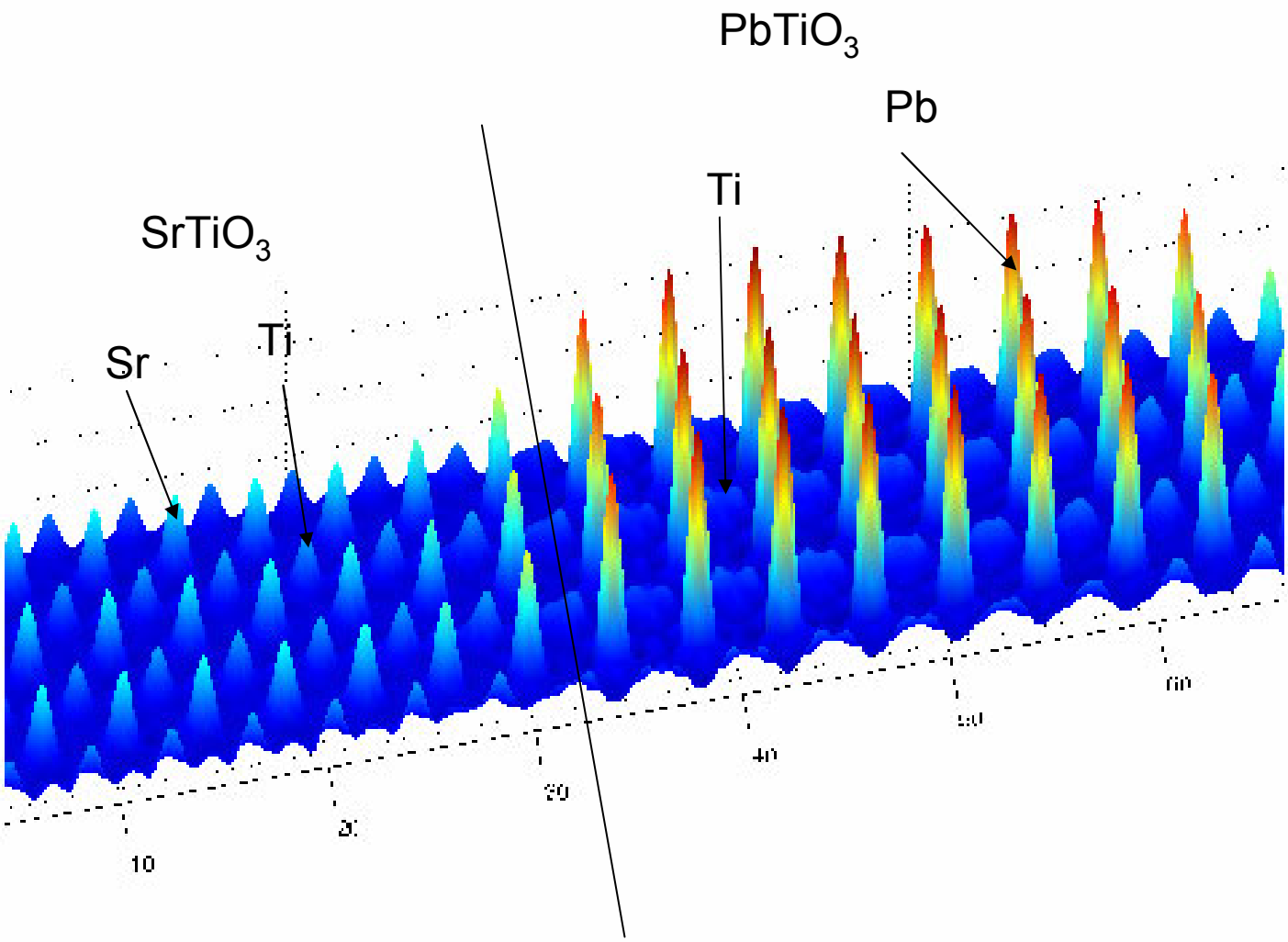


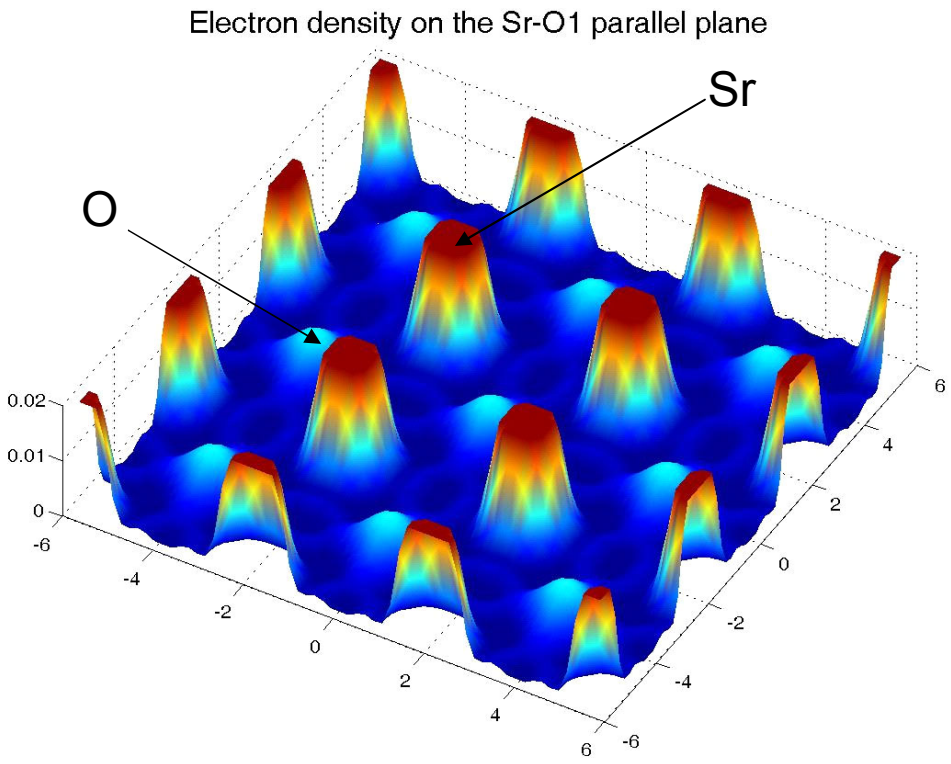

PbTiO3 – 4 unit cells
Intensity
h
4
2
0
-2
-4
-6
-8
-10
0
0.5
1
1.5
2
2.5
3
3.5
4

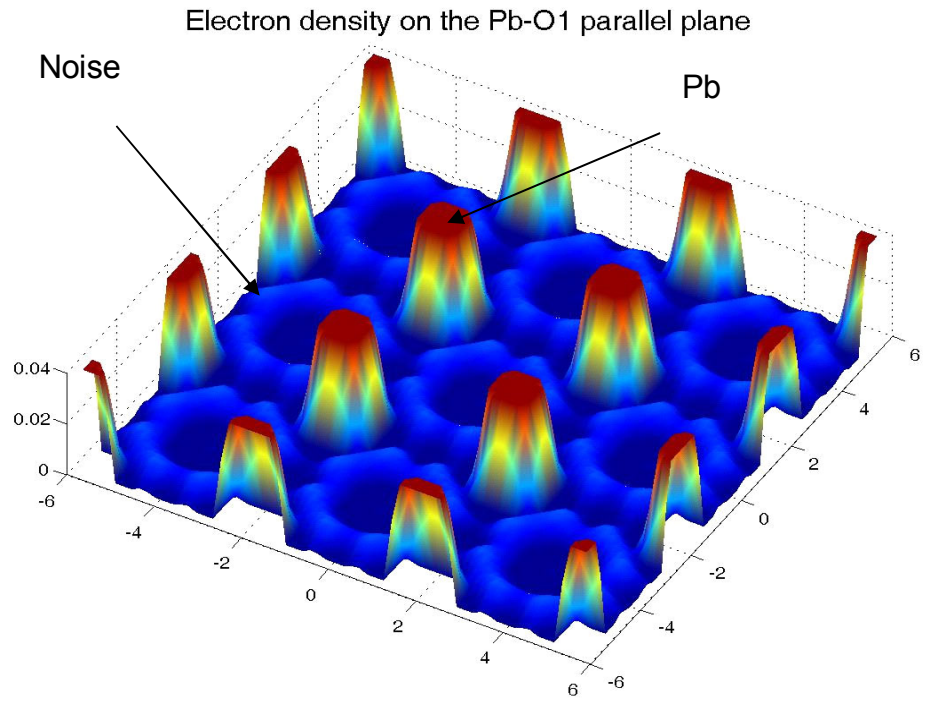

PbTiO3 – 9 unit cells
Intensity [arbitrary units]
h
4
2
0
-2
-4
-6
-8
0
0.5
1
1.5
2
2.5
3
3.5
4

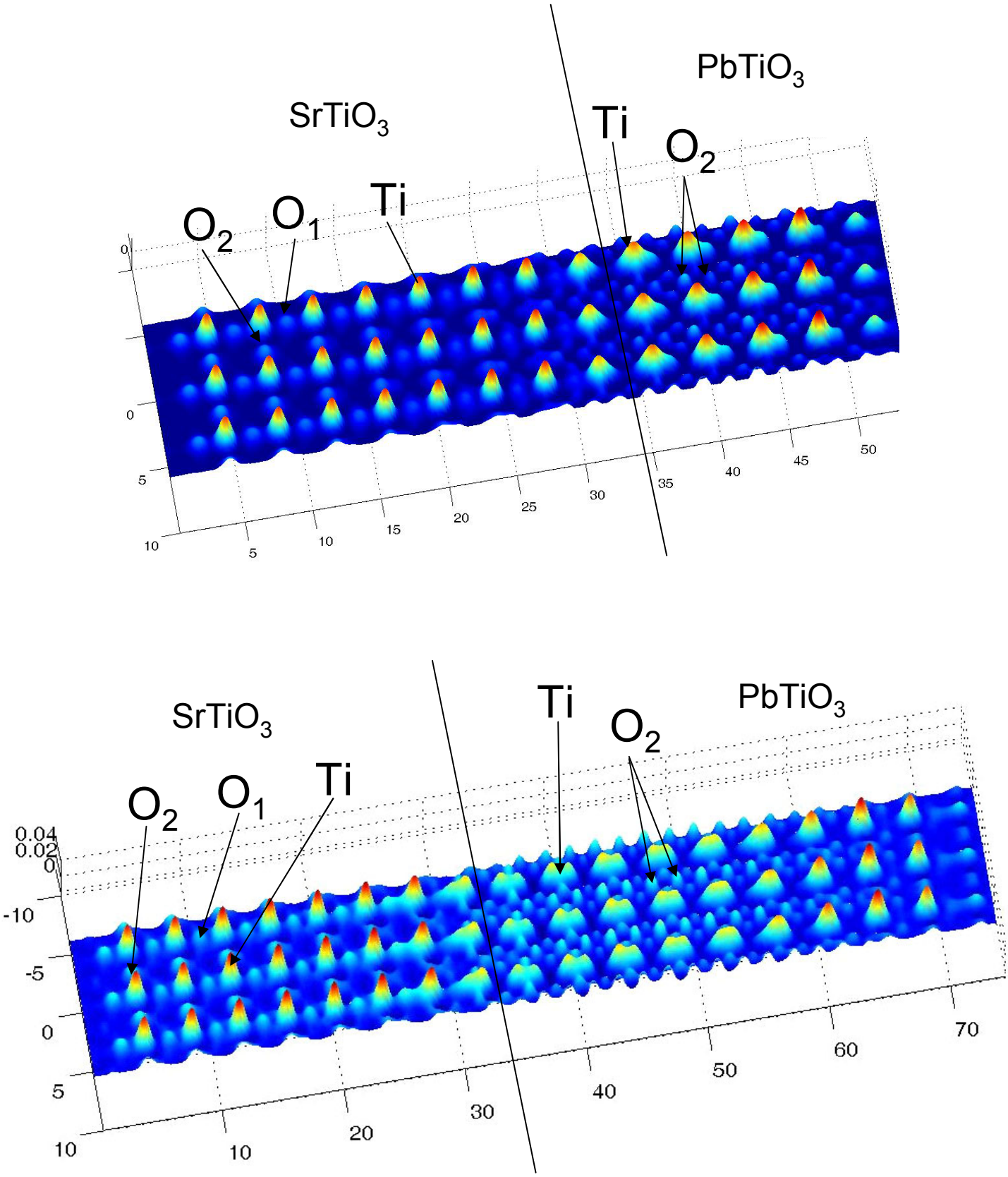
Electron density in the Pb-Ti vertical plane




PbTiO3
Pb
Ti
SrTiO3
Ti
Sr
10
20
30
40
50
60


Electron density on the Sr-O1 parallel plane
Sr
O
0.02
0.01
0
-6
-4
-2
0
2
4
6
-6
-4
-2
0
2
4
6


Electron density on the Pb-O1 parallel plane
Noise
Pb
0.04
0.02
0
-6
-4
-2
0
2
4
6
-6
-4
-2
0
2
4
6


SrTiO3
PbTiO3
O2
O1
Ti
Ti
O2
0
0
5
10
5
10
15
20
25
30
35
40
45
50
SrTiO3
PbTiO3
O2
O1
Ti
Ti
O2
0.04
0.02
0
-10
-5
0
5
10
10
20
30
40
50
60
70

Summary

X-ray Absorption Fine Structure XAFS

- XAFS advantages:
  - Sensitivity to inter-atomic distances
  - High resolution
- The main results:
  - The crystals are spontaneously distorted far above T_c.
  - The distortions are large and comparable to the distortions at 0 K.
- This led to a comprehensive understanding of the mechanism driving the phase transitions:

The phase transition takes place not when the soft mode frequency goes to zero but when the spontaneous distortions coupled to the soft mode slow down to zero.

Coherent Bragg Rod Analysis (COBRA)

- COBRA advantages:
  - The method is direct namely the structure does not depend on a pre-conceived model.
  - The structure is obtained with sub-Angstrom resolution.
- $PbTiO_3$ on $SrTiO_3$
  - The structure is very different from a naively expected structure