Invited

Visualizing Single Domains and Domain Walls with X-Rays

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The vision for Nanotechnology in both the electronics and photonics industries promises very compact, low-cost devices and components with high levels of integration and functionality ten to twenty years out. This next generation of devices will be based on new nanoscale materials and materials architectures that include quantum dots, photonic crystals, laterally confined inorganic and organic thin films and single molecules. It is often the case that the discovery and utilization of new materials for novel devices and fundamental science is intimately linked with the development of advanced materials probes. Taking advantage of the very high brightness of third generation x-ray sources and the high sensitivity of x-rays to structure, strain, chemical composition and magnetism, x-ray microscopy is emerging as an ideal probe of nanoscale materials.

In this talk, we will highlight recent progress made toward understanding the interplay between the sub-micron microscopic configuration of domains and domain walls and macroscopically observable phenomena in materials of current technological interest. The first example is an effort to understand the polarization fatigue that ultimately plagues all ferroelectric devices, used for example in non-volatile memory. Using microdiffraction with 0.2 μm resolution, we have directly imaged polarization domain switching and the evolution of domain walls in epitaxial PZT devices as they become pinned after millions of poling cycles.

In a second example, we have combined non-resonant magnetic x-ray diffraction and Fresnel focusing optics to study the nucleation and growth of antiferromagnetic domains in Chromium. Images of the incommensurate antiferromagnetic domains have shown us how the spin-flip transition near 123 K nucleates at either intrinsic domain walls between orthogonal propagation directions for the spin modulation or at artificial features imposed on the material surface. This later result points toward a method by which domains may be laterally configured for multi-layer magnetic devices that utilize antiferromagnetic coupling layers.

Advanced Materials Characterization for Future Nano-technologies

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Lucent Technologies
Bell Labs Innovations

and

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Pioneering
Science and
Technology

Visualizing Domains and Domain Walls with X-rays

September 5, 2003

3rd Industrial Users Meeting, Spring-8

Talk Overview

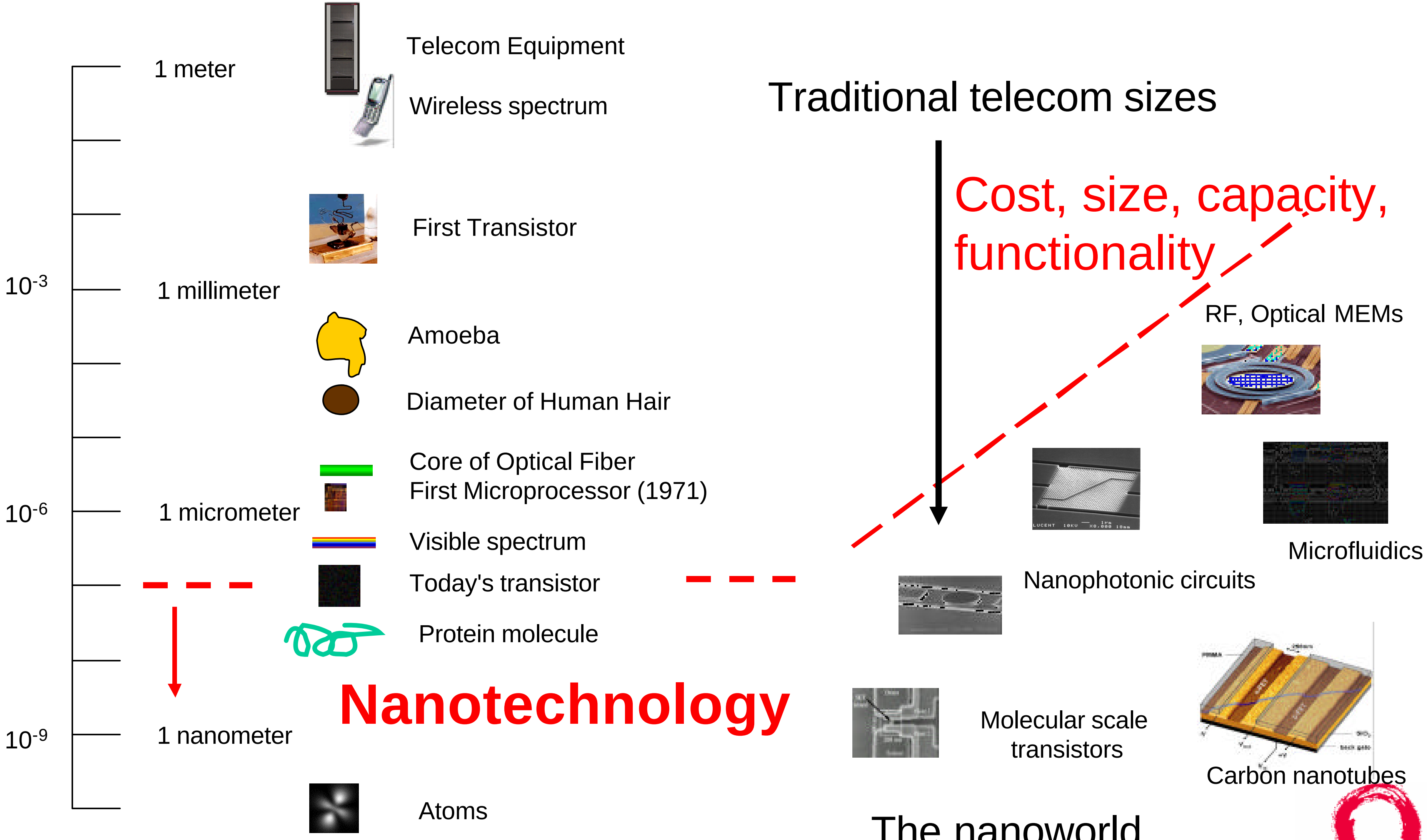
introduction

- visualizing domains and domain walls with x-rays
  - fatigue in $Pb(Zr,Ti)O_3$ ferroelectric devices
  - domain nucleation in pure chromium
- Future directions

collaborators

• Paul Evans	U. of Wisconsin, Madison
• Dal-Hyun Do	
• C-B. Eom	
• Gabriel Aeppli	University College, London
• Eric Dufresne	U. of Mich., MHATT-CAT
• Zhonghou Cai	APS, Argonne
• Barry Lai	APS, Argonne

Things continue to get smaller . . .



1 meter

Telecom Equipment

Wireless spectrum

First Transistor

10^{-3} 1 millimeter

Amoeba

Diameter of Human Hair

Core of Optical Fiber

First Microprocessor (1971)

10^{-6} 1 micrometer

Visible spectrum

Today's transistor

Protein molecule

Nanotechnology

10^{-9} 1 nanometer

Atoms

Traditional telecom sizes

Cost, size, capacity, functionality

RF, Optical MEMs

Microfluidics

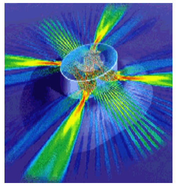
Nanophotonic circuits

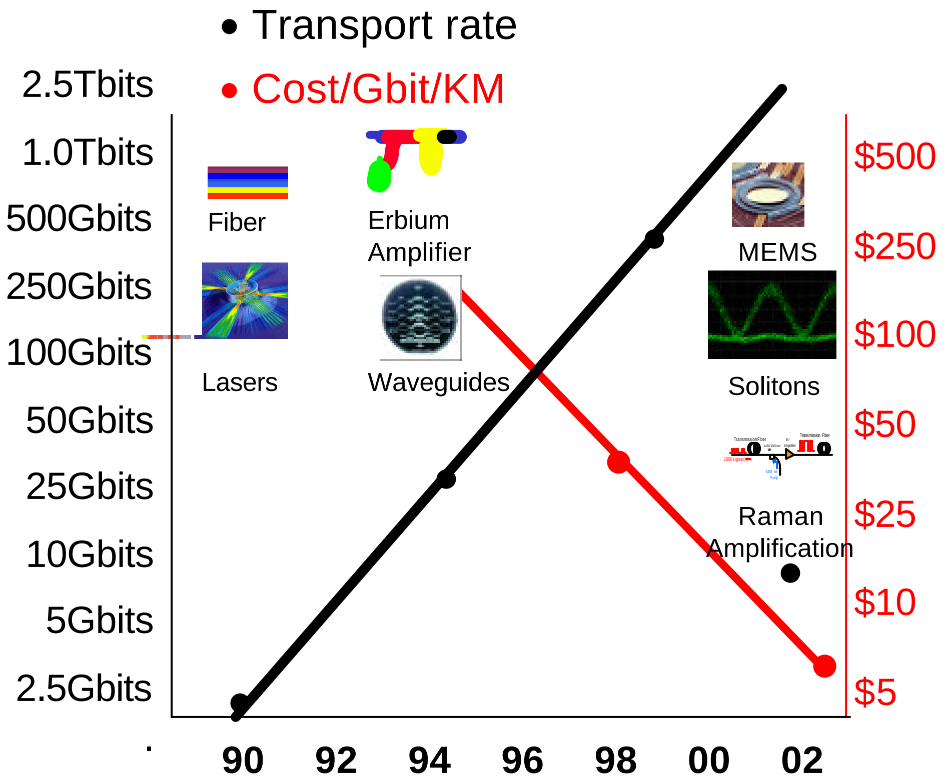
Molecular scale transistors

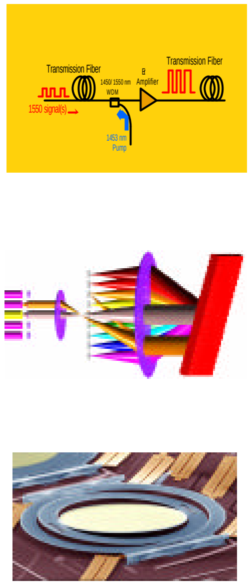
Carbon nanotubes

The nanoworld

… driven by cost, size and functionality







Laser

- Discovered 1958
- Launched the optical networking industry

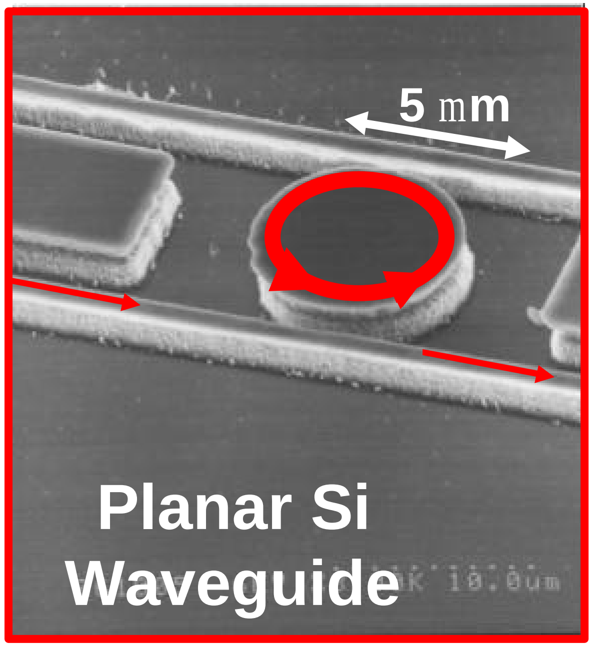
Fiber capacity

- Doubling about every 12 months
- Will exhaust in about a decade

Optoelectronics

- MEM's, Soliton's, Raman amplifiers, …
- Integrated nano-electro-optics

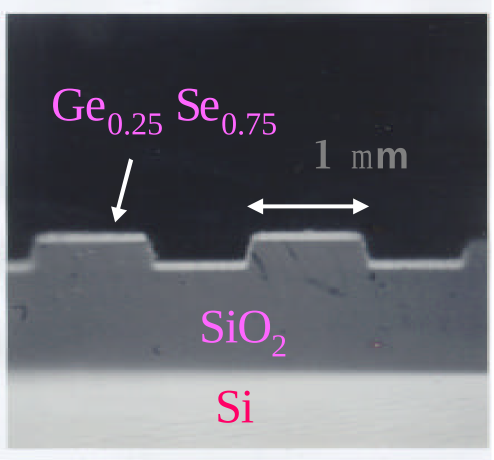
Example: Nano-Photonic Circuits



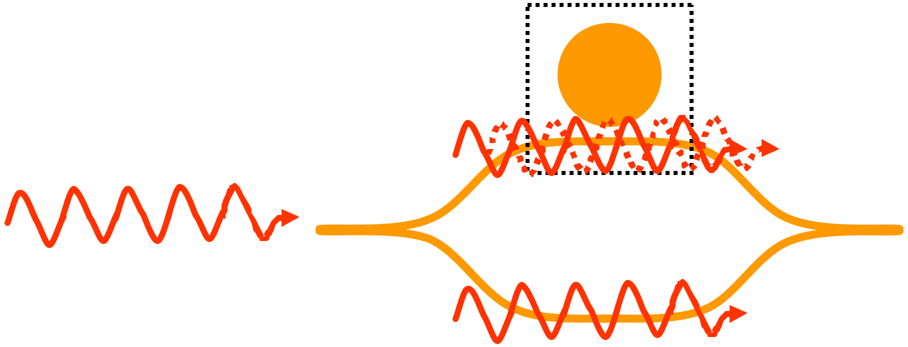
Resonant enhanced
Cavity round trips = 30
Nonlinearity = x1000
small cavity → large bandwidth

(high-index
waveguides)

Materials integration



Non-linear/EO materials
e.g., GeSe, $LiNbO_3$, PZT

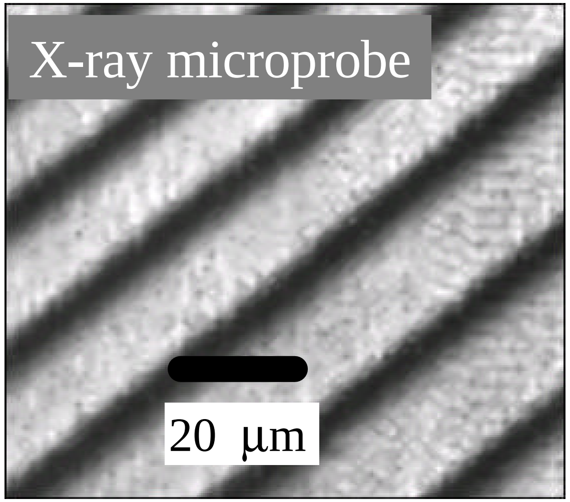


Resonantly Enhanced
Mach-Zender Interferometer

Advanced Materials Research …

substrate interactions

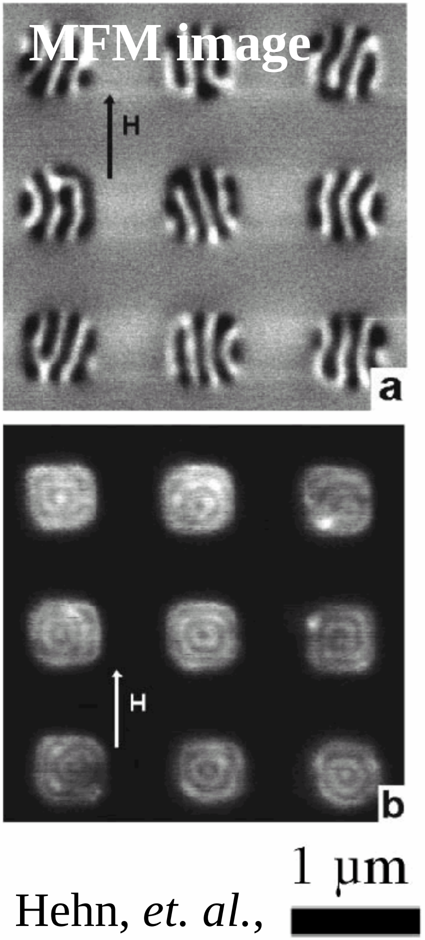
P. Evans, et al. (2001).



$BaTiO_3$ films, 90 ° domains

confinement

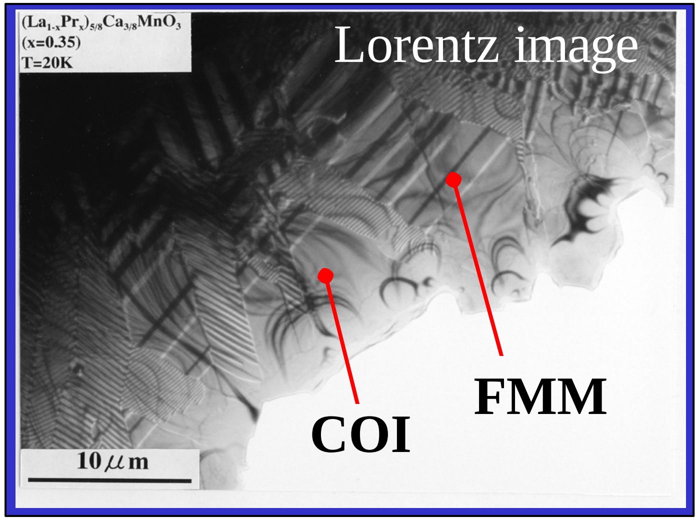
Co dots



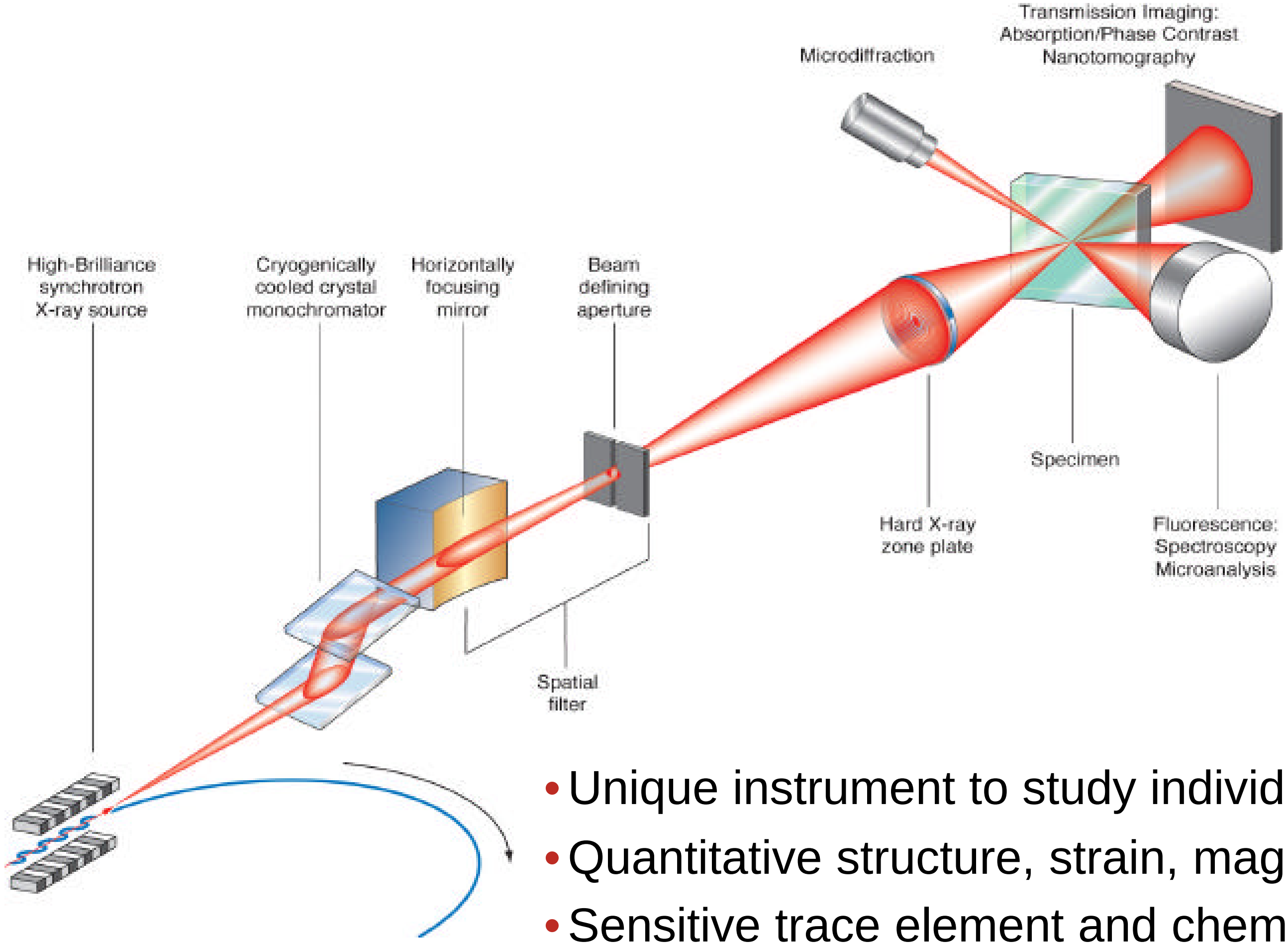
M. Hehn, *et. al.*, APL **71** 2833 (1997).

nanoscale phenomena in bulk materials

C.H. Chen, et al., Nature (1998)



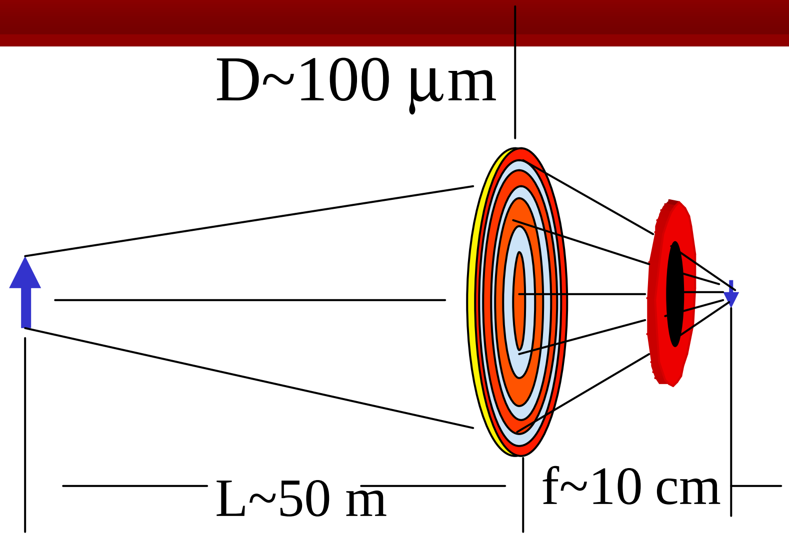
The Hard X-Ray Nanoprobe – Mastering Advanced Materials



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

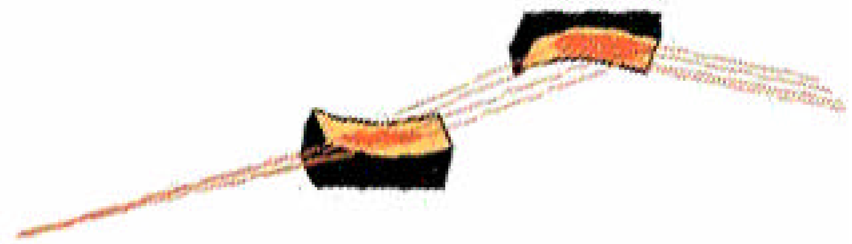
X-ray Focusing

- Fresnel Zone Plates
  - 500 eV to 30 keV
  - 10^{10} ph/s/0.01%BW
  - current spot ~ 80 x 80 nm^2
  - future ~ 10 nm (?)
  - APS 2ID, 7ID (MHATT-CAT)

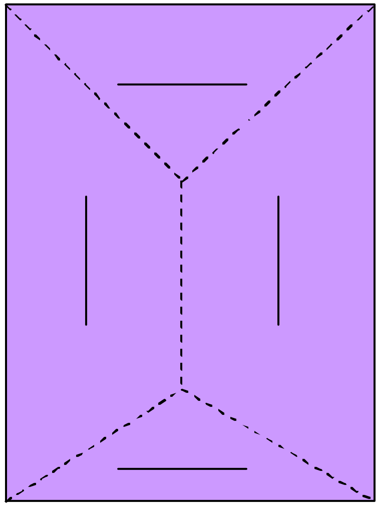


Source demagnified by L/f ≈ 500.

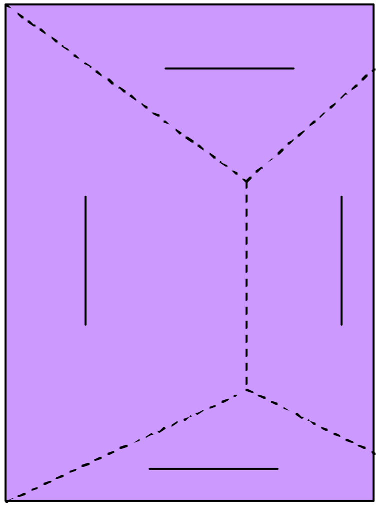
- K-B Mirrors
  - 500 eV to 100 keV
  - 100 x 100 nm^2
  - future < 10 nm (? Wolter geometry)



Ferroelectric (Ferromagnetic) Domains

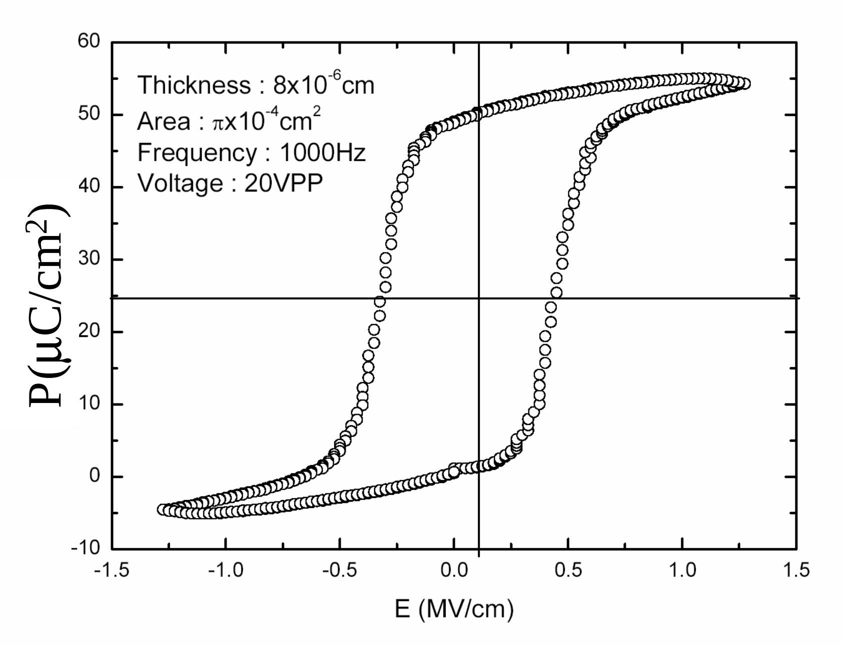


E = 0



E > 0

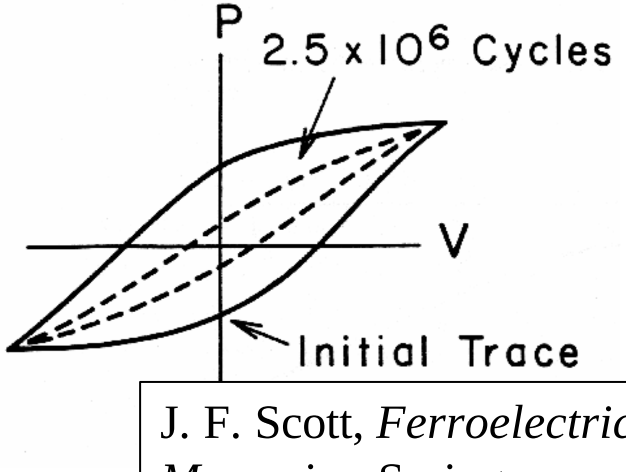
hysteresis loop



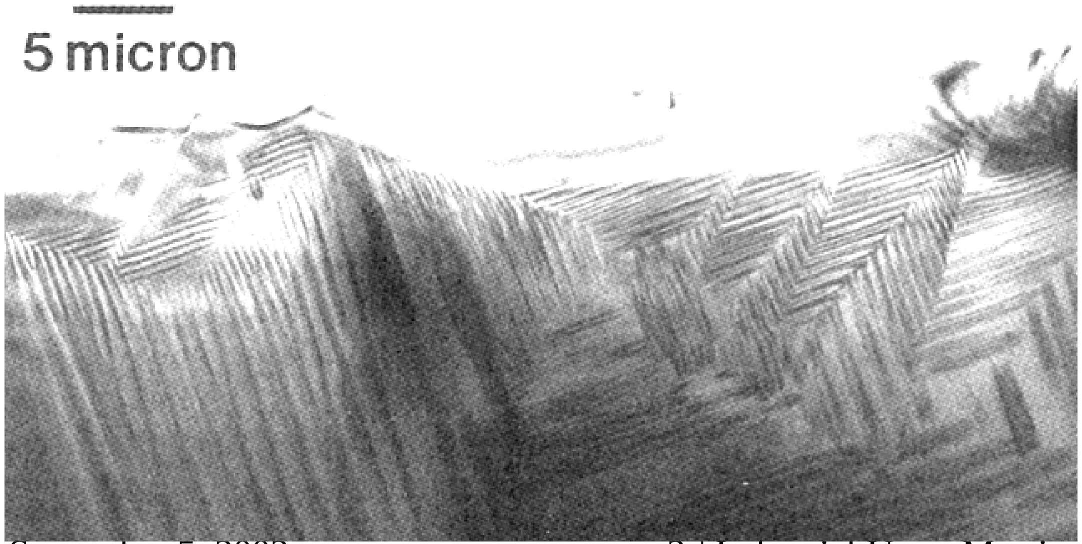
- polarization reversal by domain wall displacement
- hysteresis loop (coercive forces/remanent polarization) determined by nucleation and domain wall motion and pinning

Fatigue in Ferroelectric Devices

- Nucleation and growth of domains critical switching dynamics.
  - – Switching time
  - – Fatigue
    - – strain, pinning at defects
    - – size effects
    - – need 100 nm resolution
  - two E-field regimes of fatigue



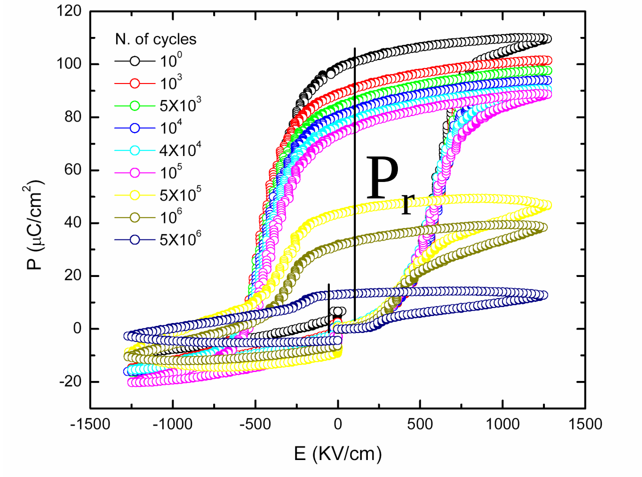
J. F. Scott, *Ferroelectric Memories*, Springer, Berlin (2000), p. 133.

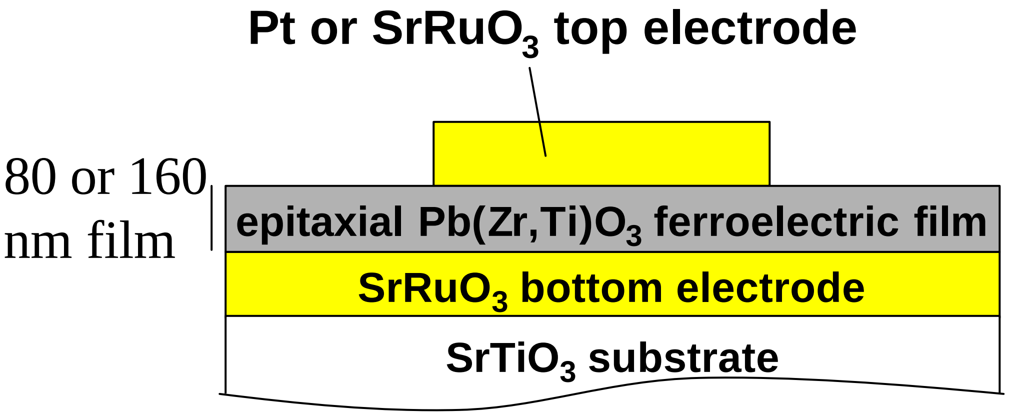


TEM study at NEC: A. Krishnan, M. E. Bisher, and M. M. J. Treacy, Mat. Res. Soc. Symp. Proc. **541** 475 (1998).

Ferroelectric Fatigue

PZT w/Pt top electrode





Pt or $SrRuO_3$ top electrode

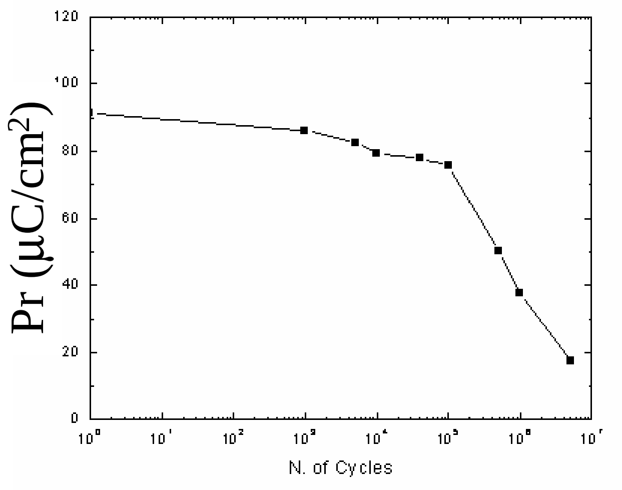
80 or 160 nm film

epitaxial $Pb(Zr,Ti)O_3$ ferroelectric film

$SrRuO_3$ bottom electrode

$SrTiO_3$ substrate

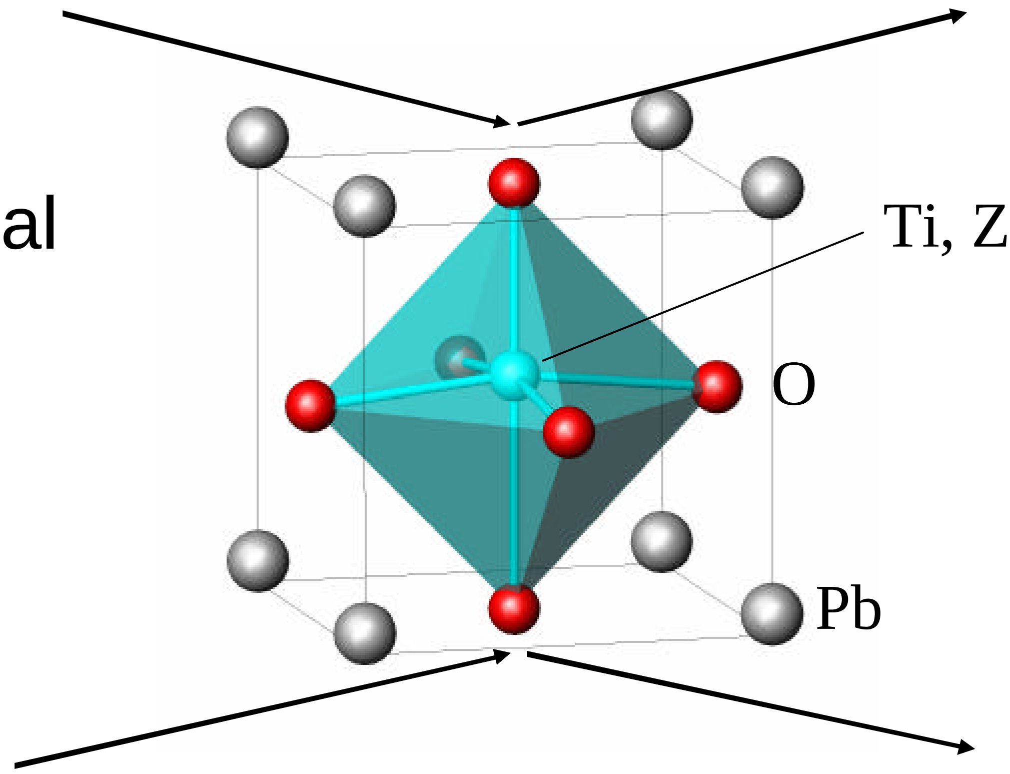
Remanent polarization vs. # cycles



Challenge:

Non-volatile RAM requires $> 10^{15}$ read/write cycles !

Imaging Domains by Breaking Friedel's Law



(002) x-ray reflection

Absorption in the crystal causes the two x-ray reflections to have the same 2θ values but different intensities

$(00\bar{2})$ x-ray reflection

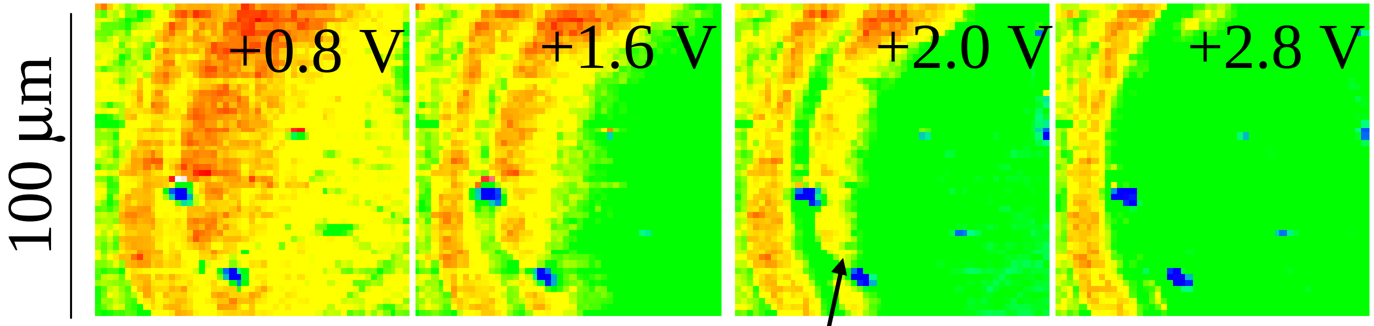
$$\frac{I^+ - I^-}{I^+ + I^-} \sim 0.3$$

@ E_i=10 keV

X-ray Visualization of remanent polarization in $PbZr_{0.6}Ti_{0.4}O_3$ (PZT)

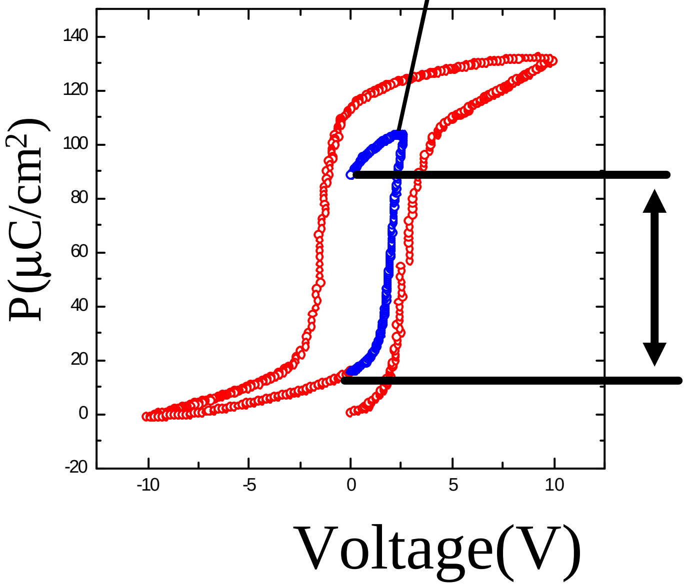
Map PZT (002) following voltage pulses to bottom electrode

MHATT-
CAT



Spot size: ~ 0.6 x 0.6 μm^2

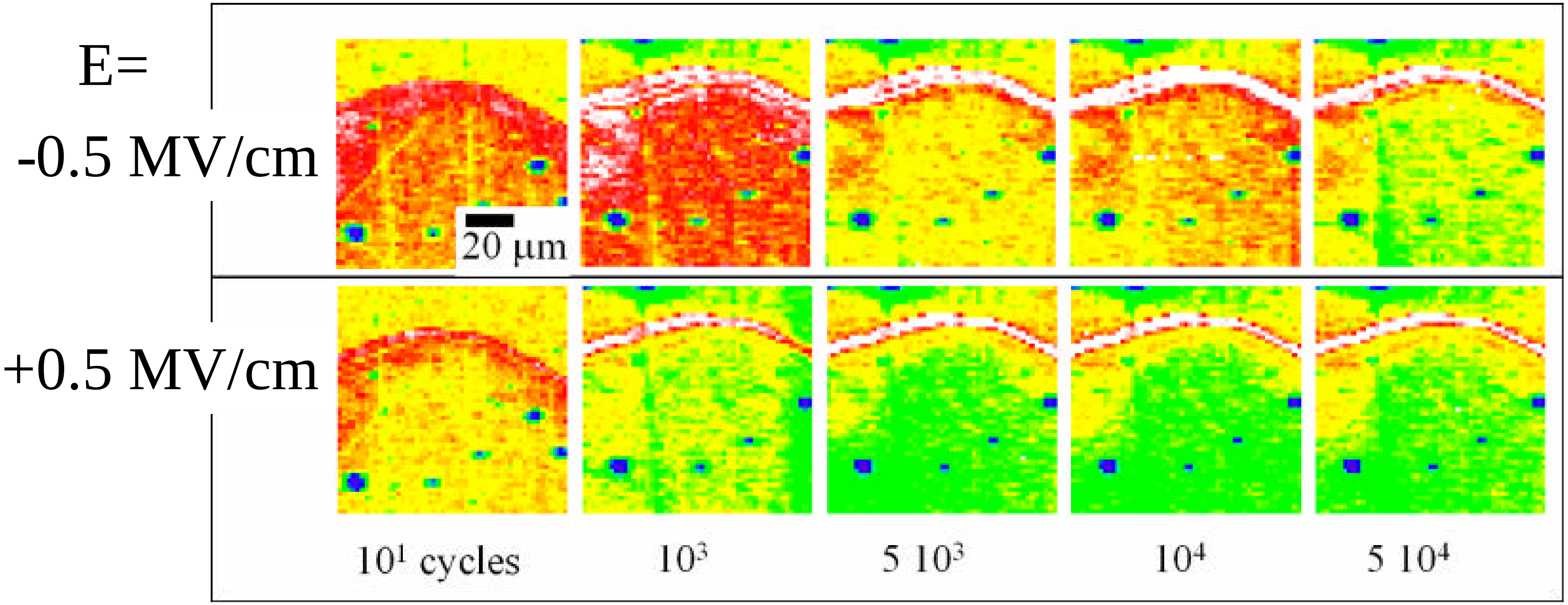
theta and theta/two-theta scans unchanged



switchable polarization, P_r

Ferroelectric Fatigue – Low-Field Regime

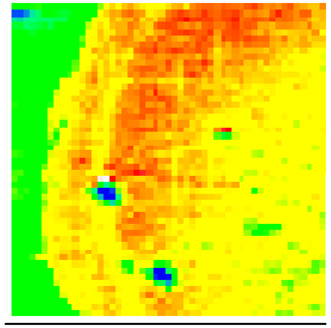
160 nm thick PZT device



- reversible - ±1.2 MV/cm restores the full switchable polarization
- no fatigue observed (<5 x 10^7 cycles) for $SrRuO_3$ top electrode; suggests chemical mechanism, e.g., oxygen diffusion
- domain wall pinning or suppression of nucleation

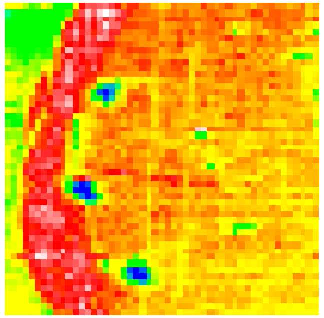
Ferroelectric Fatigue – High Field Regime

10^2 cycles

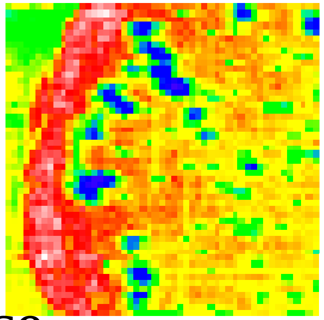


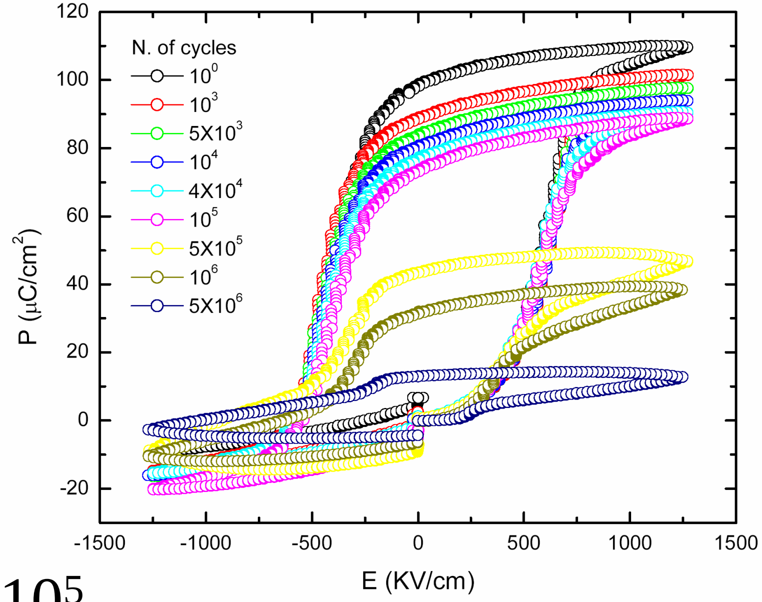
100 μm

10^4

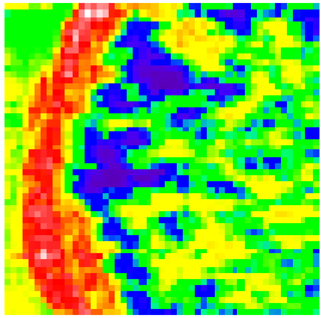


$5\text{x}10^4$

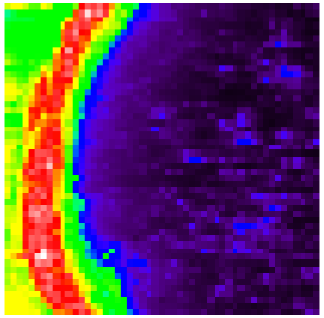




10^5



$5\text{x}10^5$



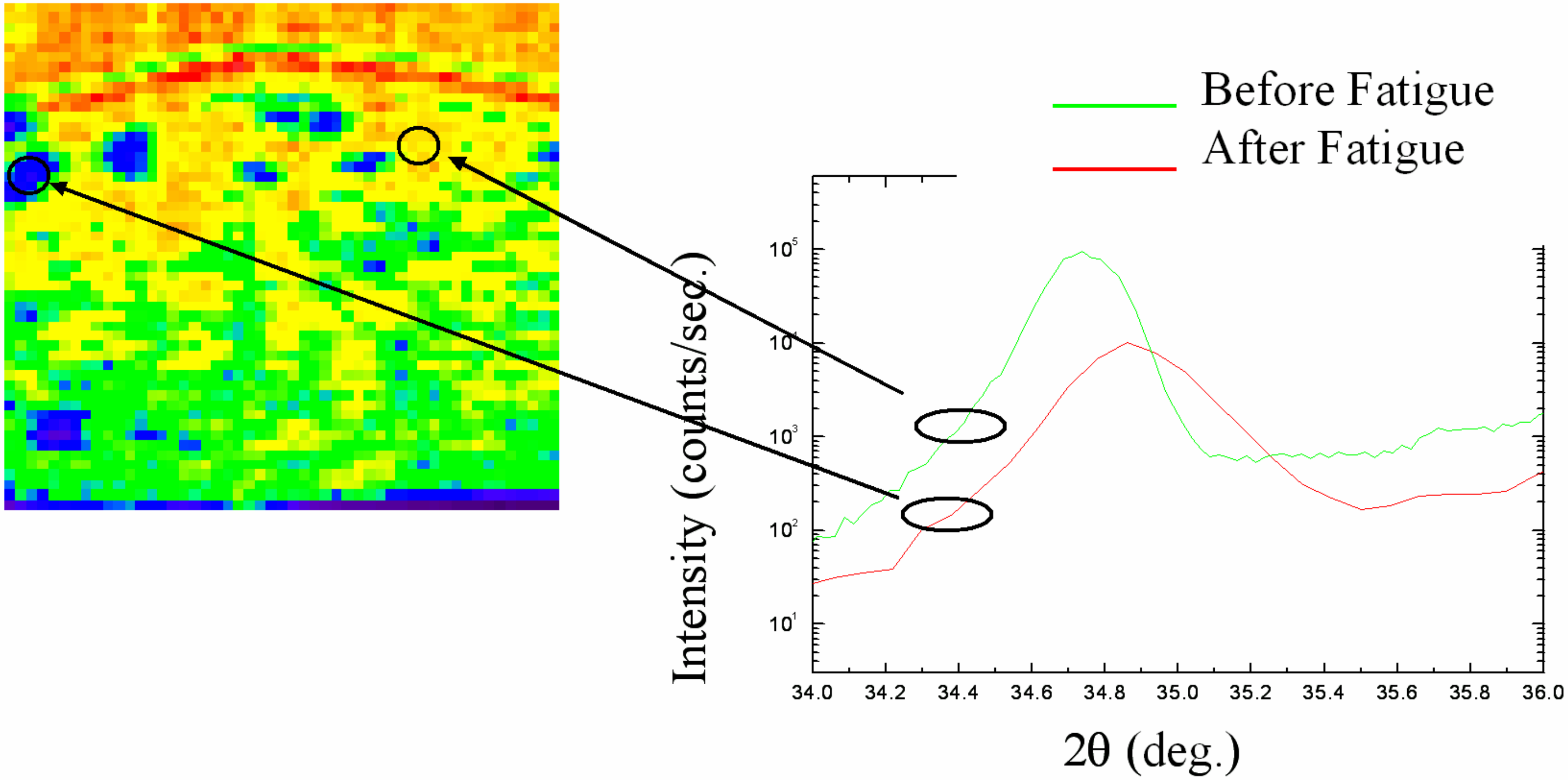
80 nm thick PZT device

E = -1.2 MV/cm (-19 V)

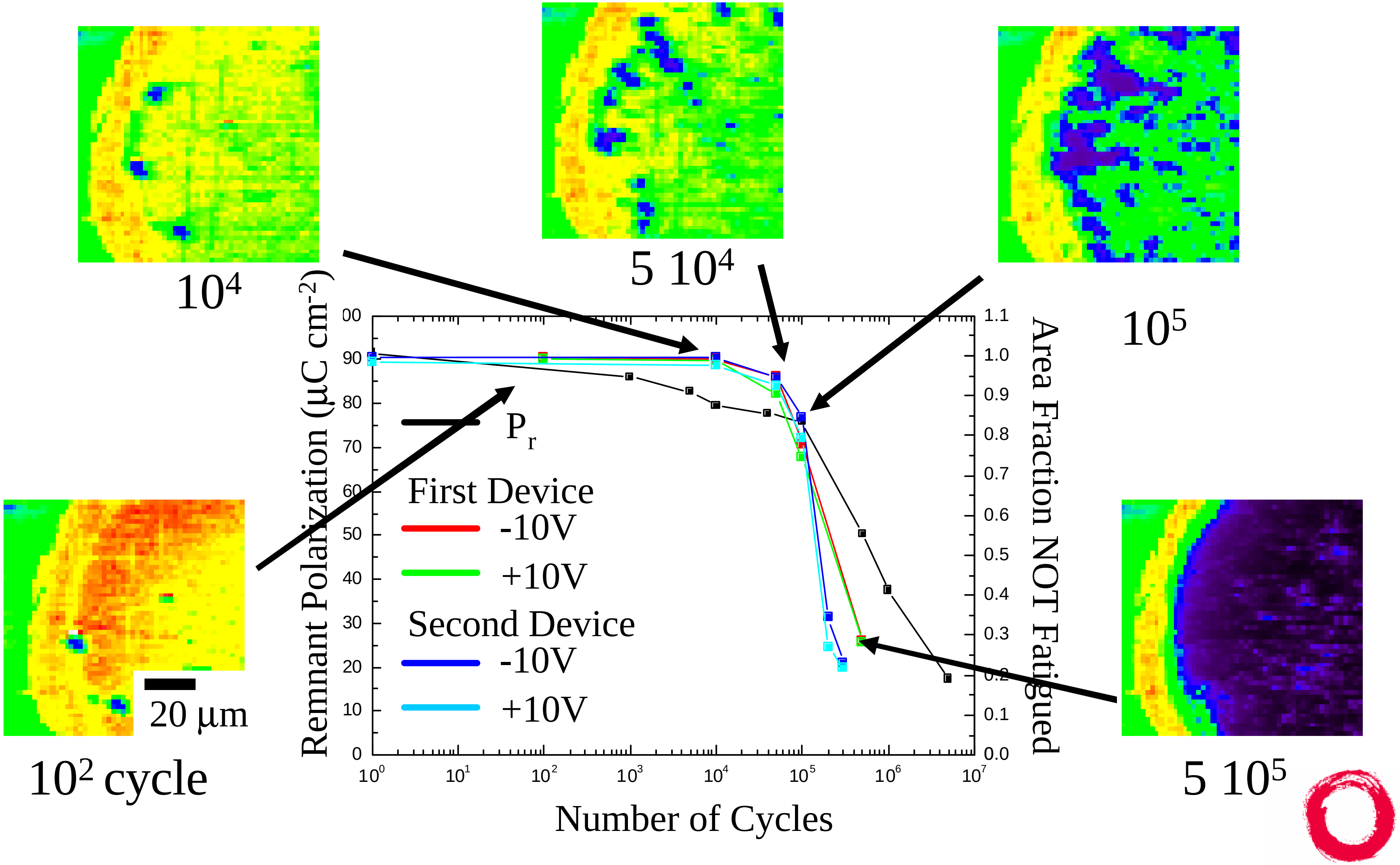
(Breakdown field ~ 2 MV/cm)

High Field Regime – lattice relaxation

E = -1.2 MV/cm



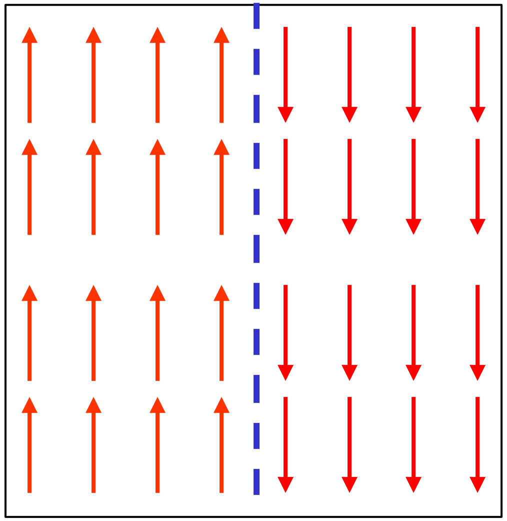
X-ray microdiffraction as an accurate probe of stored polarization



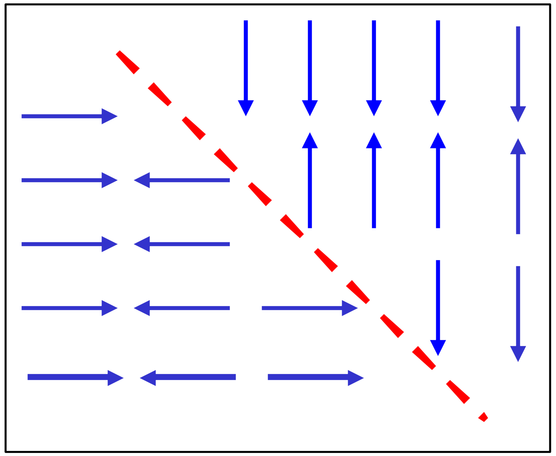
Summary

- x-ray microscopy is right tool for sorting out polarization switching and fatigue in ferroelectric devices.
  - direct structural probe of polarization switching
  - Two field regimes in fatigue
    - Low-field reversible regime (< 0.5 MV/cm)
    - High-field non-reversible regime (> 1 MV/cm)
      - ferroelectric breakdown/film relaxation
- domain wall dynamics
  - fast CCD and x-ray objective optics
  - coherent diffraction

domain wall physics



ferromagnetic



antiferromagnetic

Fundamental science

high T_C (e.g., striped phase domains)

CMR, quantum phase transitions,…

Technological importance

hard magnets, recording medium, eg., non-volatile memory (M/FRAM), etc..

Length scales

Bloch wall

$$\sigma_w \sim 2\pi\left(KJS^2/a\right)^{1/2}$$

3 Å – µm's

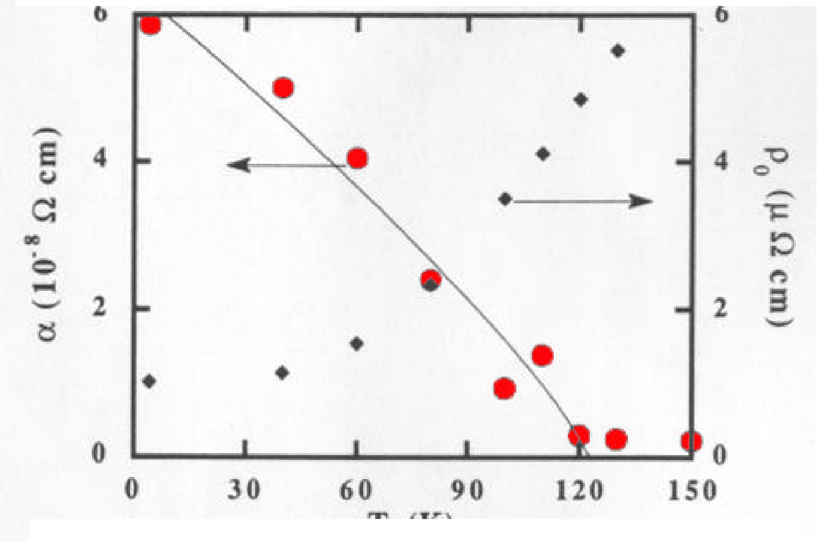
AFM ???

chromium

chromium and its common alloys are ‘simple’ bcc metals, exhibiting a range of complex behaviors including;

- complex magnetism
  - incommensurate spin density waves (TSDW and LSDW)
    - incommensurate CDW and strain wave
  - ‘chromium anomaly’ at T_N (311 K)
  - quantum critical behavior (e.g., $Cr_{1-x}V_x$)
    - x=3.5% suppresses T_N=0
    - pressure in pure Cr.

$$r(H,T) = r(H=0,T) + a(T)(H/H_0)^n$$

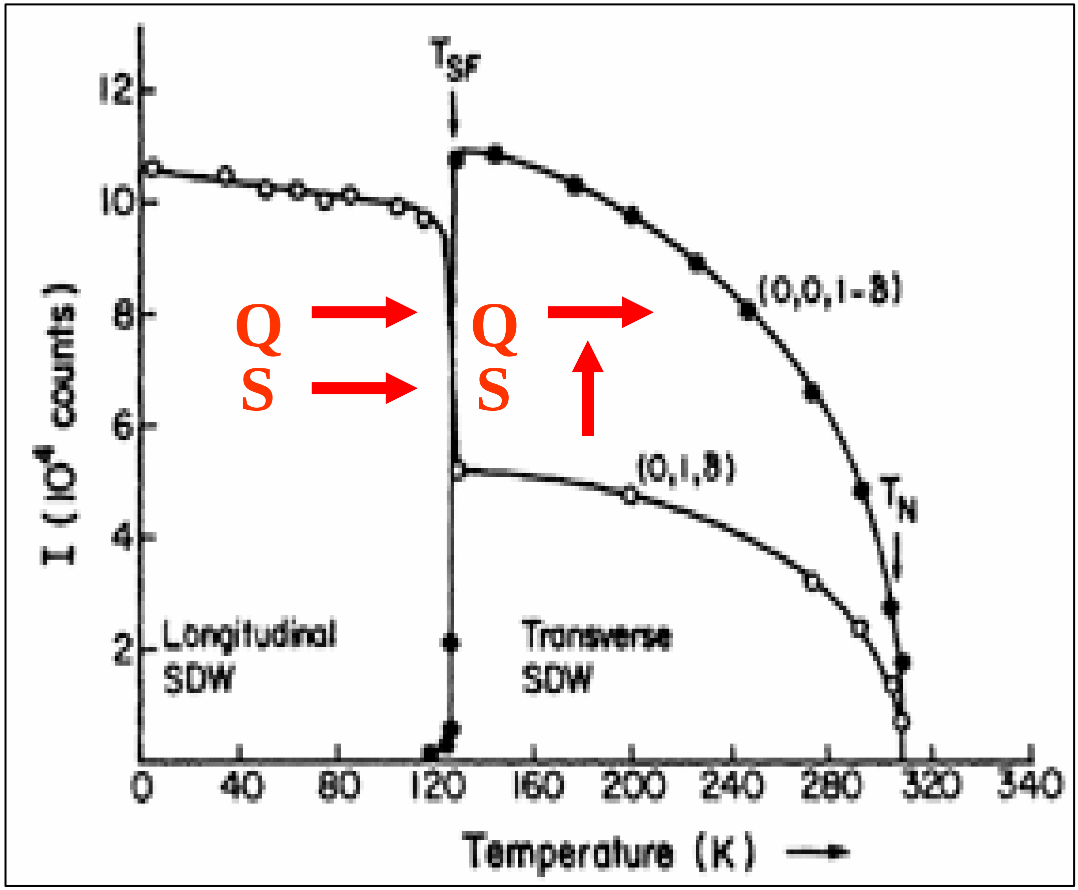


Mattson *et al.* JMMM**109** 179 (1992).

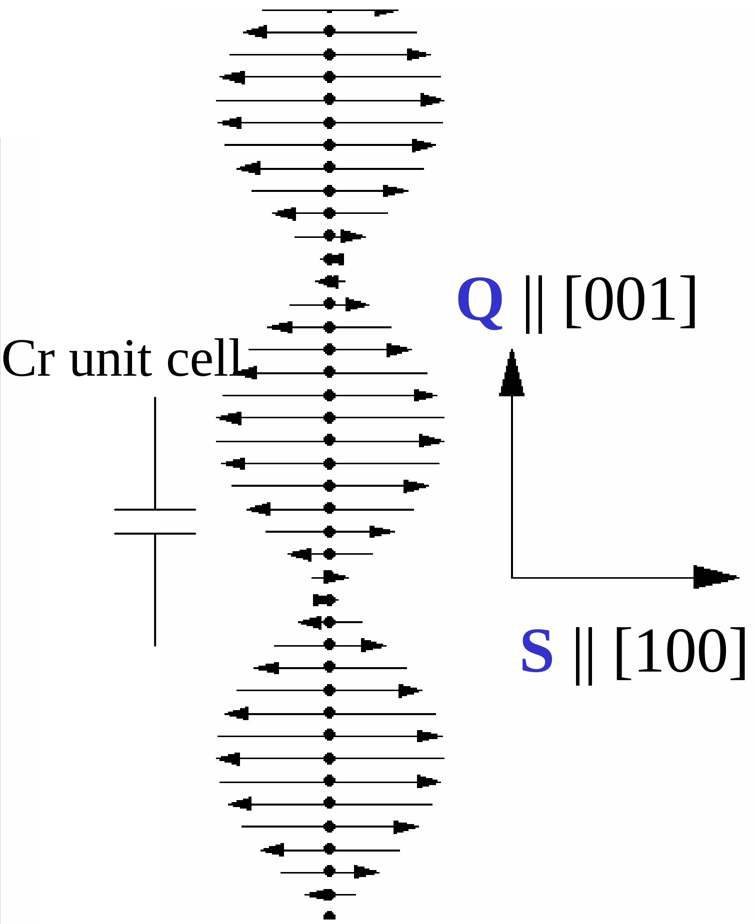
antiferromagnetic order in Cr

magnetic neutron diffraction

Fawcett, Rev. Mod Phys. 60, 209 (1988)

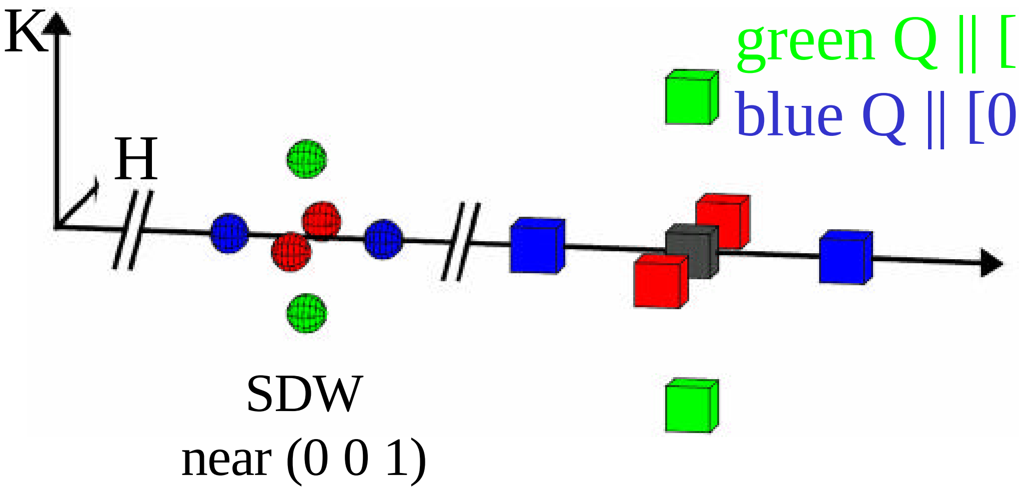


Incommensurate SDW



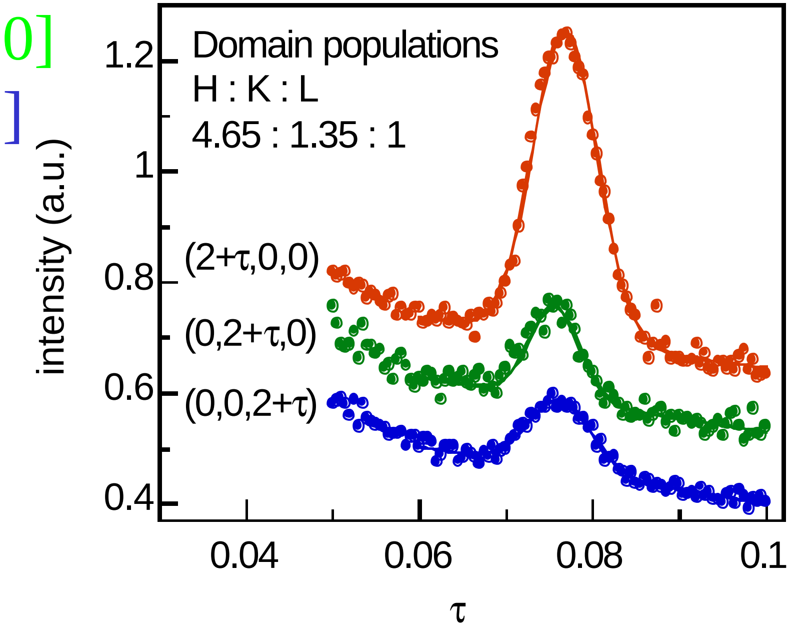
incommensurate Bragg peaks in Cr

Magnetic scattering appears near forbidden lattice reflections.



red Q || [100]
green Q || [010]
blue Q || [001]

All three domains present



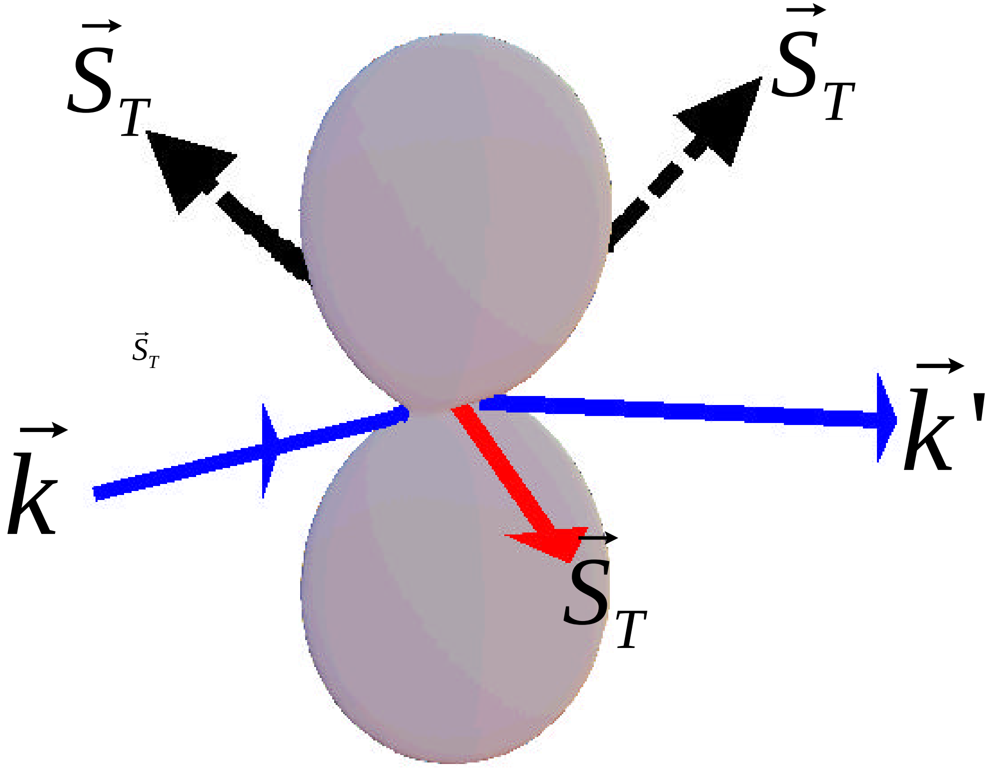
Fermi surface nesting at **Q**

Form images using either (SDW, CDW) type of reflection.

magnetic x-ray diffraction contrast in Cr

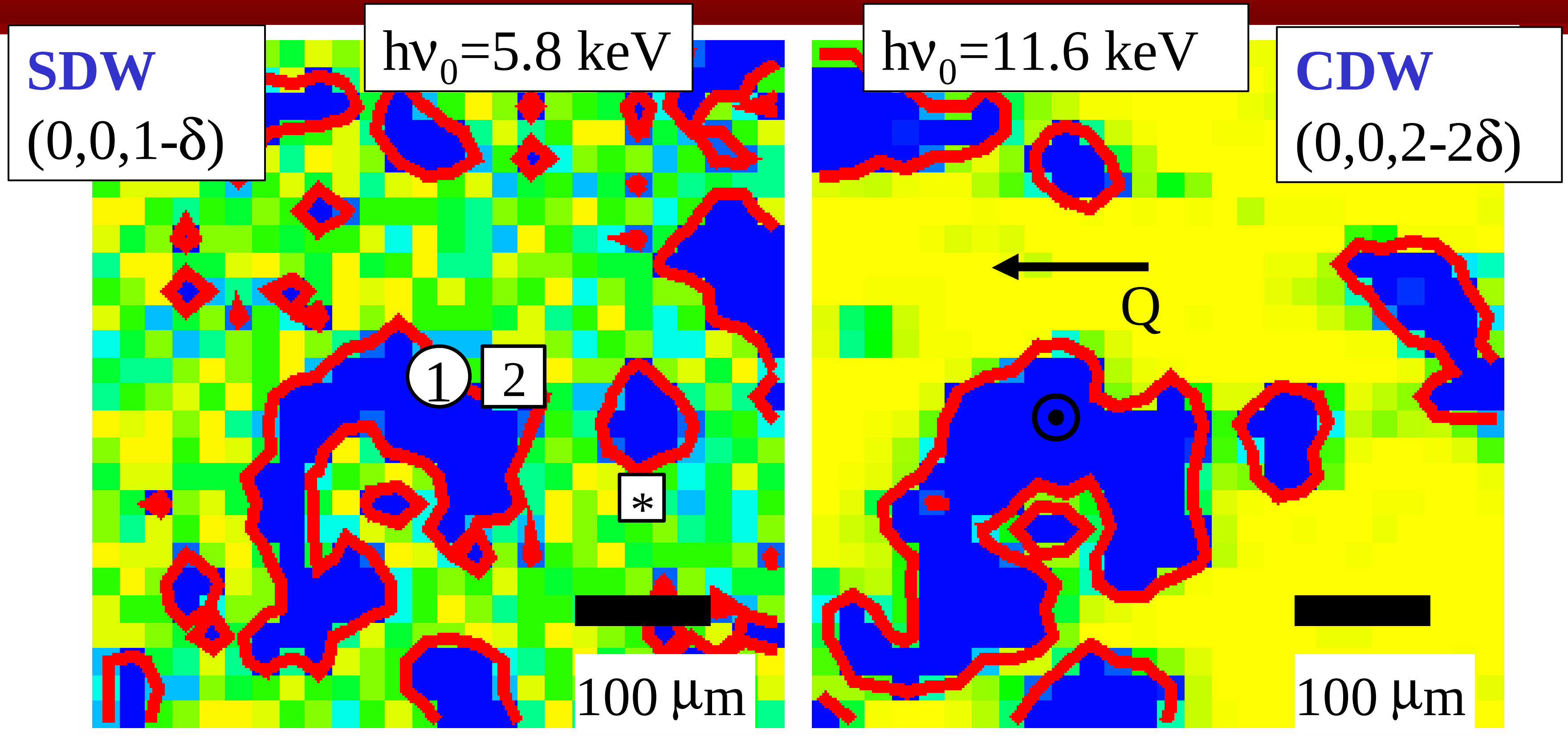
Most important term in cross section:

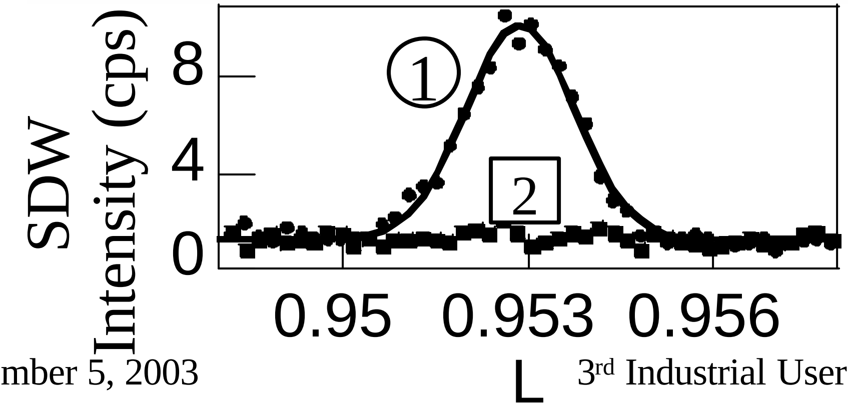
$$I \propto \left| \vec{\mathbf{S}} \cdot (\hat{\mathbf{k}} \times \hat{\mathbf{k}}') \right|^2$$



Polar plot of cross section as a function of spin direction for a **Q** || (001) domain in our geometry.

(Transverse) SDW domains at 130 K





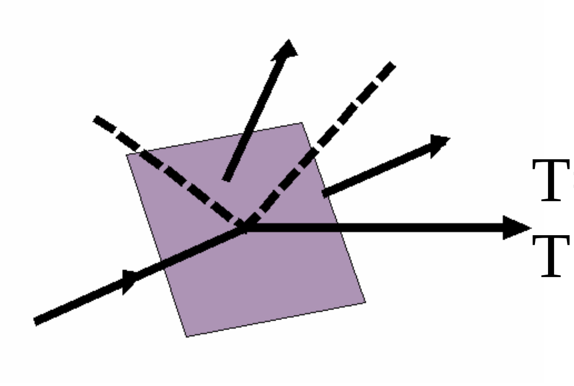
90 ° Q-domains

P.G. Evans, et. al., Science **295**, 1042 (2002).

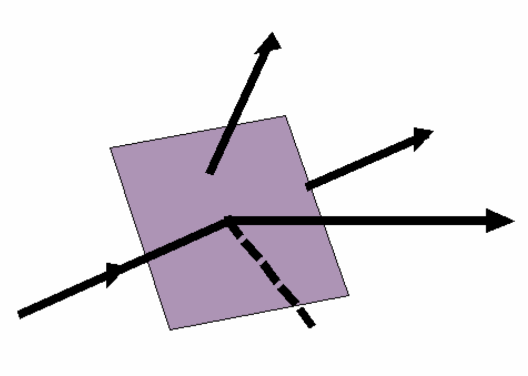
spin-flip transition in Cr

SDW Magnetic reflection

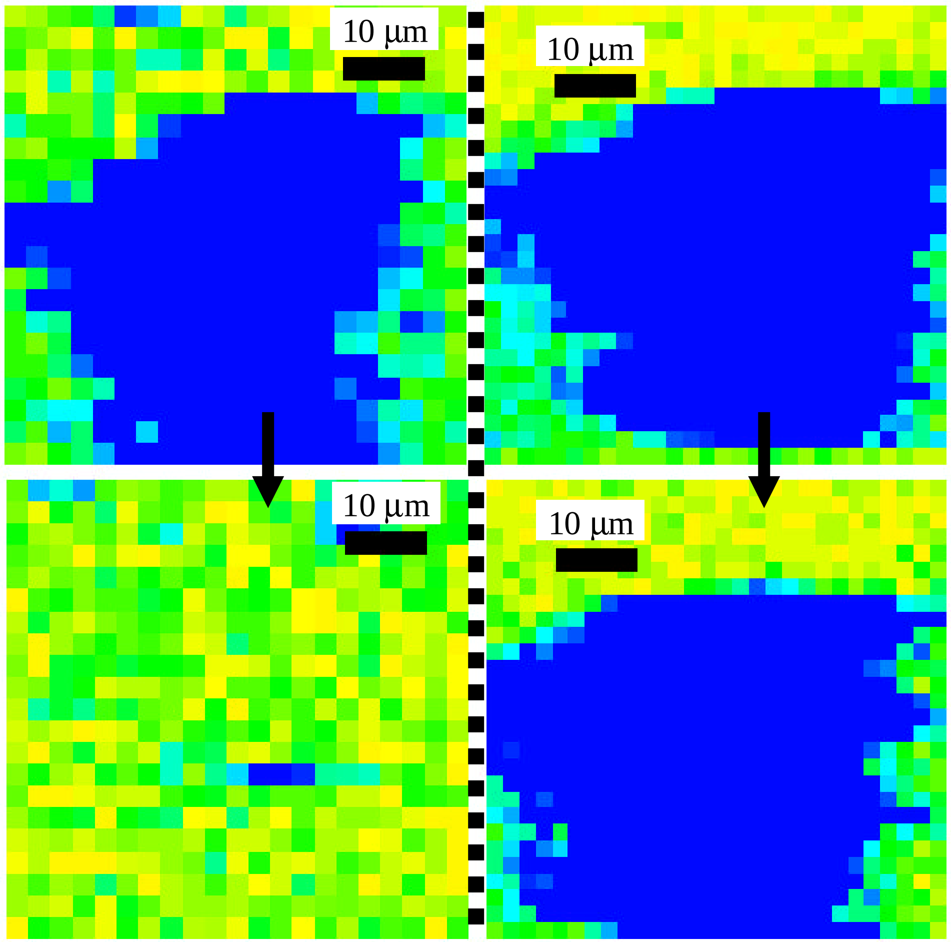
CDW Charged reflection



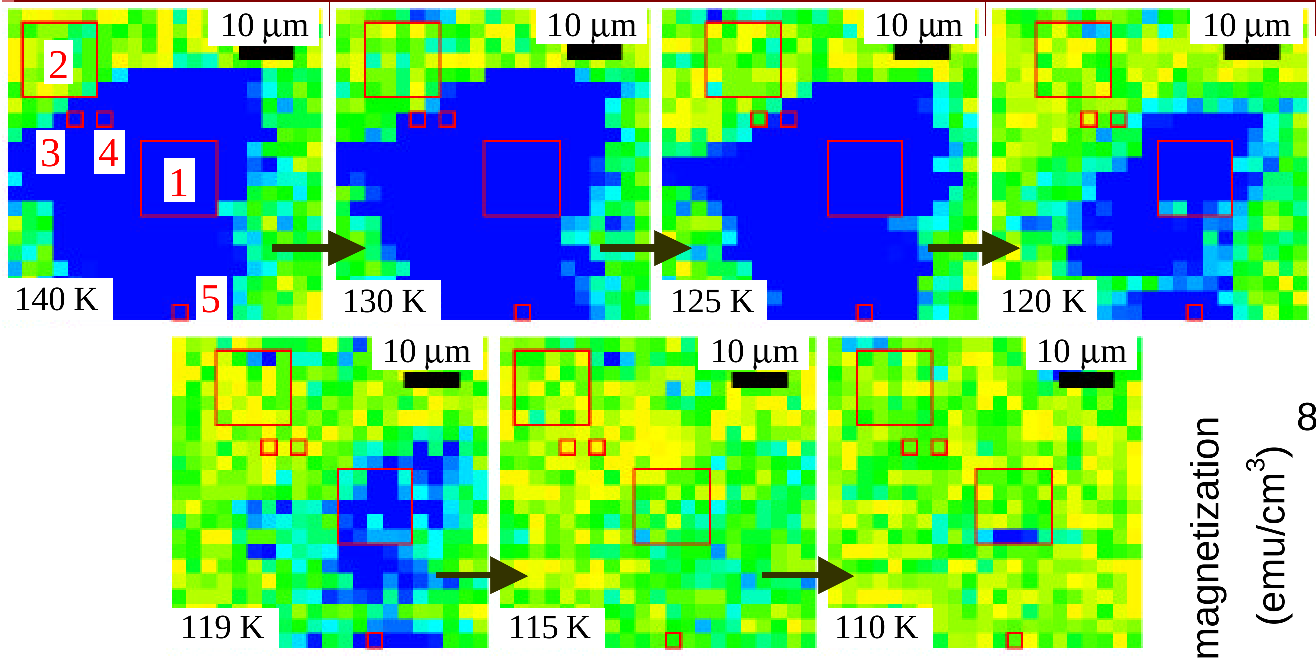
T=130 K
TSDW

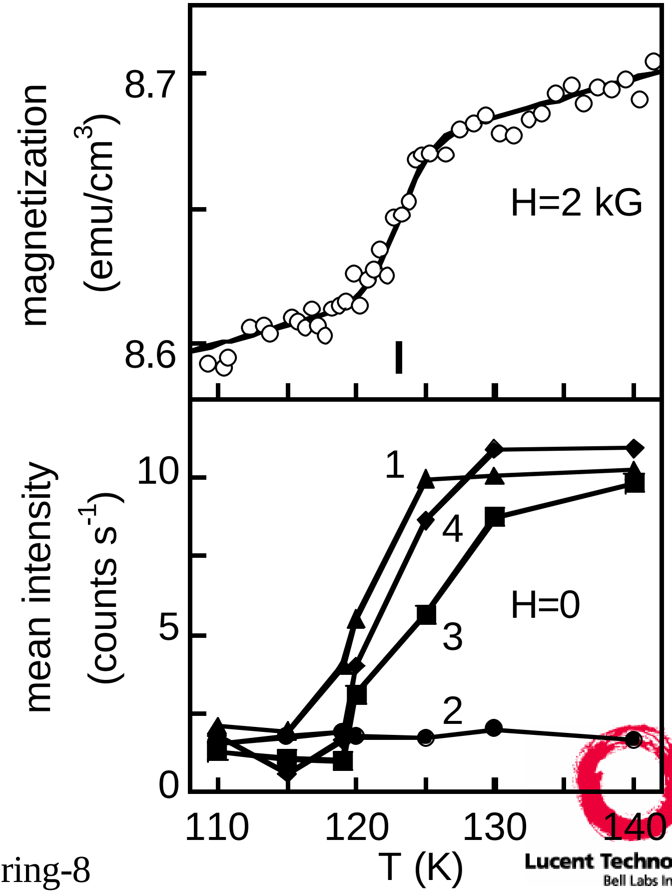


T=110 K
LSDW



Spin flip transition begins at **Q** domain edges



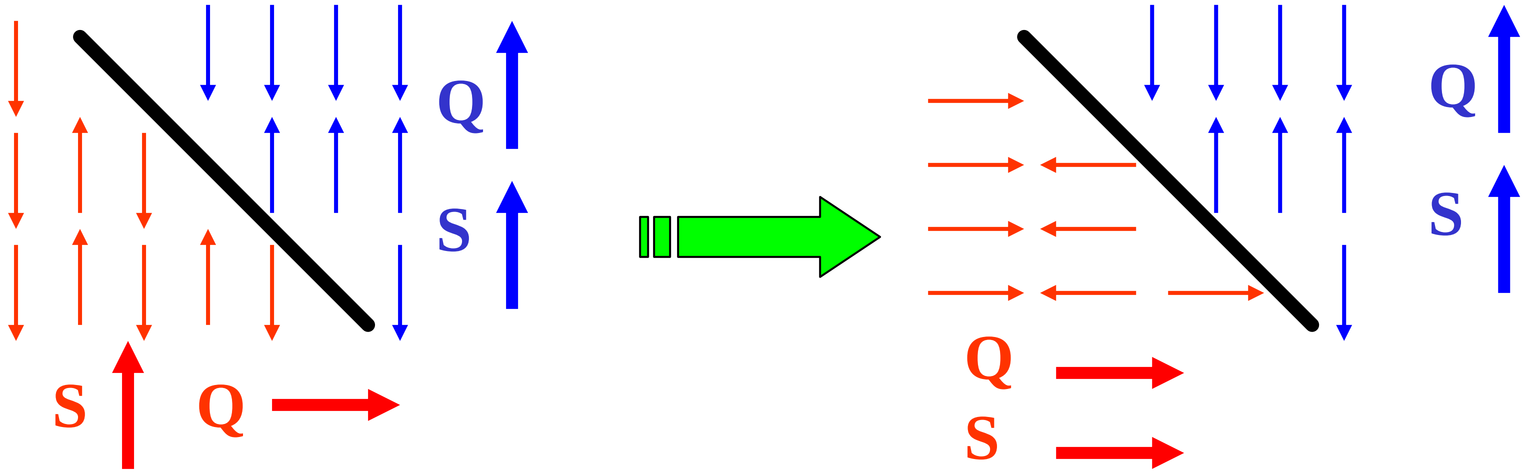


Nominally first order transition is broadened by several degrees, even at micron scale.

microscopic sources of broadening

Not much known (yet) about antiferromagnetic domain walls.
(FM/AFM interfaces are well described in comparison)

1. Magnetic interactions across domain boundary (e.g., ‘exchange-bias’)

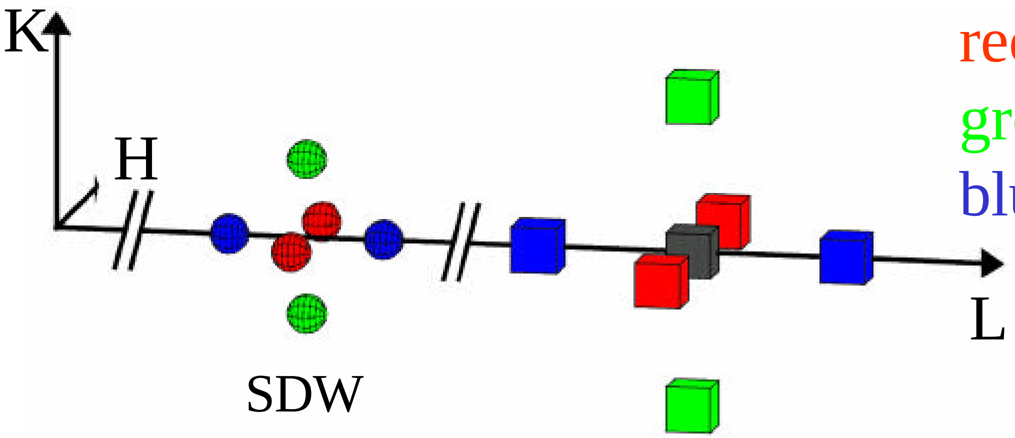


2. Fermi surface effects - simultaneous Fermi surface nesting at multiple **Q** directions is not allowed.

3. strain ($\delta T_{SF} \sim 1°$ K per $\delta d/d \sim 10^{-4}$)

Learning more about domain walls

So far we’ve looked at **Q**-domain walls.



red Q || [100]
green Q || [010]
blue Q || [001]

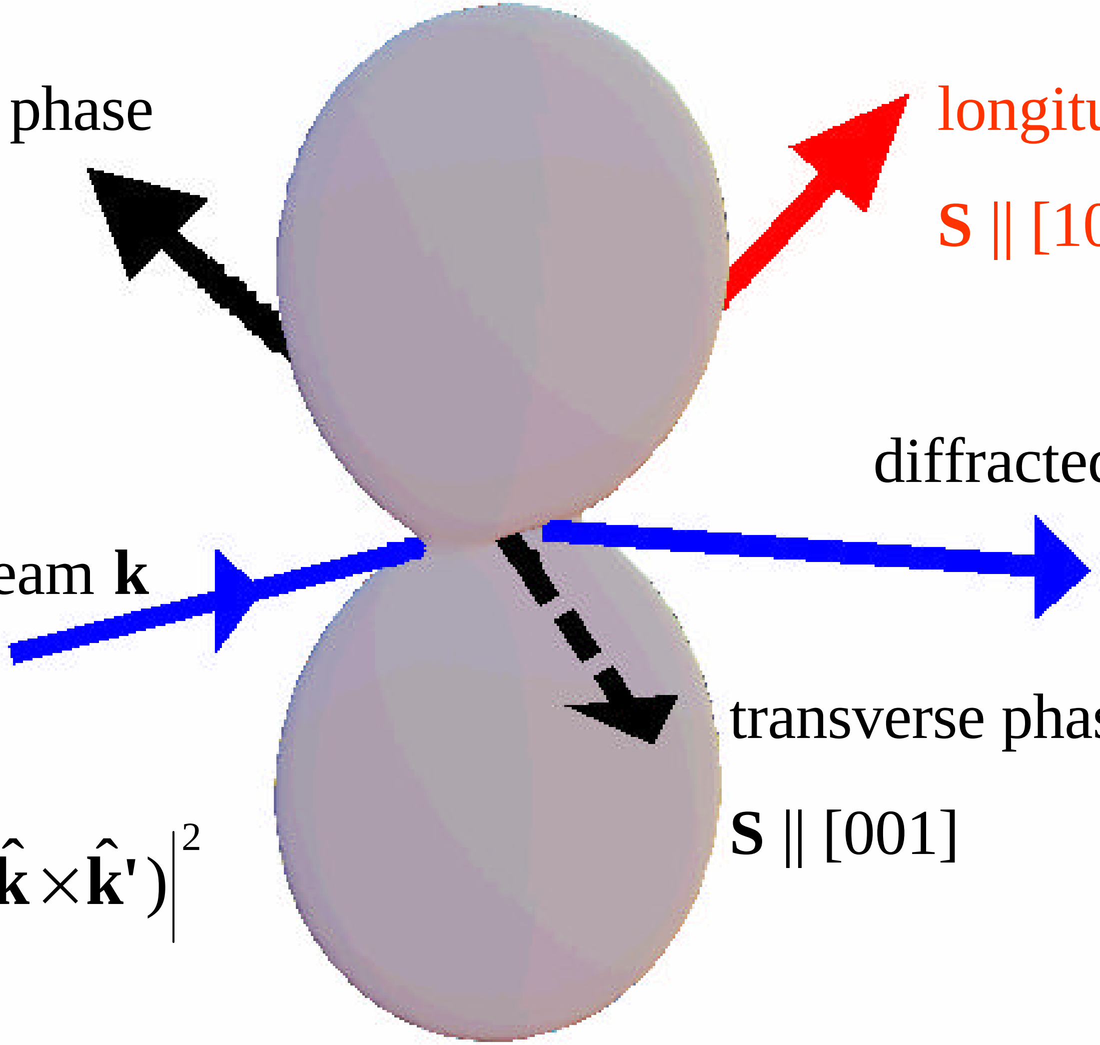
SDW
near (0 0 1)

CDW
near (0 0 2)

What about S-domain walls ?

two transverse spin polarizations (T > 123 K)

Magnetic cross sections in a **Q** || [100] domain



transverse phase

S || [010]

longitudinal phase

S || [100]

diffracted beam **k’**

incident beam **k**

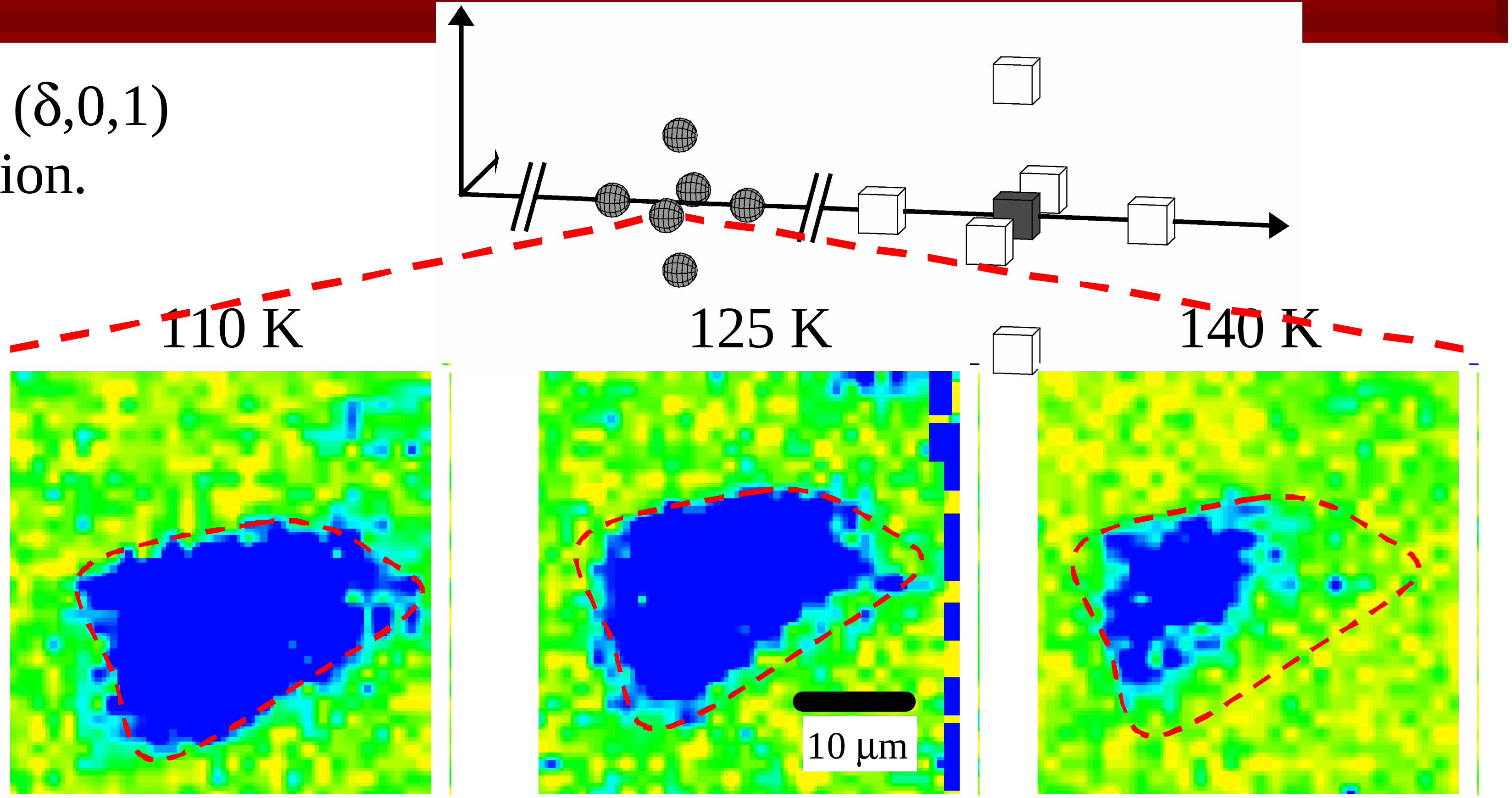
transverse phase

S || [001]

$$|M|^2 \propto \left|\vec{\mathbf{S}}\cdot(\hat{\mathbf{k}}\times\hat{\mathbf{k}}')\right|^2$$

S domains within a [100] **Q** domain

Image (δ,0,1)
reflection.



S: longitudinal | mixed | transverse

visible spins: **S** ‖ [001] ‖ **Q**

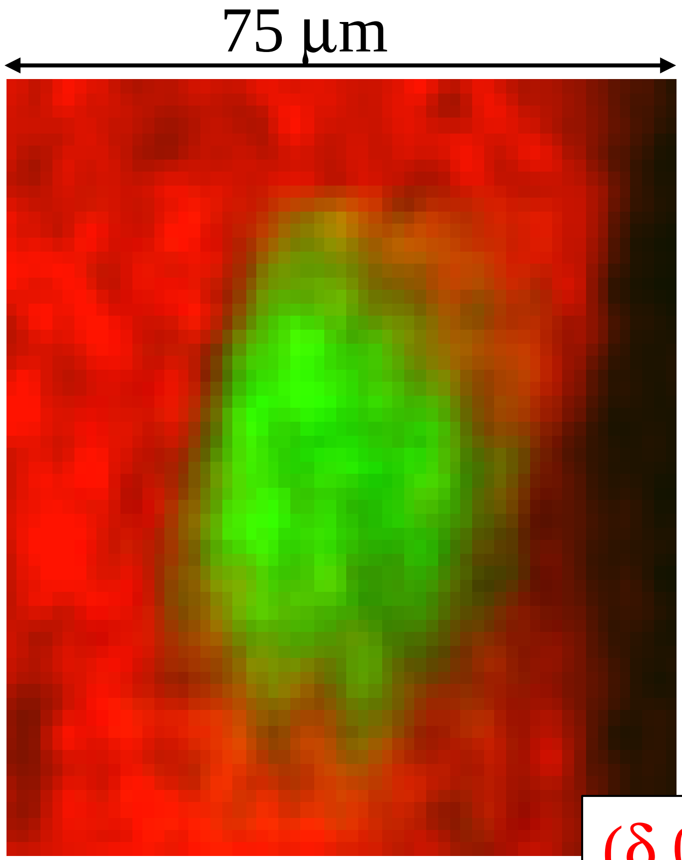
S ‖ [001] ‖ **Q** or
S ‖ [010] ⊥ **Q**

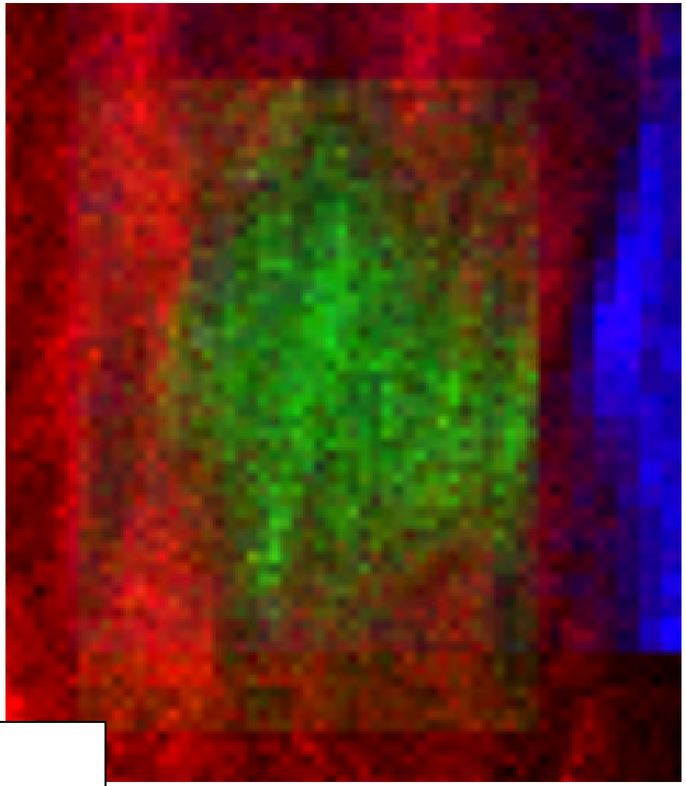
S ‖ [010] ⊥ **Q**

What's happening in adjacent domain? Width of **S** domain wall?

hints of new phenomena

composite images

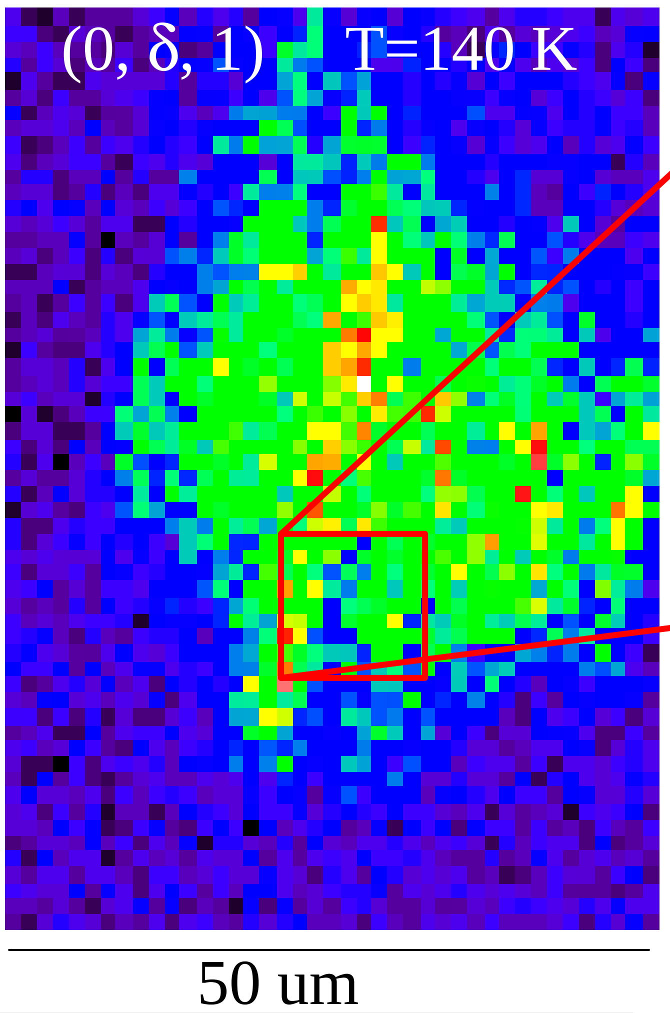


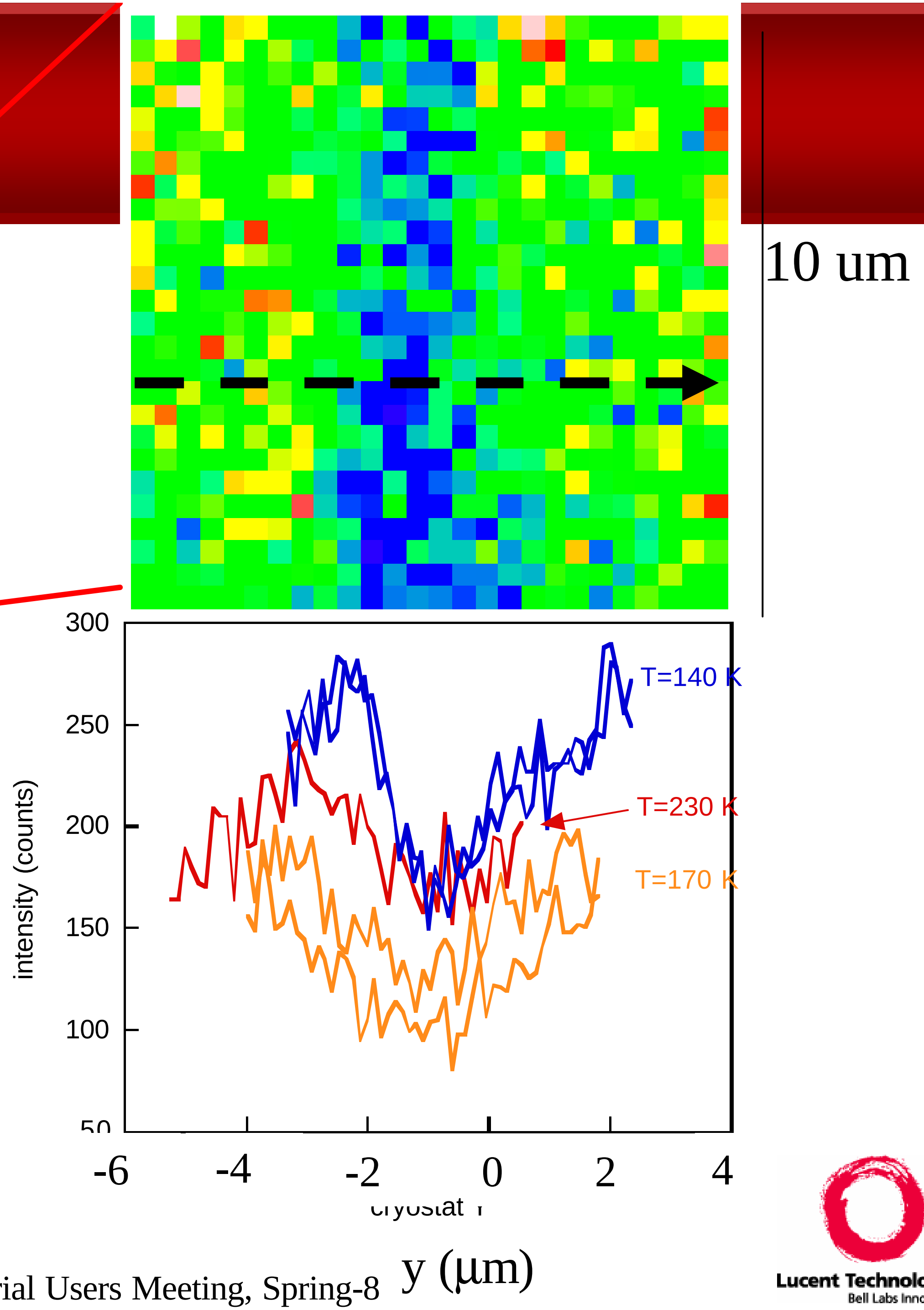


$(\delta,0,1)$ red
$(0,\delta,1)$ green
$(0,0,1+\delta)$ blue

T=110 K
LSDW

T=140 K
TSDW





Bloch Wall in FM

$$s_w \sim 2p\left(KJS^2/a\right)^{1/2}$$

$$\sim 100 \text{ nm in Fe}$$

Summary

- Self-organized domains at small scales are key to macroscopic properties in Cr.
  - magnetic x-ray microscopy (MXM) is right tool for sorting out physics of complex domain structures

- Future directions
  - Dynamics – fast CCDs and x-ray objective lenses
    - coherent x-rays ('imaging' in reciprocal space)
  - artificial domain walls
  - Quantum critical phenomena
    - domain walls should be important at quantum critical point, e.g., in $Cr_{1-x}V_x$ (e.g., quantum domain wall 'roughening')

Conclusions and Future Directions

- domain wall physics is critical to many important materials problems for technology and fundamental physics.

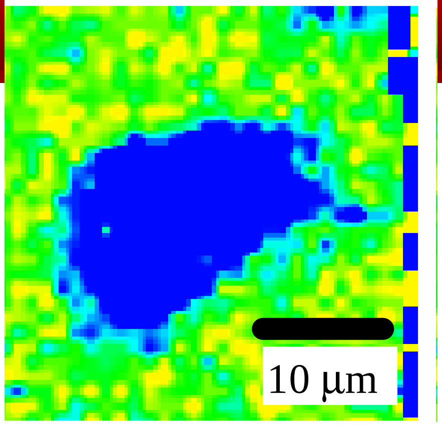
- x-ray nanoprobe (30 - 100 nm) is right quantitative tool for sorting out the physics of complex domain structures – strain, magnetism, structure, composition, etc..

Single Domains and Domain Walls

Image contrast: spin polarization

magnetic materials, quantum critical phenomena

e.g., Cr, CrV, $LiHoF_4$



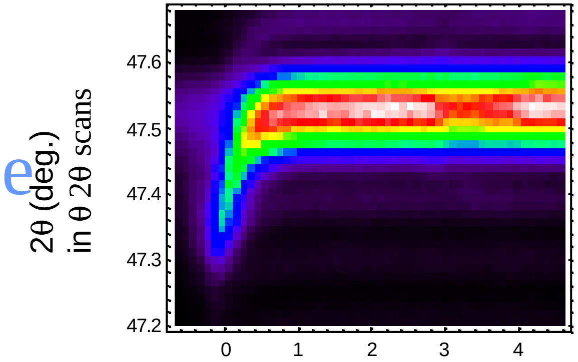
Spin density wave domains in Cr

P. Evans, *et al.*, Science **295** 1042 (2002).

Image contrast: strain

colossal magneto-resistance

$La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ bi-crystal



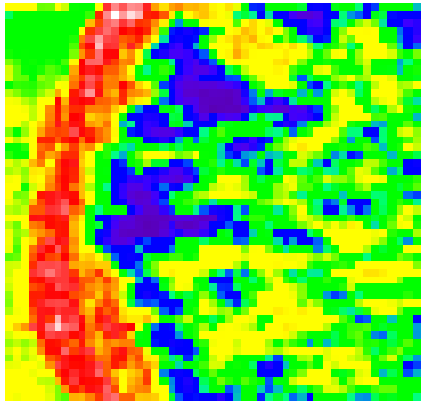
Strain relaxation at an artificial grain boundary

Y.-A. Soh, *et al.*, JAP**91**, 7742 (2002).

Image contrast: Friedel's law

ferroelectrics, fatigue

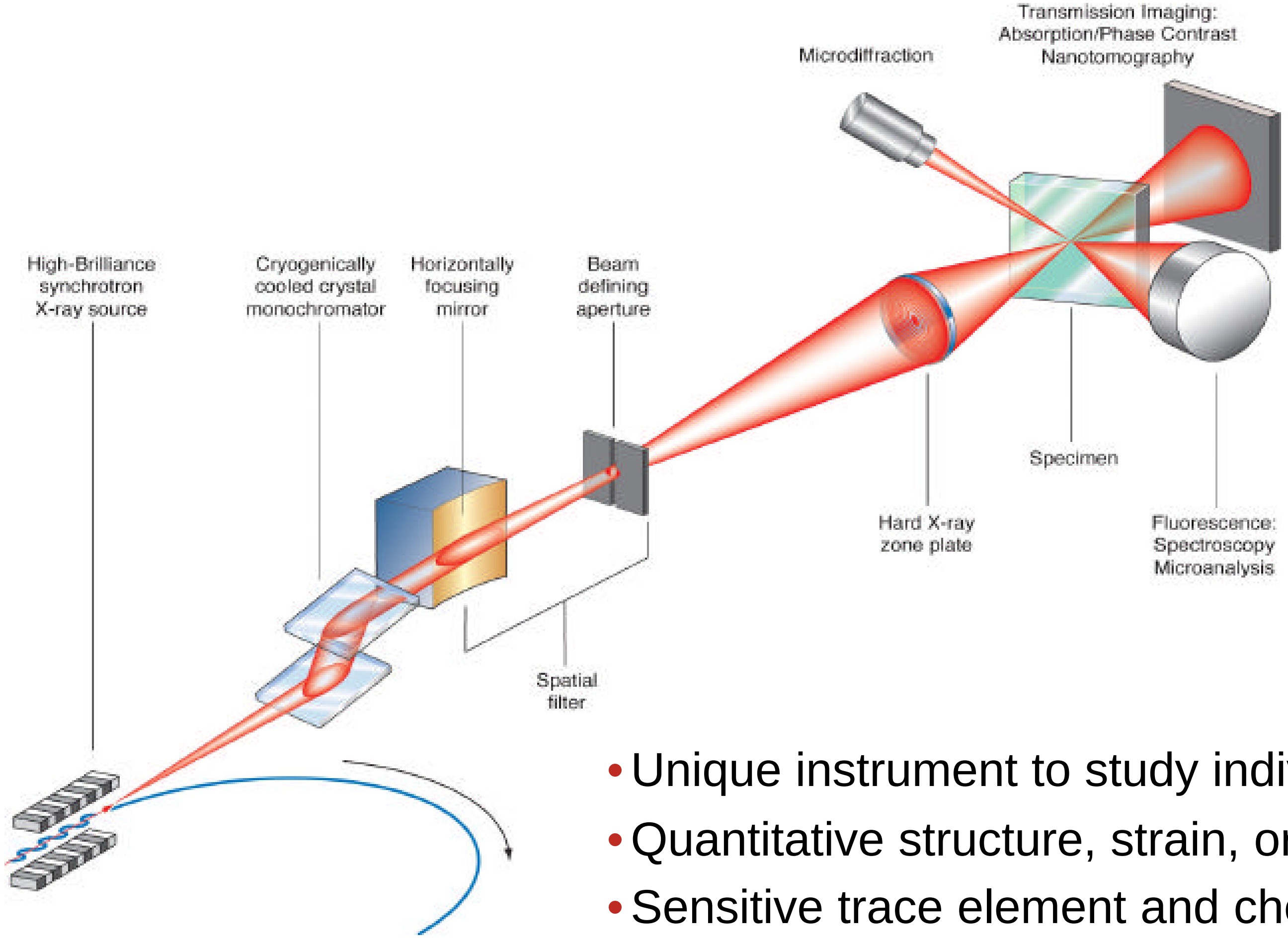
$LiNbO_3$, SBT, PZT, …



Fatigue in ferroelectric PZT device.

P. Evans, *et al.* (2003)

The Hard X-Ray Nanoprobe – Nano-CAT



- 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

Center for Nanoscale Materials Building

~85,000 gross square feet, including:

- 13,000 sq ft Laboratories
- 11,000 sq ft Cleanroom Facilities
- 33,000 sq ft Offices & Public Spaces

- Capital Investment

• IL	$36 M	Building Construction
• DOE	$36 M	Instrumentation