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Phase Transitions, Domain Structure & Dynamics, and Surface Chemistry in Ferroelectrics Studied by X-Rays

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THE UNIVERSITY OF CHICAGO

Office of Science
U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by The University of Chicago

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  - G.B. Stephenson, R.-V. Wang, F. Jiang, T. Fister, M. Highland, M.-I. Richard, D.D. Fong, J.A. Eastman, and P.H. Fuoss (Materials Science Division, ANL)
  - Carol Thompson
    (Dept. of Physics, Northern Illinois University)

- **$SrRuO_3$ Films**
  - D.-M. Kim, K.-J. Choi and C.-B. Eom (U. Wisconsin - Madison)

- **Theory**
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Overview

- Introduction to and motivation for utilizing synchrotron x-rays

- Size effects on the ferroelectric phase transition in $PbTiO_3$ and relationship to 180° domain structure

- Surface interactions with the gas phase and relationship to polarization state

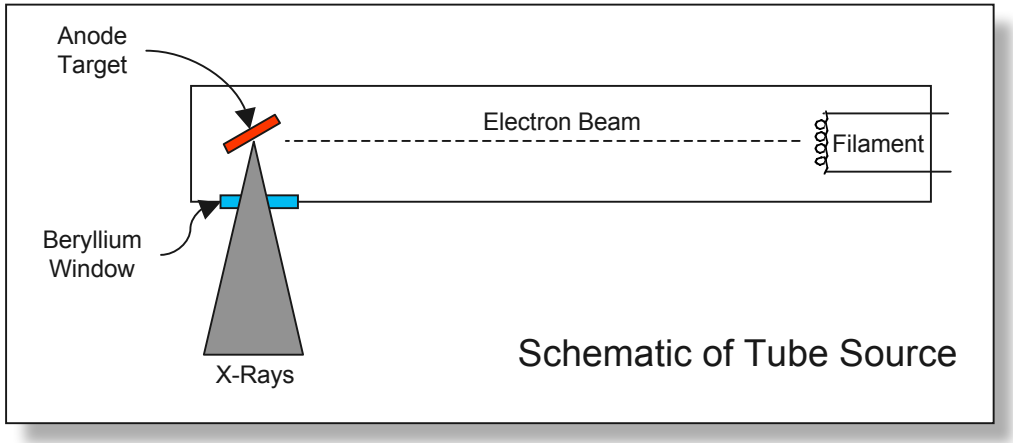
A good general reference:

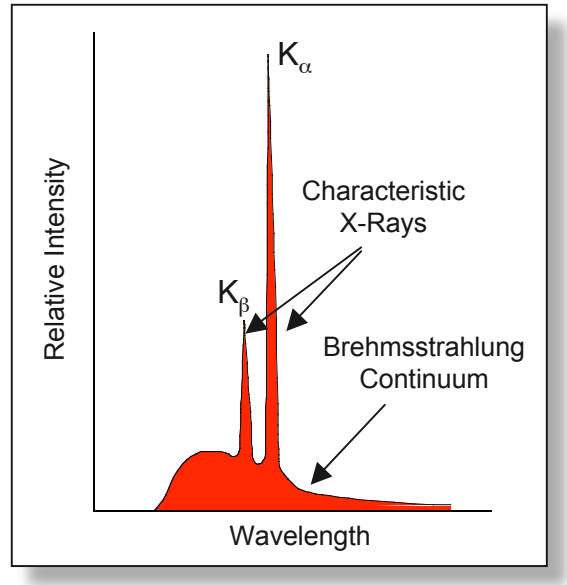
Elements of Modern X-Ray Physics, Jens Als-Nielsen and Des McMorrow (Wiley and Sons, 2001)

Also see: www.aps.anl.gov

www.lightsources.org

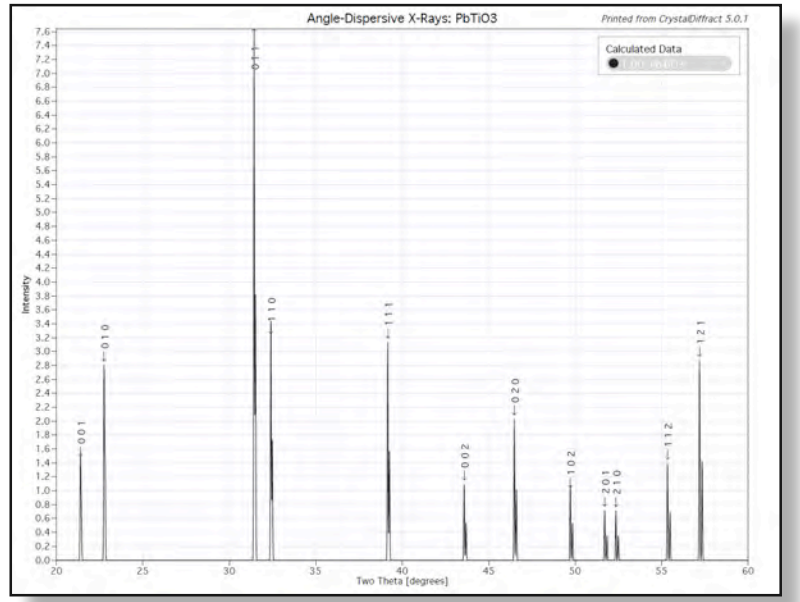
Tube Source and Bragg's Law





Bragg's Law

$n\lambda=2d\sin\theta$



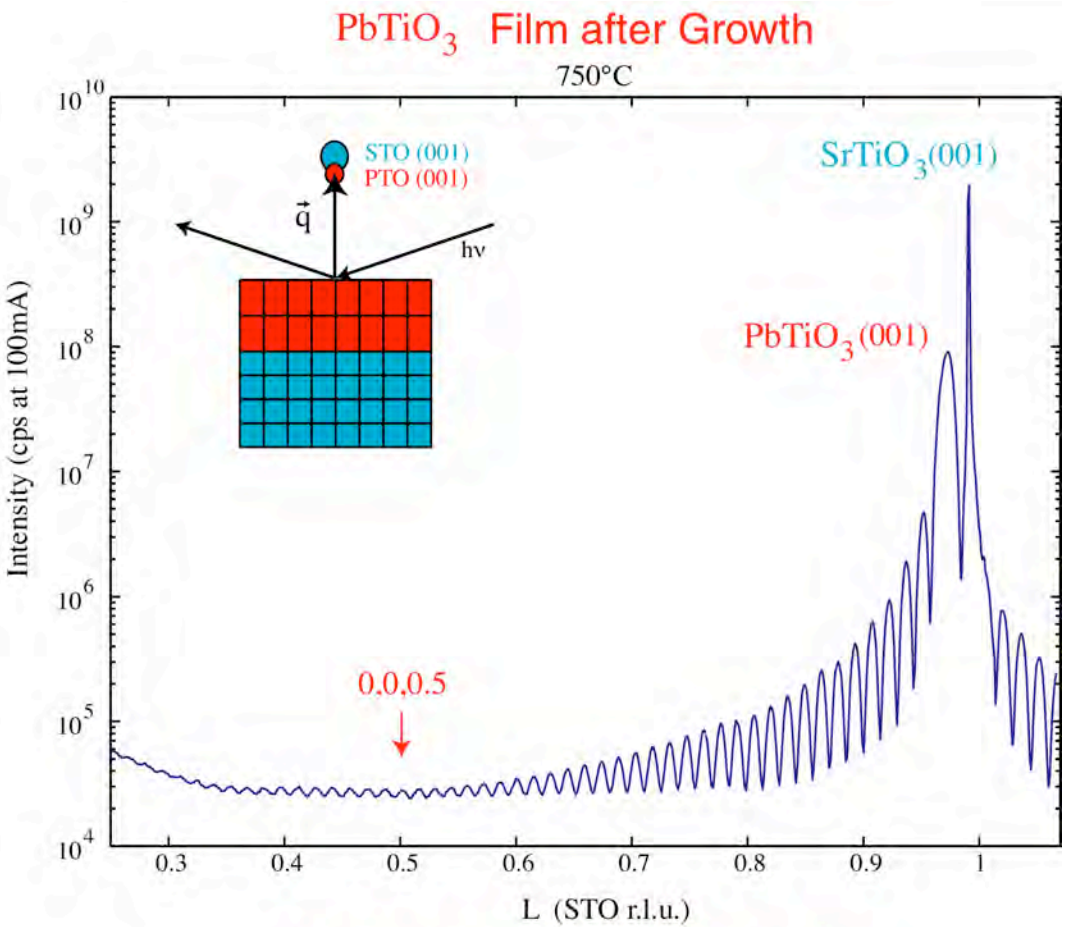
What Can We Do Better For Studies of Ferroelectric Films?

- Films are microstructurally complex
  - X-ray scattering is a measure of the Fourier transform of the structure being probed
  - Don't just measure the "average" structure as represented by the Bragg peaks

- Films are not random crystals
  - Measure the three-dimensional structure using multiple angles to position the sample relative to the x-ray beam, with an x-ray beam that is sufficiently non-divergent and monochromatic, and of a suitable energy/wavelength to see ***all*** the details

- Films are grown and manipulated in complex environments
  - Utilize an x-ray probe that is sufficiently brilliant to penetrate such environments
  - If at all possible, do measurements in real time!

Doing Better: Real Films of Finite Thickness

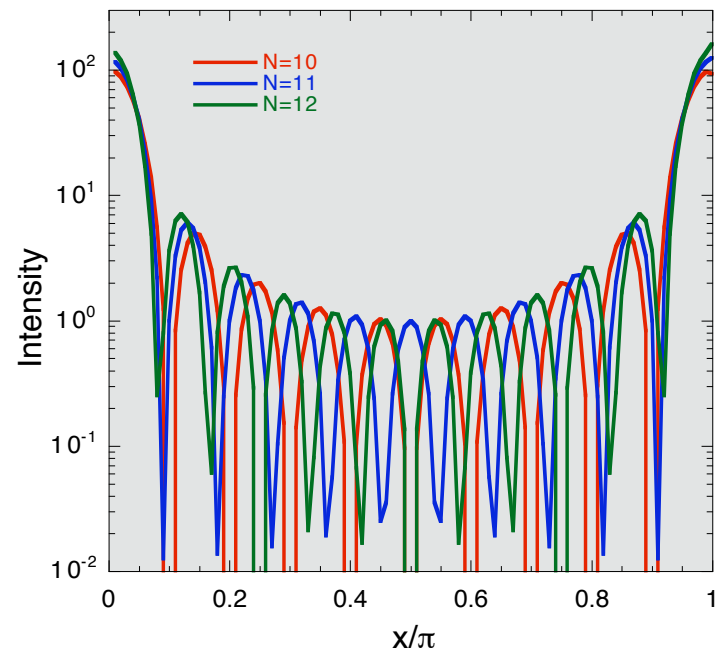


Thickness fringes from 300Å $PbTiO_3$ film
Tetragonal distortion of the epitaxial film

Thickness fringe period:

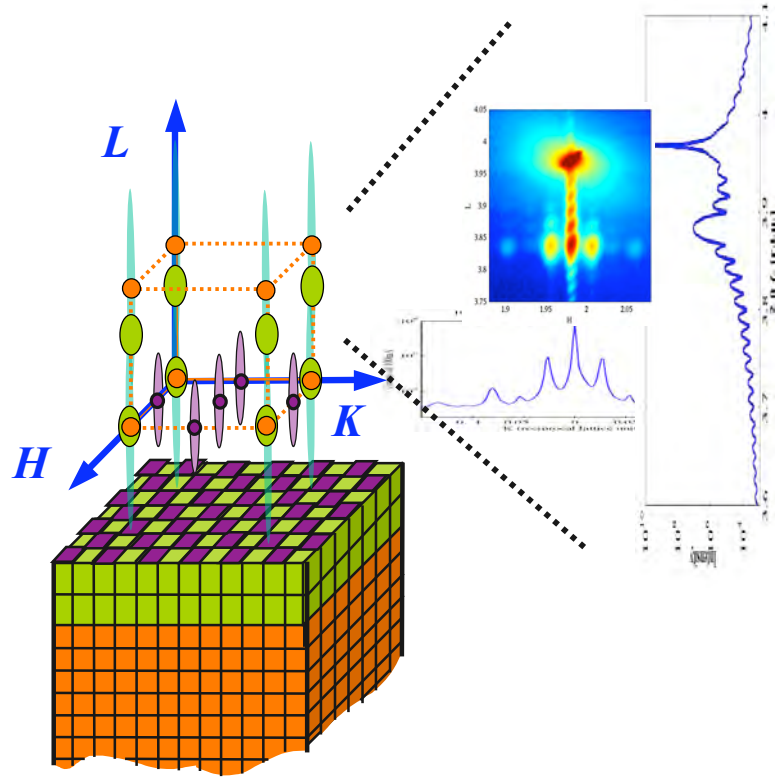
$$\frac{\sin^2 Nx}{\sin^2 x}, \quad x = \frac{\pi}{\lambda}(s - s_o)$$

$$L=(0,0,0.5) \Rightarrow x=\pi/2$$



The Goal: Seeing Dynamic Structure in Real Time

- Reciprocal space
  - Substrate Bragg peaks
  - Film Bragg peaks
  - Crystal truncation rods (CTR) and finite size oscillations
    - *Truncation of crystal at surface causes streaks of intensity extending out of Bragg peaks, perpendicular to the surface*
    - *Tilt of rods show miscut*
  - Surface reconstruction Bragg peaks
  - Diffuse scattering from defects
    - *Islands*
    - *Planar defects*
    - *Structural modulations*



X-Ray Surface Scattering

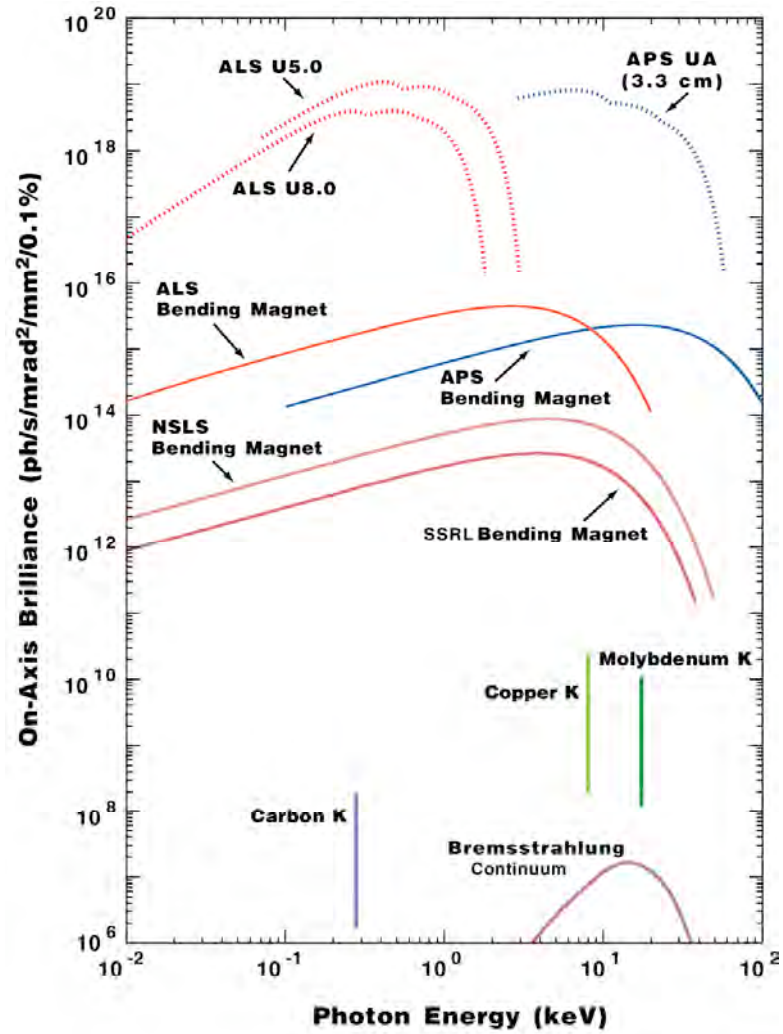
Why Use a Synchrotron X-Ray Source?

- **High brightness:** synchrotron light is extremely intense and highly collimated.
- **Wide energy spectrum:** synchrotron light is emitted with energies ranging from the infrared to hard, energetic (short wavelength) x-rays.
- **Tunable:** through sophisticated monochromators and insertion devices it is possible to obtain an intense beam of any selected wavelength.
- **Highly polarized:** the synchrotron emits highly polarized radiation, which can be linear, circular or elliptical.
- **Emitted in very short pulses:** pulses emitted are typically less than a nano-second (a billionth of a second).

Why Use A Synchrotron X-Ray Source?

E (keV)	λ (Å)
0.8	15.0
8.0	1.5
40.0	0.3
100.0	0.125

	Brightness ($s^{-1}\ m^{-2}\ ster^{-1}$)	*dE/E* (%)	*Divergence* ($mrad^2$)	*Flux* ($s^{-1}\ m^{-2}$)
Neutrons	10^{15}	2	10 x 10	10^{11}
Rotating Anode	10^{16}	3	0.5 x 10	5×10^{10}
Bending Magnet	10^{24}	0.01	0.1 x 5	5×10^{17}
Wiggler	10^{26}	0.01	0.1 x 1	10^{19}
Undulator (APS)	10^{33}	0.01	0.01 x 0.1	10^{24}

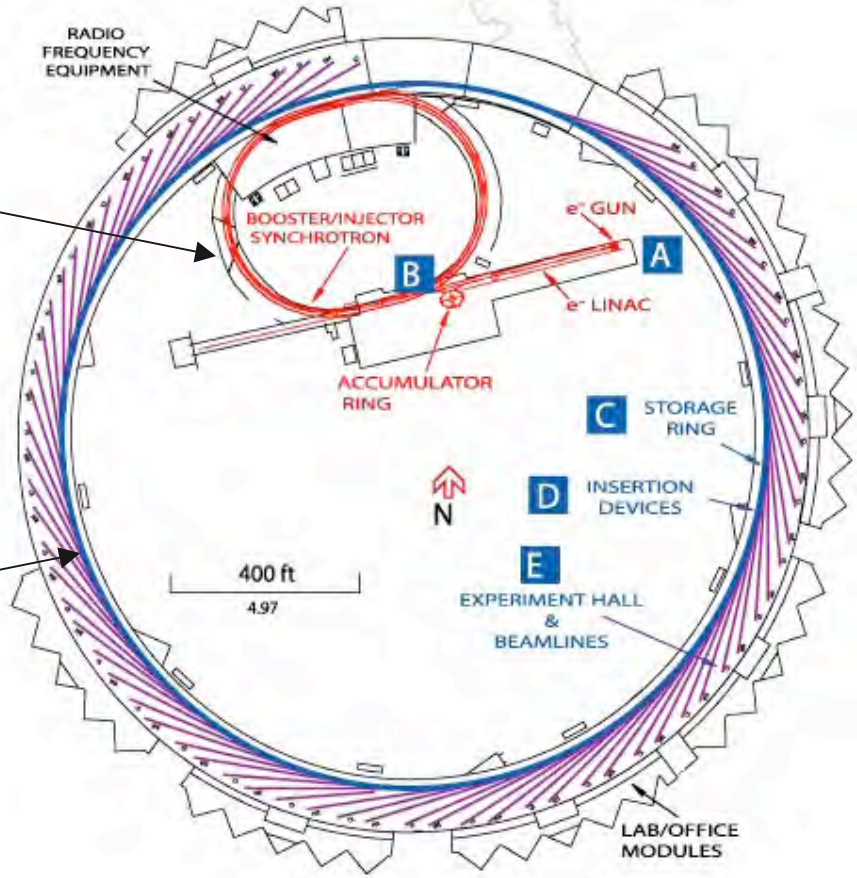


What is a Synchrotron?

Acceleration of a charged particle causes it to give off energy as photons

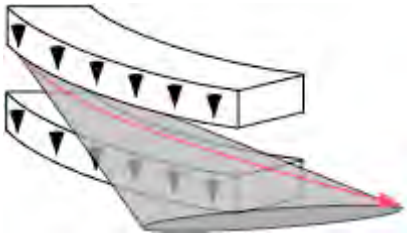
- Electrons (or positrons) are accelerated to almost the speed of light by a linear accelerator (linac) and booster ring. They are then transferred to an outer storage ring.

- The electrons are confined to the "circular" orbit by a series of bending magnets separated by straight sections.

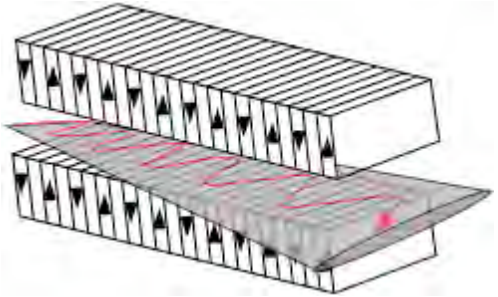


What is a Synchrotron?

- As the electrons are deflected through the magnetic field created by the bending magnets, they give off electromagnetic radiation, so that at each bending magnet a beam of synchrotron light is produced.

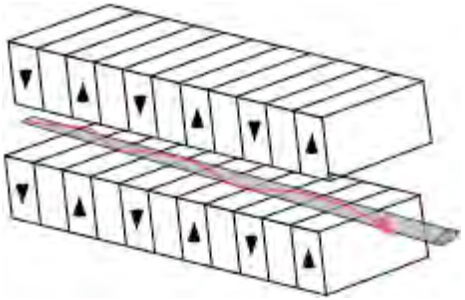


Bending Magnet: Deflection of the electron path yields a fan of radiation with a broad energy spectrum



Wiggler: Intensities add with the number of wiggles

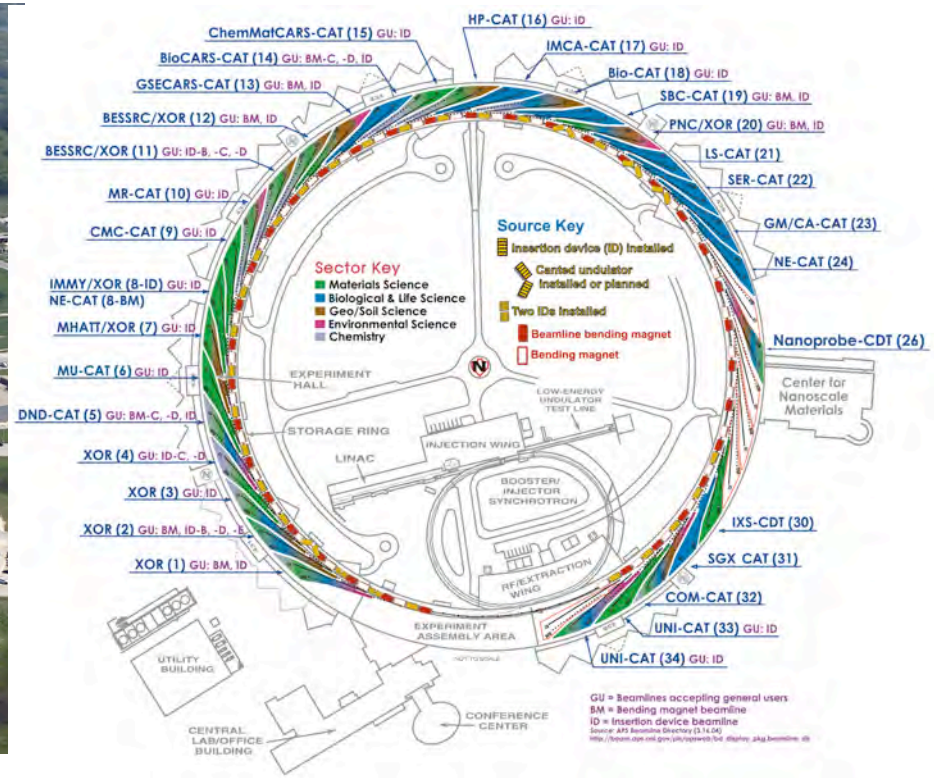
- Electrons passing through “insertion devices” in the straight sections of the ring give off an extremely intense beam of light



Undualtor: Radiation from each undulation interferes constructively, yielding a narrow energy spectrum with high brilliance

- Energy is added back to the electron beam using rf cavities

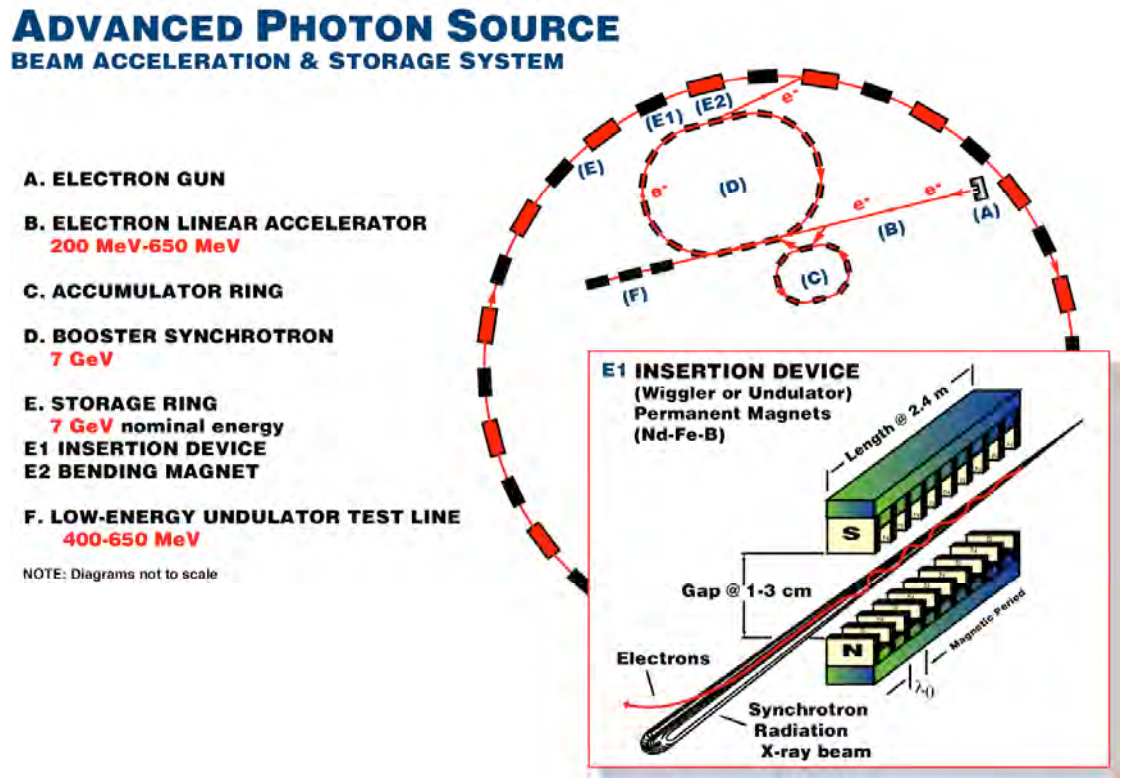
The Advanced Photon Source at Argonne National Laboratory

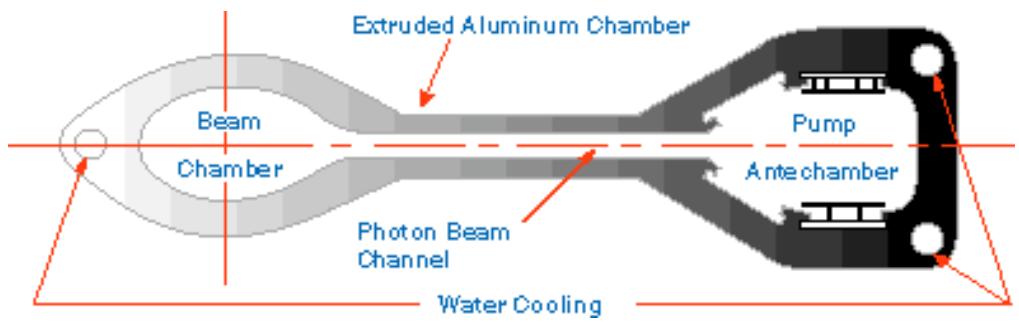


- 7 GeV storage ring completed in 1995
- Construction cost: $467 million
- Number of APS operations staff: ~450
- Outer diameter of the APS experiment hall: 390 meters (1,225 feet)
- Height of the Sears Tower in Chicago: 436 meters (1,454 feet)
- Total gross floor space of all APS buildings: 86,310 square meters (959,000 square feet)
- Annual operating budget ~$100M/year or ~$1000/hr per station

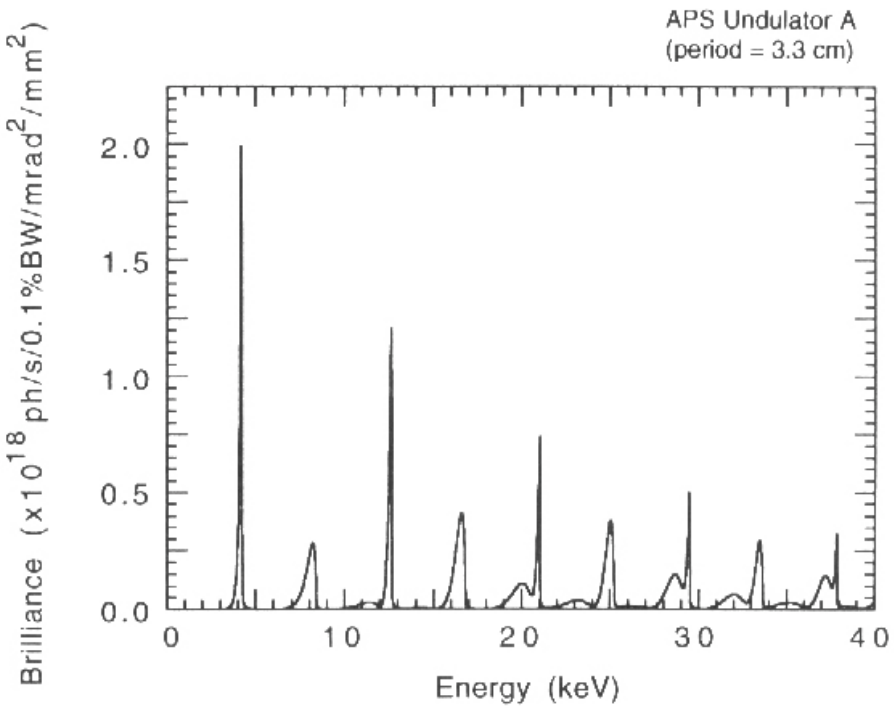
How X-Rays are Produced

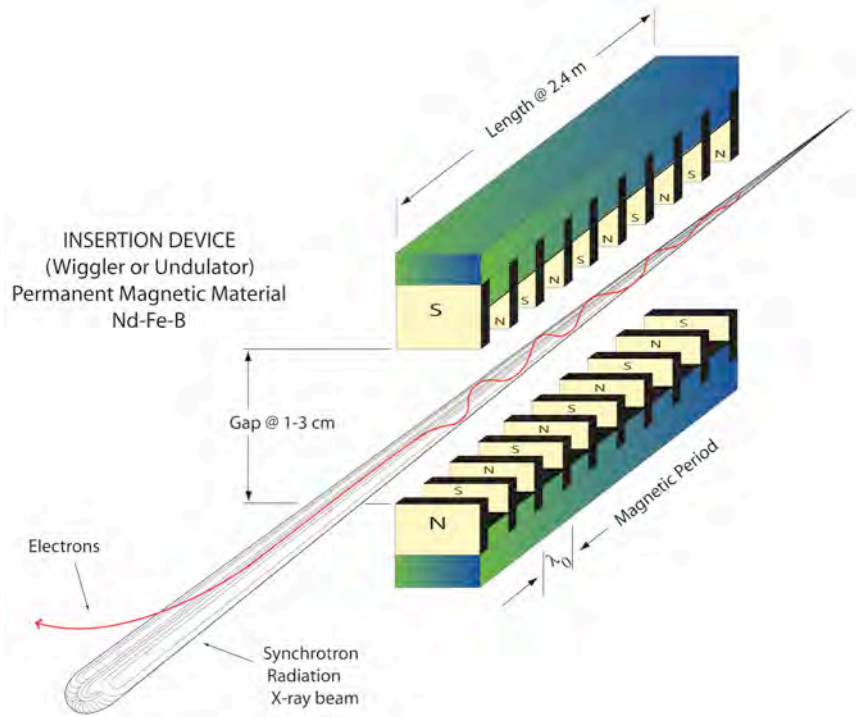
- Electrons injected into the 1104-m circumference storage ring orbit the ring more than 271,000 times per second.
- The beam of electrons is steered and focused by 1097 powerful electromagnets as it travels within a closed system of 240 aluminum alloy vacuum chambers.
- The beam decelerates at a rate of about 6 MeV per turn as it emits synchrotron radiation. This energy loss is replaced by the 352-MHz storage ring rf systems





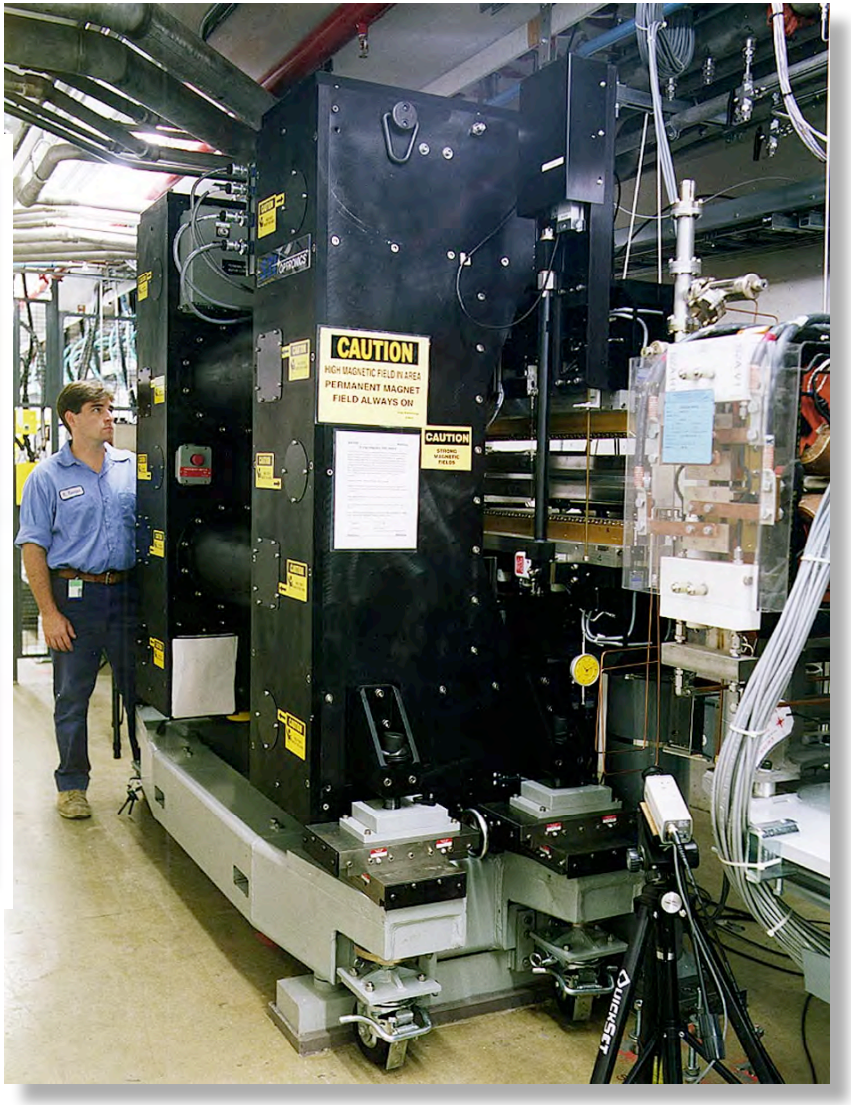
Advanced Photon Source Undulator A



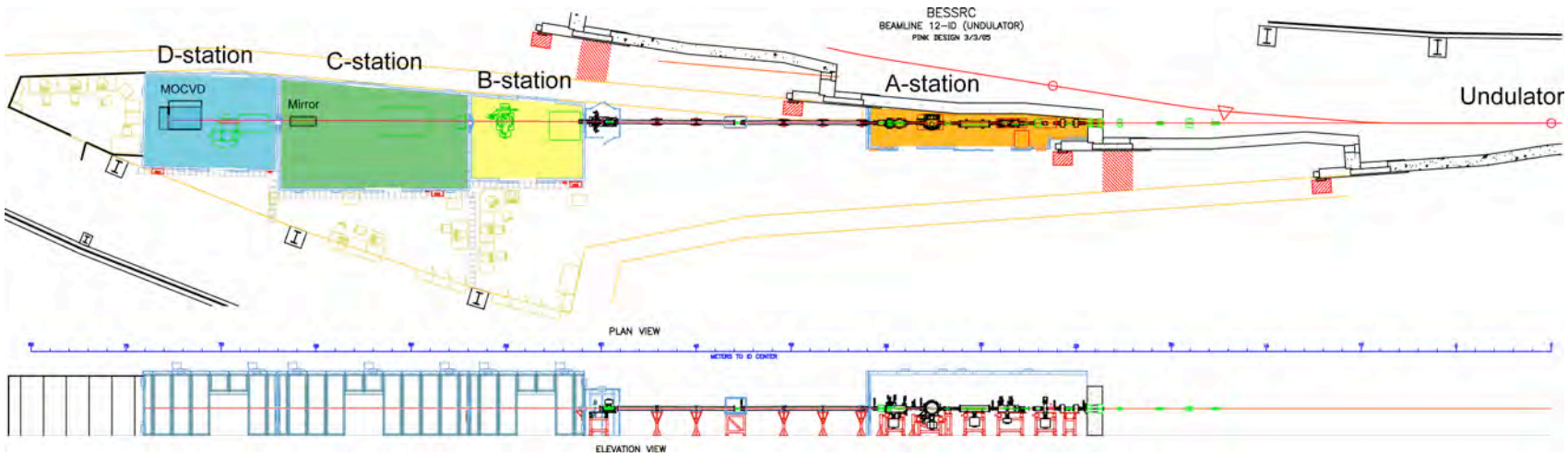


Typical Storage Ring Sector

Undulator Insertion Devices



Experimental Stations: APS Beamline 12-ID

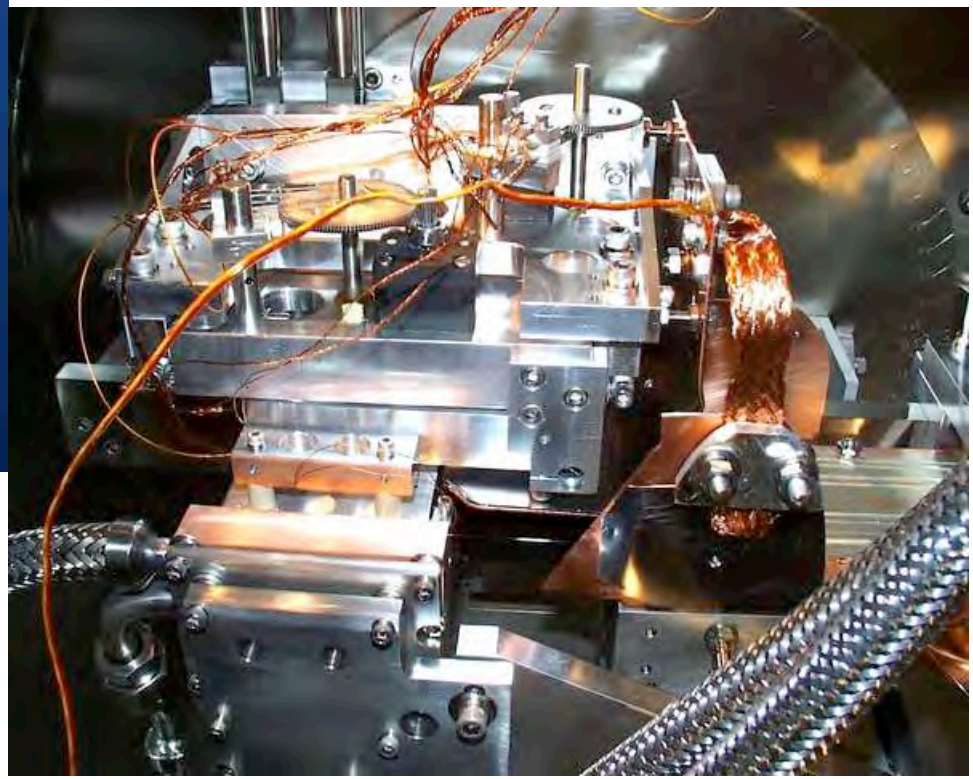


Source size: 50μm (vertical) x 300μm (horzontal)

Beamline optics: Pink-beam Pt-mirror at 4mrad (A-station)
Constant offset double-crystal Si(111) monochromater (A-station)
Focusing Pt-mirror (C-station)
Defining slits: 10μm vertical x 2mm horizontal (D-station)

Incident beam: 2×10^{11} photons/sec @ 28.3 keV

Monochromators for Wavelength Selection



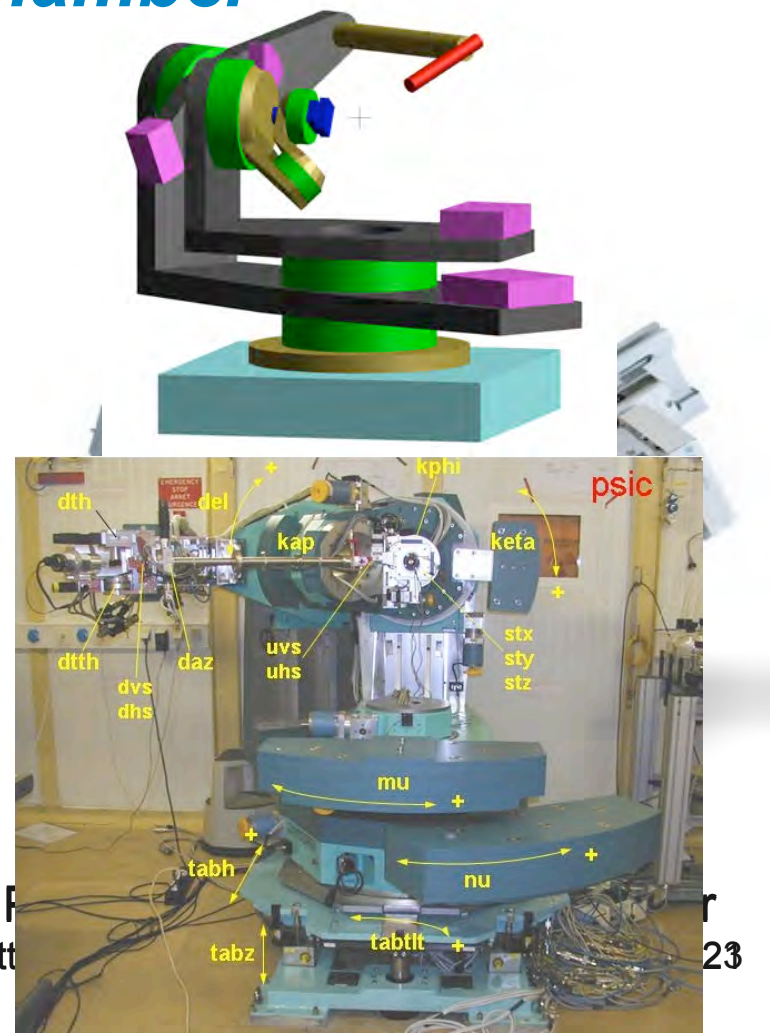
Monochromator used to select x-ray energy

In vacuum and LN_2 cooled

Important to align monochromator (angle) and undulator (gap) energy

Supporting and Manipulating the Sample and Processing Chamber

- Spectrometer must:
  - Provide many degrees of freedom for motion
  - Support the weight of the processing chamber
  - Provide open paths for incident and exit beams and for detectors, and for necessary connections to the chamber
- Motional degrees of freedom
  - Position and orient sample with respect to the x-ray beam (beam is asymmetric!)
  - Control many angles (more than the 3 Eulerian angles)
    - *Scattering conditions are underconstrained*
    - *Allows additional constraints to be imposed that facilitate different types of measurements!*
      - Fixed incidence angle
      - Fixed exit angle
      - Incidence angle = exit angle
      - Fixed azimuth



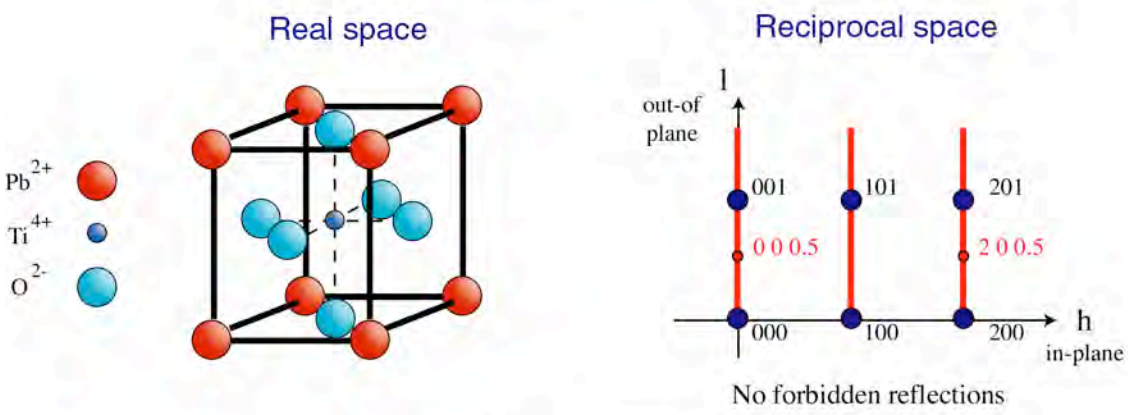
Huber 6-Circle Diffractometer at ESRF Beamline 32ID

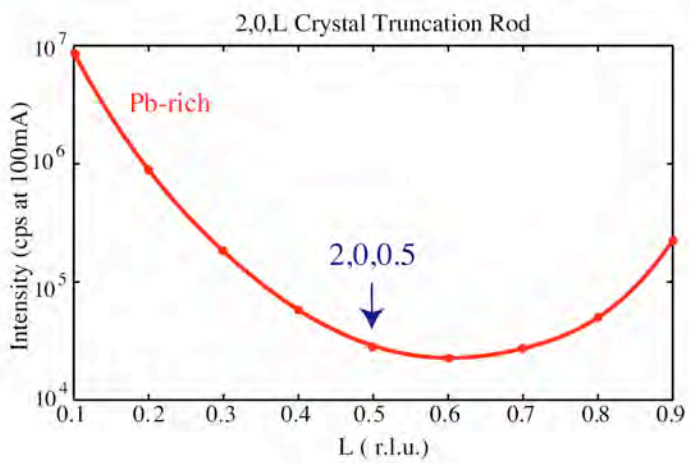
http://www.esrf.eu/UsersAndScience/Experiments/SurfaceScience/ID32/Beamline/diffractometer

Types of Synchrotron X-Ray Methods

- Scattering and Diffraction
  - Very high resolution
  - Penetration into sample can be tuned by the incidence angle
  - Tunable wavelength: anomalous scattering - element specific
  - High energy - penetrating
  - Dynamical scattering
  - Small-angle scattering
  - Inelastic scattering, magnetic scattering
- Spectroscopy
  - Penetration into sample can be tuned by the incidence angle
  - Fluorescence
  - X-ray absorption fine structure
- Microscopy
- Time-Resolved Measurements

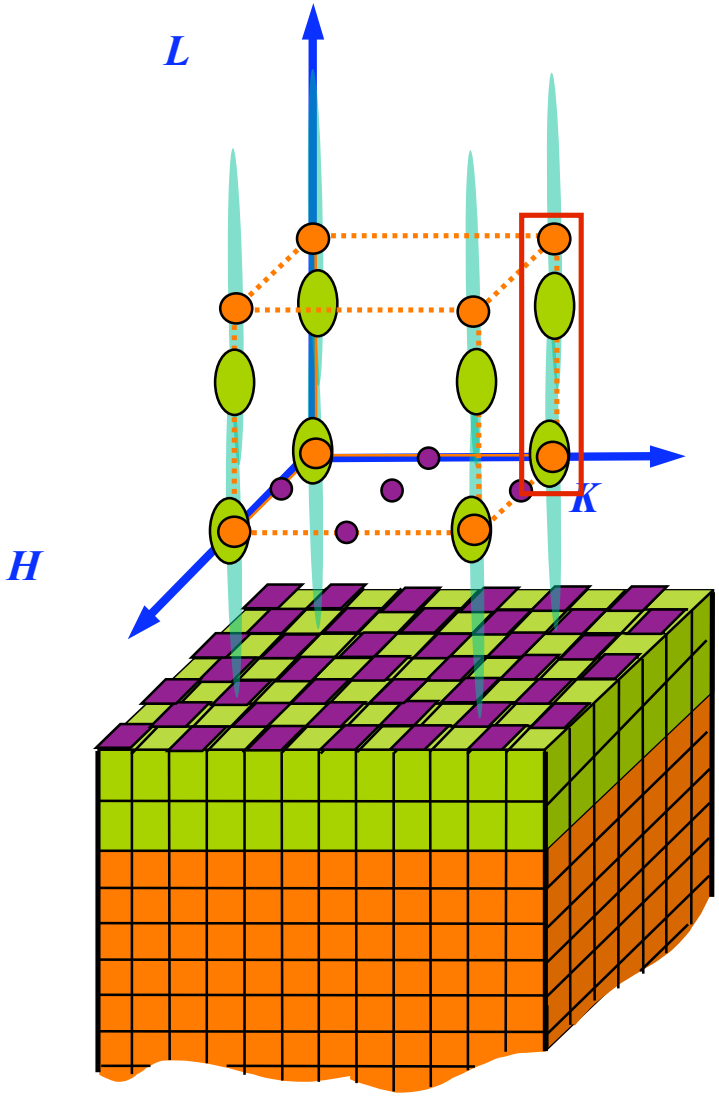
Crystal Truncation Rods (CTRs)

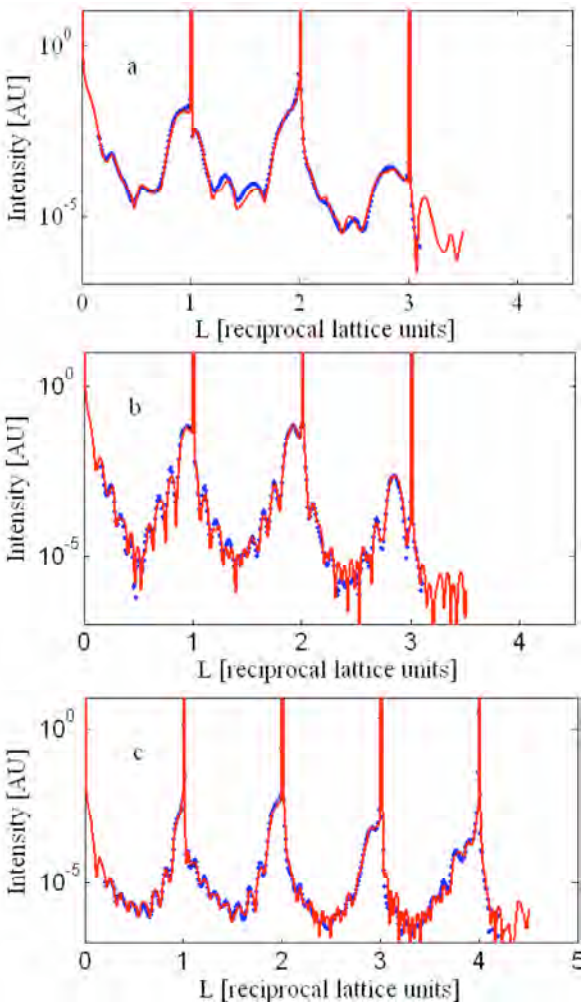




- Truncation of crystal at surface causes streaks of intensity to extend away from Bragg peaks, perpendicular to the surface

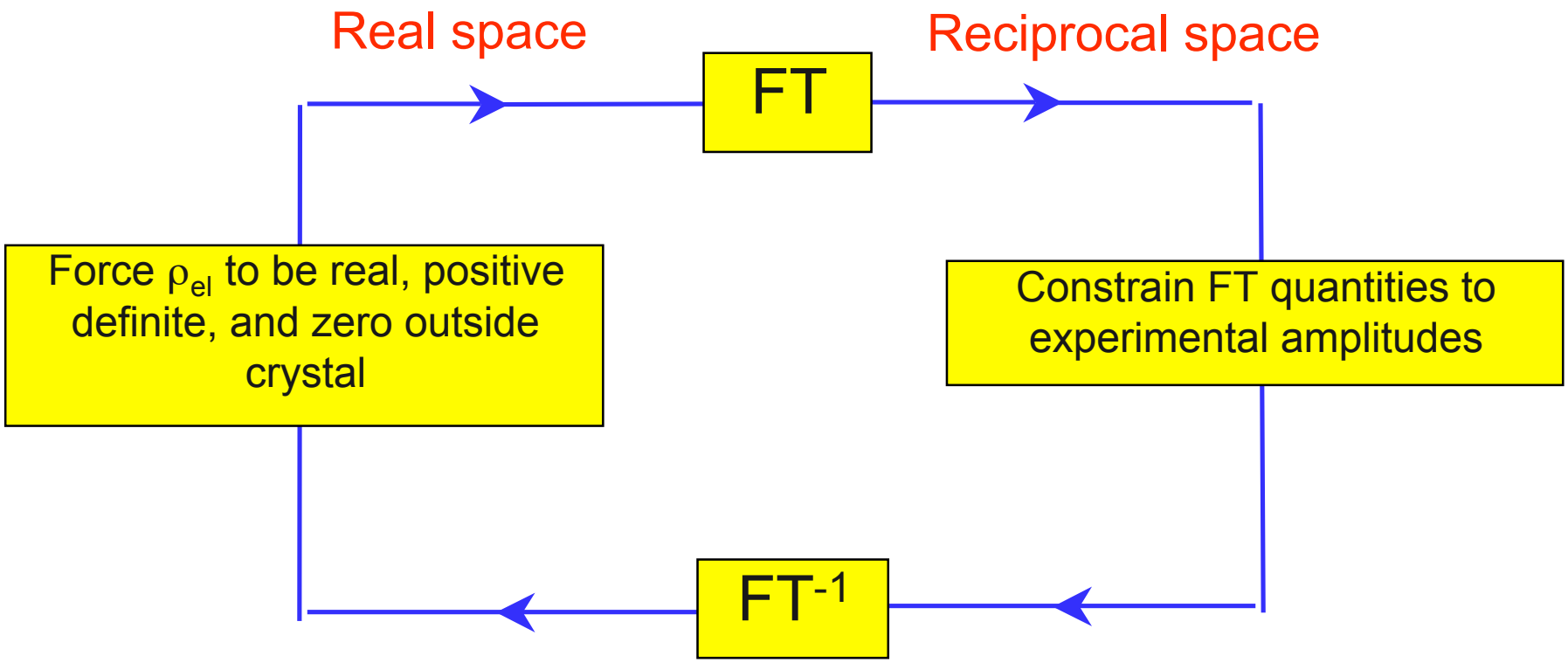
Measuring as much as you can in reciprocal space (oversample) to solve the real space structure





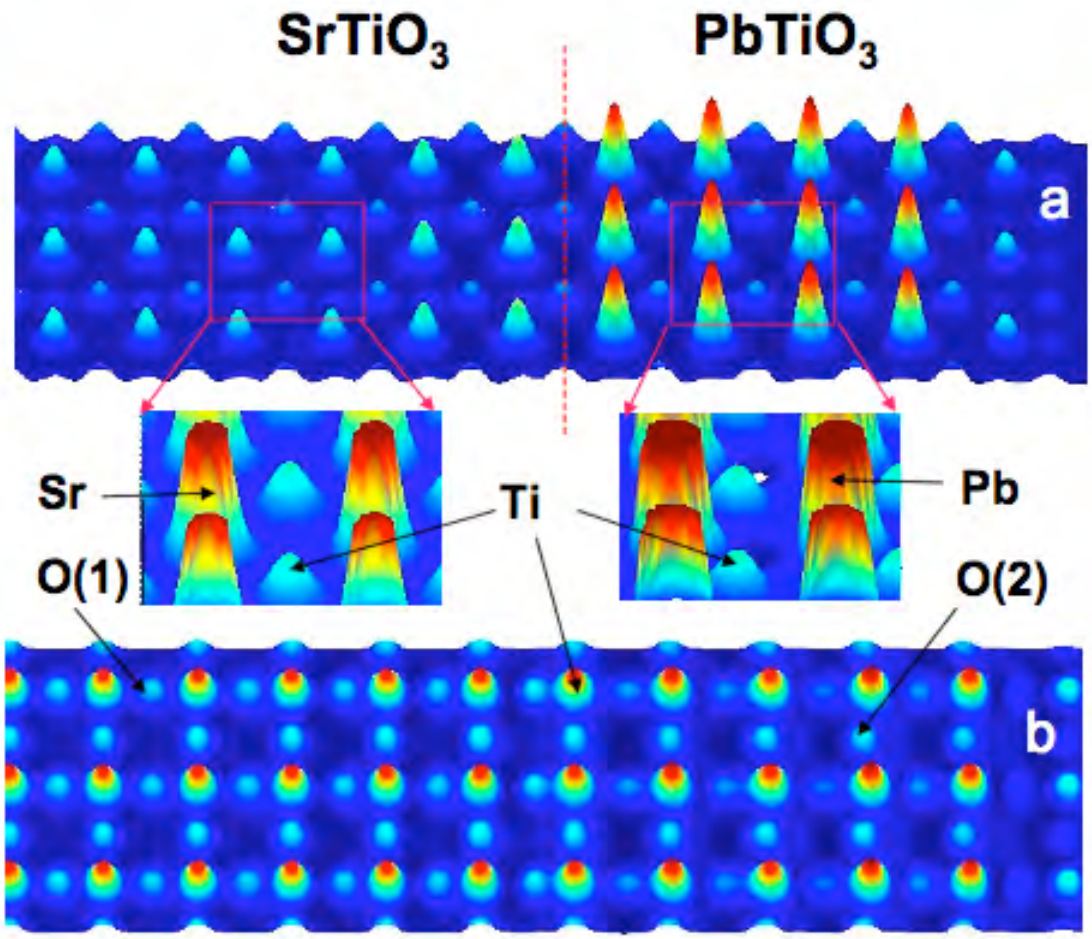
How do you solve the phase problem?

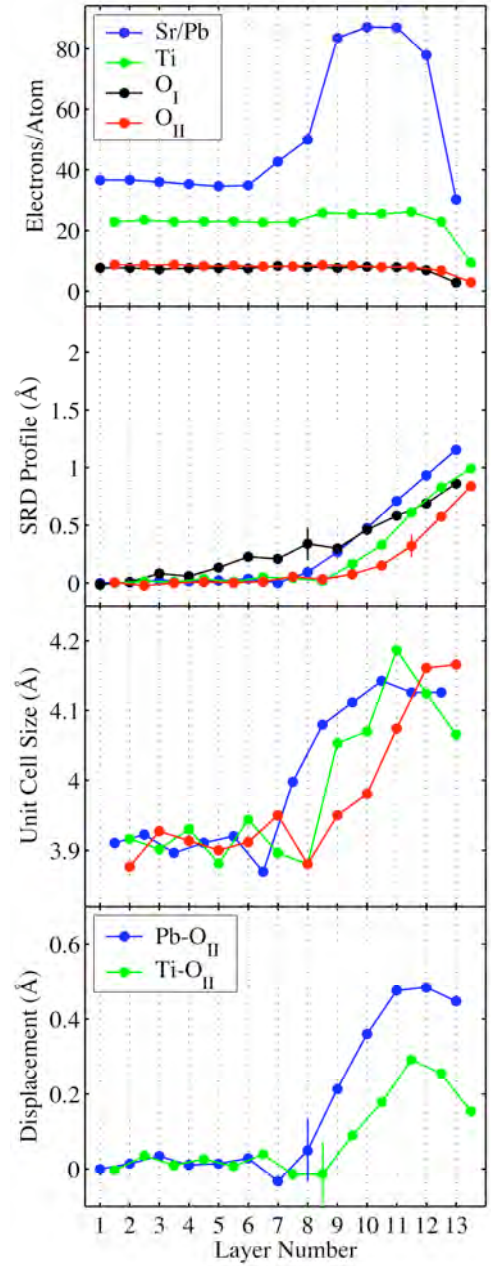
- Electron density (ρ_{el}) found by iterating between real and reciprocal space



- COBRA (Yacoby et al., J. Phys.: Condens. Matter **12,** 3929 (2000) and PRB **66,** 205311 (2002).
- Fienup algorithm (I. K. Robinson, D. K. Saldin, et al.)

Real space structure for $PbTiO_3/SrTiO_3(001)$





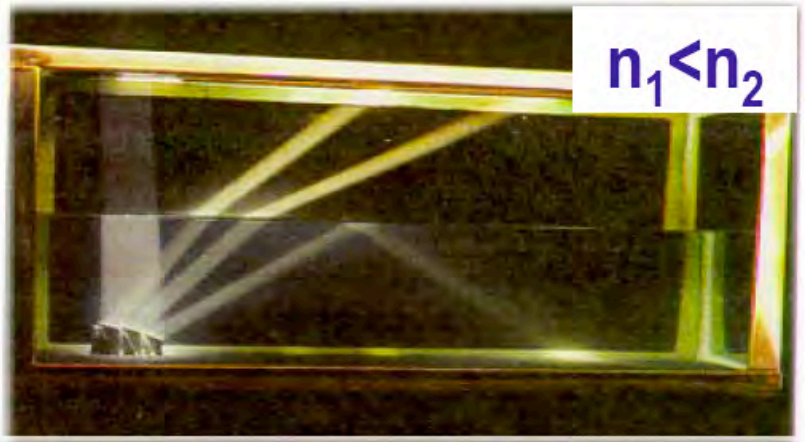
- Fong et al. PRB **71,** 144112 (2005).

Total External Reflection

X-Ray Reflectivity: Principle

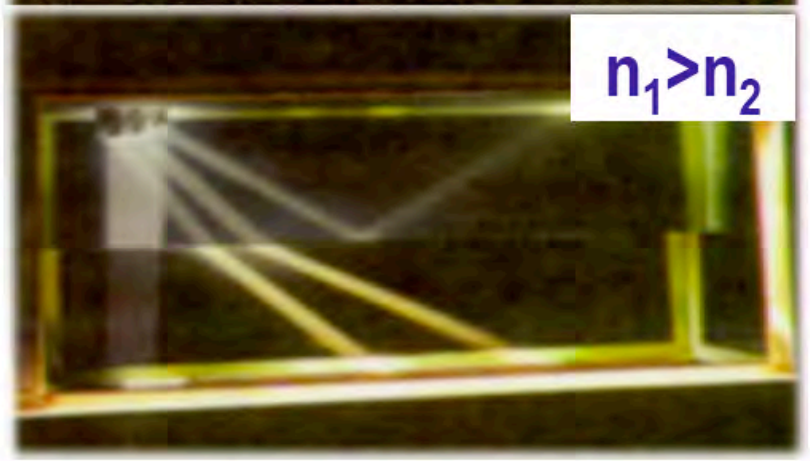
Visible Light Reflectivity: $\frac{n_1}{n_2}$

$n_2 > 1$



X-Ray Reflectivity: $\frac{n_1}{n_2}$

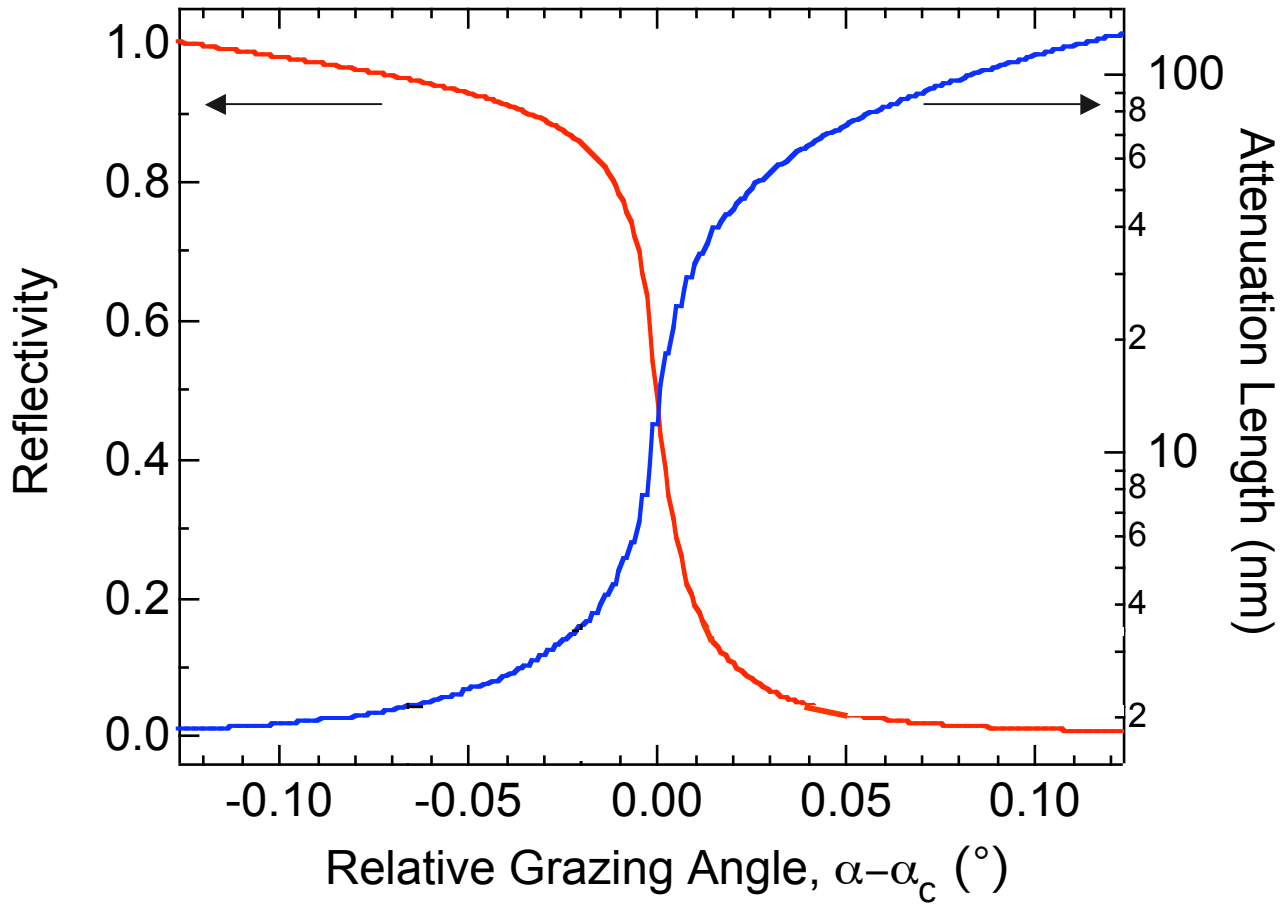
$n_2 < 1$



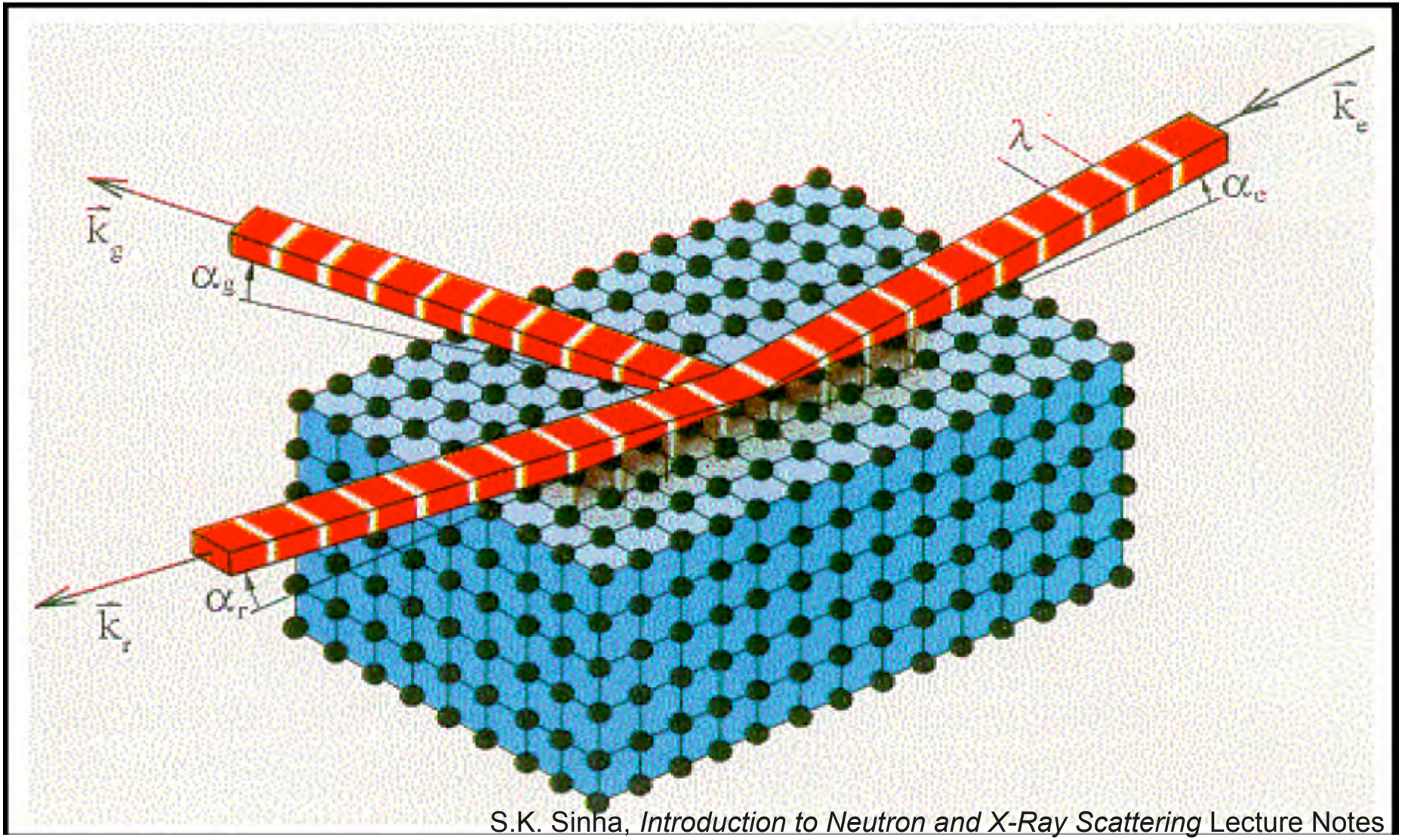
S.K. Sinha, *Introduction to Neutron and X-Ray Scattering* Lecture Notes

Reflectivity and Penetration Depth About the Critical Angle α_c

Calculation for $PbTiO_3$, 24keV x-rays,
using http://www-cxro.lbl.gov/optical_constants/mirror2.html



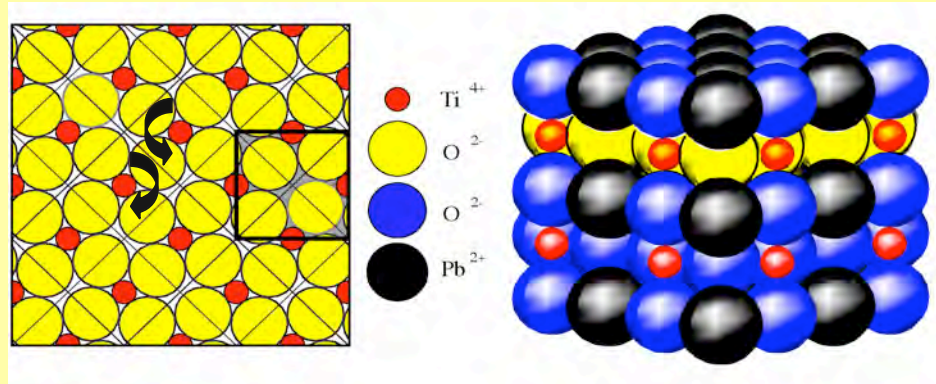
Grazing-Incidence-Diffraction



S.K. Sinha, *Introduction to Neutron and X-Ray Scattering* Lecture Notes

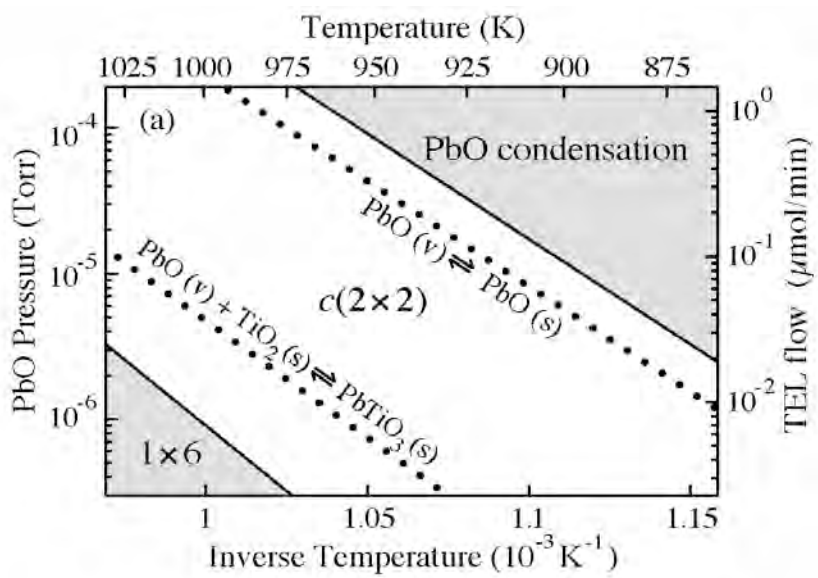
Measuring Surface Structure

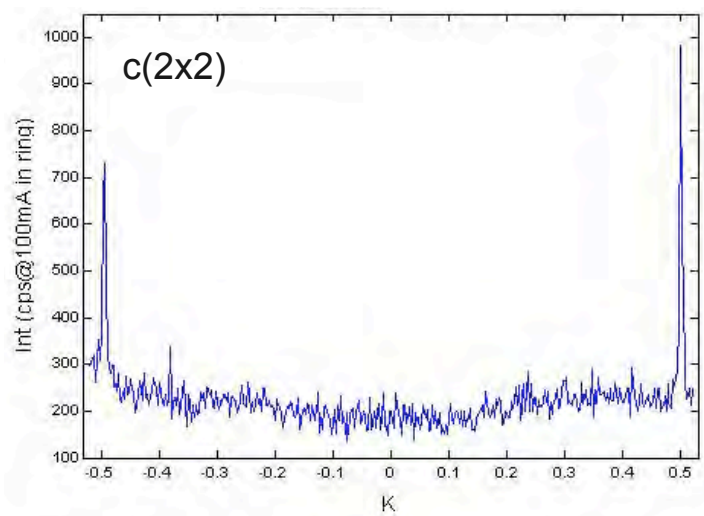
- PbO pressure controlled by changing precursor flows
  - PbO terminated surface (c(2x2) reconstruction)



PbO-terminated surface has an antiferrodistortive structure, obtained by 10° oxygen octahedral rotations.

A. Munkholm *et al.*, *PRL*, **88**, 016101 (2001)

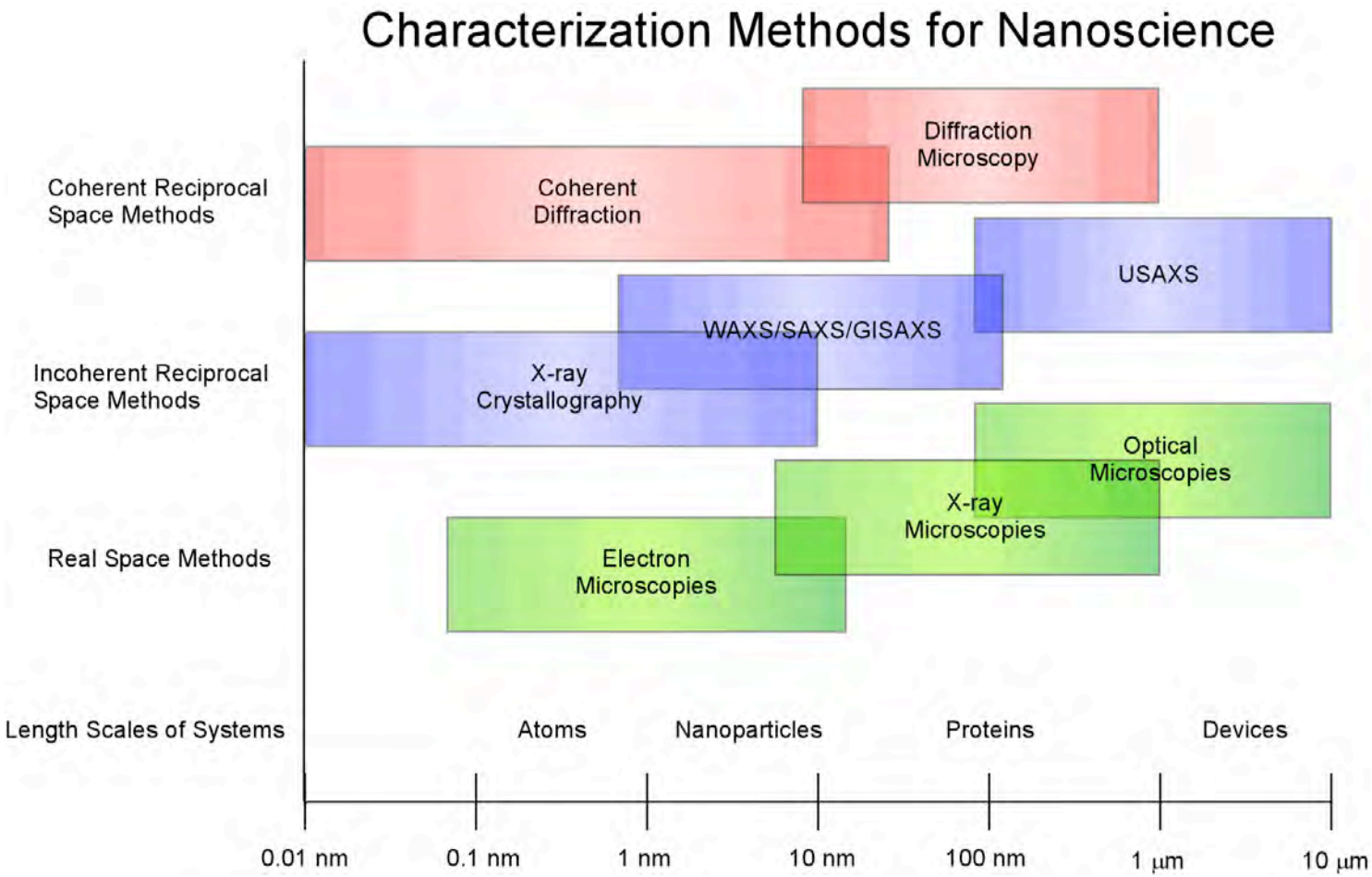


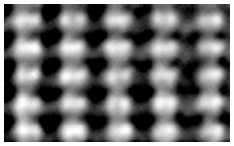


Does surface termination affect compensation and ferroelectric phase stability?

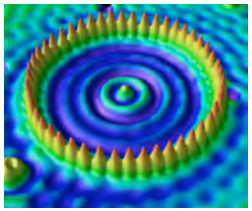
Why Build an X-ray Microscope?

- X-rays are penetrating and not charged!

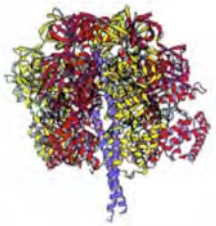




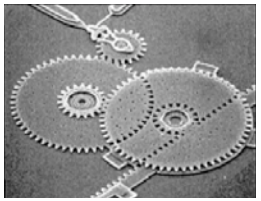
Atoms of silicon spacing 0.078 nm



Iron atom quantum corral 14 nm wide



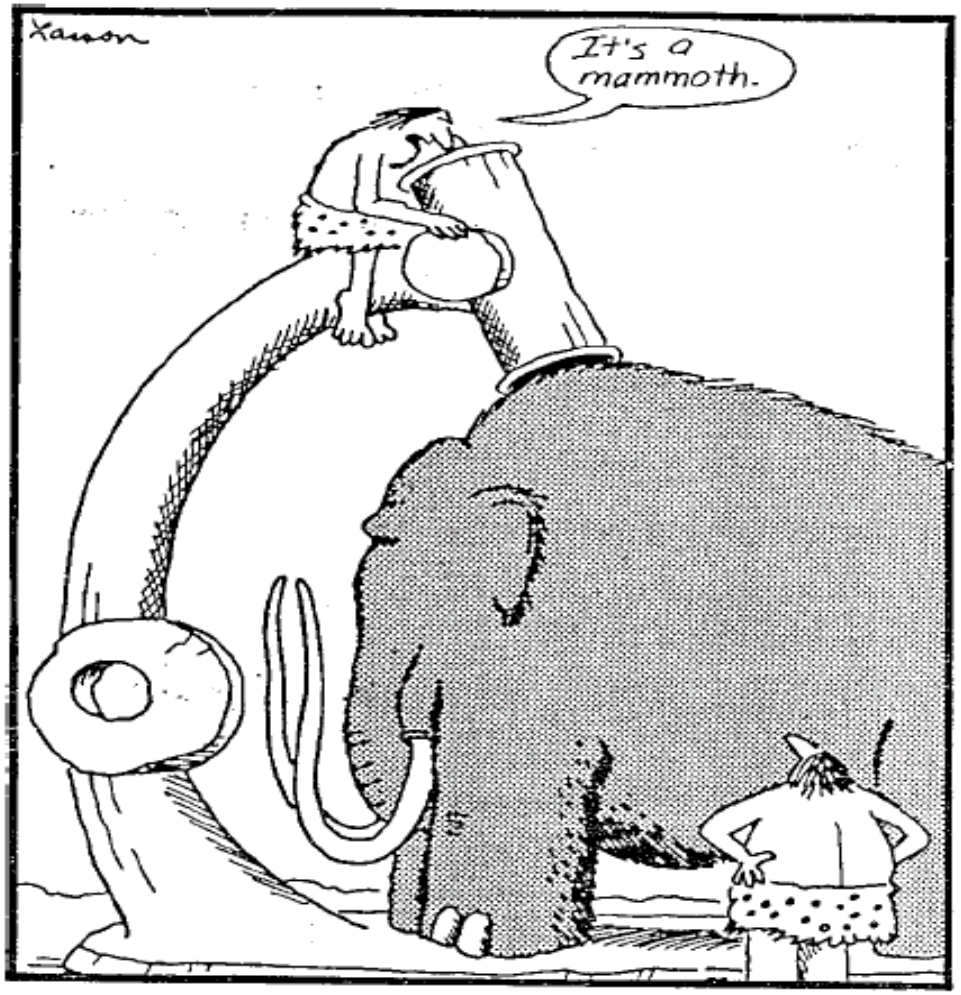
ATP synthase about 10 nm wide



MEMS devices 10-100 µm wide

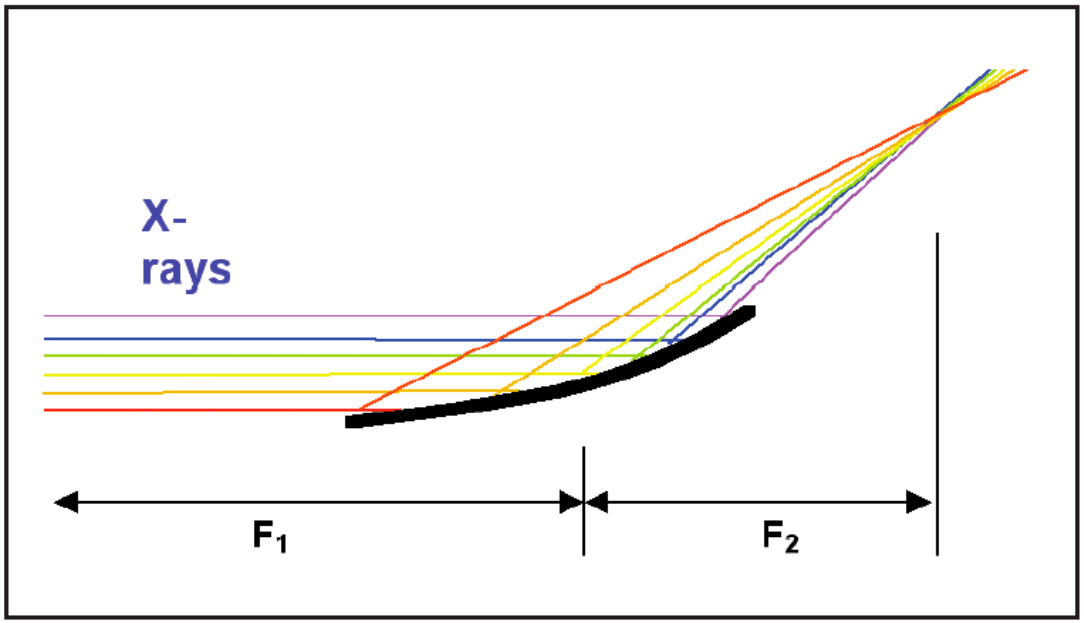
www.science.doe.gov/bes/scale_of_things.html

Seeing is believing….



Early microscope

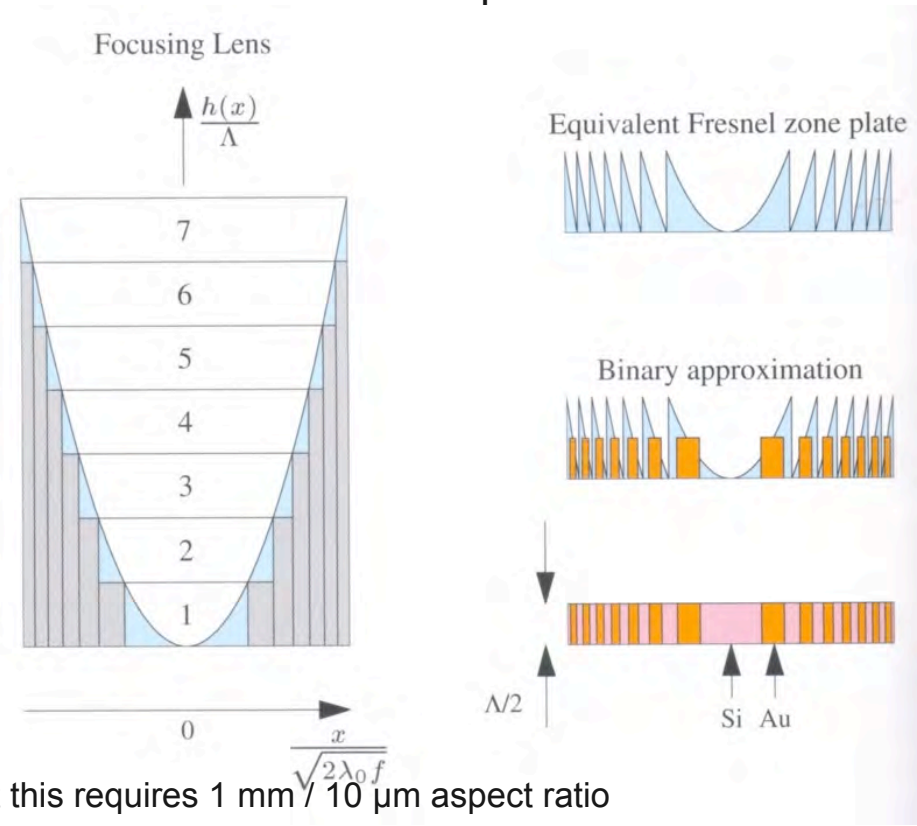
Microscopy: Focusing Mirrors

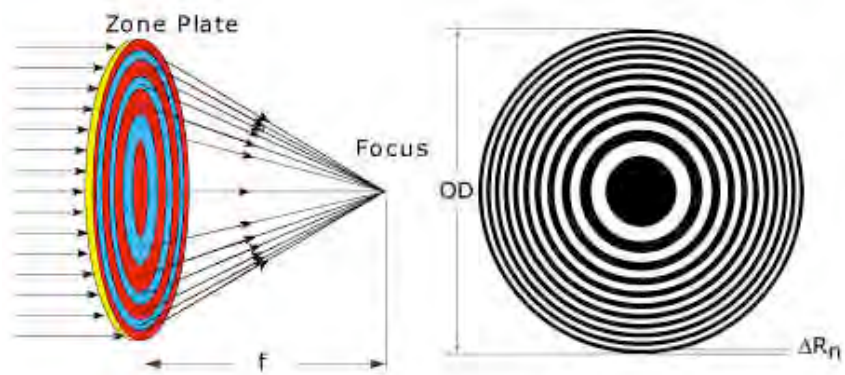


- A *bent flat mirror* is used to give to focusing (for instance in the vertical direction).
- The term *cylindrical mirror* is traditionally used to refer to a mirror not bent, but rather concave-figured in the other direction to focus the beam horizontally.
- Bending a cylindrical mirror along the long axis produces a *toroidal mirror* that focuses in both directions.
- The special case where you have two flat mirrors, one reflecting vertically, the next reflecting horizontally and both independently bendable is called a *Kirkpatrick–Baez pair*.

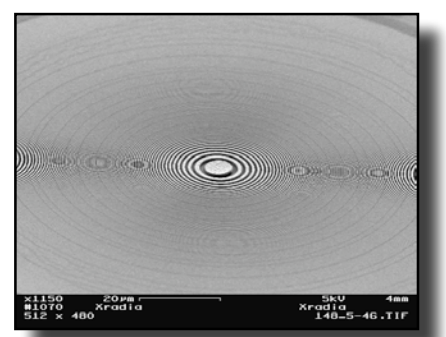
Probing local structure with lenses

- The above dealt with ensemble averages of thin films or nanoparticles on a substrate
  - x-ray beam is focused vertically but wide (~ 2mm) horizontally (larger than coherence length)
  - averages the scattering unit (ex., the average unit cell in the horizontal dimension)
- What if you don't want the average information but local information (e.g., microscope)?
  - Fresnel zone plate





- OD ~ 100 μm
- now can resolve to ~ 30 nm

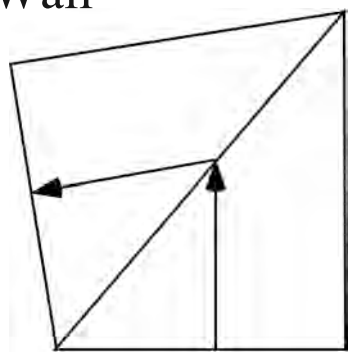


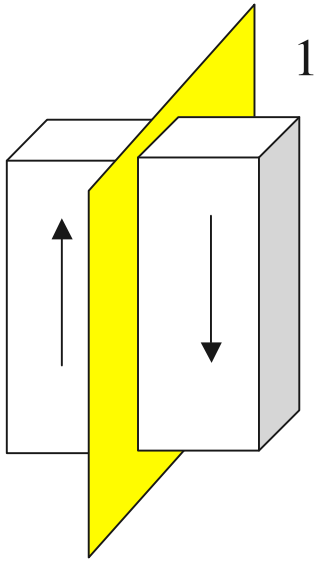
- but this requires 1 mm / 10 μm aspect ratio

Domains

- Domains are different orientations of the ferroelectric phase with respect to the higher symmetry prototype phase
- Domains separated by domain walls
- Domains may be ferroelectric/ferroelastic (polarization and shape change across domain wall) or purely ferroelectric (polarization change only)

90° Ferroelastic/Ferroelectric Domain Wall





180° Ferroelectric Domain Wall

Calculating Intensities

$$f = f_o + \Delta f' + i\Delta f''$$

$$F_{\Delta\mathbf{k}} = \sum_j f_j e^{-i\Delta\mathbf{k}\cdot\mathbf{r}_j}$$

$$I_{\Delta\mathbf{k}} = |\psi_{\Delta\mathbf{k}}|^2 \propto |F_{\Delta\mathbf{k}}|^2$$

- Friedel's Law: Bragg reflections related by inversion through the origin have equal amplitude and opposite phase.

- **However,** Friedel's Law is broken by anomalous scattering, i.e. when the imaginary part of f is non-negligible.

Imaging Polarization Using X-Rays

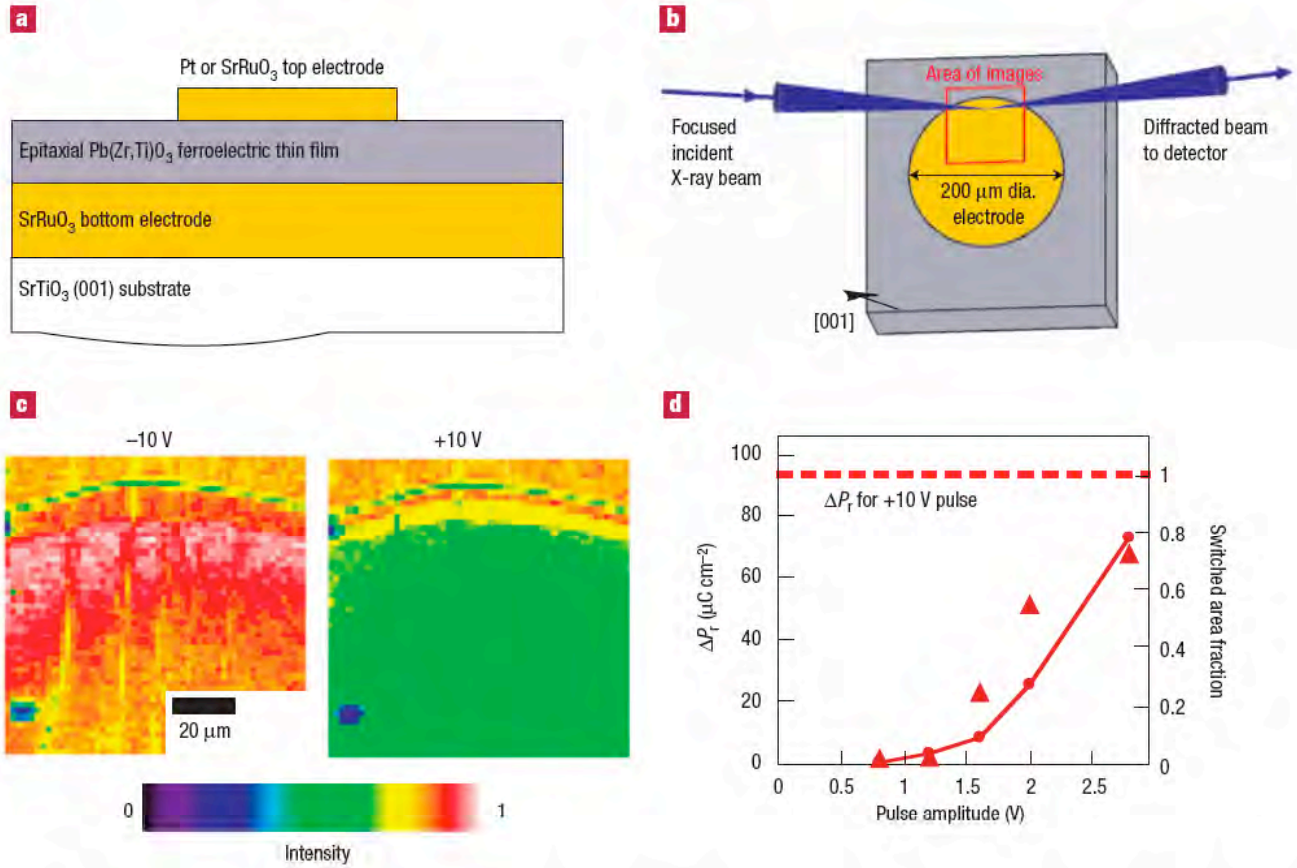
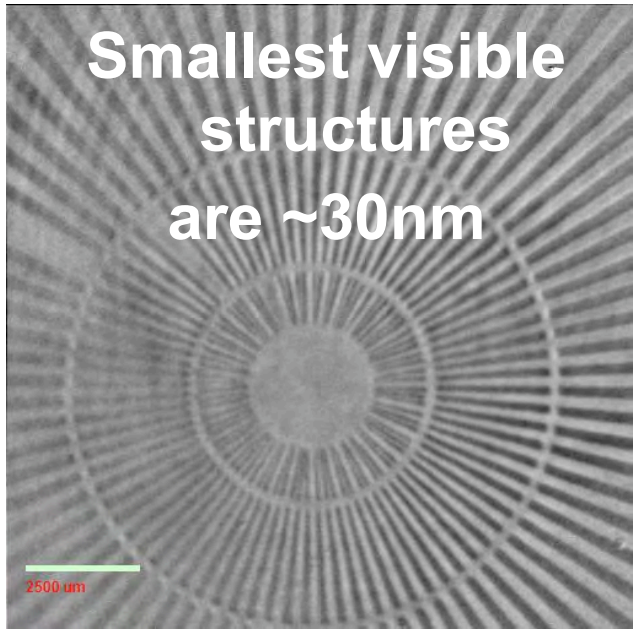


Figure 1 Polarization switching in a PZT thin-film capacitor. a, Epitaxial ferroelectric capacitor fabricated on an (001) oriented $SrTiO_3$ substrate. **b**, A diagram of the synchrotron X-ray microdiffraction experiment. **c**, Real-space images of the intensity of the (002) reflection of $Pb(Zr,Ti)O_3$ following −10 V and +10 V pulses to the bottom electrode of the capacitor device. The intensity of the X-ray reflection varies with the local ferroelectric polarization, and changes by 30% upon polarization switching. Each image required ~30 min to acquire. **d**, The area of the region in which the intensity has changed (triangles) and the total switched polarization ΔP_r (solid line) are proportional, and provide independent observations of the switching process. There was no change in the intensity of the (002) reflection in the area of the PZT film not covered by the top electrode.

Do, Evans, et al., Nature Materials **3**, 365 (2004)

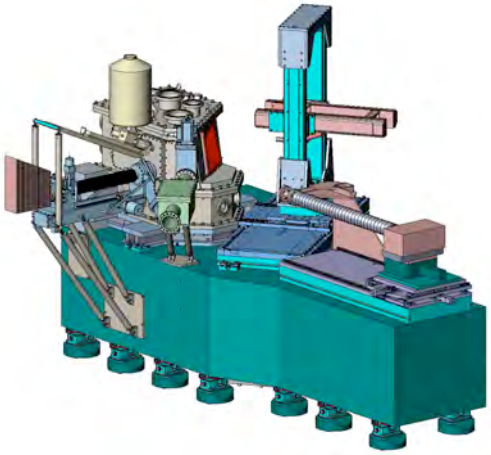
CNM & APS Partnership at Sector 26-ID
The Hard X-Ray Nanoprobe

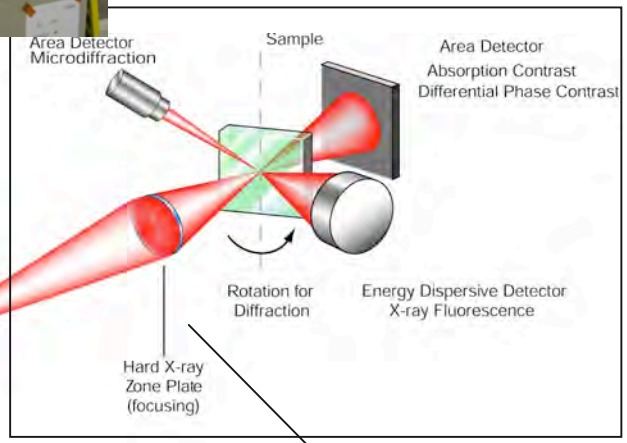
- Unique instrument to study individual nanostructures
- Quantitative structure, strain, orientation imaging
- Sensitive trace element and chemical state analysis
- Ability to penetrate overlayers, environments, fields
- 30 nanometer spatial resolution

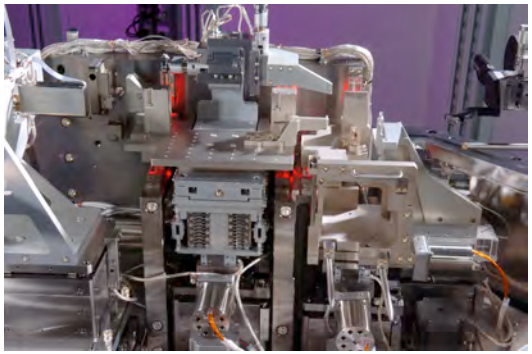


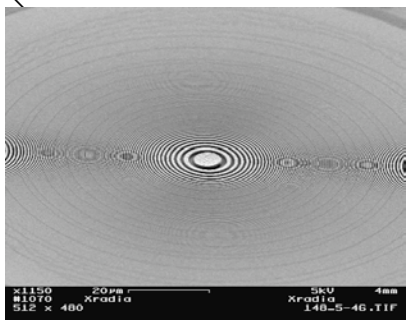
Jointly staffed and managed by CNM & APS

The World's Premier Hard X-ray Nanoprobe: 30 nm and Beyond





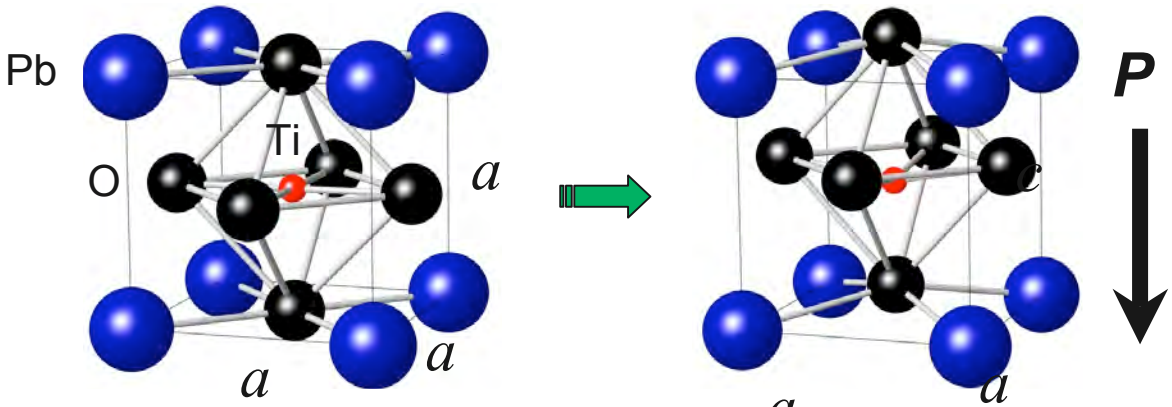




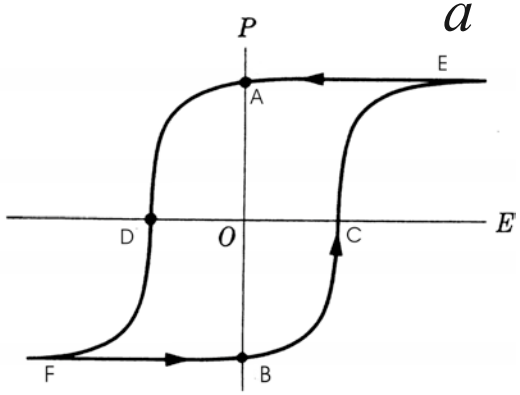
Xradia Zone Plate and instrument (CNM/APS)

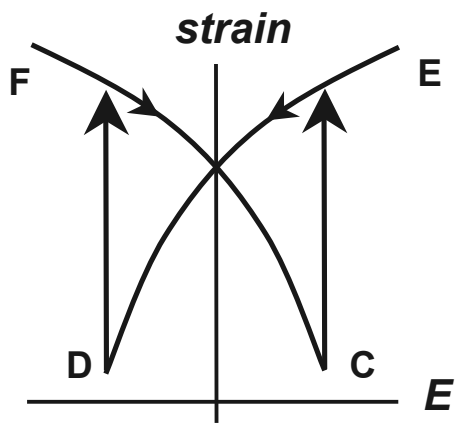
Background: Ferroelectricity

Above T_c: paraelectric 492°C Below T_c: ferroelectric



Ferroelectric Transition
$PbTiO_3$-Based System





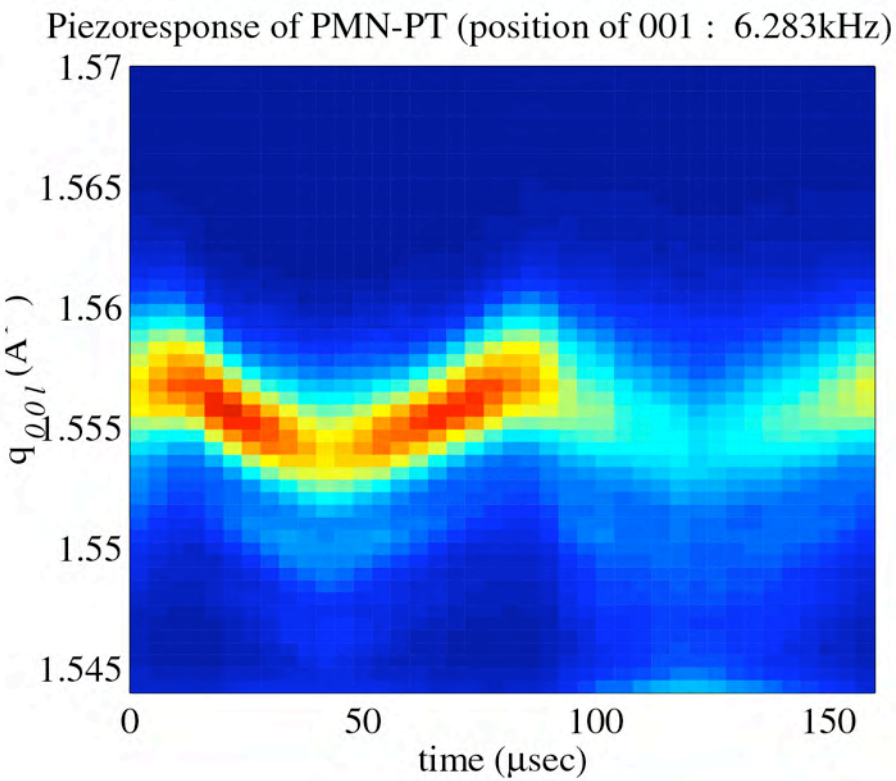
- The strain can be linked to the polarization through LGD phenomenological theory

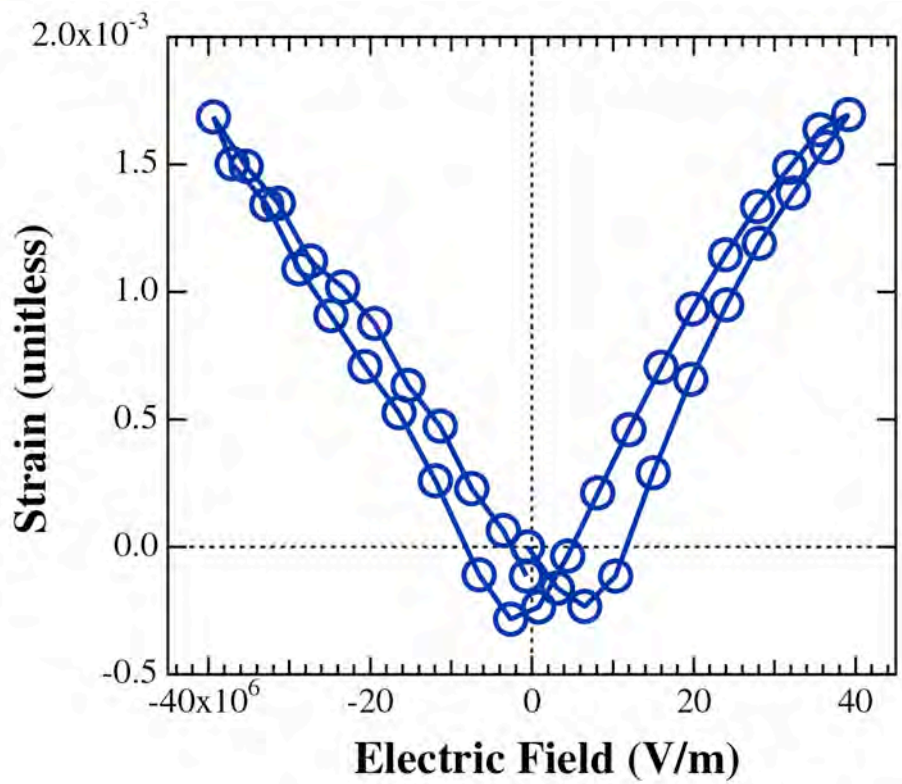
For c-oriented monodomain

$$P = \left(\frac{x - x_0}{Q_{11} - 2 s_{12} Q_{12} / (s_{11} + s_{12})} \right)^{1/2}$$

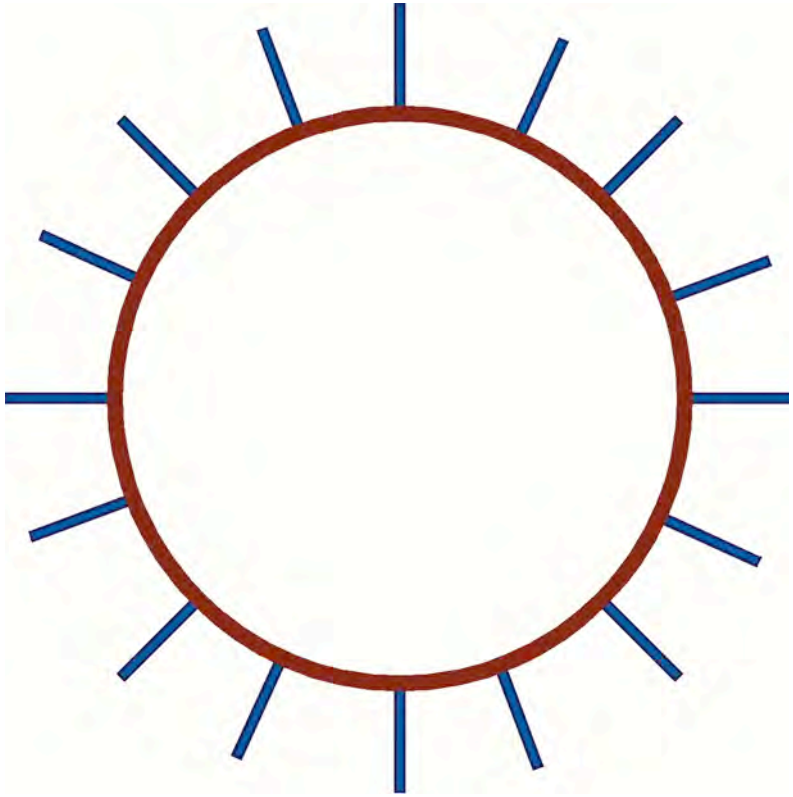
Time-Resolved Synchrotron X-Ray Scattering

- Data taken on 250 nm PMN-PT film (PT≈30-35%)



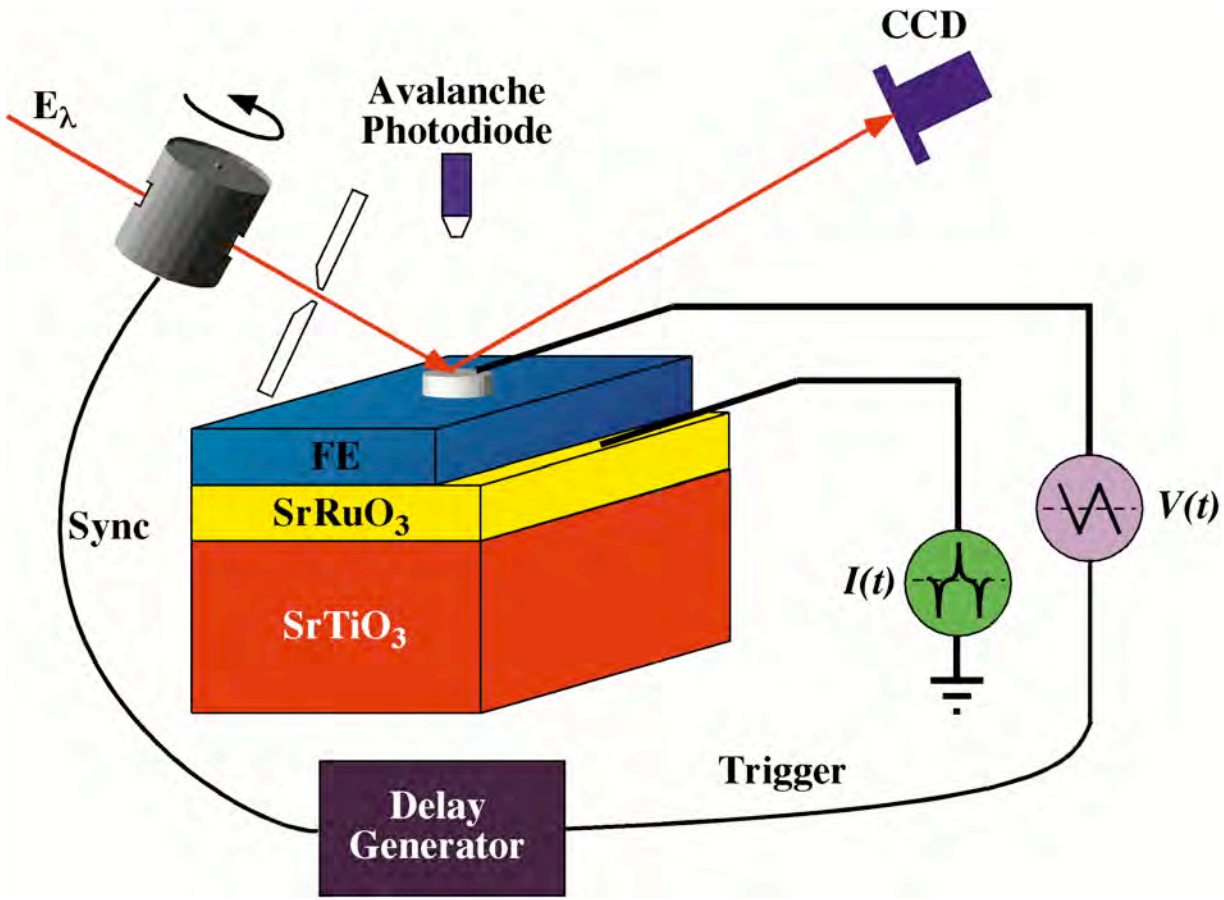


Storage Ring Filling



- X-rays generated by electron bunches circulating around ring with 3.68μs period
- Bunch width is about 100ps

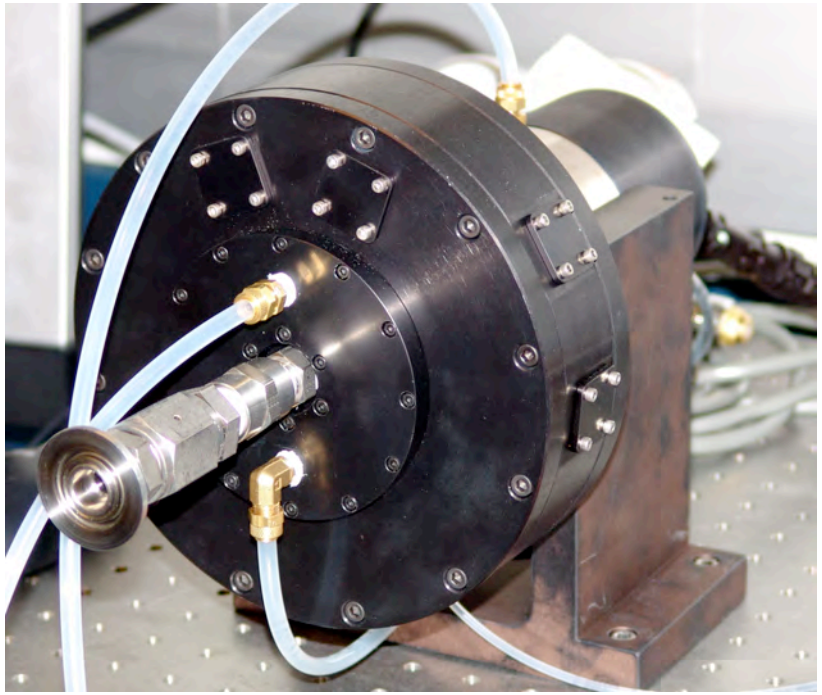
Time Resolved, Stroboscopic Methods



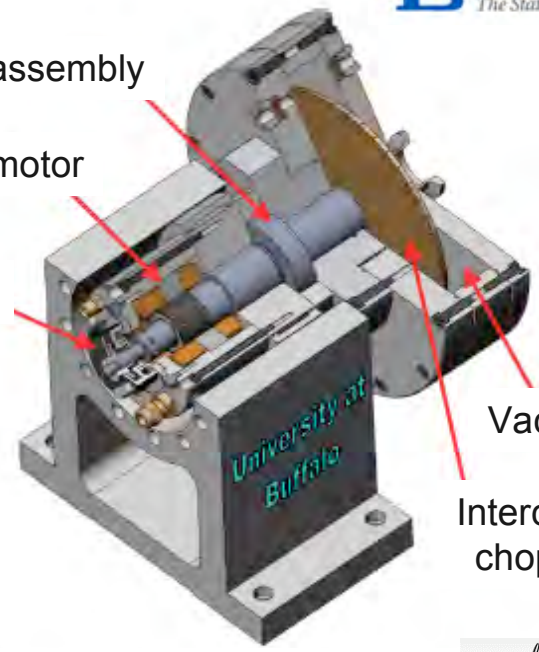
- At each voltage, collect all 2θ
- Utilizes rocking curve of sample to "scan" θ

Chopper

- Ability to select individual ~ 100 picosecond pulses from the storage ring fill pattern (during special asymmetric fill modes) for time-resolved studies

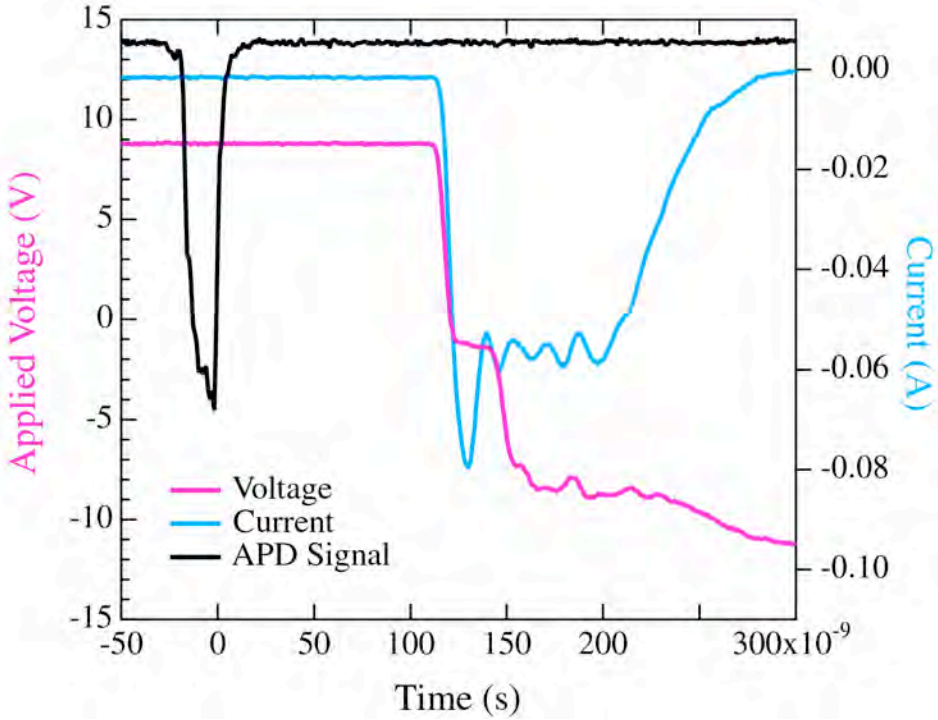


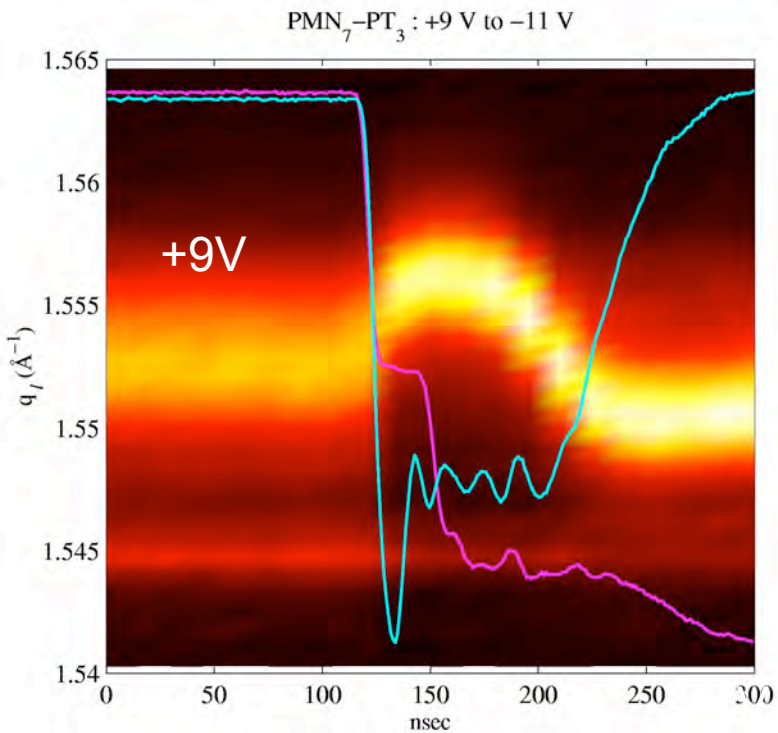
University at Buffalo
The State University of New York



Professional Instruments company

PMN_7-PT_3 Response to a Step Voltage

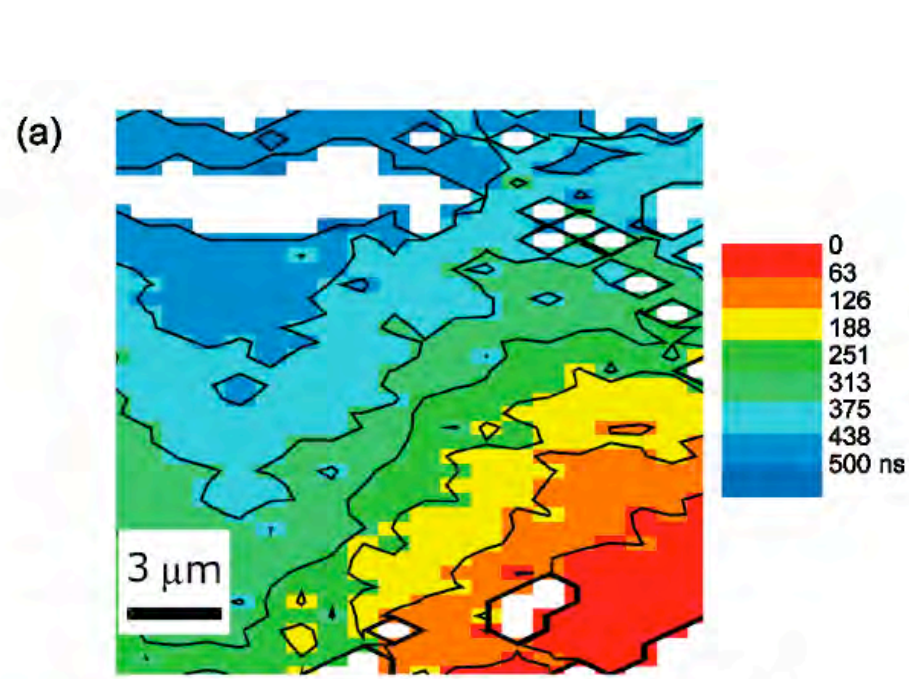




- $\Delta P \sim 80 \mu C/cm^2$; agrees well with 100kHz hysteresis loop
- RC time constant of circuit ~ 15ns, given current device size

Measuring Domain Wall Velocity

- Grigoriev, et al., Phys. Rev. Lett. **96**,187601 (2006)
- APS Sector 7, 10keV, 115nm spot



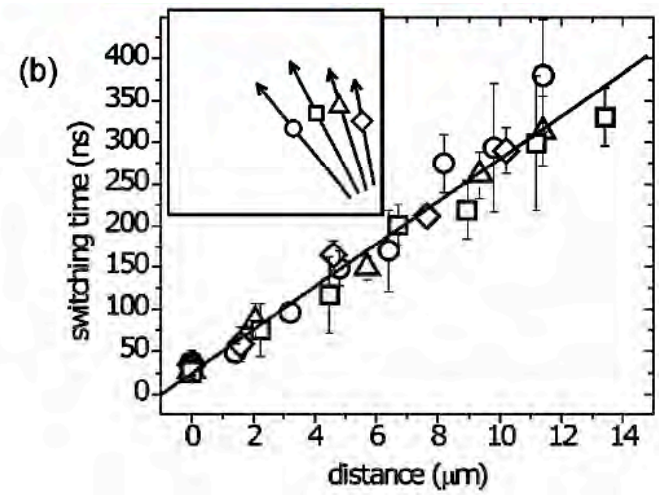


FIG. 4 (color). (a) Polarization switching times in a $20 \times 20\ \mu m^2$ area of the thin film capacitor. The earliest and latest switching times are red and blue, respectively. It was not possible to unambiguously assign switching times to the white areas. (b) Polarization switching time as a function of a distance along the arrows shown in the inset. The solid line is a linear fit giving a $40\ m\,s^{-1}$ domain wall velocity. The error bars correspond to the uncertainty associated with assigning the switching time.

Overview

- Introduction to and motivation for utilizing synchrotron x-rays
- **Size effects on the ferroelectric phase transition in $PbTiO_3$ and relationship to 180° domain structure**
- Surface interactions with the gas phase and relationship to polarization state

Ferroelectric Physics: The Ferroelectric Size Effect

- Ultimately interested in 3D structures
- Problems:
  - Difficult to change size without changing other parameters
    - *Domain structure*
    - *Stress*
    - *Chemistry, defect content*
  - Two correlations to consider
    - *Longitudinal*
    - *Transverse*
  - Hard to characterize
    - *Surface structure*
    - *Particle shape*
    - *Size distribution*
- Use coherent epitaxial ultrathin films as a model system with precise control of:
  - stress/strain
  - chemistry
  - electrical boundary conditions

Tybell et al. [*Appl. Phys. Lett.* **75**, 856 (1999)] observed stable ferroelectricity in 10 unit cells thick (4 nm) $Pb(Zr_{0.2}Ti_{0.8})O_3$ films on $SrTiO_3$

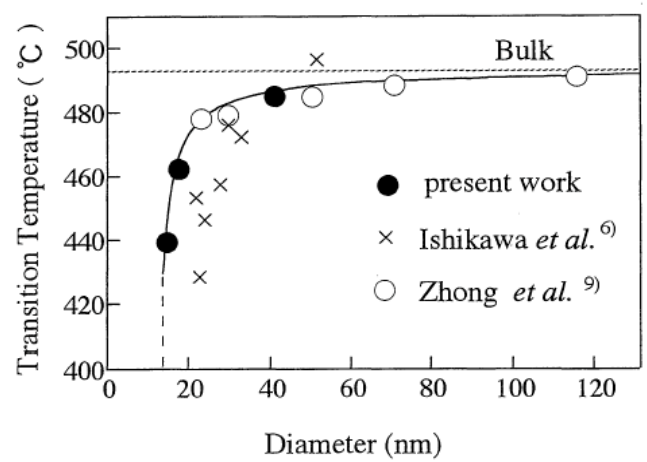
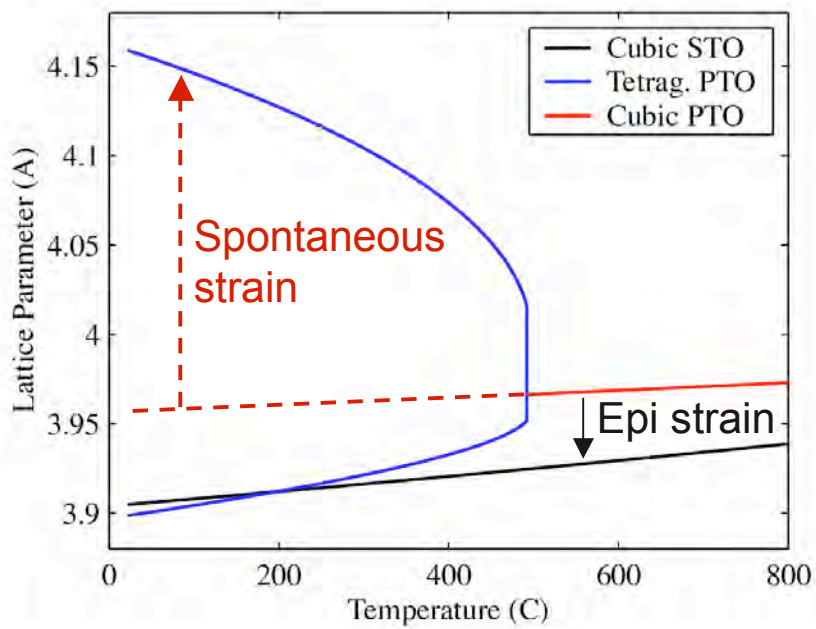
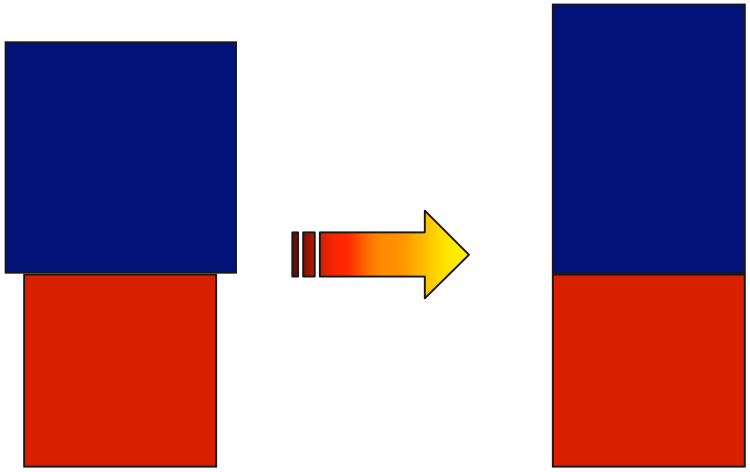


Fig. 4. Shift of T_c as a function of particle size. ●: present work, ×: our previous work,[6] ○: Zhong *et al.*[9]

Ishikawa, et al., JJAP **35**, 5196 (1996): $PbTiO_3$ D_{crit} = 10.7nm

Spontaneous Strain, Epitaxial Strain

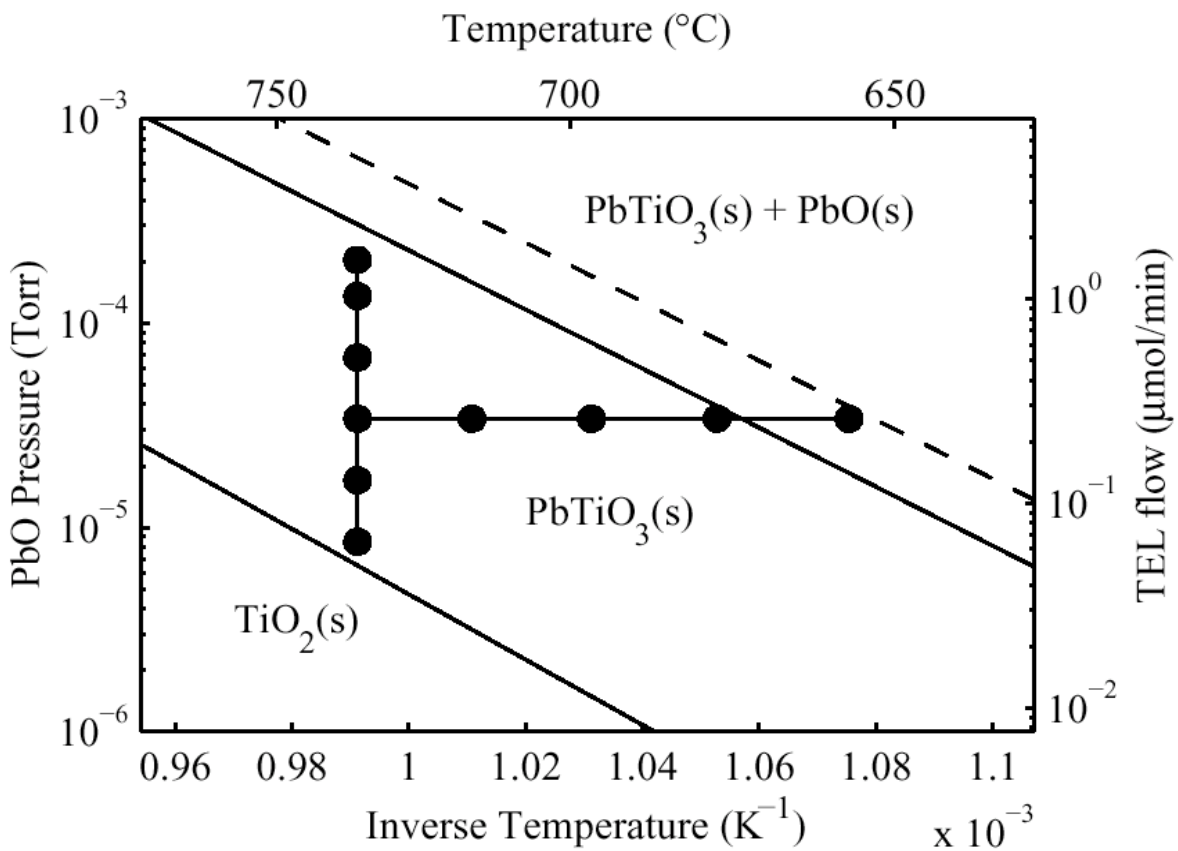




- Take reference frame for describing the phase transition as the fictitious cubic lattice parameter
- Spontaneous strains occur at zero stress through strain-polarization coupling

Model System: Epitaxial $Pb(Zr_xTi_{1-x})O_3$ on $SrTiO_3$

- Large polarization, spontaneous strains and atomic displacements
- Easy to explore interaction between interfaces & spontaneous polarization.



Growth using:

Tetraethyl Lead (TEL)

Titanium Isopropoxide (TIP)
Titanium tert-Butoxide (TTB)

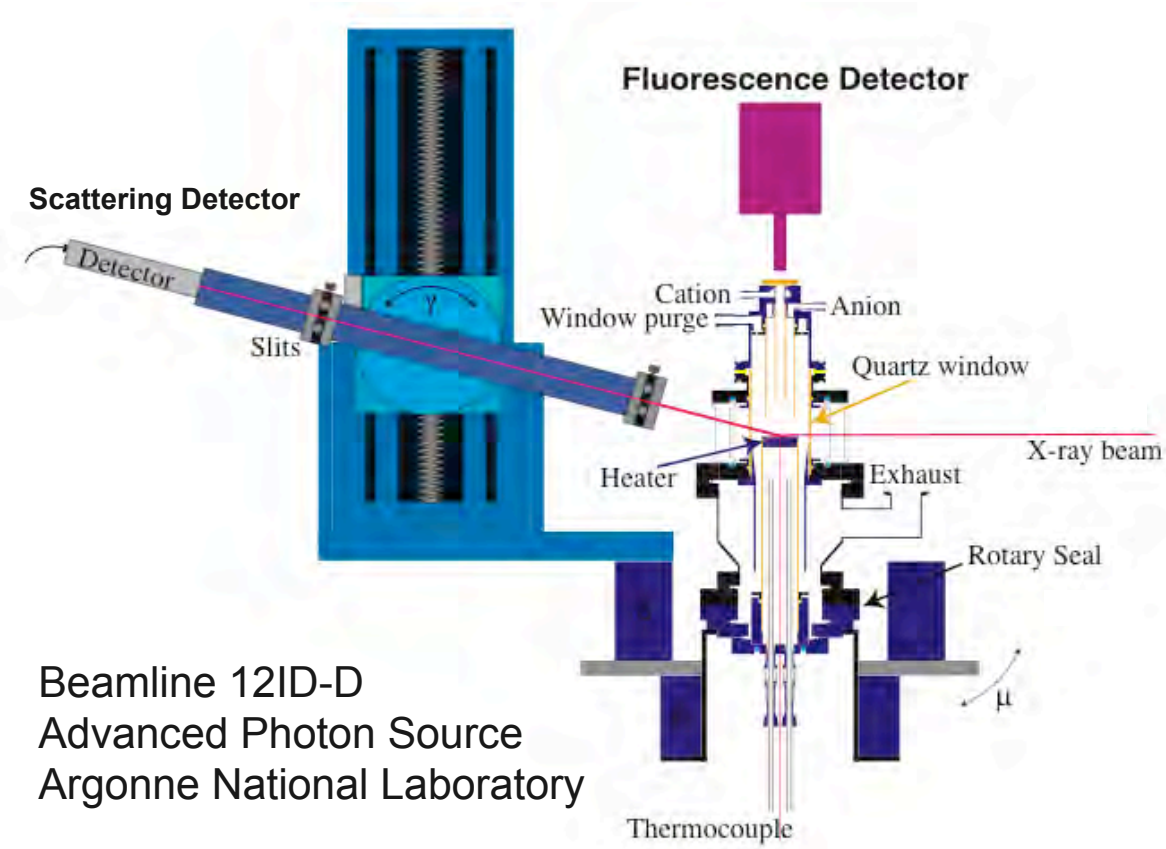
Zirconium tert-Butoxide (ZTB)

10 Torr chamber pressure

600-800 °C growth temperature

After C.D. Theis, at al., Thin Solid Films **325**, 107 (1998)
Phase boundaries calculated from I. Barin, *Thermochemical Data of Pure Substances*, 3rd Edn., VCH, New York, 1995

Experimental Approach



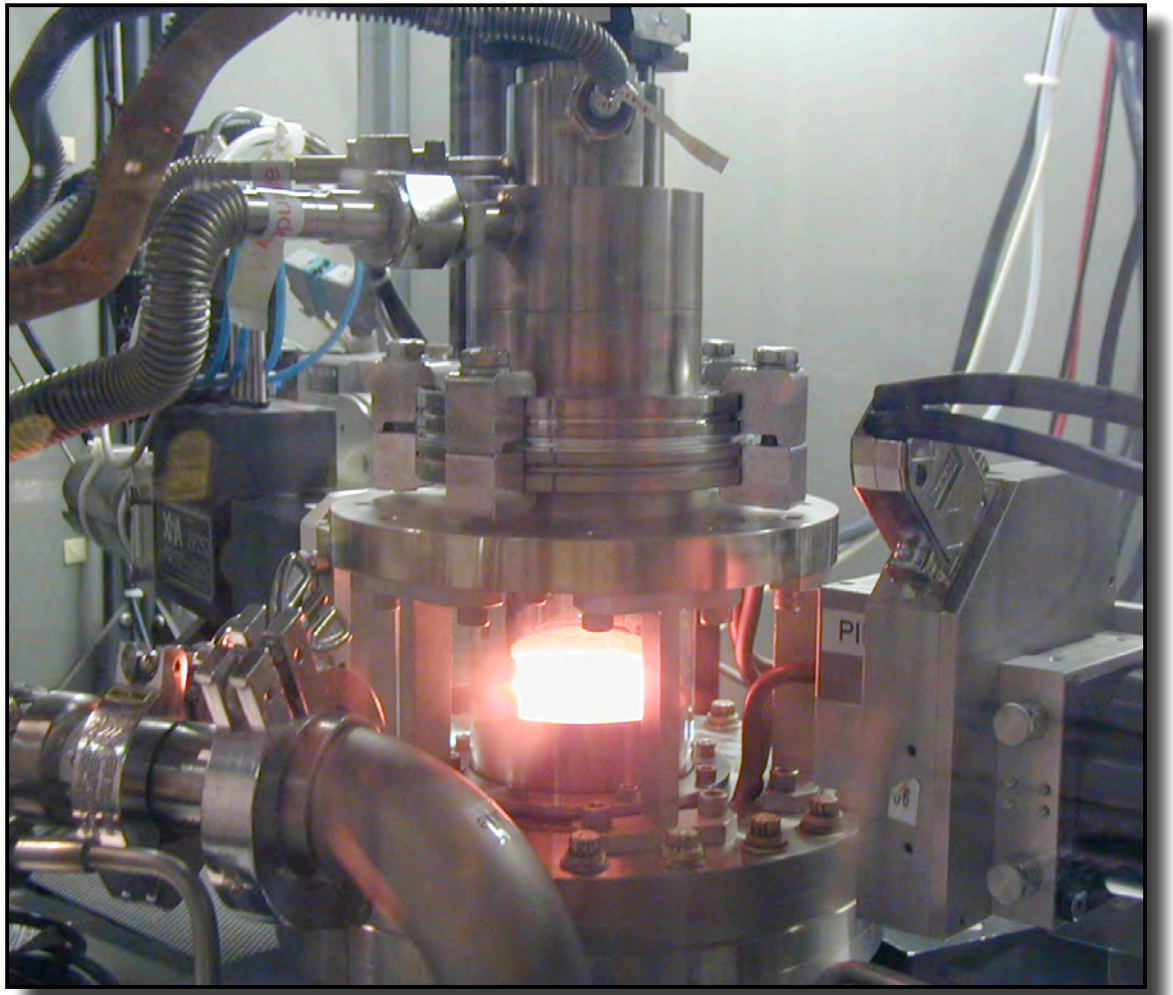
Beamline 12ID-D
Advanced Photon Source
Argonne National Laboratory

Grazing incidence geometry (28.3 keV)

G.B. Stephenson, *et al., MRS Bull.* **24** (1) 21 (1999)
M.V.R. Murty, et al., *Appl. Phys. Lett.* **80**, 1809 (2002)
G.B. Stephenson, et al., *Physica B* **336**, 81-89 (2003)

- Grow epitaxial $PbTiO_3$ films on $SrTiO_3$ or $SrRuO_3$/ $SrTiO_3$ substrates by metalorganic chemical vapor deposition (MOCVD) at ~700°C
- Chamber Pressure: 10 Torr (usually kept at 2.3 Torr O_2)
- In-situ growth allows precise control of film thickness to sub-unit-cell accuracy
  - We study films 1-100 unit cells (0.4 - 40 nm) in thickness
  - Films have crystalline quality equivalent to substrate (ω~ 0.005°)
- Study structure at various *T* as we cool to room temperature

Experimental Approach



G.B. Stephenson, *et al., MRS Bull.* **24** (1) 21 (1999)
M.V.R. Murty, et al., *Appl. Phys. Lett.* **80**, 1809 (2002)
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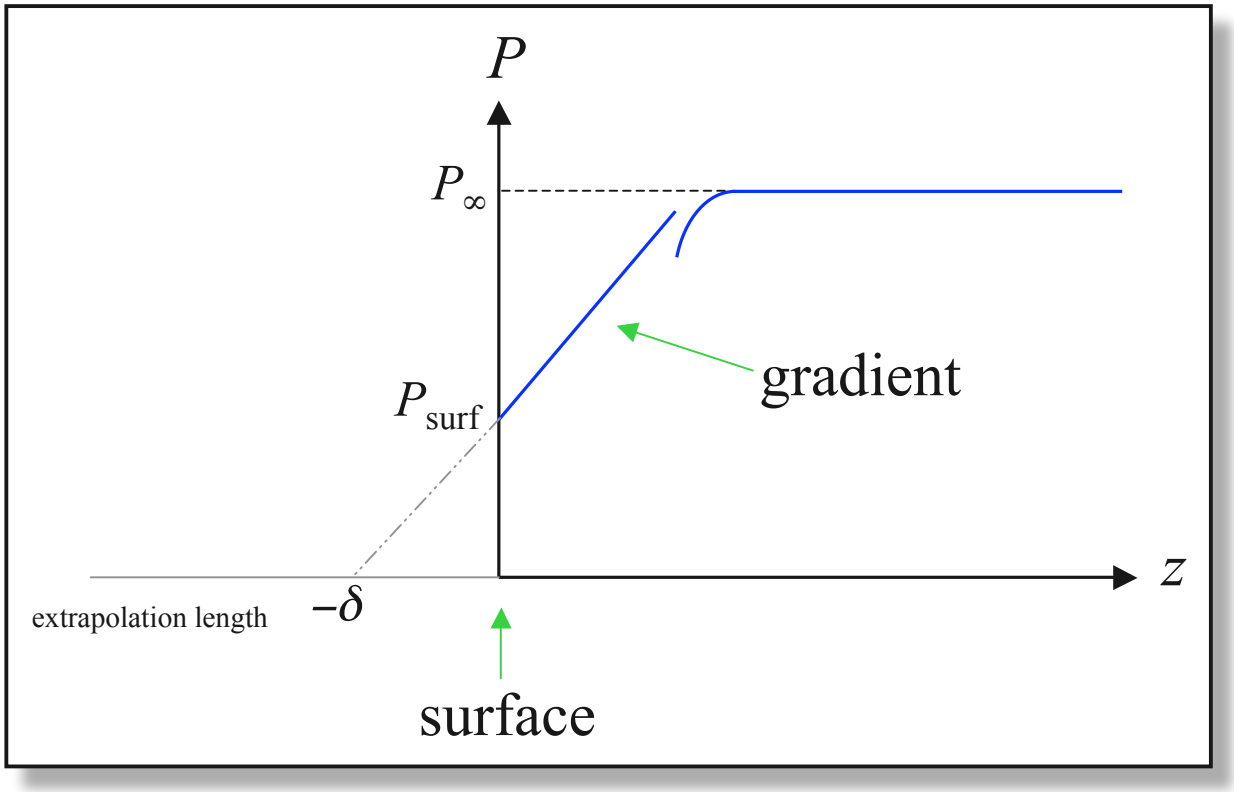
  - Films have crystalline quality equivalent to substrate (ω~ 0.005°)
- Study structure at various *T* as we cool to room temperature

Intrinsic Surface Effect

- Polarization near surface can differ due to surface properties
  - Surface energy
- Can explain suppression of T_C if surface "prefers" lower polarization



Adapted from Kretschmer & Binder, *Phys. Rev. B* **20**, 1065 (1979).

The Depolarizing Field Effect

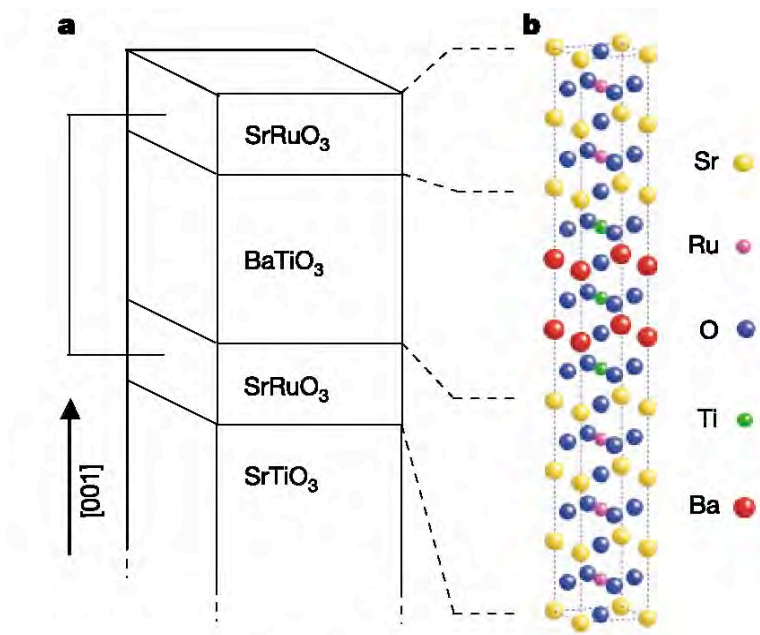


Figure 1 Structure of a typical ferroelectric capacitor. **a**, Schematic view of the system considered here: a $BaTiO_3$ film between $SrRuO_3$ electrodes that are short-circuited. The whole structure is grown on top of a $SrTiO_3$ substrate. The epitaxy is such that $SrTiO_3$ (001) || $SrRuO_3$(001) || $BaTiO_3$ (001)|| $SrRuO_3$(001). **b**, Atomic representation of the related supercell that is simulated (for the case $m = 2$).

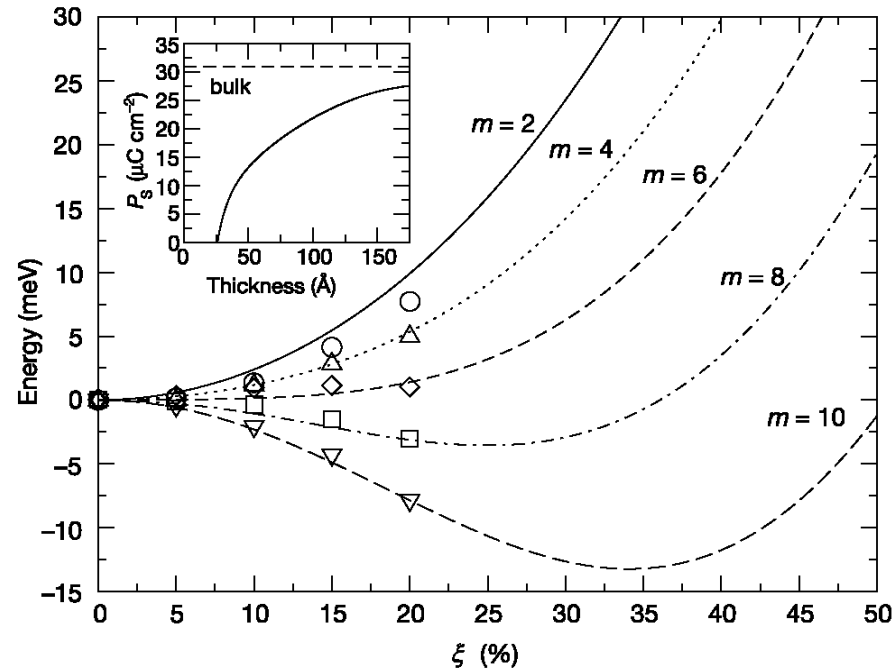


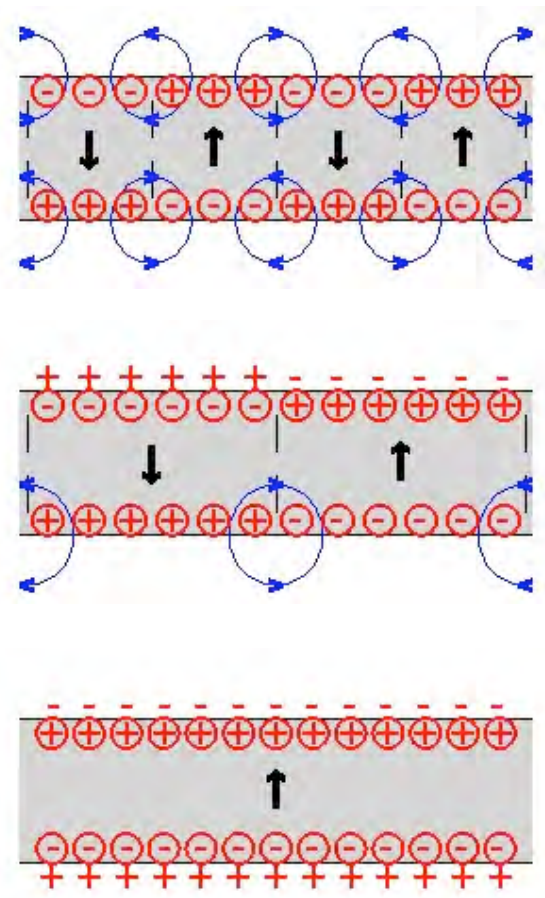
Figure 2 Evolution of the energy as a function of the soft-mode distortion ξ. First-principles results (symbols) and electrostatic model results (lines) are shown for different thicknesses of the ferroelectric thin film: $m = 2$ (circles, full line), $m = 4$ (upward-pointing triangles, dotted), $m = 6$ (diamonds, short-dashed), $m = 8$ (squares, dot-dashed), and $m = 10$ (downward-pointing triangles, long-dashed). The magnitude of ξ is reported as a percentage of the bulk soft-mode displacements of $BaTiO_3$ atoms ($\xi = 1$ corresponds to the distortion of the bulk tetragonal ferroelectric phase).The energy of the paraelectric phase is taken as reference. Inset, evolution of the spontaneous polarization, P_s, with thickness. For each thickness, P_s is deduced from the amplitude of ξ at the minimum.

– J. Junquera, P. Ghosez, Nature **422**, 506 (2003)

Stability of the Ferroelectric Phase

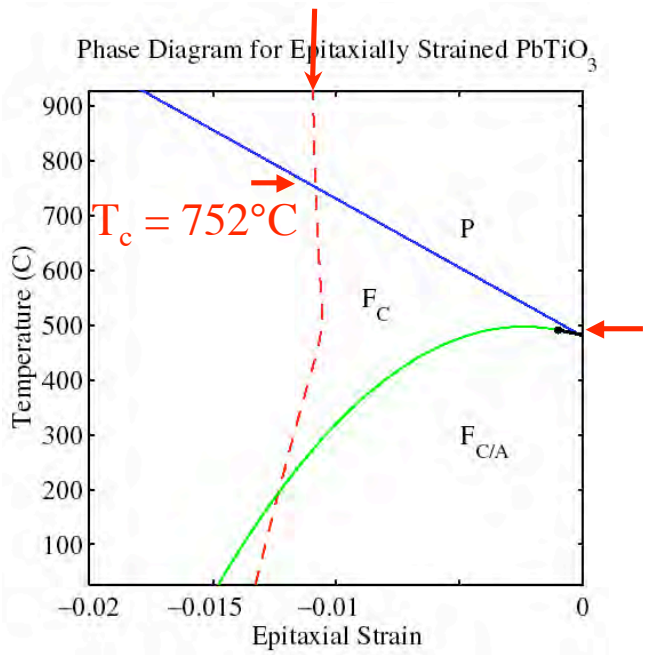
If the depolarizing field is uncompensated, the ferroelectric phase transition in $PbTiO_3$ is destroyed

- Depolarizing field E_D is the electric field arising from polarization
- E_D can be partially compensated by:
  - Domain formation
    - *Equilibrium stripe domain period determined by trade-off between field and domain wall energies*
  - Free charge at surface/interface from
    - *Conducting or semiconducting electrodes*
    - *Charged surface adsorbates*
- Given residual depolarization, ferroelectricity is maintained to surprisingly small thicknesses in ultrathin $PbTiO_3$



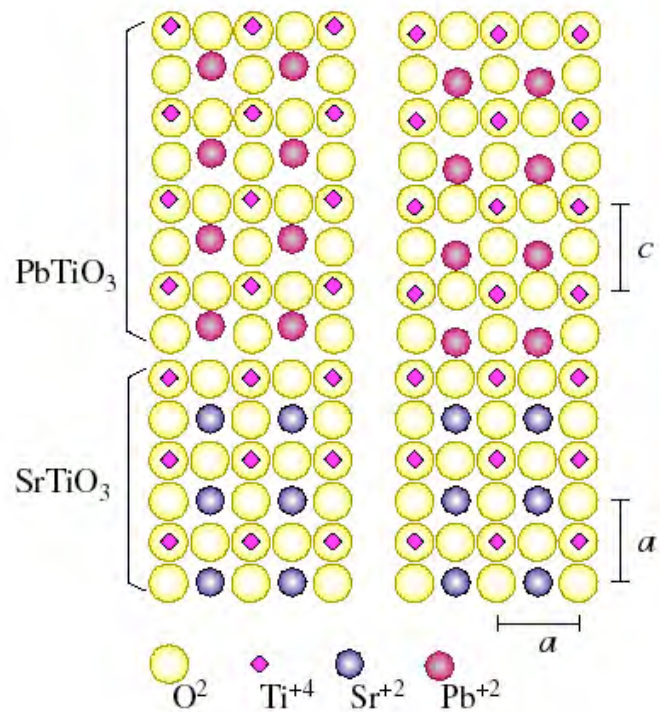
Phase Transitions in $PbTiO_3$

Strain
$PbTiO_3$ on $SrTiO_3$ substrate



after N. A. Pertsev and V. G. Koukhar ***PRL* 84**, 3722 (2000).

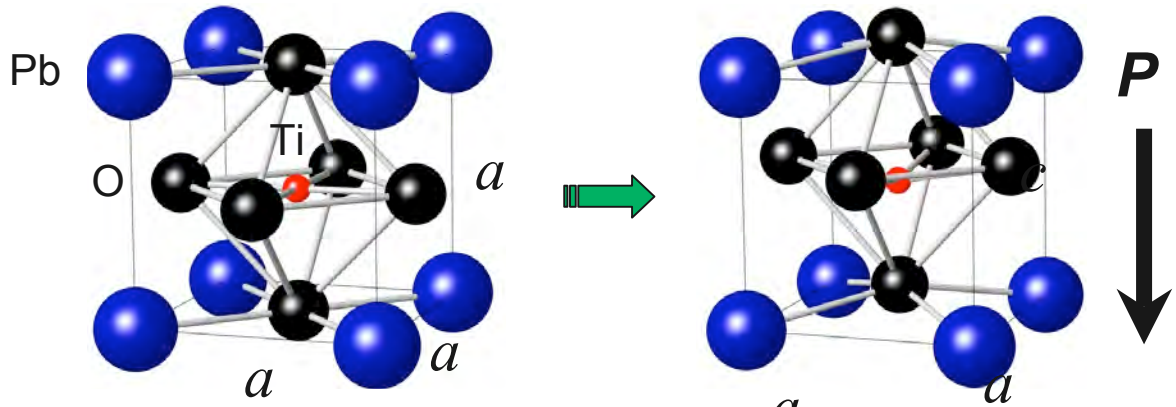
T_c(zero stress) = 492°C



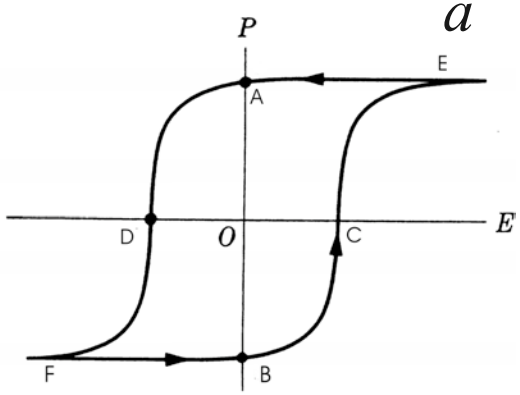
- Thin films can be grown that are fully lattice matched (unrelaxed)
- Paraelectric-to-ferroelectric phase transition T_c predicted to depend on epitaxial strain
  - 260°C enhancement predicted in T_c for $PbTiO_3$ on $SrTiO_3$

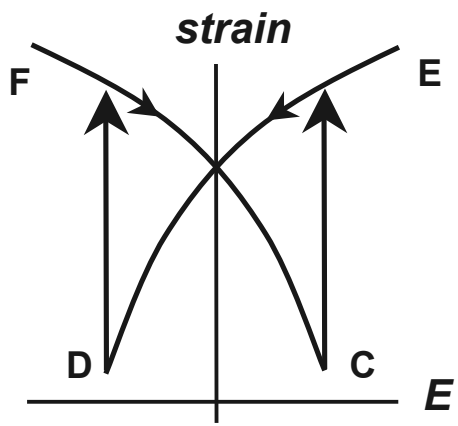
Background: Ferroelectricity

Above T_c: paraelectric 492°C Below T_c: ferroelectric



Ferroelectric Transition
$PbTiO_3$-Based System



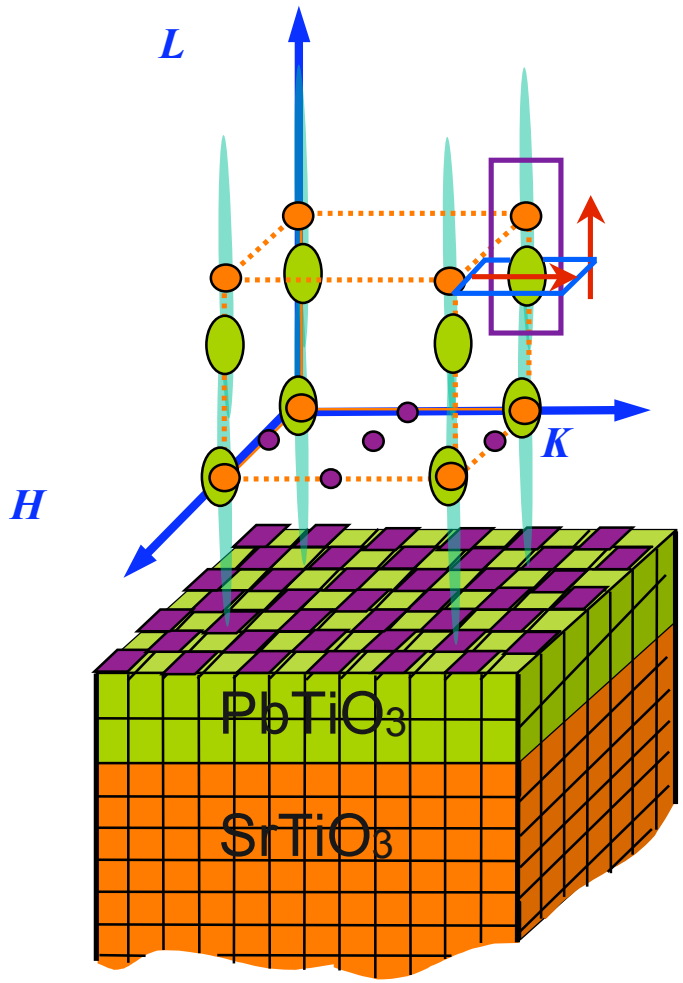


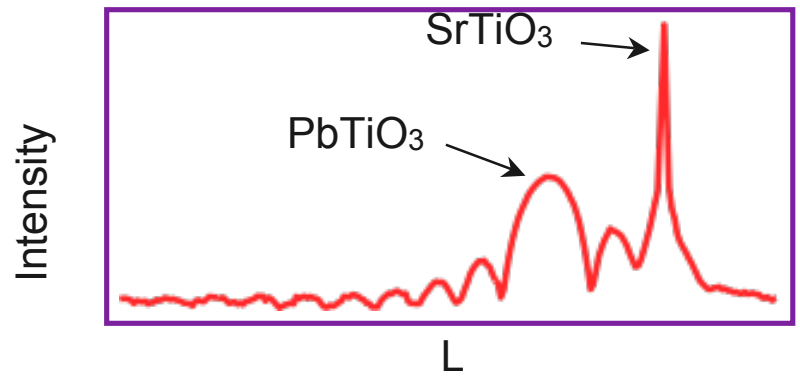
- The strain can be linked to the polarization through LGD phenomenological theory

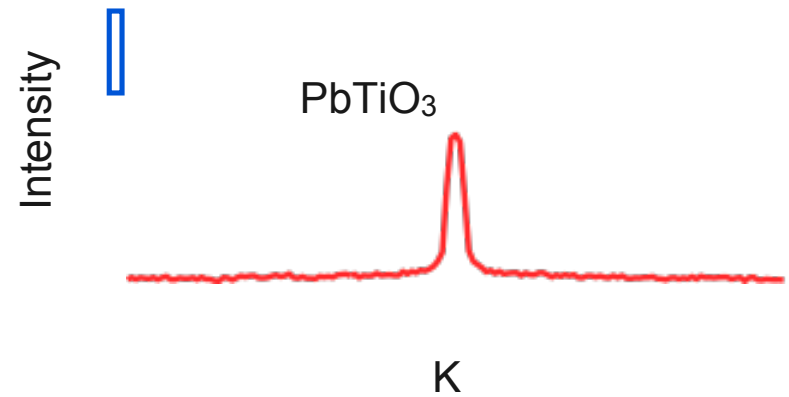
For c-oriented monodomain

$$P = \left(\frac{x - x_0}{Q_{11} - 2 s_{12} Q_{12} / (s_{11} + s_{12})} \right)^{1/2}$$

Reciprocal Space

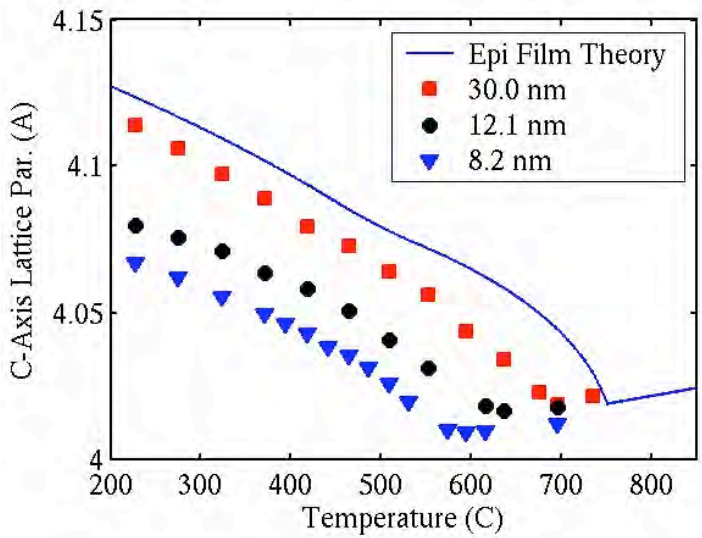


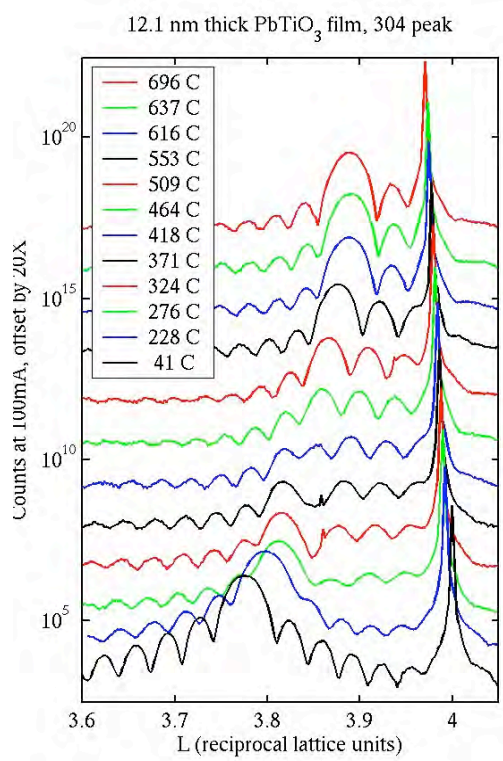


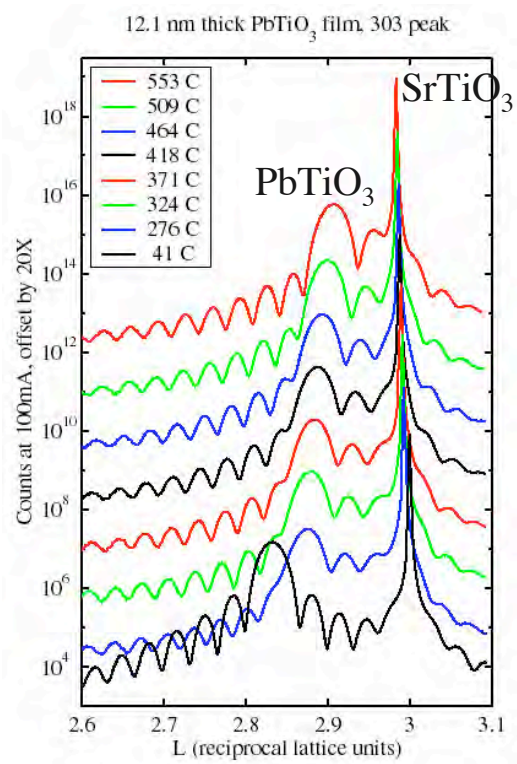


Determination of T_c from Lattice Parameter

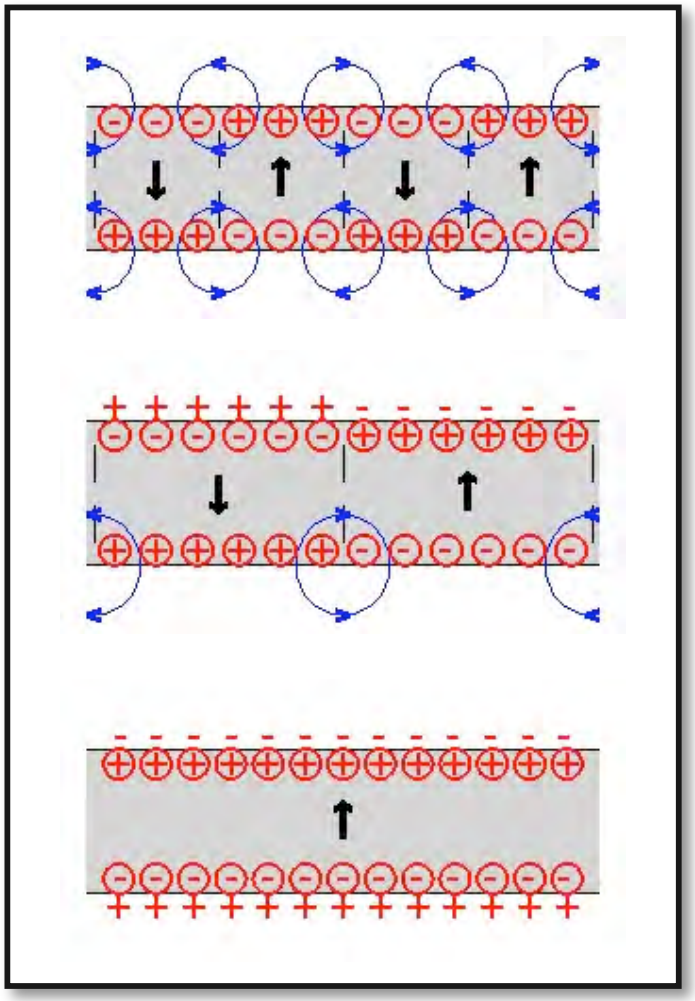
- Ferroelectric phase transition identified by measuring lattice parameter of $PbTiO_3$ as function of temperature
- Phase transition is continuous
- T_c suppressed below *E*=0 LGD theory

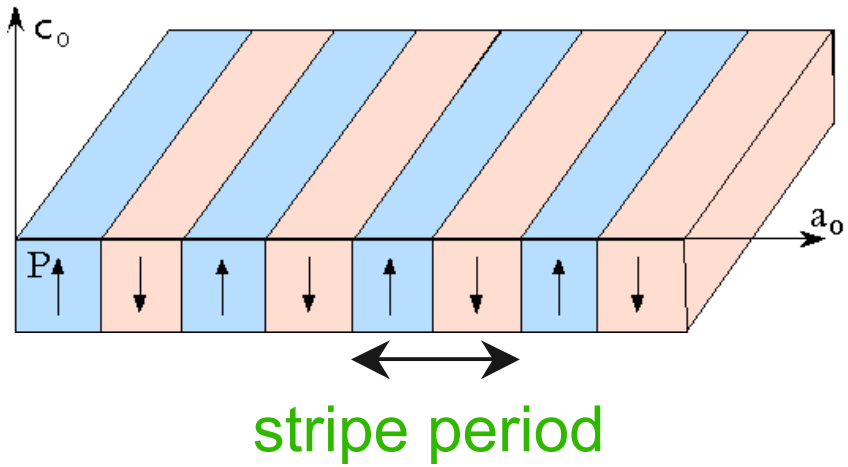






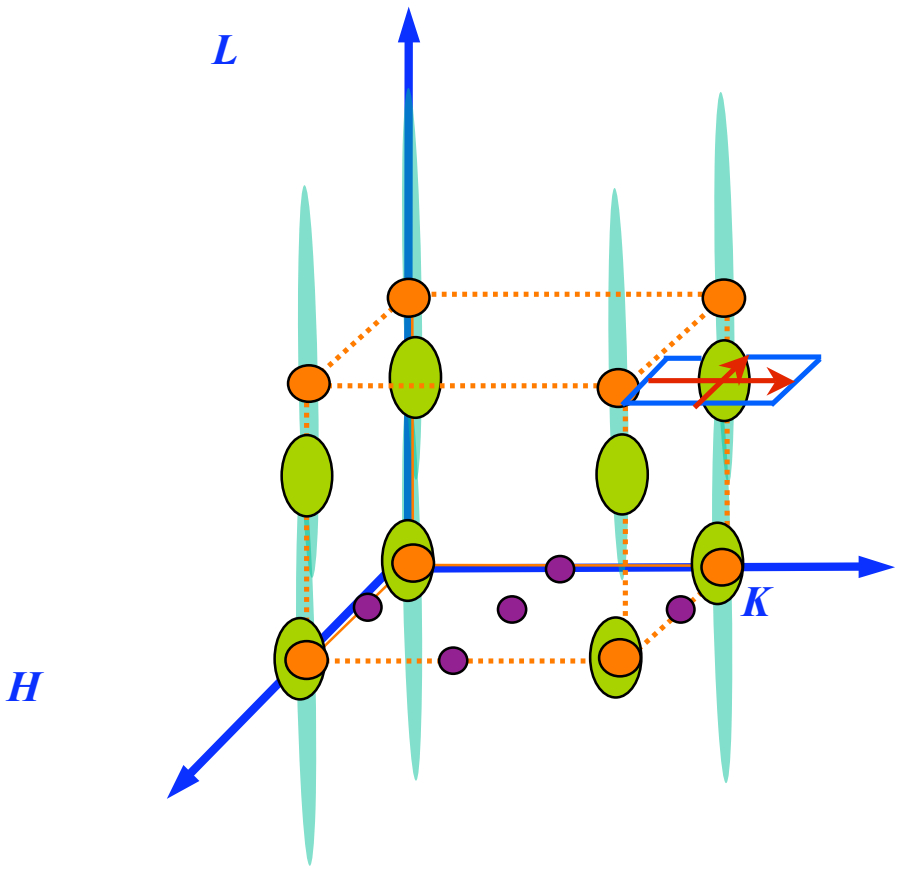
PTO/STO: Ordered 180° stripe domains



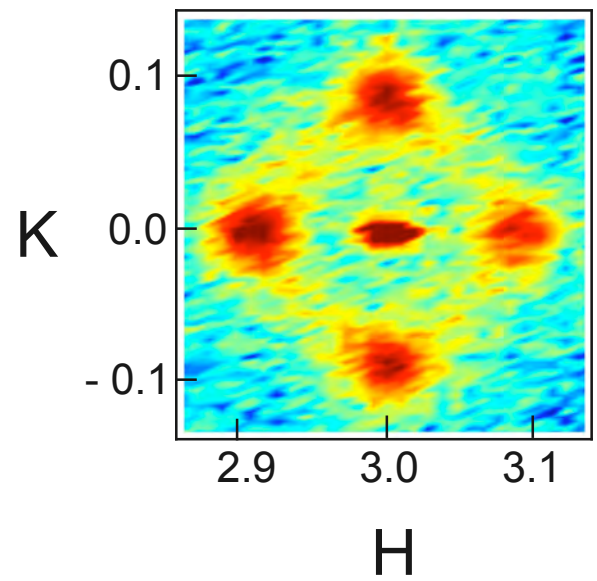


- Domain formation minimizes energy of depolarizing field that arises from growth on an insulator ($SrTiO_3$)

PTO/STO: Satellites → 180° stripe domains

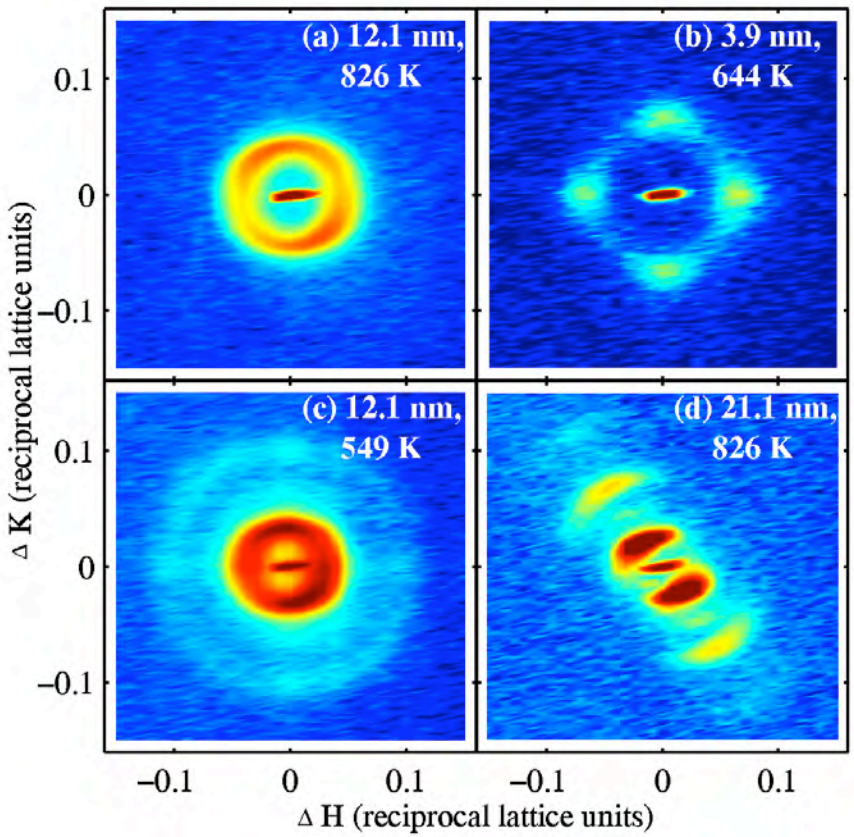


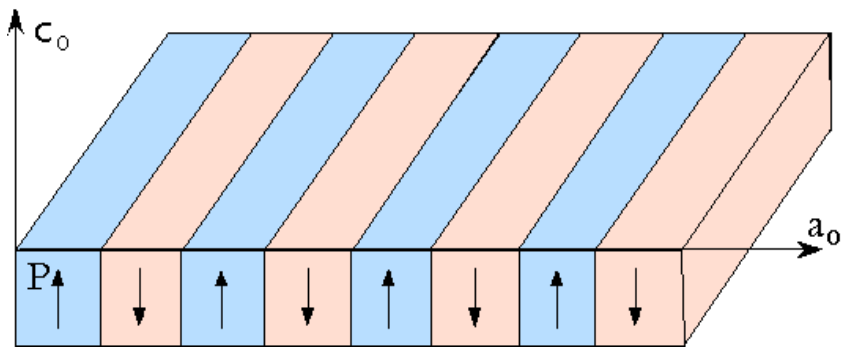
In-plane map
around PTO 304



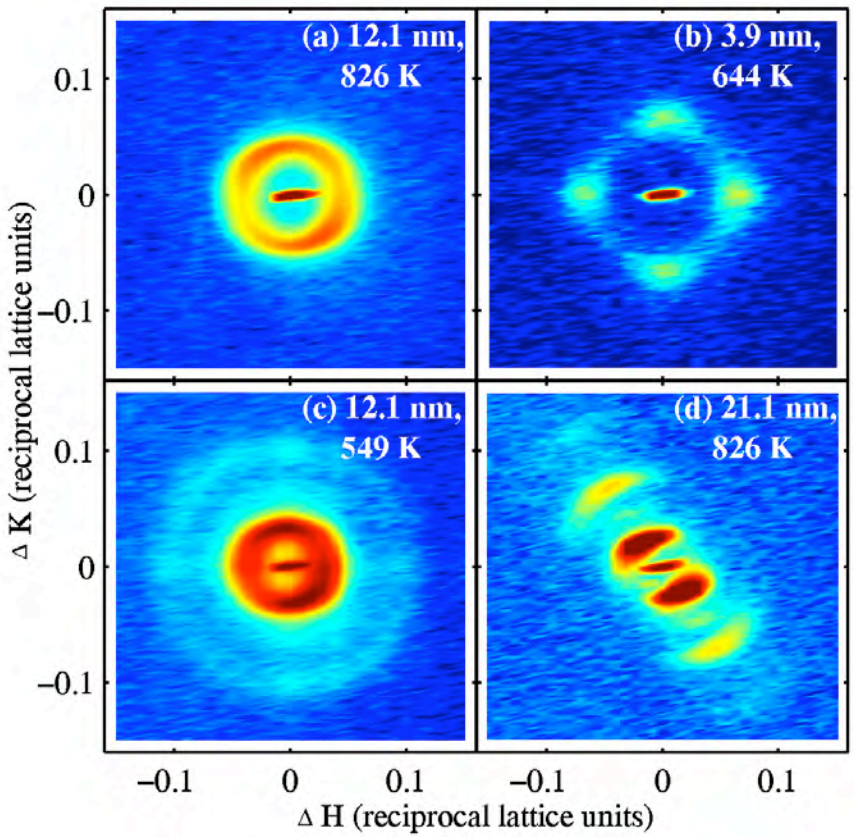
S.K. Streiffer et al., *PRL* **89**, 067601 (2002)

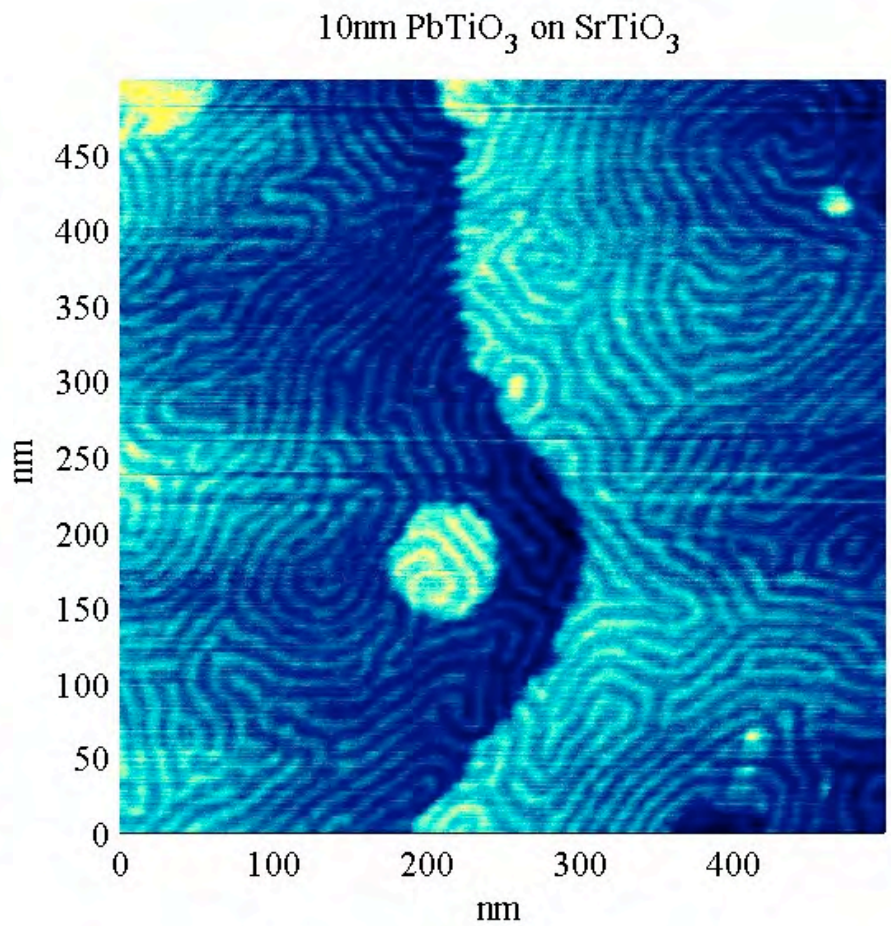
Diffuse Scatter Originates from 180° Stripe Domains





Diffuse Scatter Originates from 180° Stripe Domains

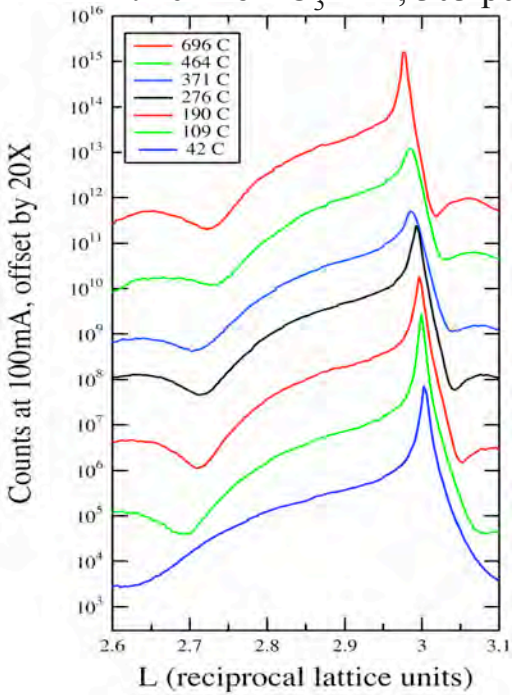




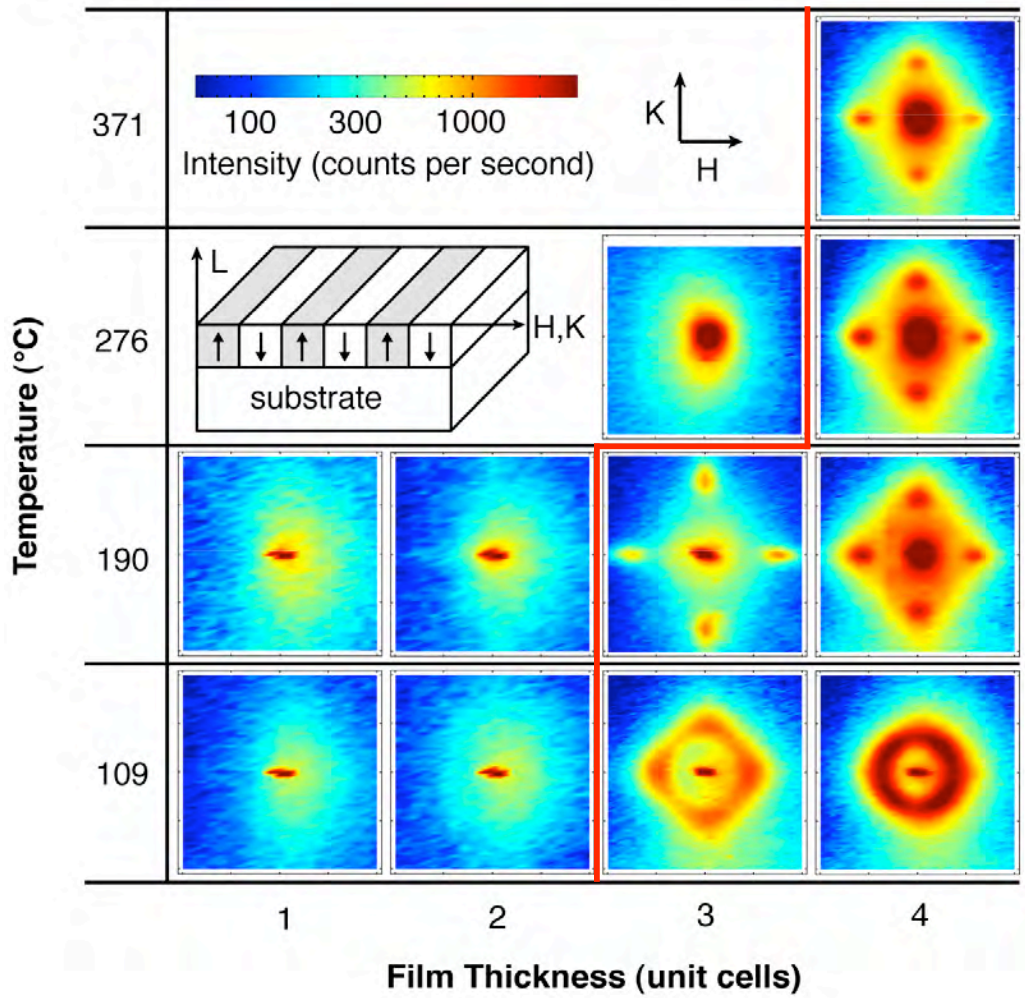
Ex situ AFM
(C. Thompson, submitted to APL)

T_C in Ultrathin Films

2 nm thick $PbTiO_3$ film, 303 peaks

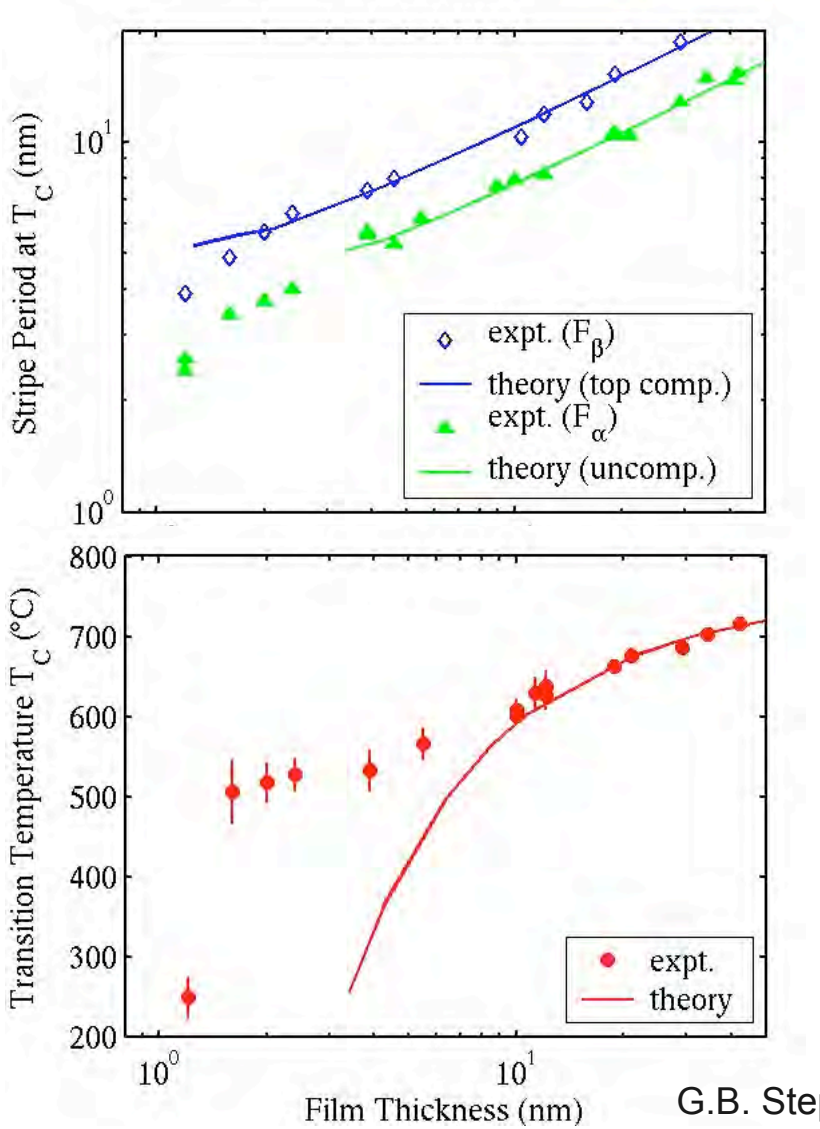


Satellite appearance is a more sensitive measure of T_C than lattice parameter measurements - useful for ultrathin films



Fong et al. *Science* **304**, 1650 (2004)

Landau Theory Analysis of Depolarization Effects



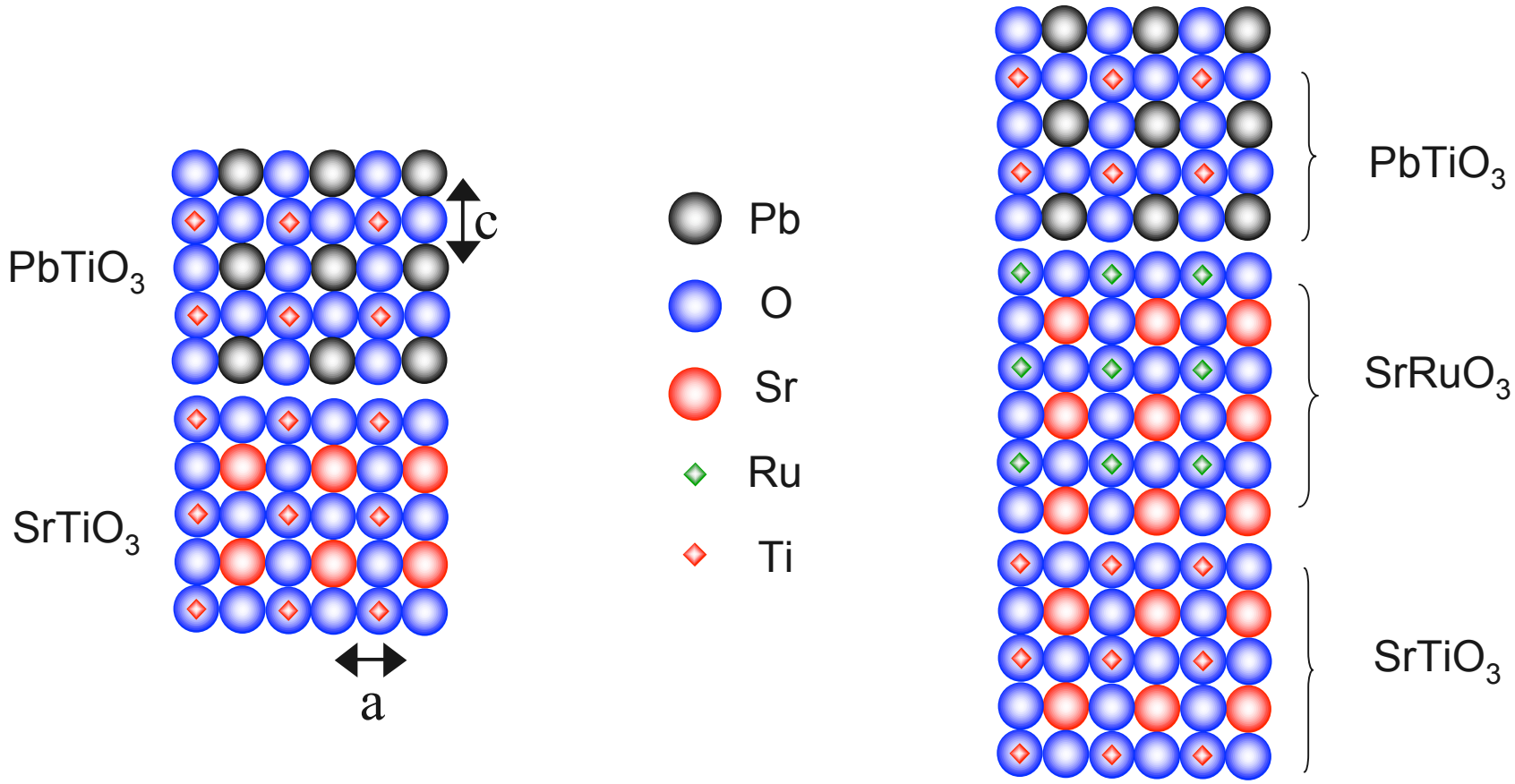
- Non-linear Landau-Ginzburg-Devonshire theory solved using phase field approach (collaboration with Ken Elder, Oakland Univ.)
- Single free parameter (domain wall energy) gives agreement with periods of both "phases", assuming F_α has two uncompensated boundaries and F_β has a compensated top surface
- Get agreement with observed T_C suppression for thicknesses larger than 10 nm
- Ultrathin films have a ***higher*** T_C than predicted, indicating that intrinsic surface effect *enhances* polarization

G.B. Stephenson and K.R. Elder, *J. Appl. Phys.* **100**, 067601 (2006)

Overview

- Introduction to and motivation for utilizing synchrotron x-rays
- Size effects on the ferroelectric phase transition in $PbTiO_3$ and relationship to 180° domain structure
- **Surface Chemistry: Surface interactions with the gas phase and relationship to polarization state**

Model Systems: Coherently Strained $PbTiO_3$



- $PbTiO_3$-on-$SrTiO_3$ misfit strain ≈ -1% at growth temperature
- Films remain coherently strained up to thicknesses of 40 nm
- This favors polarization axis (*c*) normal to the film surface

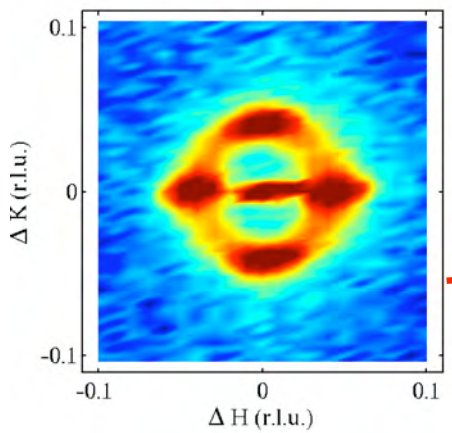
Boundary Conditions - Conducting Substrate

- Deposit on $SrRuO_3/SrTiO_3$ provided by Eom group

reactive atmosphere

$PbTiO_3$

$SrTiO_3$ (001)

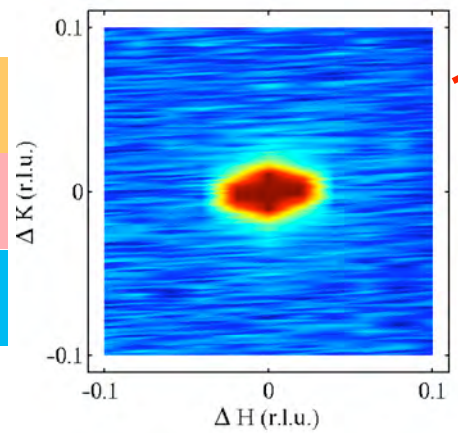


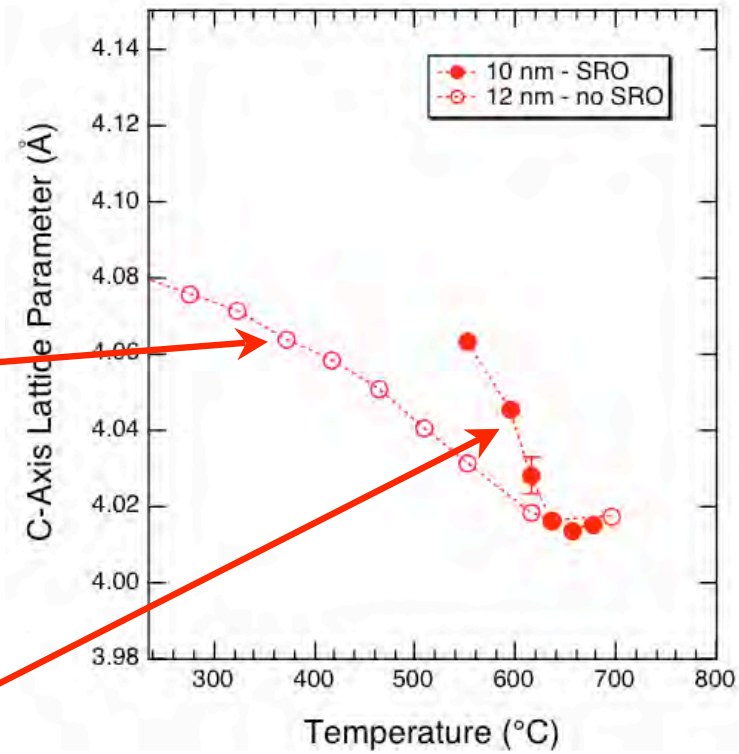
reactive atmosphere

$PbTiO_3$

$SrRuO_3$

$SrTiO_3$ (001)



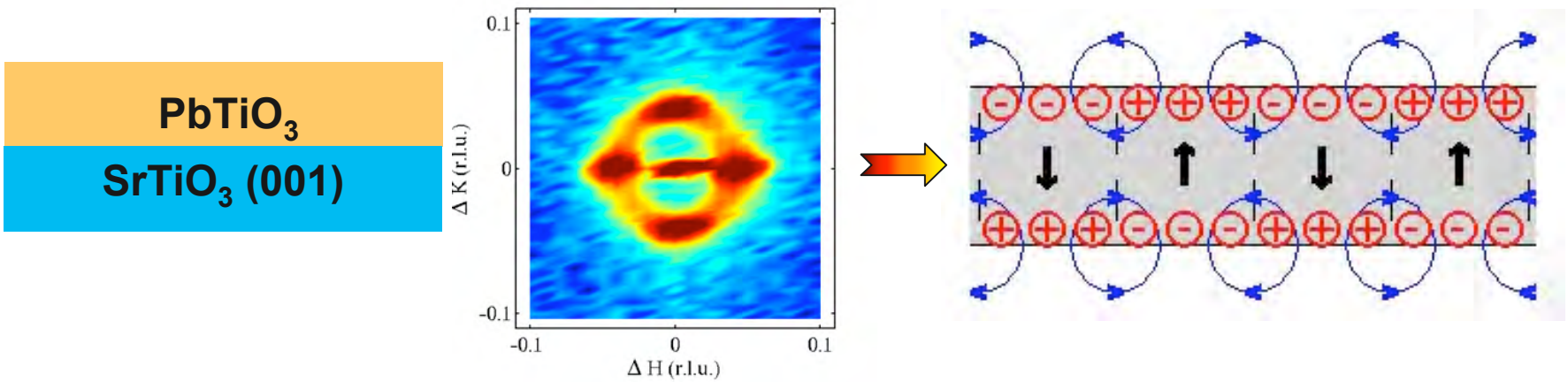


No stripe phase, instead monodomain films with larger polarization than films with 180° stripe domains form.

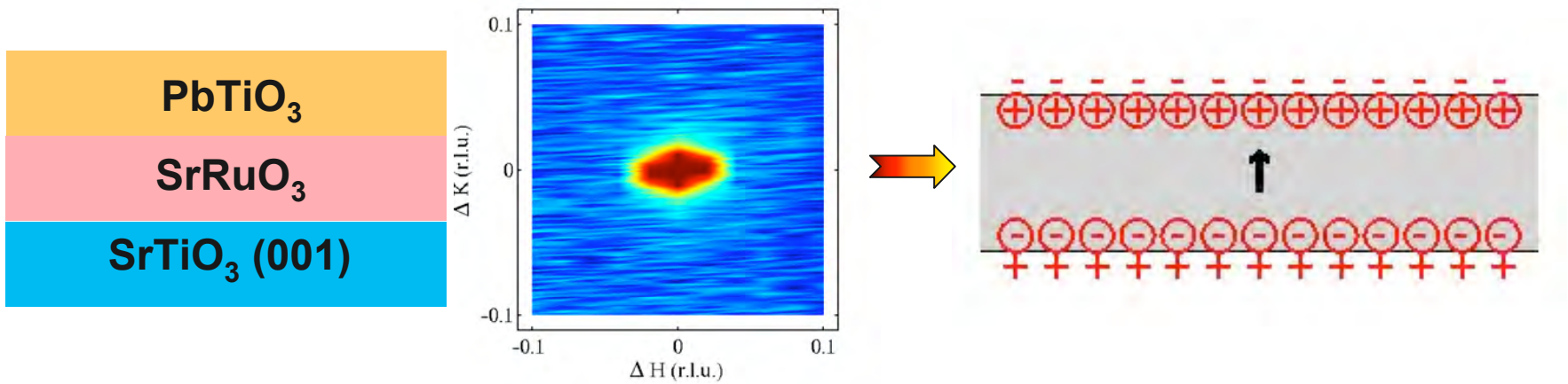
Boundary Conditions - Conducting Substrate

- Deposit on $SrRuO_3/SrTiO_3$ provided by Eom group

reactive atmosphere



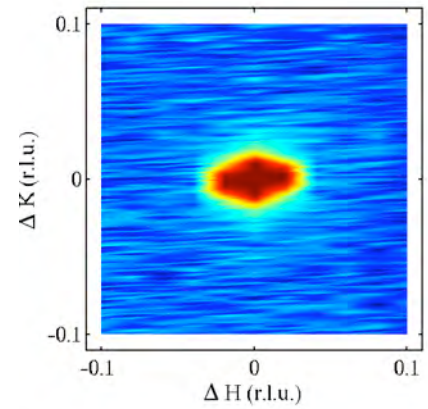
reactive atmosphere

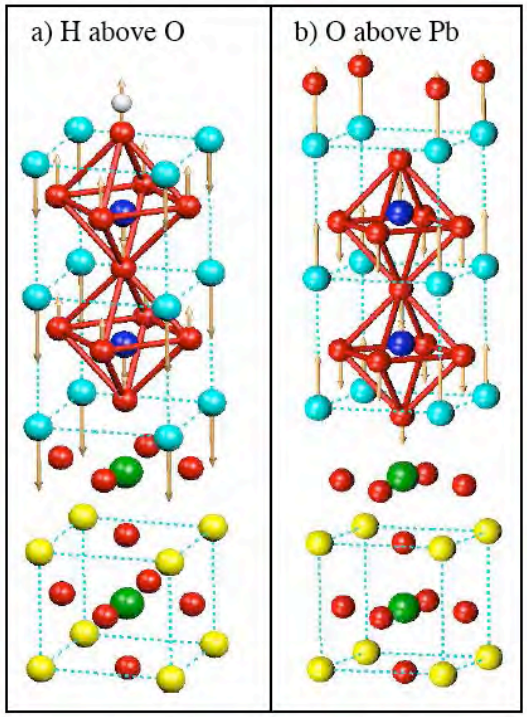


$PbTiO_3$ Films on Conductive $SrRuO_3$

For films grown on conductive $SrRuO_3$ layers, we see a direct transition to the monodomain state with higher T_C than for films on $SrTiO_3$

- Piezoresponse AFM confirms that films on conductive substrates are monodomain, polarized "up"
- For monodomain ferroelectric phase, charge compensation ***must*** occur at both interfaces
- DFT calculations show that 3-unit-cell-thick films of $PbTiO_3$ on $SrRuO_3$ are non-polar when no adsorbates are present. Adsorption of H or O ions stabilizes polarizations of opposite sign (collaboration with A.M. Rappe *et al.*, Univ. Pennsylvania)

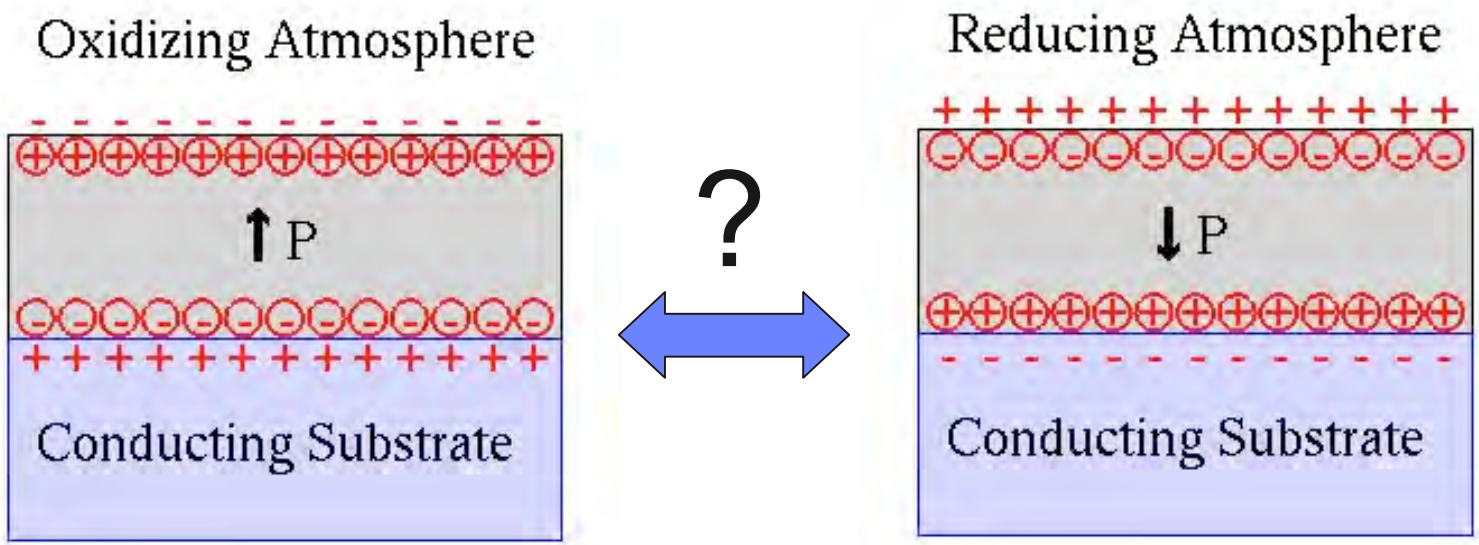




D.D. Fong *et al.*, *Phys. Rev. Lett.* **96**, 127601 (2006)

"Chemical Switching" of a Ferroelectric Film

- Can we switch the polarization by changing the chemistry of the environment?
- Conversely, how does the sign of polarization affect surface chemistry?



D.D. Fong *et al.*, Phys. Rev. Lett. **96**, 127601 (2006)

Conclusions

- In situ hard x-ray techniques are extremely powerful for probing torr-level deposition and controlled environment systems.
- In situ methods have allowed us to develop for the first time truly quantitative control of synthesis of a complex oxide film.
- This quantitative control has allowed deep insight into the physics of the ferroelectric phase transition.

- Different environments have the potential to interact differently with the perovskite surface.
  - The nature of interfacial charge that compensates the depolarizing field determines the polarization structure of ultrathin ferroelectric films
    - *Equilibrium 180º stripe domains are observed in films on insulating substrates with an uncompensated interface*
    - *Monodomain polarization is observed in films on conductive substrates*
    - *Direction of polarization can be chemically switched by changing* pO_2 *of environment*

- The game is in tuning between competing interactions and interactions.