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In-Situ Measurement of Crystalline Lattice Strains in Fluoropolymers by Neutron Diffraction

Eric N Brown, Bjørn Clausen, Donald W Brown, Thomas A. Sisneros, Dana M Dattelbaum, Philip J Rae, E Bruce Orler

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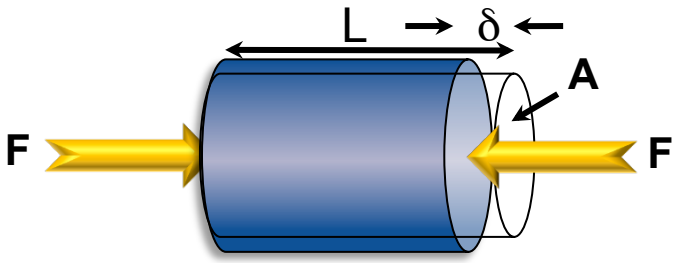
Outline

- Intro to important engineering parameters and diffraction measurements
- Intro to the pressure and temperature dependence of the crystalline phases of polytetrafluoroethylene (PTFE, Teflon)
- Using SMARTS to measure the lattice strains in the crystalline domains of a semi-crystalline polymer
- Observation of a new strain path to inducing a phase transition in PTFE

When tensile and compressive forces are applied to a body, stress is the force per unit area upon which it acts and strain is the unitless deformation



Engineering Stress $= \sigma = \dfrac{\textbf{Force}}{\textbf{Area}} = \dfrac{F}{A}$

(Unit is Pascal (Pa) or N/m^2)

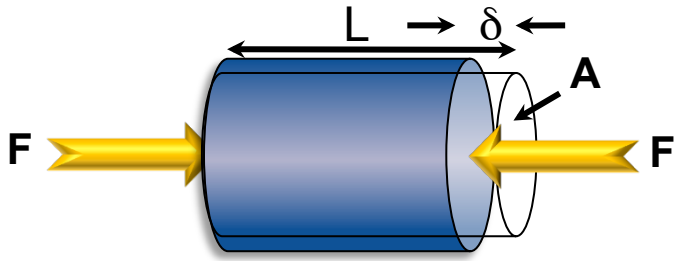
Engineering Strain $= \varepsilon = \dfrac{\textbf{displacement}}{\textbf{initial length}} = \dfrac{\delta}{L}$

(Unitless)

Poisson's ratio $= \nu = -\dfrac{\textbf{transverse strain}}{\textbf{axial strain}} = \dfrac{\varepsilon_y}{\varepsilon_x}$

(Unitless, typically 0 to 0.5)

Hookes's Law states the deformation of a spring is directly proportional to the force. This proportionality in terms of stress and strain is the Young's modulus (*E*)

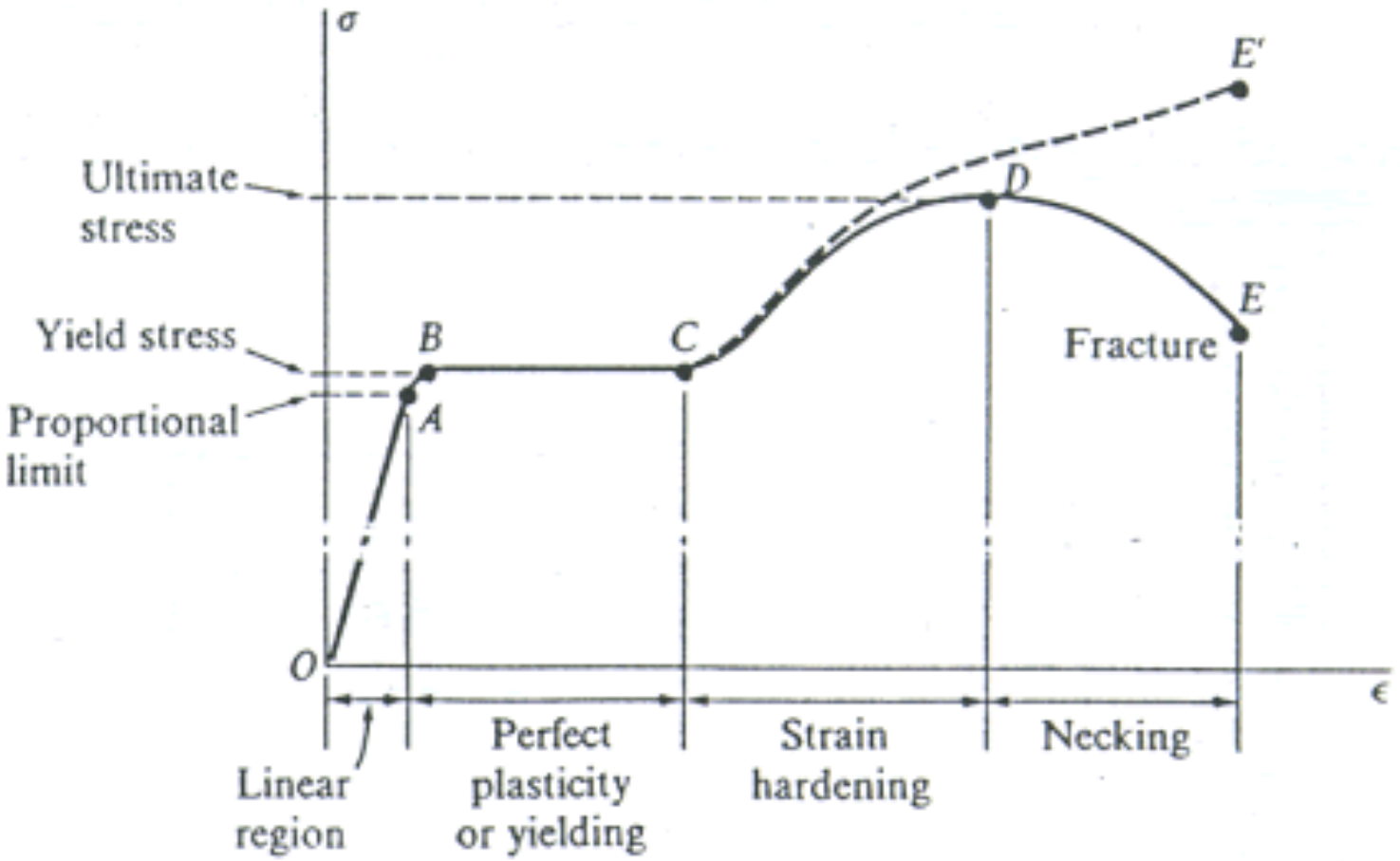


$$\sigma = \frac{F}{A}$$

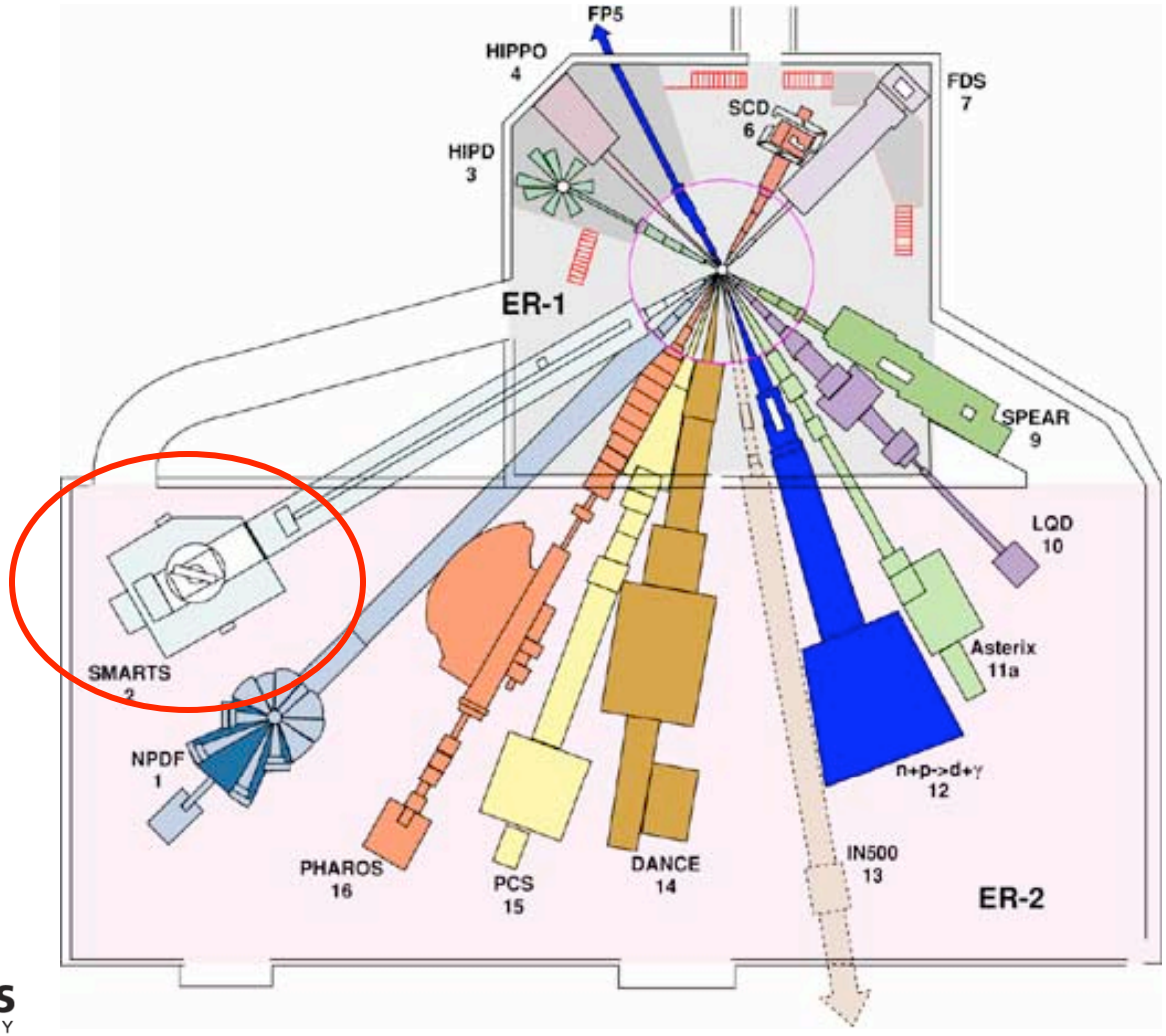
$$E = \frac{\sigma}{\varepsilon} = \frac{FL}{A\delta}$$

$$\varepsilon = \frac{\delta}{L}$$

Representative Stress-Strain Diagram

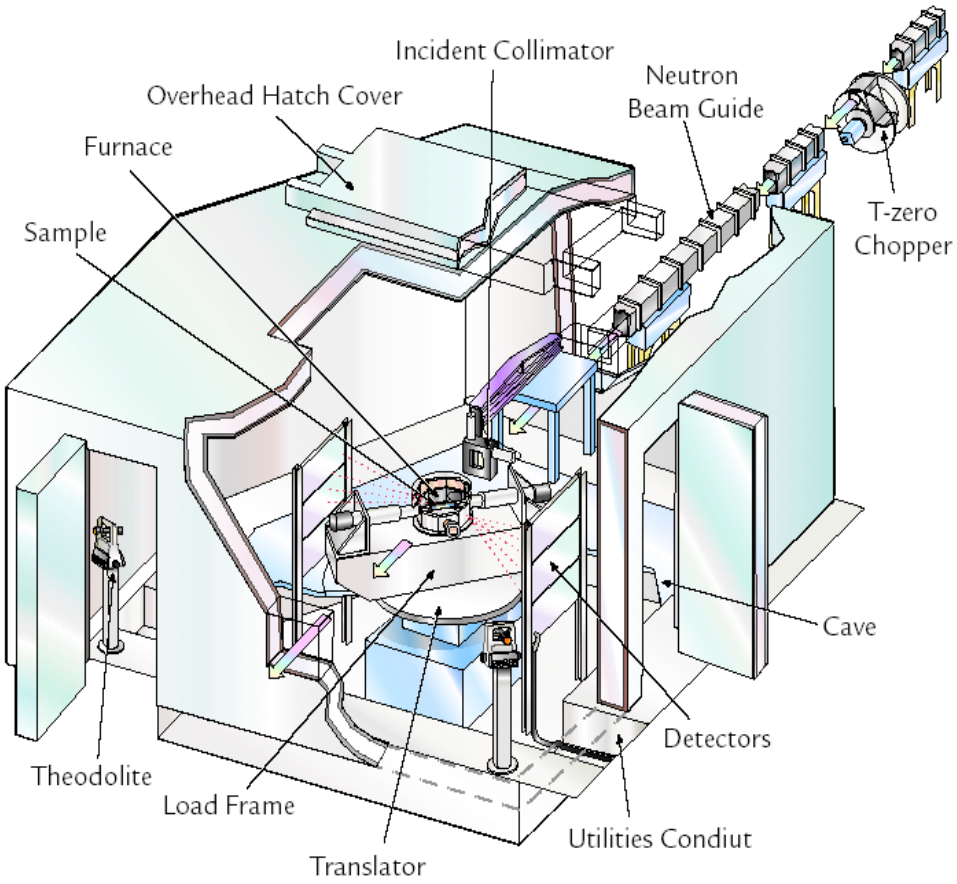


Neutron Diffraction Instruments at the Lujan Center



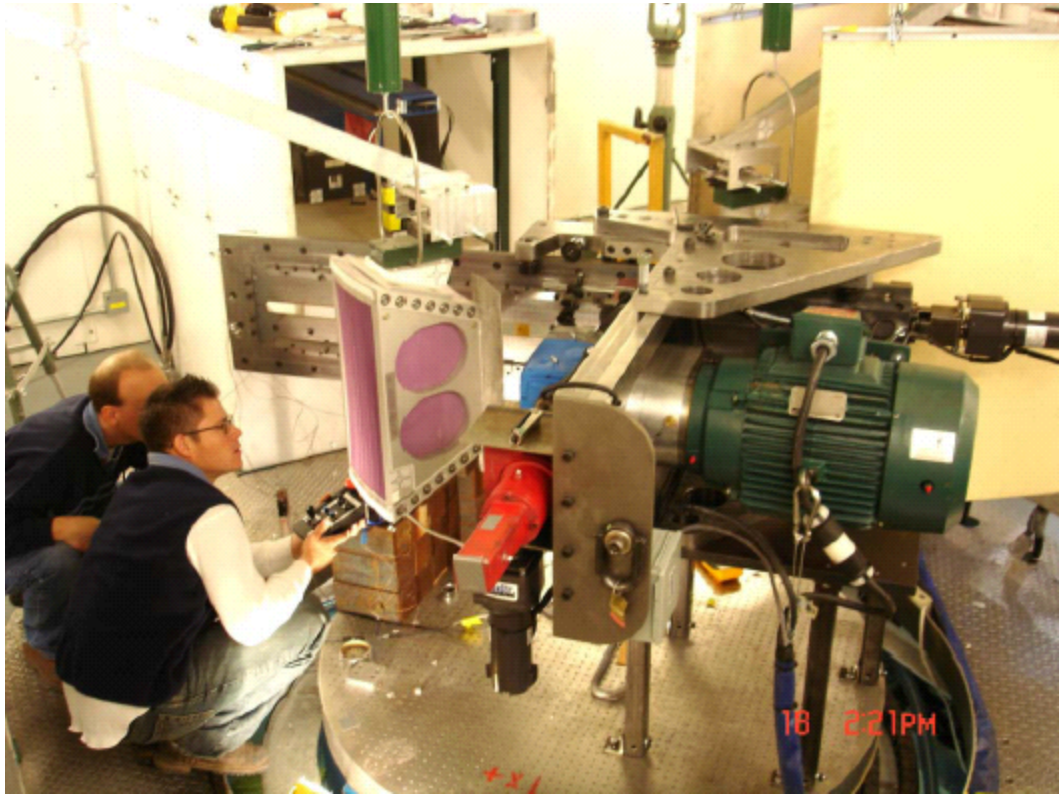
SMARTS

- **Spectrometer for MAterials Research at Temperature and Stress**
- **Spatially resolved measuremen**
  - Residual strains in components
- ***In situ* measurements**
  - Strains as a function of stress, temperature, environment, …
- **Instrument Scientists:**
  - Donald W. Brown
  - Bjørn Clausen



SMARTS Operation

The large cave at SMARTS allows for easy installation of ancillary equipment and large samples

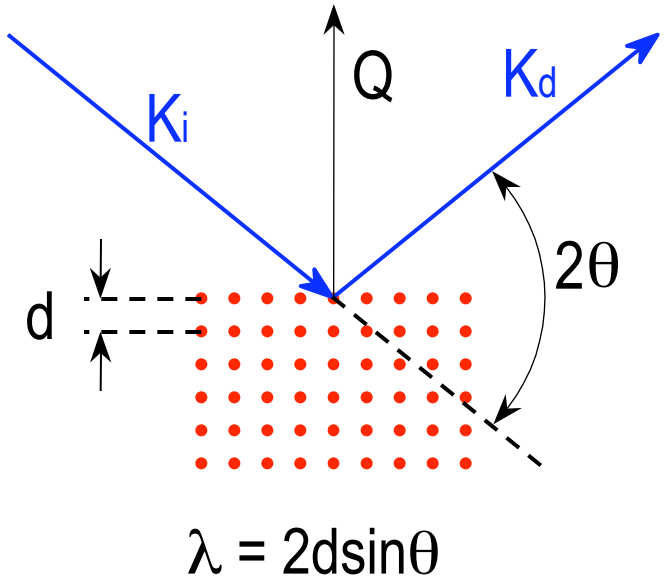


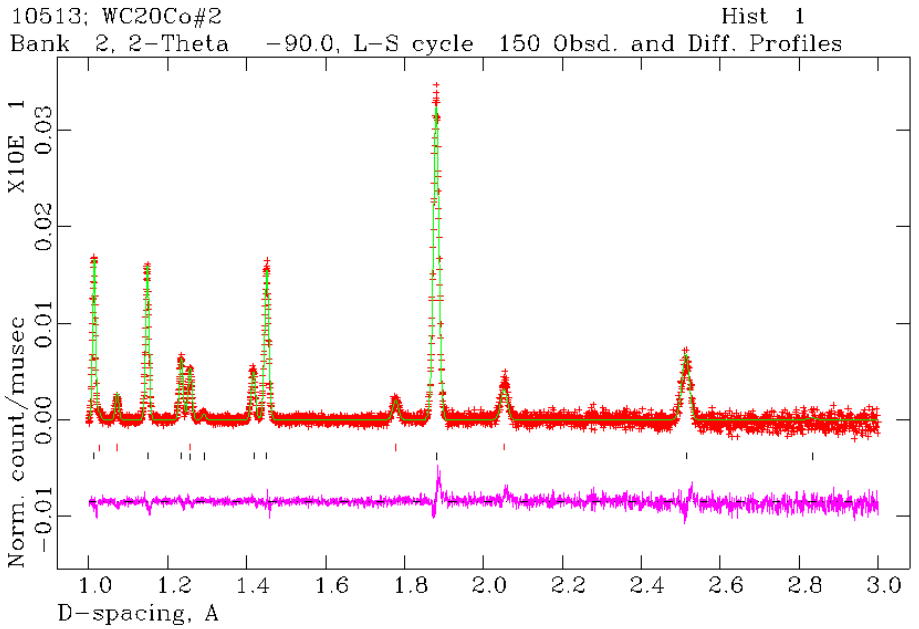
Diffraction Specifications

- **2nd generation Time-of-Flight (TOF) engineering powder diffractometer:**
  - 31 meter primary flight path
  - 1.5 meter secondary flight path
  - Detector coverage: ±13° horizontal and vertical
  - Resolution at 90° (wavelength dependent): ~0.4% FWHM
  - Nominal count time for 1 cm^3 under load at temperature: ~10 minutes
  - Nominal count time for 1 mm^3 in 10-mm-thick Fe plate: ~60 minutes
- **Time-of-flight:**
  - Full diffraction pattern (0.4 - 3.75 Å)
  - Single peak or Rietveld analysis
  - Strain resolution (fitting ESD):
    - Single peak analysis: ±50με
    - Rietveld analysis: ±20με

Information Obtained from Diffraction Measurements

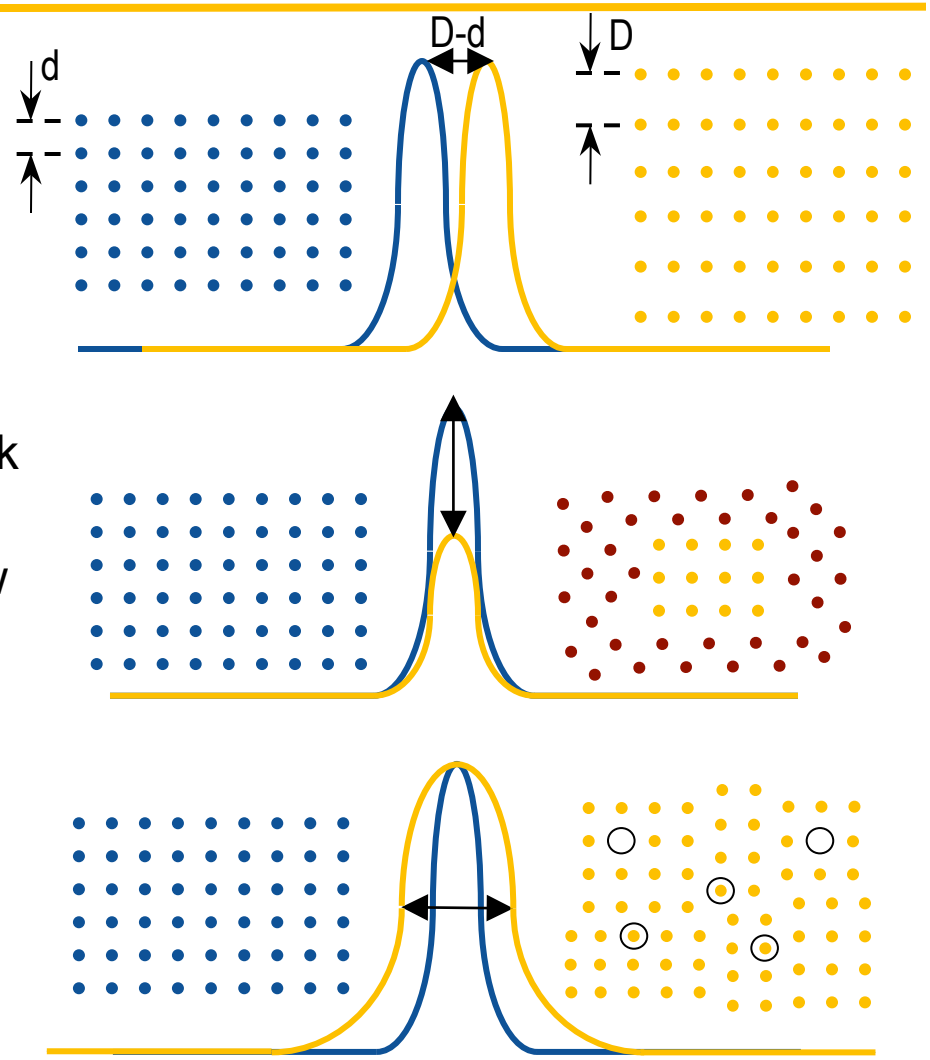
Bragg's law relates the wavelength, the lattice spacing and the scattering angle





Information Obtained from Diffraction Measurements

- **Peak position**
  - Elastic lattice strain from changes in peak position
  - Intergranular strains
- **Peak intensity**
  - Texture change from changes in peak intensities
  - Phase transition form appears of new peaks and loss of initial peaks
- **Peak width**
  - Depends on defect concentration and grain size
    - Generally increases with plastic deformation



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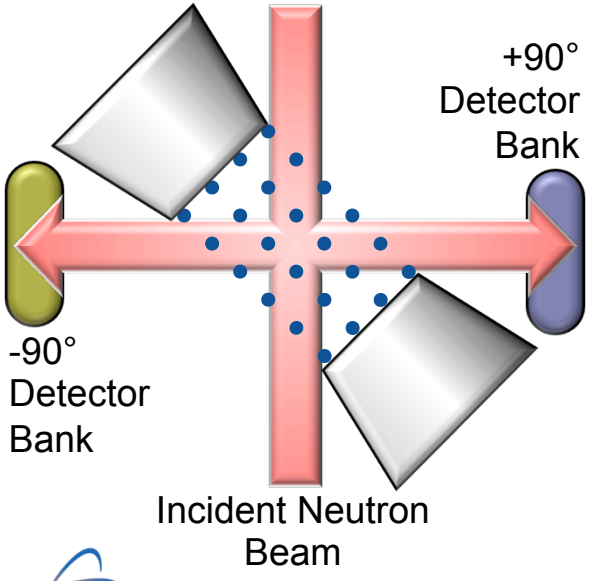
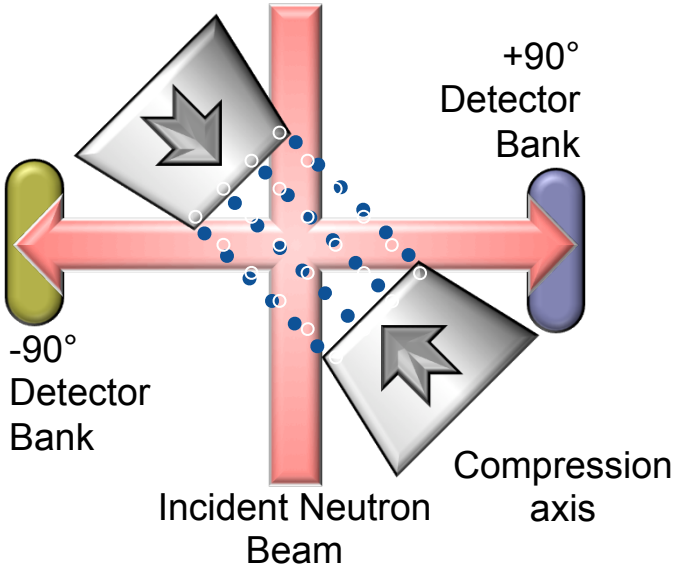
SMARTS Operation

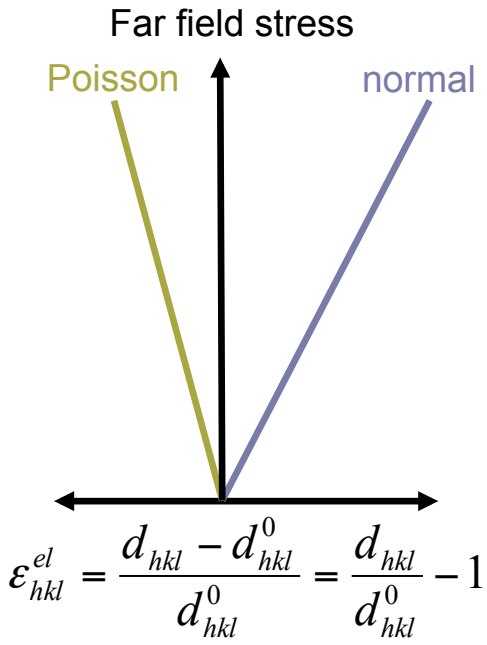
- **In-situ measurements**
  - Strains as a function of stress, temperature, environment, …
  - Measurements of 2 strain components simultaneously: Longitudinal and Transverse

Undeformed Reference – d^0



Deformed state – d

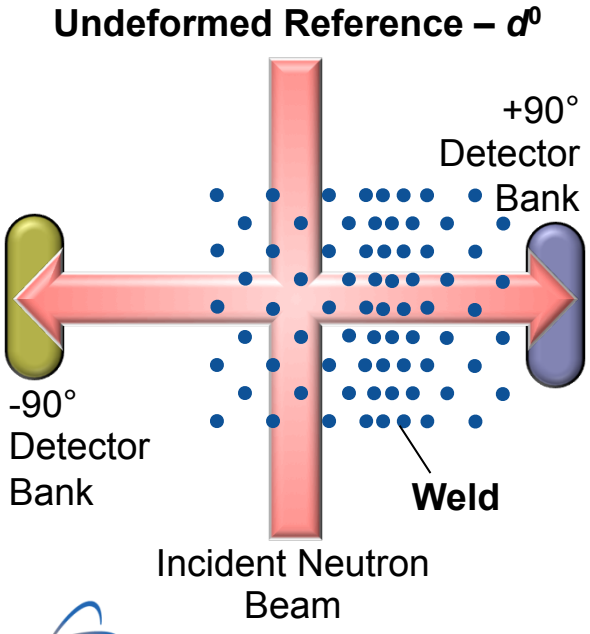


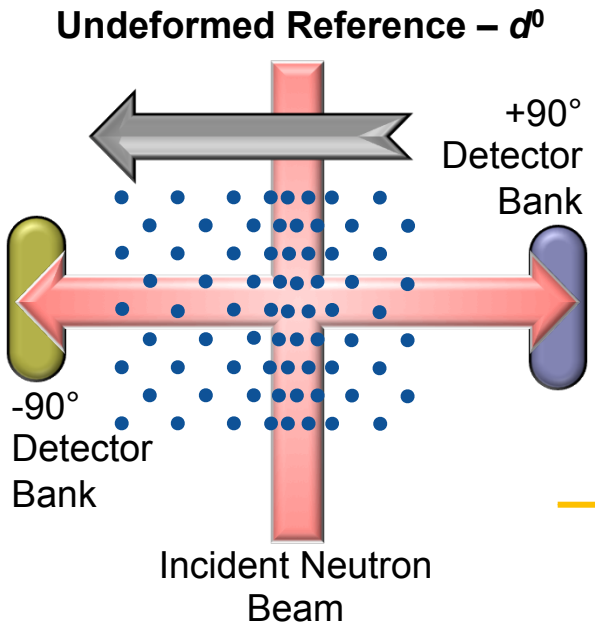


$$\varepsilon_{hkl}^{el} = \frac{d_{hkl} - d_{hkl}^0}{d_{hkl}^0} = \frac{d_{hkl}}{d_{hkl}^0} - 1$$

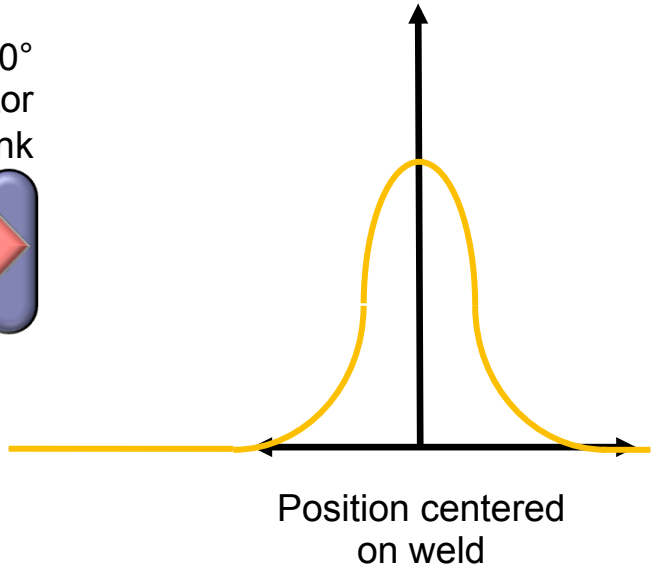
SMARTS Operation

- **Spatially resolved measurements**
  - Residual strains in components
  - Measurements of 2 to 6 strain components to determine full strain tensor



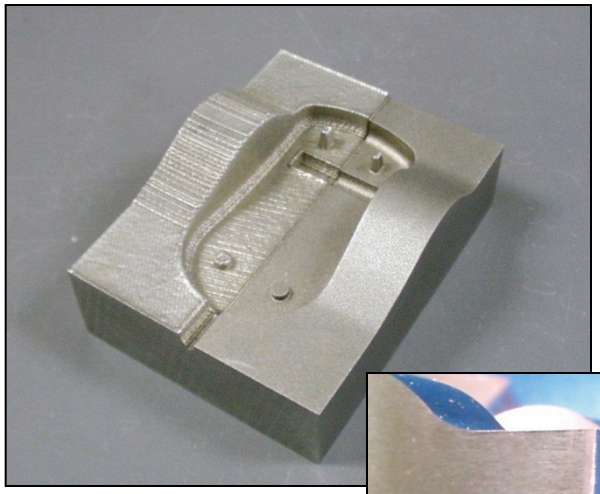


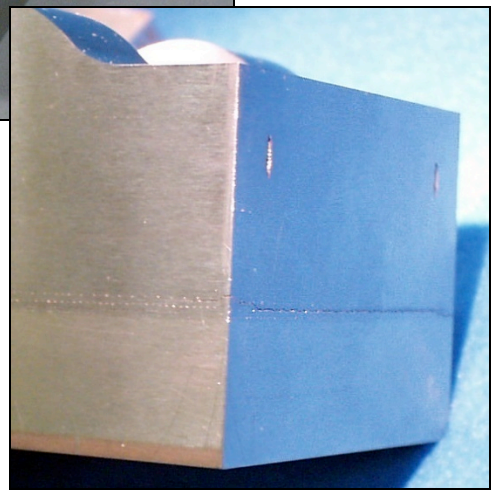
$$\varepsilon_{hkl}^{el} = \frac{d_{hkl} - d_{hkl}^0}{d_{hkl}^0} = \frac{d_{hkl}}{d_{hkl}^0} - 1$$



Materials Science and Engineering With Neutron Diffraction

- **Typical issues**
  - Residual stress in processed parts
  - Intergranular strains
  - Deformation mechanisms of advanced materials
  - Phase stress in multi-phase materials (composites)
  - Structural (solid/solid) phase transformation
  - Development of texture





LASER
ENGINEERED
NET
SHAPING

Materials Science and Engineering With Neutron Diffraction

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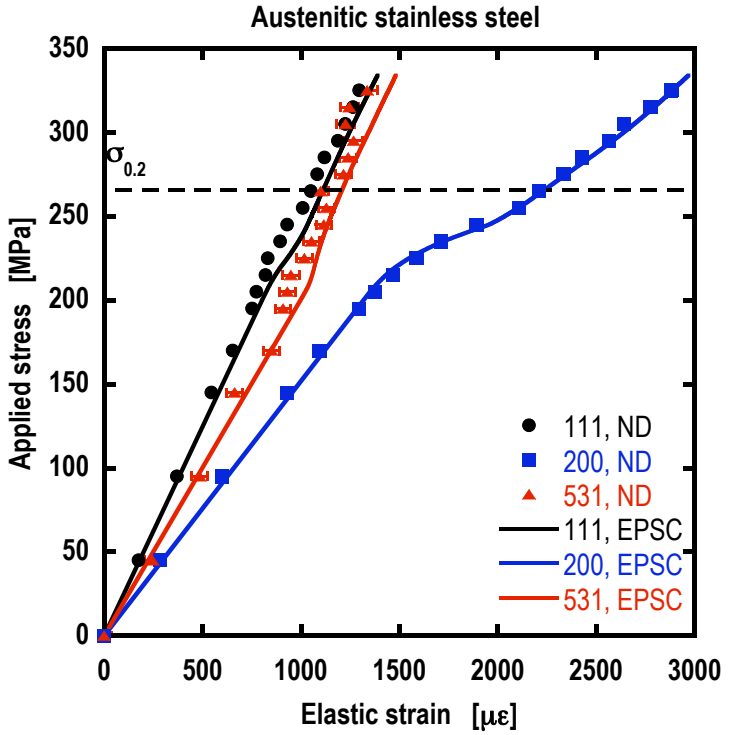

Materials Science and Engineering With Neutron Diffraction

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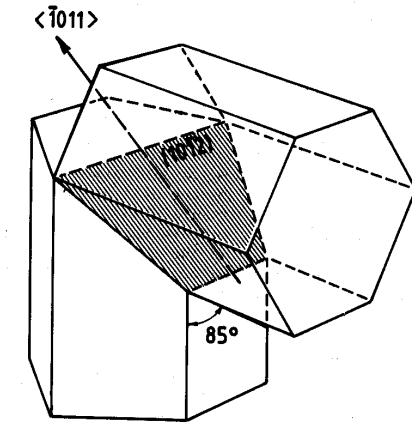

Twinning in *hcp* materials

Materials Science and Engineering With Neutron Diffraction

- **Typical issues**
  - Residual stress in processed p
  - Intergranular strains
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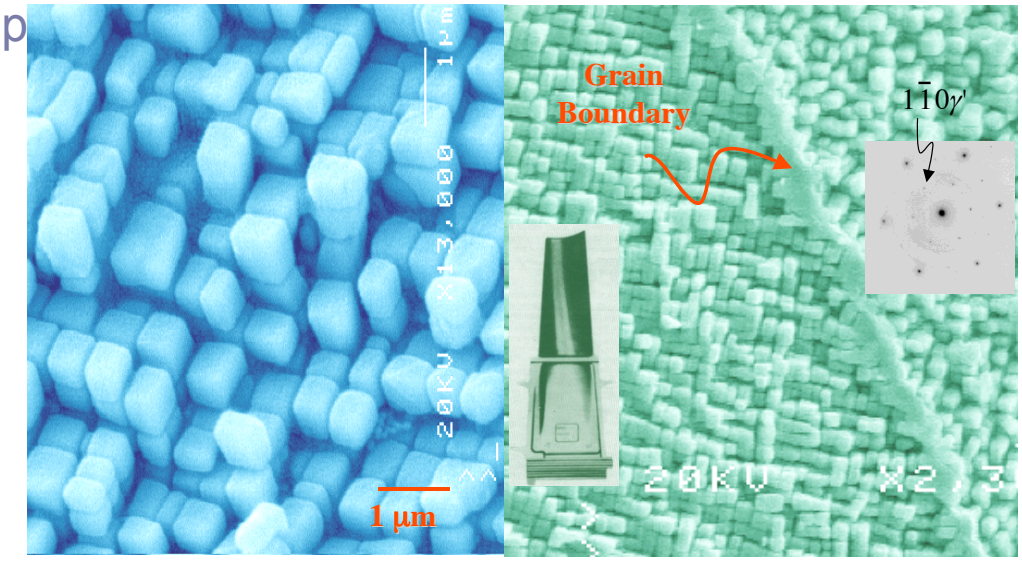

Materials Science and Engineering With Neutron Diffraction

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  - Residual stress in processed parts
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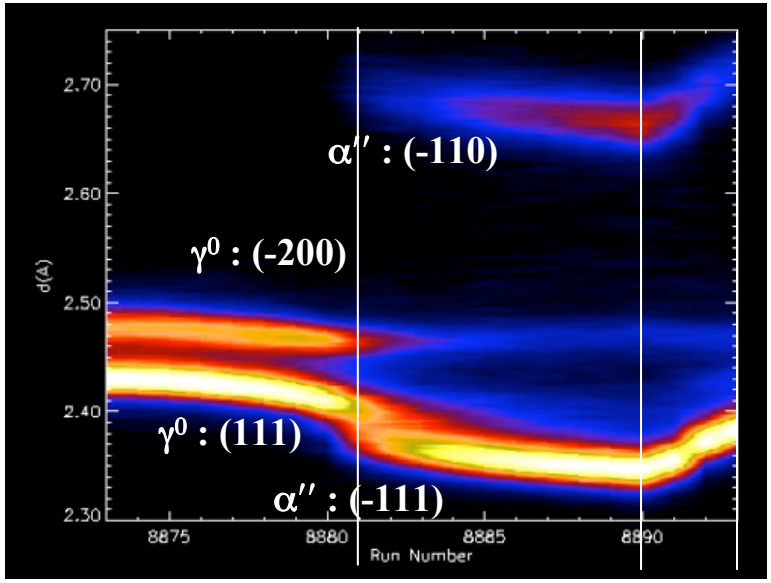
U 6 wt.% Nb



200MPa 450MPa Unloaded

Materials Science and Engineering With Neutron Diffraction

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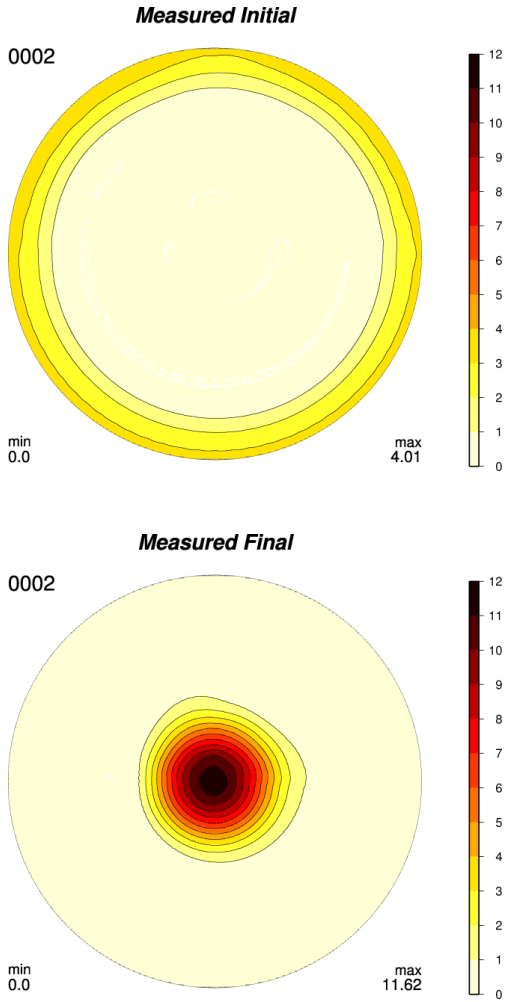

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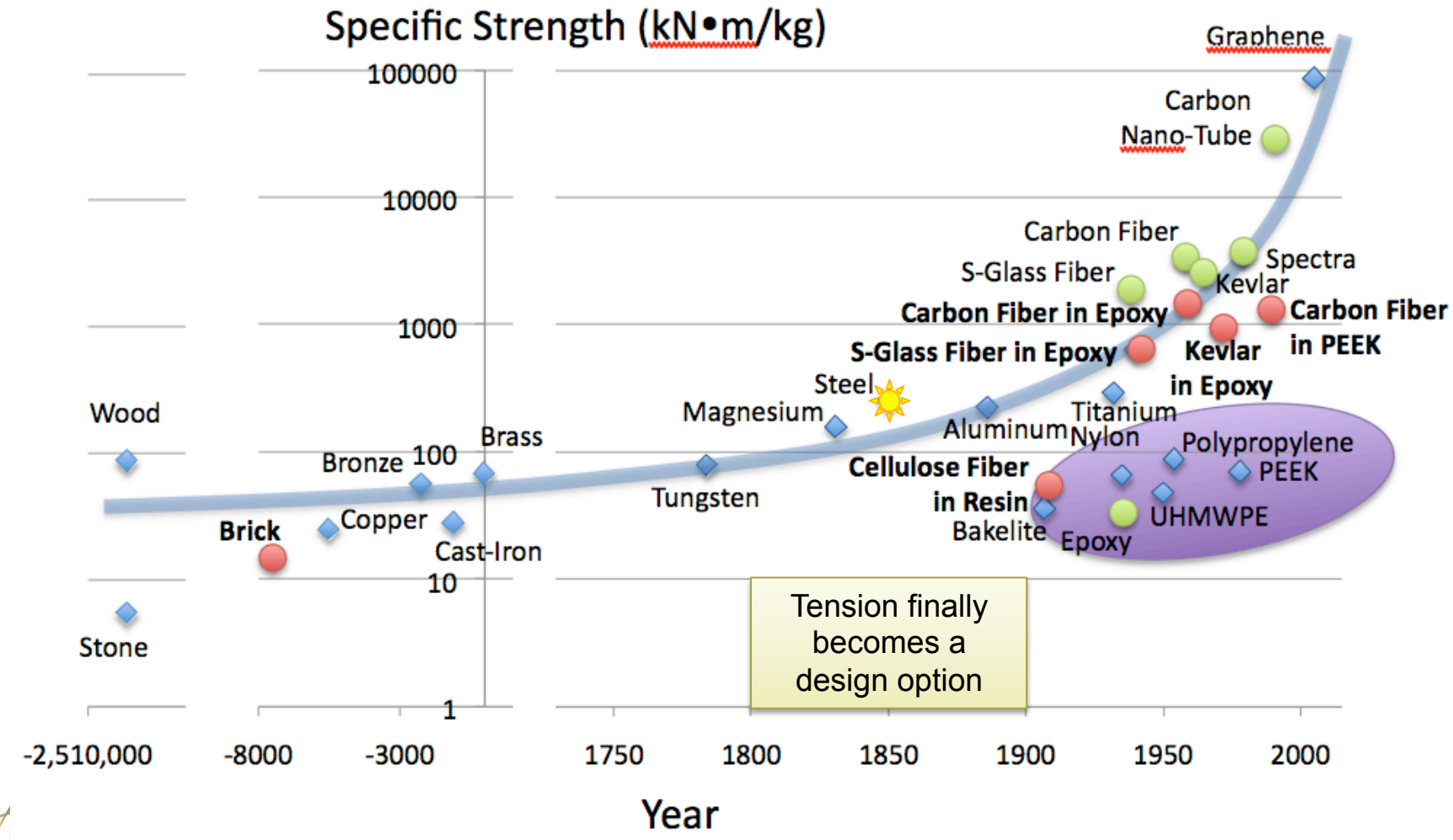
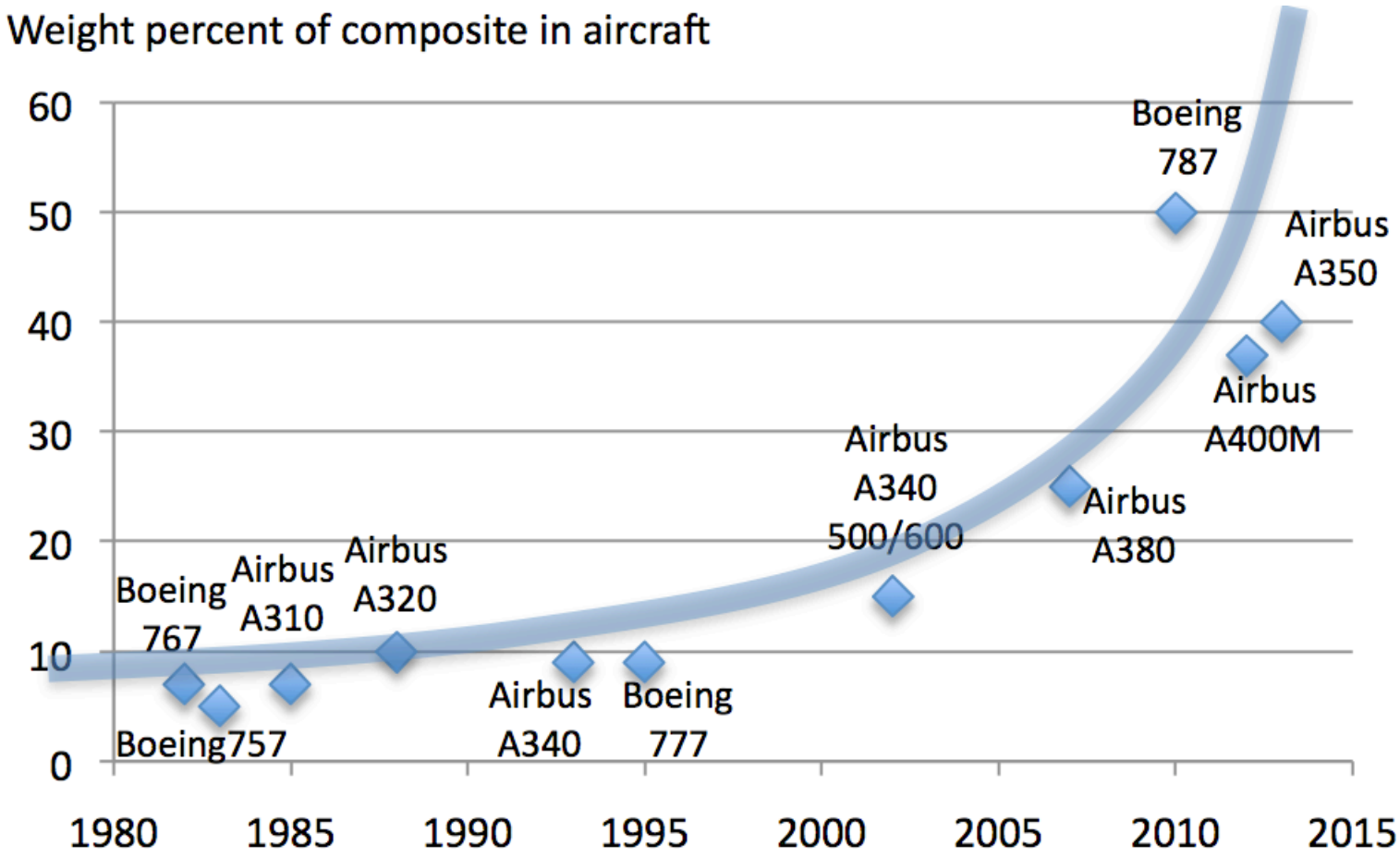
In-Situ Measurement of Crystalline Lattice Strains in Fluoropolymers by Neutron Diffraction

Polymers and composites offer unique properties and material design space



Polymers and composites are finding their way into many critical applications historically reserved for metals, many of which involve materials under extremes



The massive human and economic costs from material failure motivated my interest in deformation, damage and fracture

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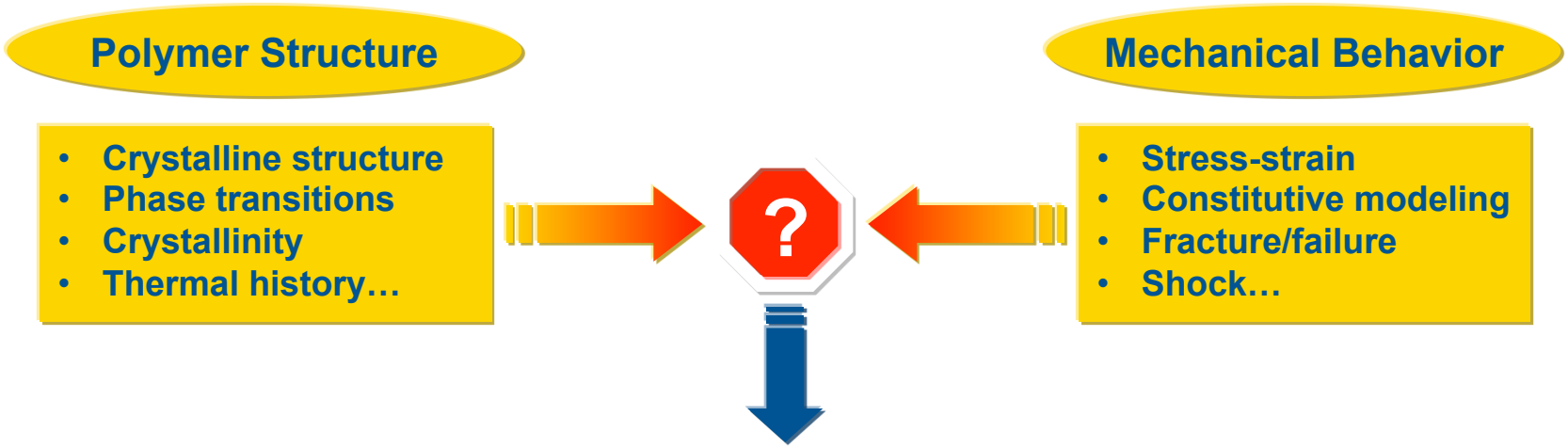
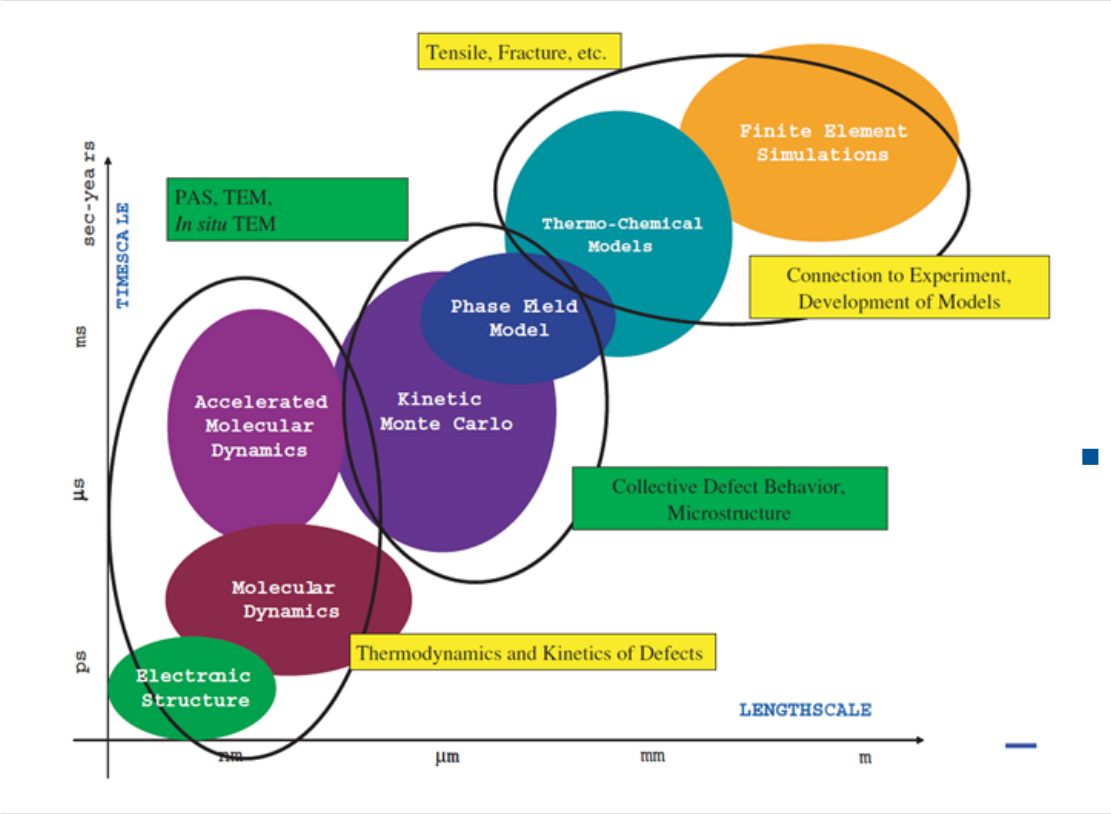
Most studies in the current literature focus on two equally important BUT segregated areas of study. Progress lies at the interface.

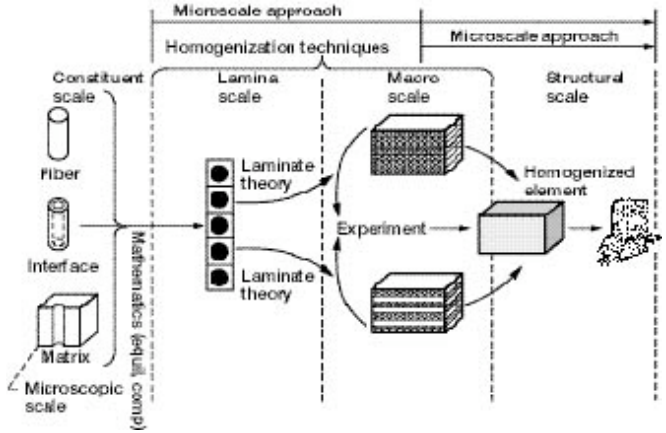


- The current work investigates the interplay between mechanical behavior of semicrystalline polymers with polymer structure, percent crystallinity, crystalline lattice deformations using
  - Atomic Force Microscopy (AFM)
  - Scanning Electron Microscopy (SEM)
  - Neutron Diffraction
  - He pycnometry
  - Differential Scanning Calorimetry (DSC)

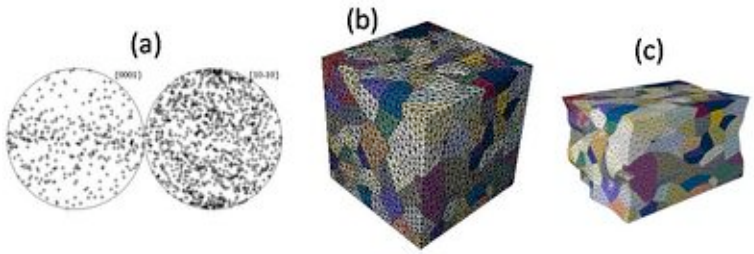
Multiscale modeling requires multiscale experiments and attention to QMU

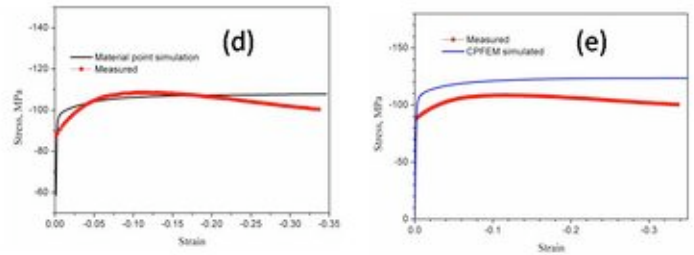


- **Generalized method of cells**



- **Explicate microstructure modeling**





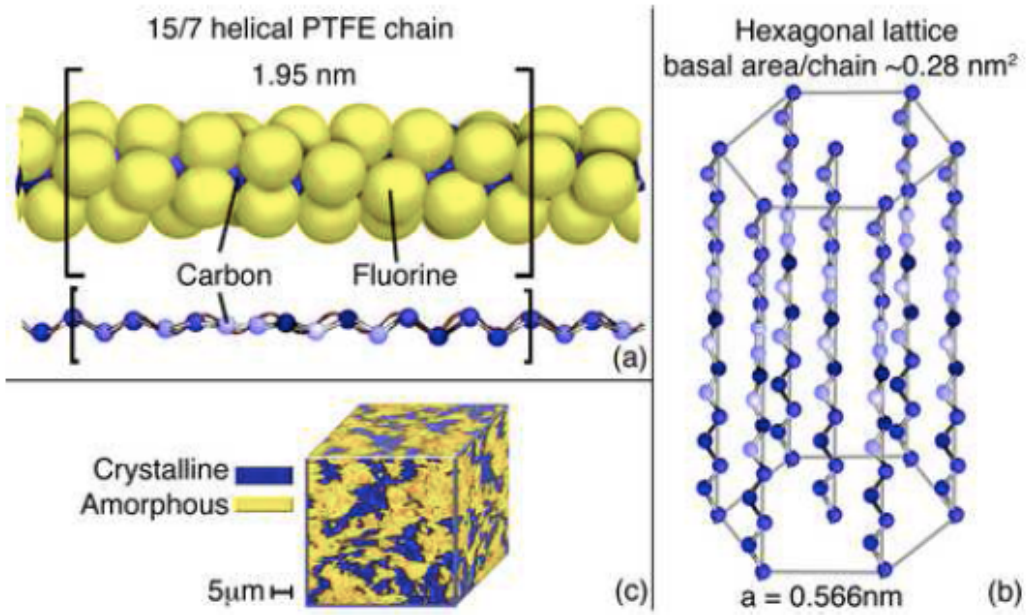
Polytetrafluoroethylene (PTFE, Teflon) Introduction

- **PTFE (CF_2-CF_2) is semi-crystalline, with its linear chains forming complicated phases near room temperature and ambient pressure**
- **PTFE possesses a combination of desirable chemical and physical properties including:**
  - excellent thermal stability
  - chemical resistance
  - dielectric properties
  - extremely low coefficient of friction
- **Applications of PTFE include:**
  - surgical implants
  - aerospace components
  - motor seals
  - barriers for hazardous chemicals

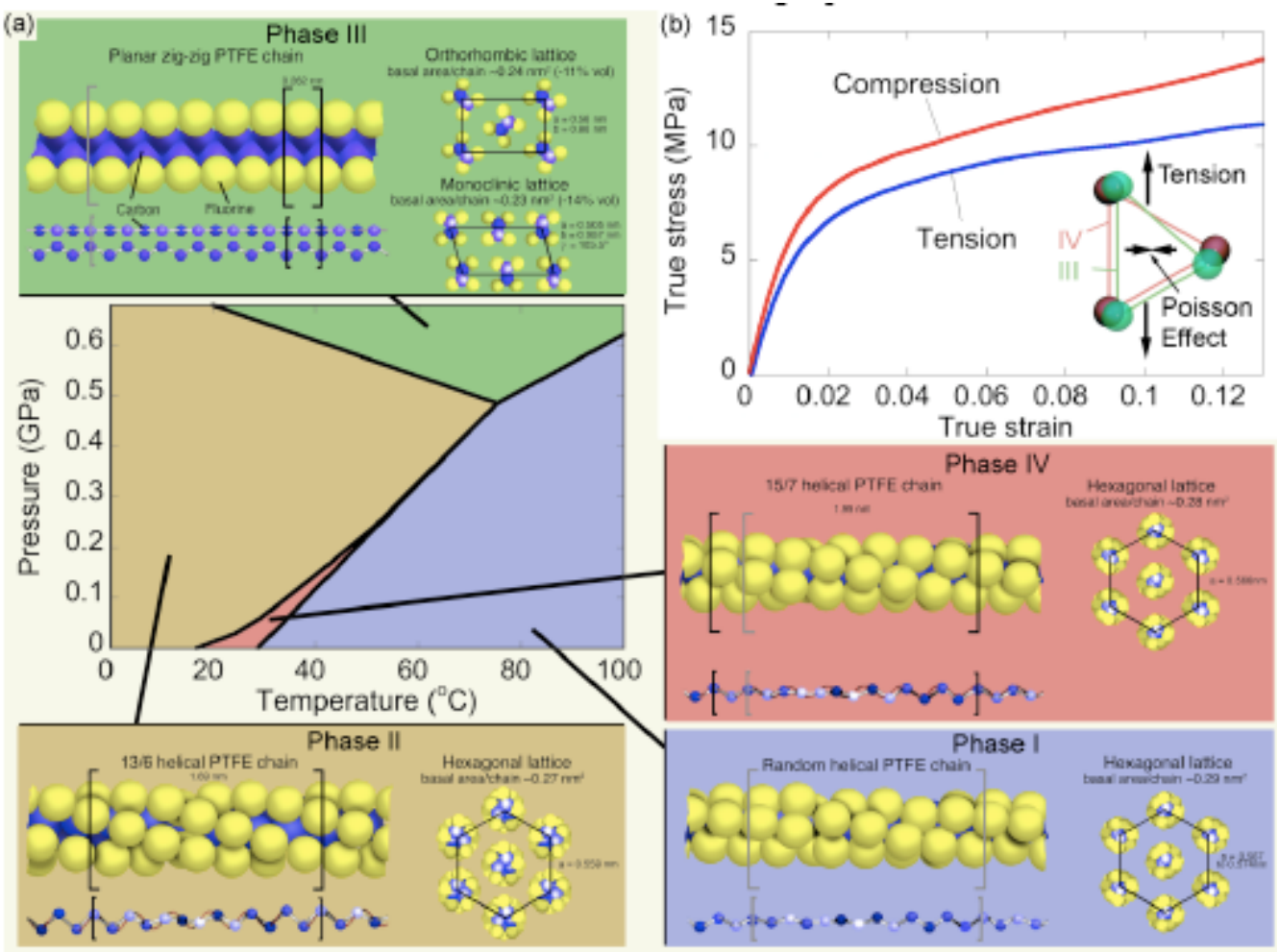
- **This study focuses on PTFE 7C:**
  - Molding powder (DuPont) is pressed and sintered by Balfor Industries according to the ASTM standard ASTM-D-4894-98a
  - Molding powder has the unique feature of consisting of small (~20 μm) irregularly shaped, fibrous particles
  - Molding powder is ~85% crystalline (by density)
  - Pressed PTFE is ~48% crystalline (by density)

Crystalline structure of PTFE for Neutron Diffraction

- **Crystalline phase defines both the short range (in chain) and long range (chain folding/packing) structure**
- **From C—C—C bond length and angle the translational advance is consistently 0.13 nm/CF_2.**
- **BUT the representative repeat length c (if one exists) is n x 0.13 nm (n = 2,13,15).**
- **Amorphous PTFE has the chemical compositions as crystalline PTFE but without short or long range order.**



Previously Reported Pressure-Temperature Phase Diagram for PTFE



Measurement Methods for Crystallinity

- Several methods have been reported in the literature, including Raman, IR, X-ray and NMR

- Moreover, because 100% amorphous and 100% crystalline PTFE are not experimental obtainable, these constants must often be extrapolated based on one or more methods

DSC

$$X_c = \frac{\Delta H_f^S}{\Delta H_f^0} \qquad (1)$$

Where ΔH_f^S is the measured sample heat of fusion, and

ΔH_f^0 is the theoretical heat of fusion for 100% crystalline PTFE

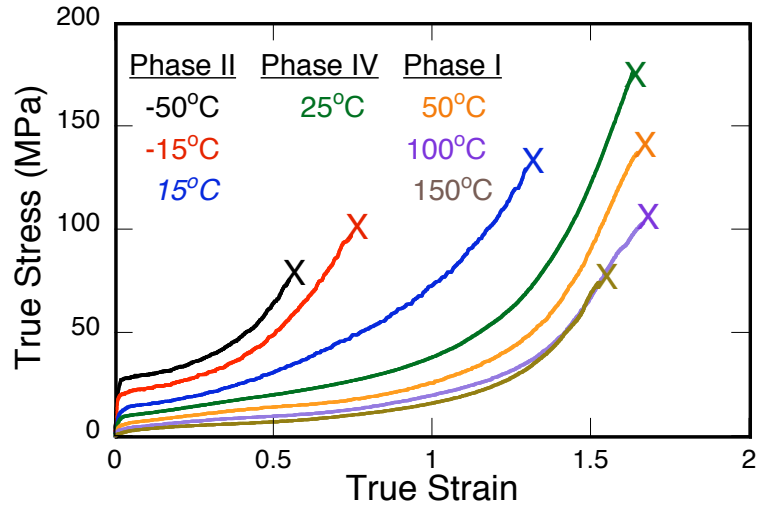
Density

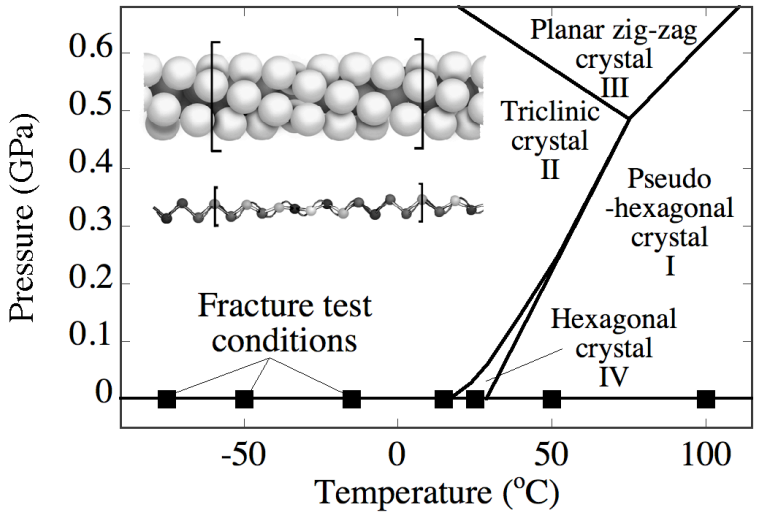
$$X_c = \frac{\rho_c}{\rho}\frac{\rho - \rho_a}{\rho_c - \rho_a} \qquad (2)$$

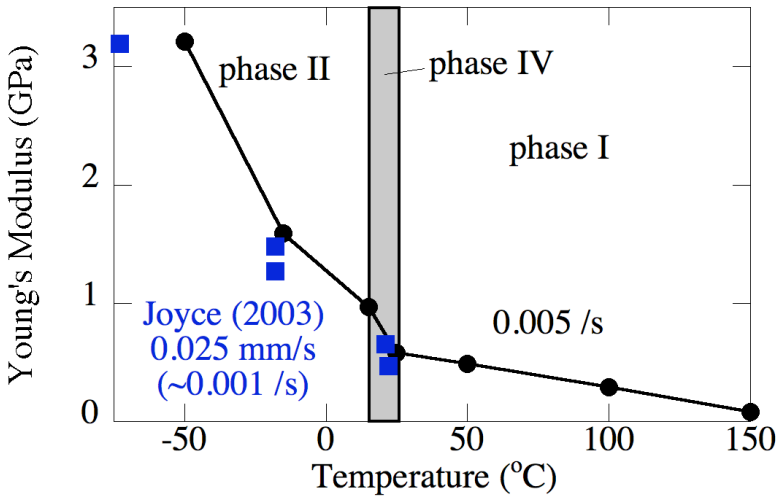
Where ρ is the measured sample density, and

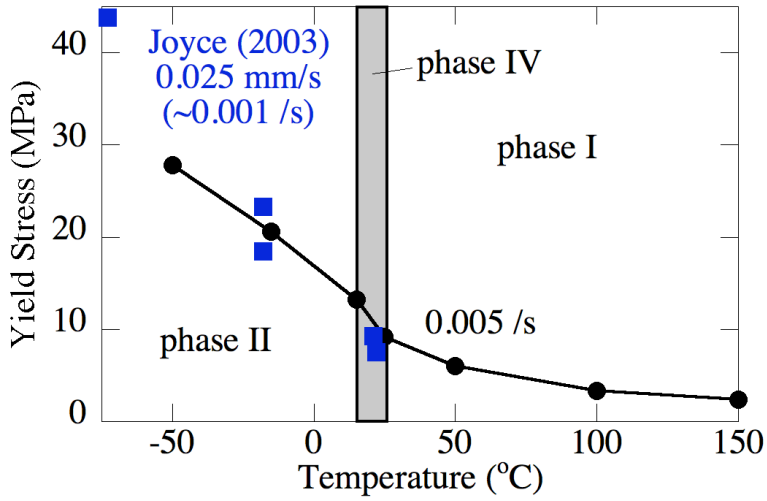
ρ_a and ρ_c are the extrapolated density for 100% amorphous and 100% crystalline PTFE respectively

Manifestation of the Crystalline Phase in theTensile Behavior

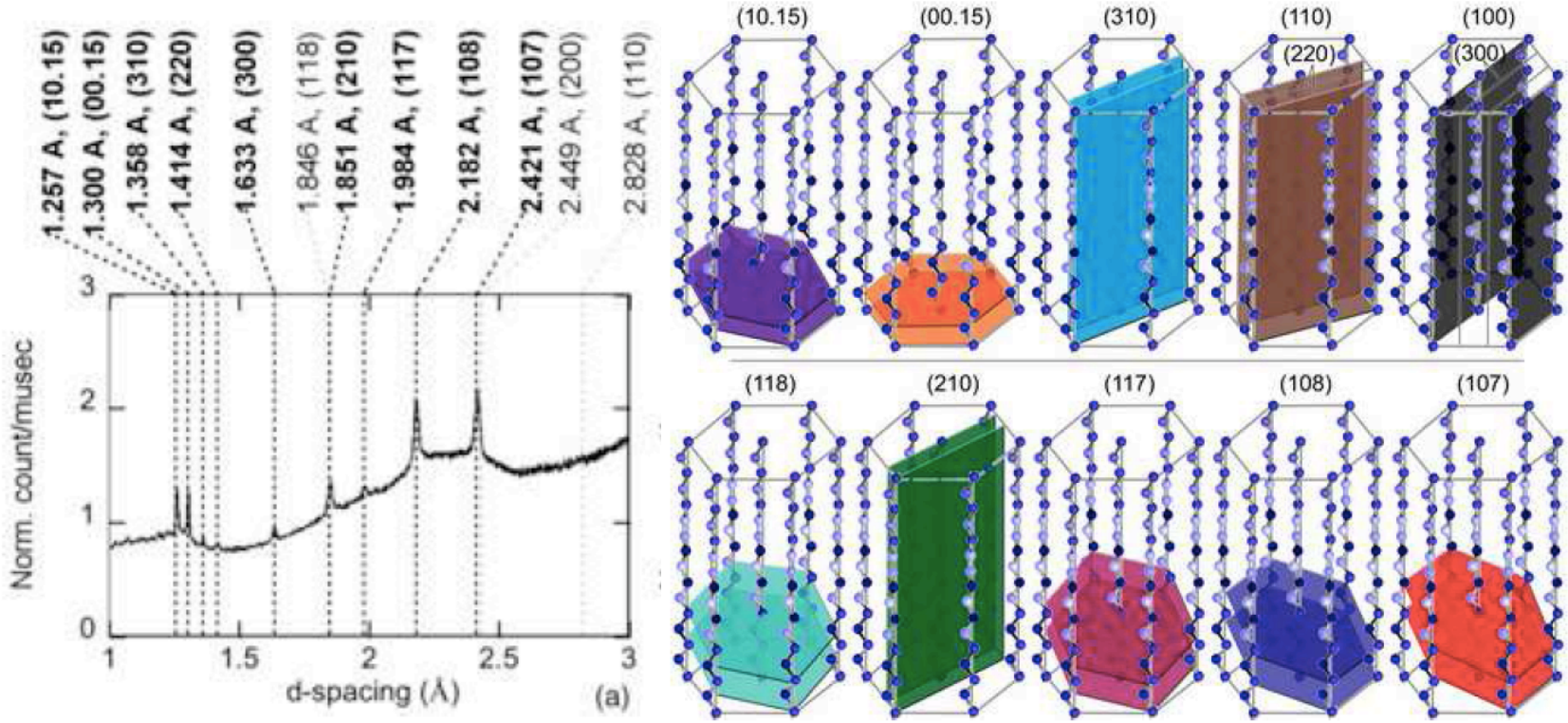








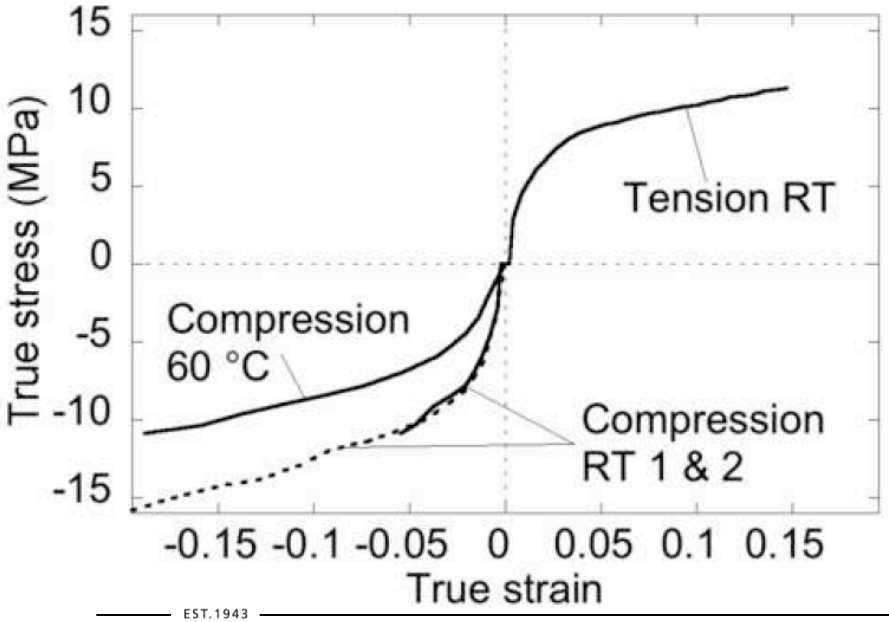
Neutron Diffraction of Undeformed PTFE 7C

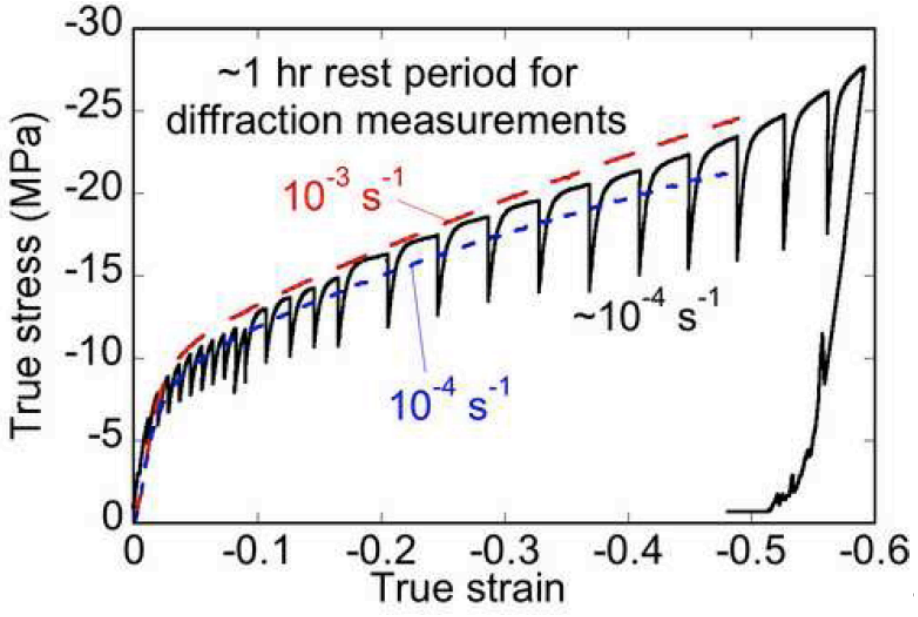


- **All of the observed peaks can be assigned based on literature x-ray data**
  - Kimmig *Macromol.* **27** (1994)
  - Weeks *Polymer* **22** (1981)
  - Clark *Z. Kristallogr.* **117** (1962)
  - Clark *J. Macromol. Sci. Phys.* **B1** (1967)

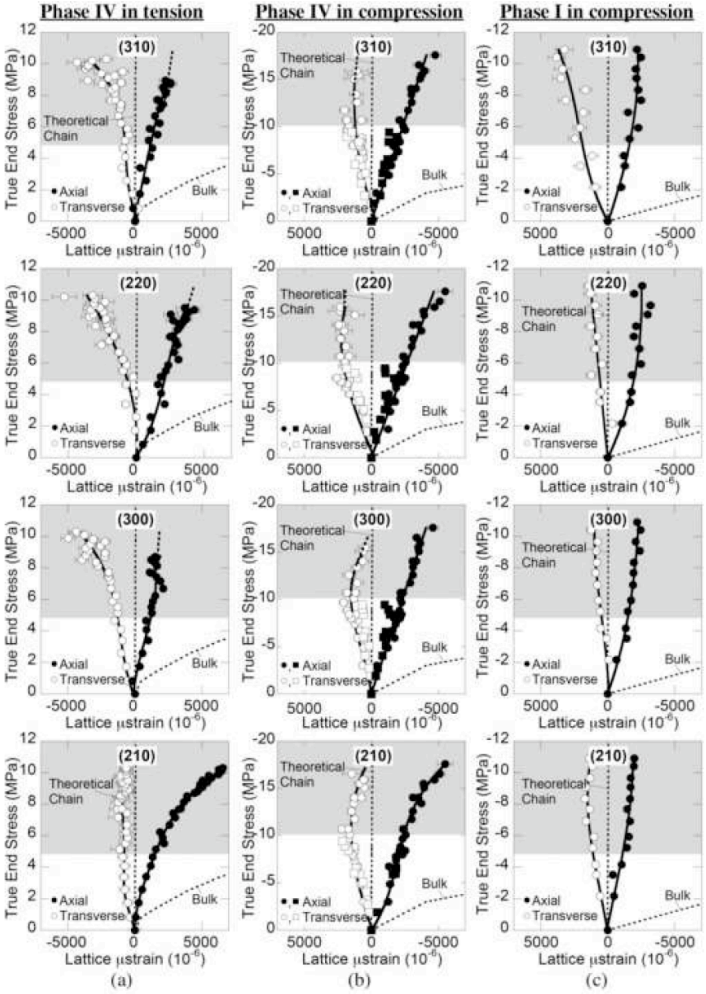
Loading conditions

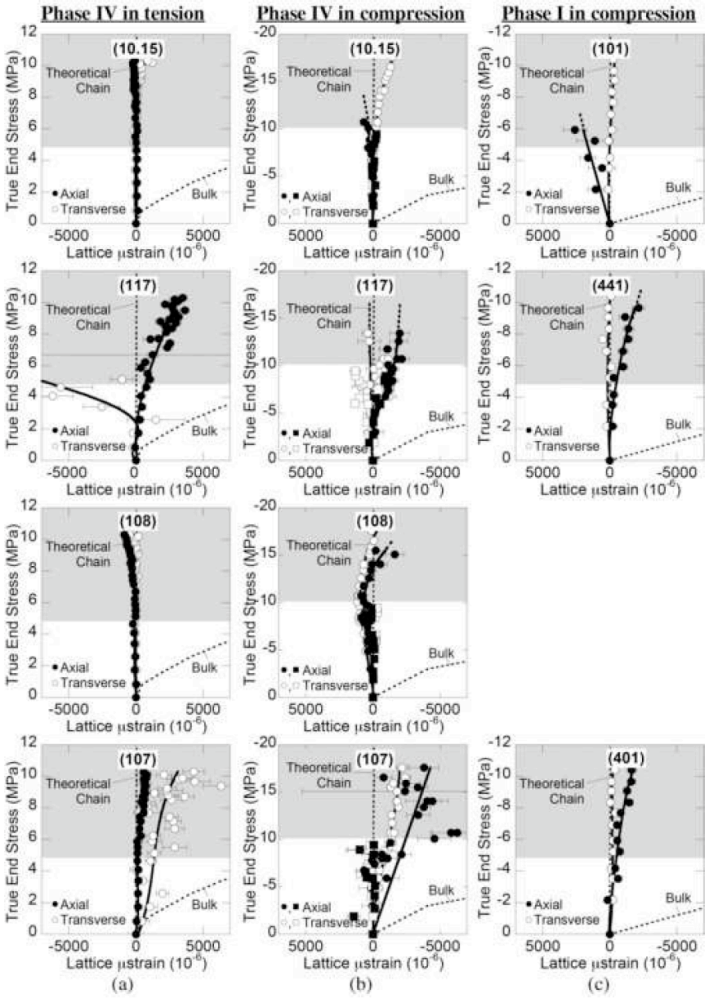
- **The response is measured at ambient temperature (phase IV) in tension and compression and elevated temperature (phase I) in compression**
- **Relaxation is observed during diffraction measurements at constant strain**
- **Reasonable agreement with quasi-static data**
  - P. J. Rae, D. M. Dattelbaum, Polymer 2004, 45, 7615
  - P. J. Rae, E. N. Brown, Polymer 2005, 46, 8128.



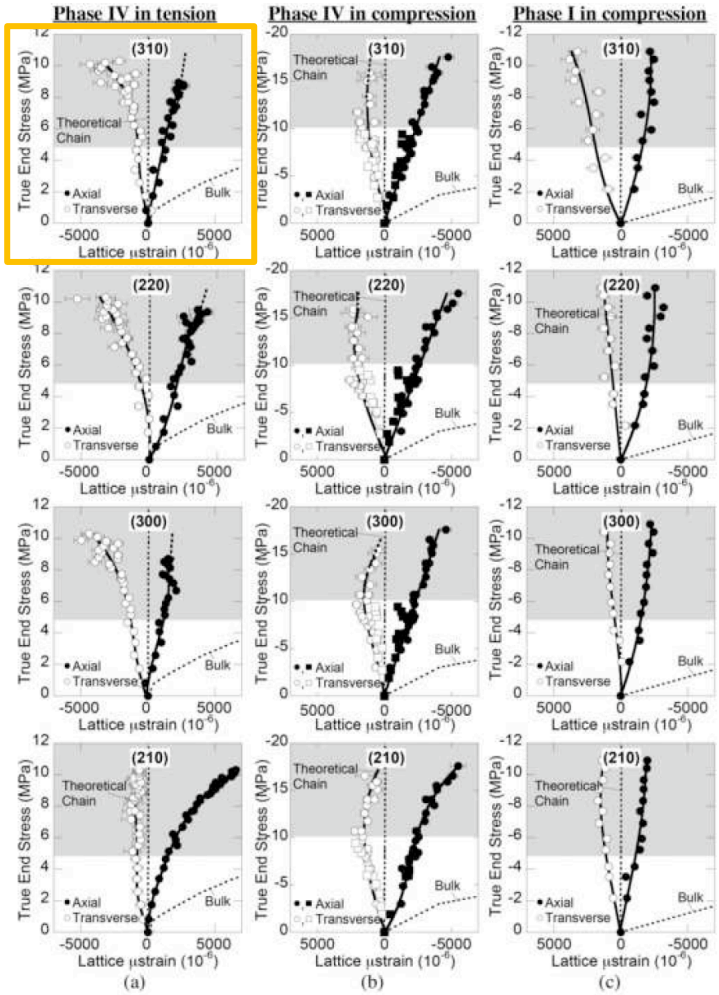


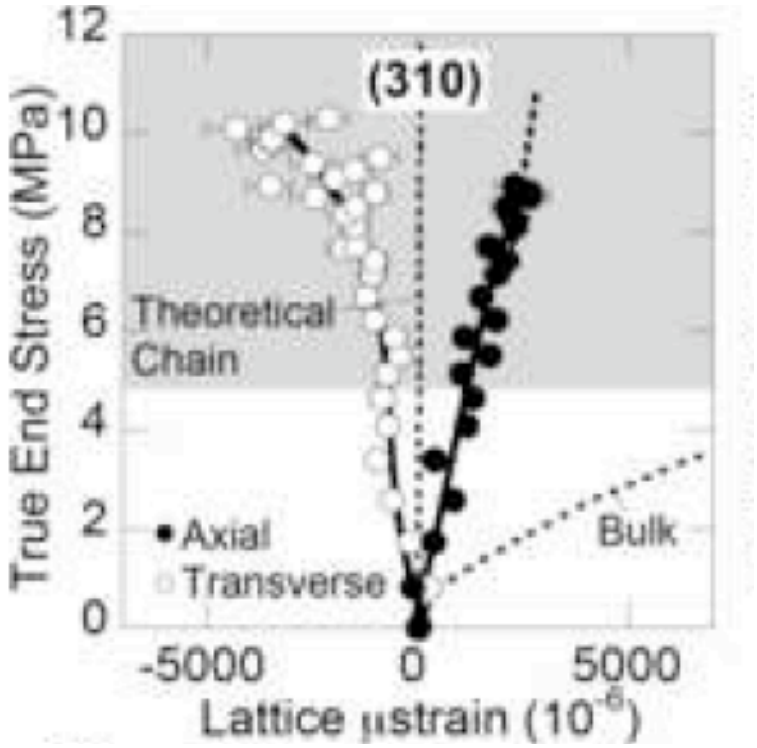
Stress–strain response of the individual prismatic *(left)* and pyramidal *(right)* crystalline lattice planes





Stress–strain response of the individual prismatic *(left)* and pyramidal *(right)* crystalline lattice planes





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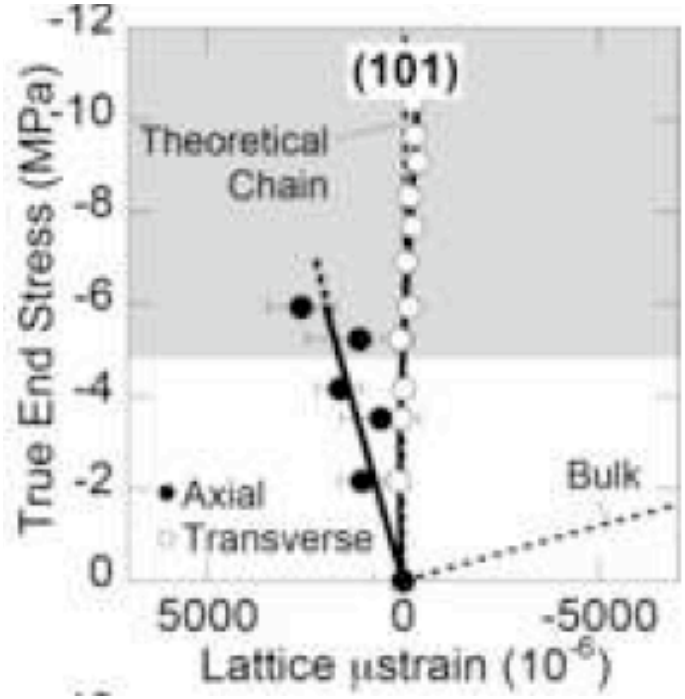
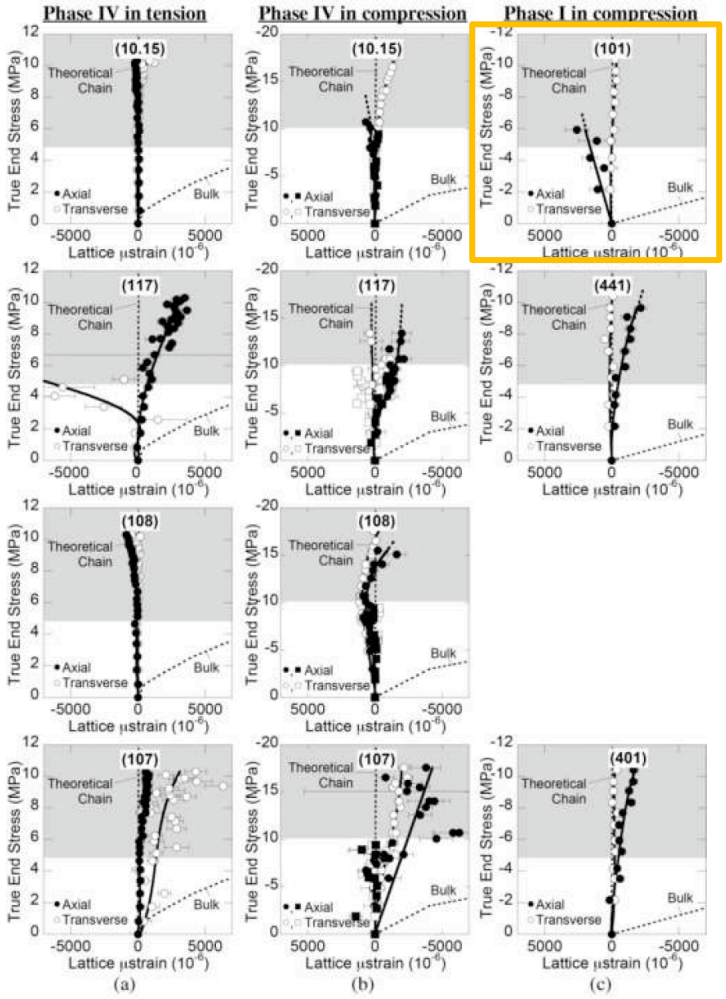
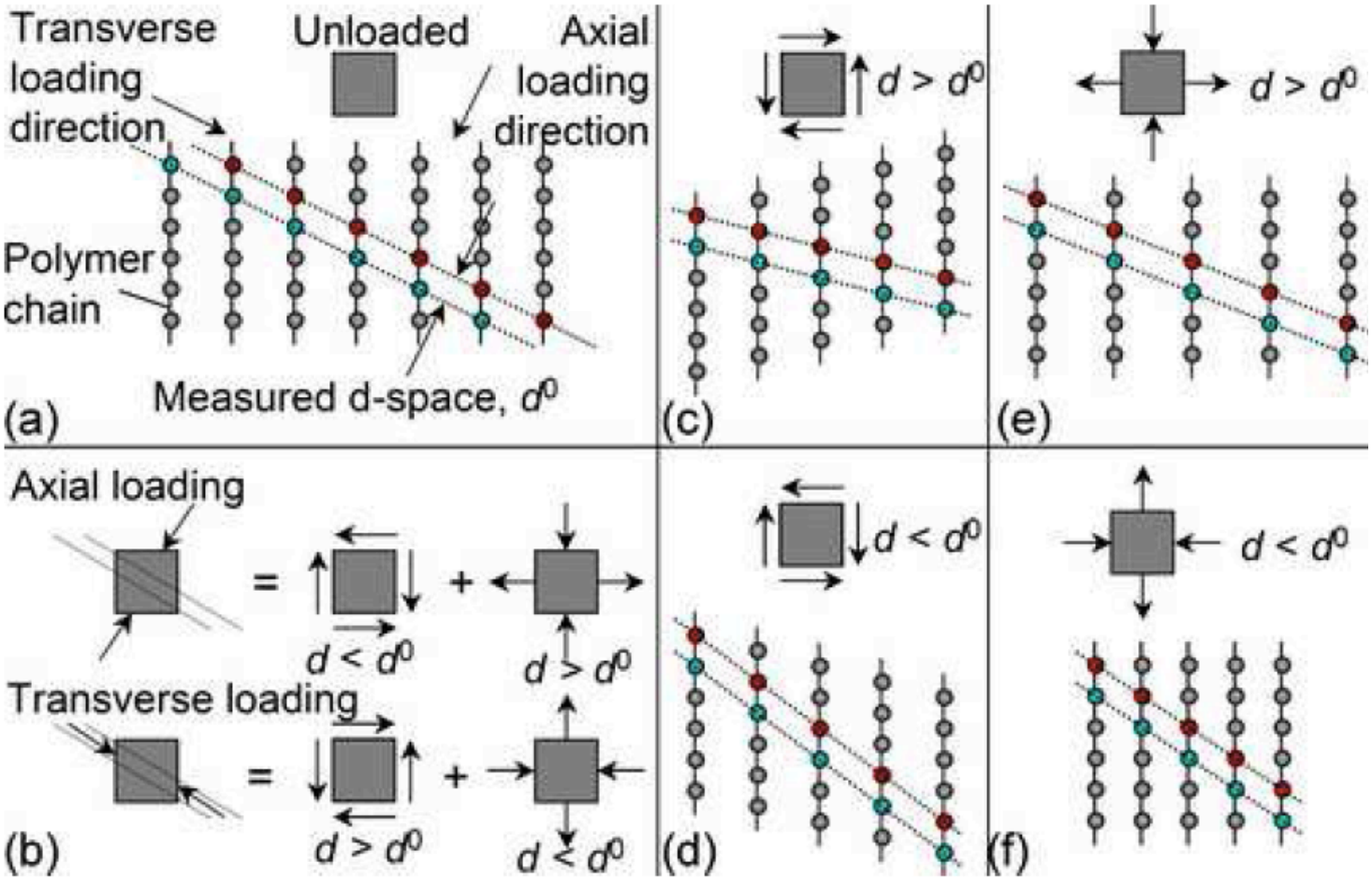
Stress–strain response of the individual pyramidal crystalline lattice planes



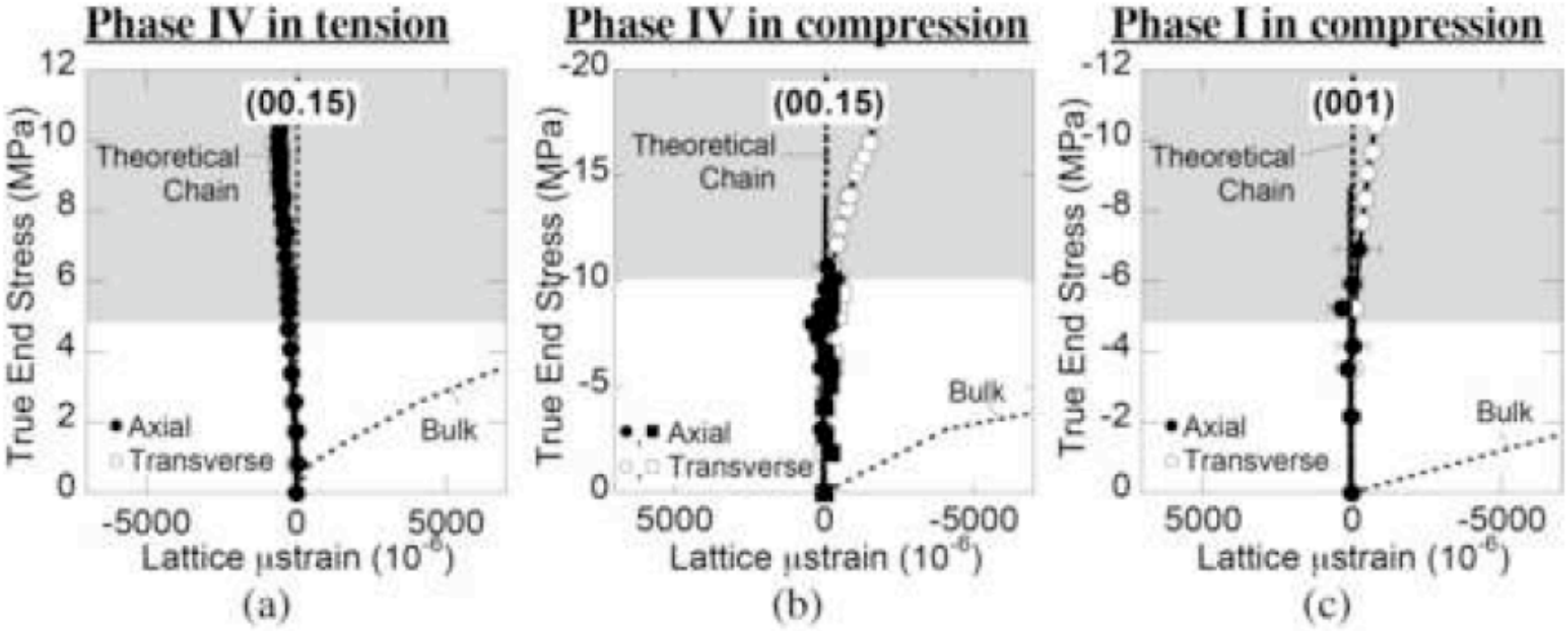


Proposed pyramidal deformation mechanisms incorporating shear



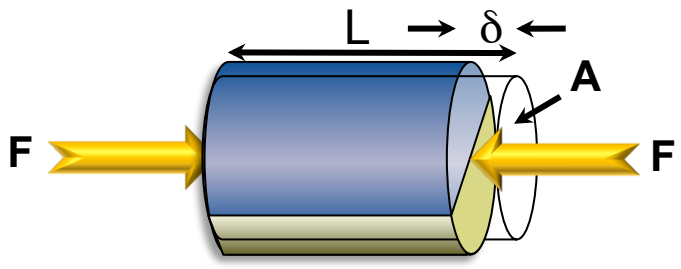
Stress–strain response of the individual basal crystalline lattice planes

- **Within experimental error the basal response corresponds to theoretical value**
  - Bartha F, Bogar F, Peeters A, Van Alsenoy C, Van Doren V (2000) Density functional calculations of the elastic properties of some polymer chains. Phys Rev B 62(15):10142–10150



Composite stiffness can be predicted using a micro-mechanics approach termed the rule of mixtures.

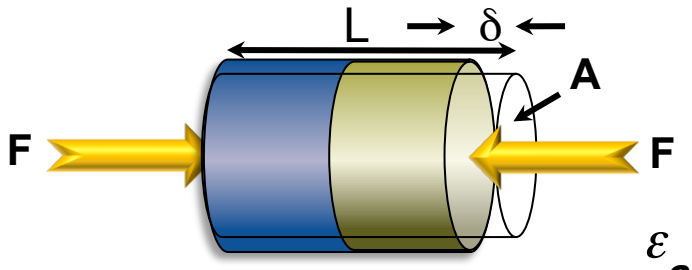
- **Longitudinal Rule-of-Mixtures (Constant Strain)** $\varepsilon_c = \varepsilon_1 = \varepsilon_2 = \varepsilon$



$$F_c = F_1 + F_2 \Leftrightarrow \sigma_c A_c = \sigma_1 A_1 + \sigma_2 A_2$$

$$\frac{\sigma_c}{\varepsilon} = \frac{\sigma_1}{\varepsilon} V_1 + \frac{\sigma_2}{\varepsilon} V_2 \Leftrightarrow \boxed{E_c = E_1 V_1 + E_2 (1 - V_1)}$$

- **Transverse or Inverse Rule-of-Mixtures (Constant Stress)**



$$\sigma_c = \sigma_1 = \sigma_2 = \sigma$$

$$\delta_c = \delta_1 + \delta_2 \Leftrightarrow \varepsilon_c L_c = \varepsilon_1 L_1 + \varepsilon_2 L_2$$

$$\frac{\varepsilon_c}{\sigma} = \frac{\varepsilon_1}{\sigma} V_1 + \frac{\varepsilon_2}{\sigma} V_2 \Leftrightarrow \boxed{E_c = 1 \Big/ \left(\frac{1}{E_1} V_1 + \frac{1}{E_2} (1 - V_1) \right)}$$

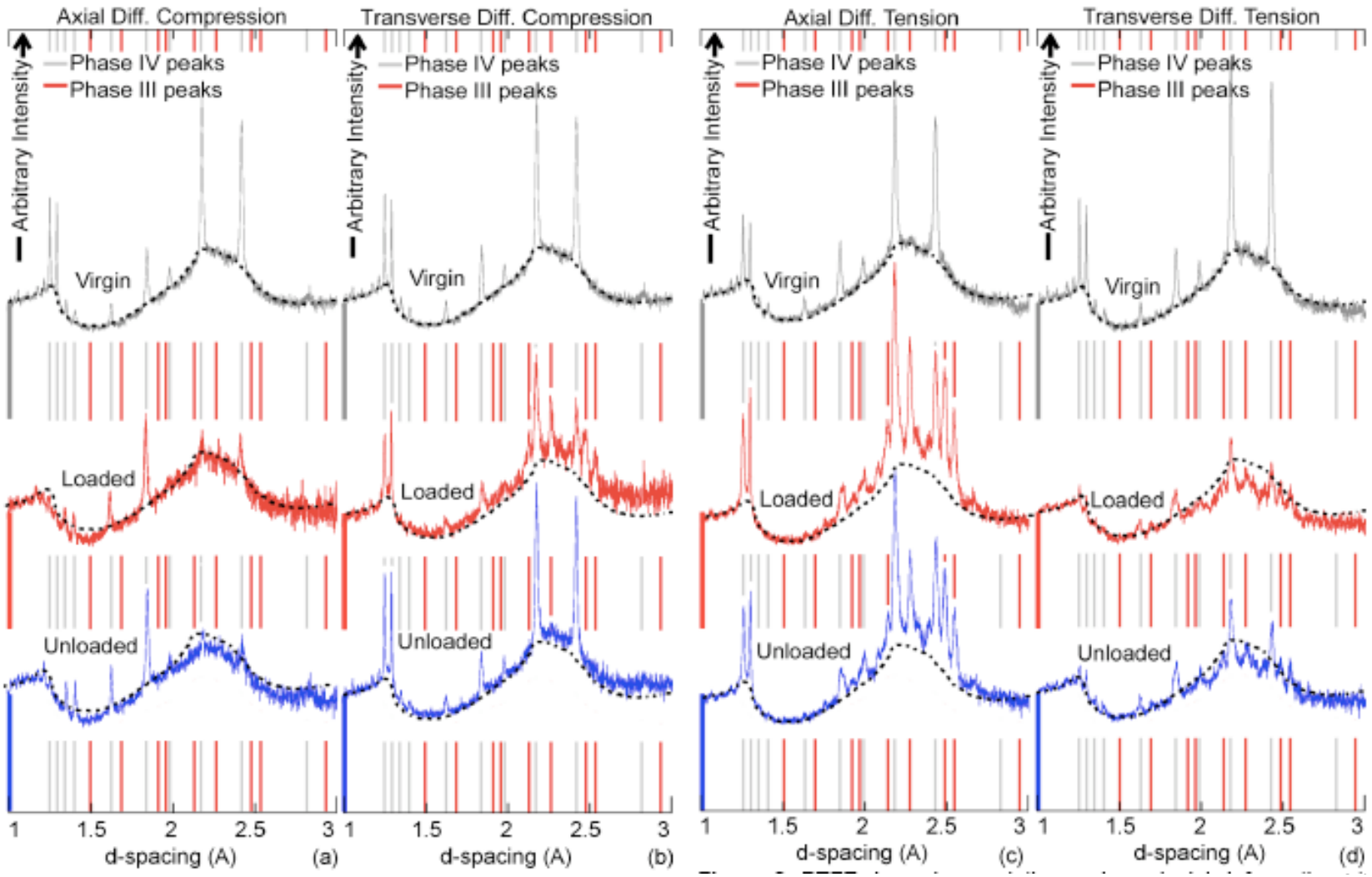
Elastic Constants

- **Assume constant stress**

(hkl)	Elastic constants (GPa)		
	Tension RT	Compression RT	Compression 60 °C
Bulk behavior	0.5[1]	0.6[1]	0.2[1]
Theoretical PTFE chain	220.5[2]	220.5[2]	~220[3]
2 1 0	3.8	1.8	5.4
3 0 0	4.8	5.1	3.0
2 2 0	2.2	5.4	2.3
3 1 0	4.1	5.8	3.1
0 0 .1 5	na	~220	—
0 0 1	—	—	~220

- $$E_{amor} = 0.62\left[E_{bulk}^{-1} - 0.038\left[E_{107}^{-1} + E_{108}^{-1} + E_{117}^{-1} + E_{210}^{-1} + E_{118}^{-1} + E_{300}^{-1} + E_{220}^{-1} + E_{310}^{-1} + E_{00.15}^{-1} + E_{10.15}^{-1}\right]\right]^{1}$$
- **At room temperature the elastic modulus of the amorphous PTFE is 0.32 and 0.38 GPa in tension and compression respectively**
- **At 60 °C under compression the elastic modulus of the amorphous PTFE is 0.13 GPa.**

d-spacing evolution under uniaxial deformation at ambient temperature and pressure



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Under small strains Phase III structure observed

a (hkl)	Phase IV measured d-space (Б) at zero stress	Relative intensity
100	4.902	Off range
110	2.822	W
200	2.423	Under 107
107	2.424	VS
108	2.178	VS
117	1.986	M
210	1.847	S
118	1.845	Under 210
300	1.631	M
220	1.411	M
310	1.357	M
00.15	1.299	S
10.15	1.257	S

b (hkl)	Phase III literature d-space (Б) at 1.2 GPa hydrostatic[1]	Measured d-space (Б) under uniaxial stress	Relative intensity
010	4.89	Off range	
210	2.97	2.985	W
101	2.52	2.541	VS
020	2.45	2.482	VS
-111	2.31	2.272	VS
111	2.17	2.130	S
-420	1.94	1.945	VW
410	1.90	1.895	VW
-121	1.84	Under IV 210	S
311	1.75	1.754	M
420	1.48	1.484	W
321	1.42	Under IV 220	M
002	1.31	Under IV 00.15	S
012	1.28	Under IV 10.15	S

For More Information

- E.N. Brown, P.J. Rae, D.M. Dattelbaum, B. Clausen, D.W. Brown. "In-situ measurement of crystalline lattice strains in polytetrafluoroethylene" *Experimental Mechanics* 2008 48 (1) 119–131.

- E.N. Brown, D.M. Dattelbaum, D.W. Brown, P.J. Rae, B. Clausen. "A new strain path to inducing phase transitions in semi-crystalline polymers" *Polymer* 2007 48 (9) 2531–2536.

- E.N. Brown, B. Clausen, D.W. Brown. "In-Situ Measurement of Crystalline Lattice Strains in Phase IV Polytetrafluoroethylene," *Journal of Neutron Research* 2007 15 (2) 139–146.

Conclusions on PTFE

- The lattice strains in the crystalline domains with semi-crystalline PTFE have been measured in situ during tension and compression
- Assuming constant stress, elastic moduli have been measured
- The stiffness along the polymer chain backbone agree with theoretical predictions
- Pyramidal plains accommodate a dilatational response through shear
- Deformation is primarily accommodated in the compliant amorphous domain and inter-chain prismatic deformation in the crystal
- Uniaxial deformation induces a phase transition into a structure equivalent to phase III previous only reported under high hydrostatic pressure

Conclusions on SMARTS

- **Neutron diffraction is a powerful tool in materials science and engineering providing:**
  - Bulk residual/internal strain measurements
  - Bulk texture measurements
- **Large penetration depth enables beam to easily go through "windows" in ancillary equipment**
  - Vacuum or environmental chambers
  - High temperature furnaces
  - Cryogenic temperatures

Abstract

A novel application of in situ neutron diffraction under applied uniaxial strain is presented; measuring the crystalline domain evolution in a semi-crystalline polymer under bulk deformation. PTFE is shown to respond to uniaxial deformation by undergoing a crystalline phase transition previously believed to occur only at very high hydrostatic pressure. Discovery of this phase transition under applied uniaxial-strain fundamentally changes our understanding of the deformation mechanisms in semi-crystalline polymers and how they need to be modeled. Under compression parallel to the basal plane normal (i.e., parallel to the molecular axis) the modulus is ~1000× bulk dominated by intra-polymer chain compression, providing experimental validation of theoretical predictions. Deformation parallel to the pyramidal plane normal exhibit both axial and transverse strains of the opposite sign as the applied load, suggesting the crystalline lattice is accommodating deformation by shearing along the prismatic planes.