Enhancing Oxide Properties: The Approach of the Modern Alchemist

Darrell G. Schlom

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Cornell University

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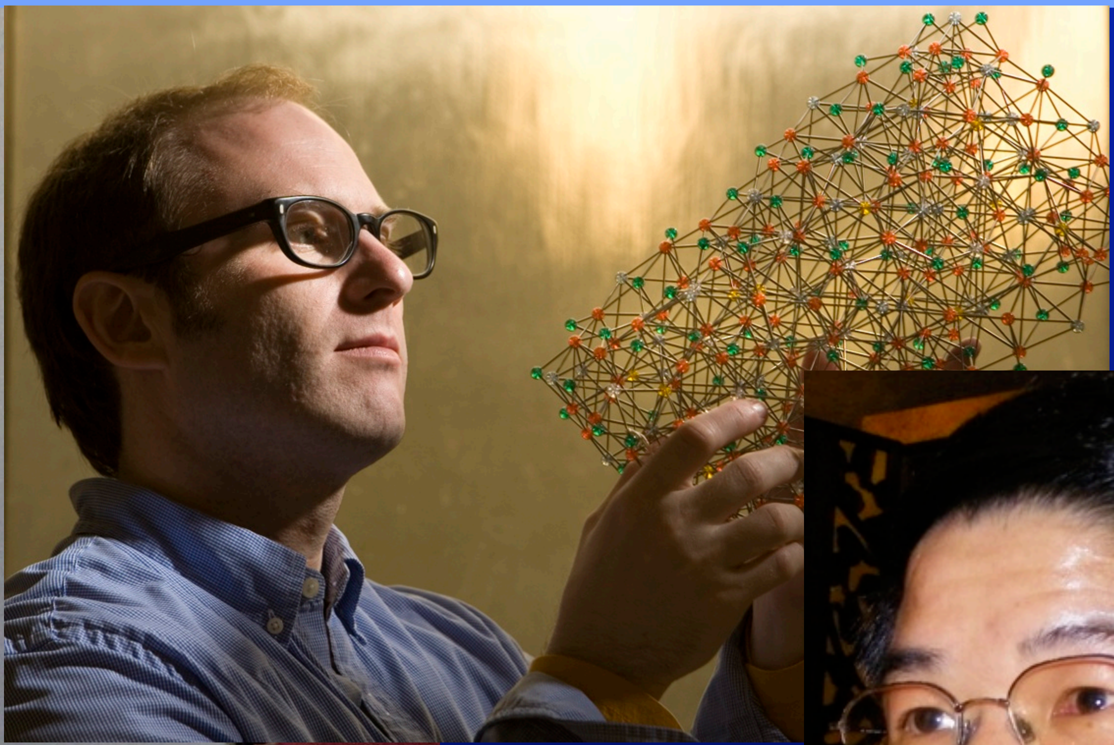
The Sorcerers

Karin Rabe (Rutgers)



Craig Fennie
(Cornell)

LongQing Chen
(Penn State)

What's New? — Motivation

- **Theoretical Predictions**
  - **Effect of Strain on Ferroelectric Properties of $SrTiO_3$, $BaTiO_3$, $BaTiO_3$ / $SrTiO_3$ Superlattices**

N.A. Pertsev, A.G. Zembilgotov, and A.K. Tagantsev, *Phys. Rev. Lett.* **80**, 1988 (1998).

J.B. Neaton and K.M. Rabe, *Appl. Phys. Lett.* **82**, 1586 (2003).

Y.L. Li and L.Q. Chen, *Appl. Phys. Lett.* **88**, 072905 (2006).

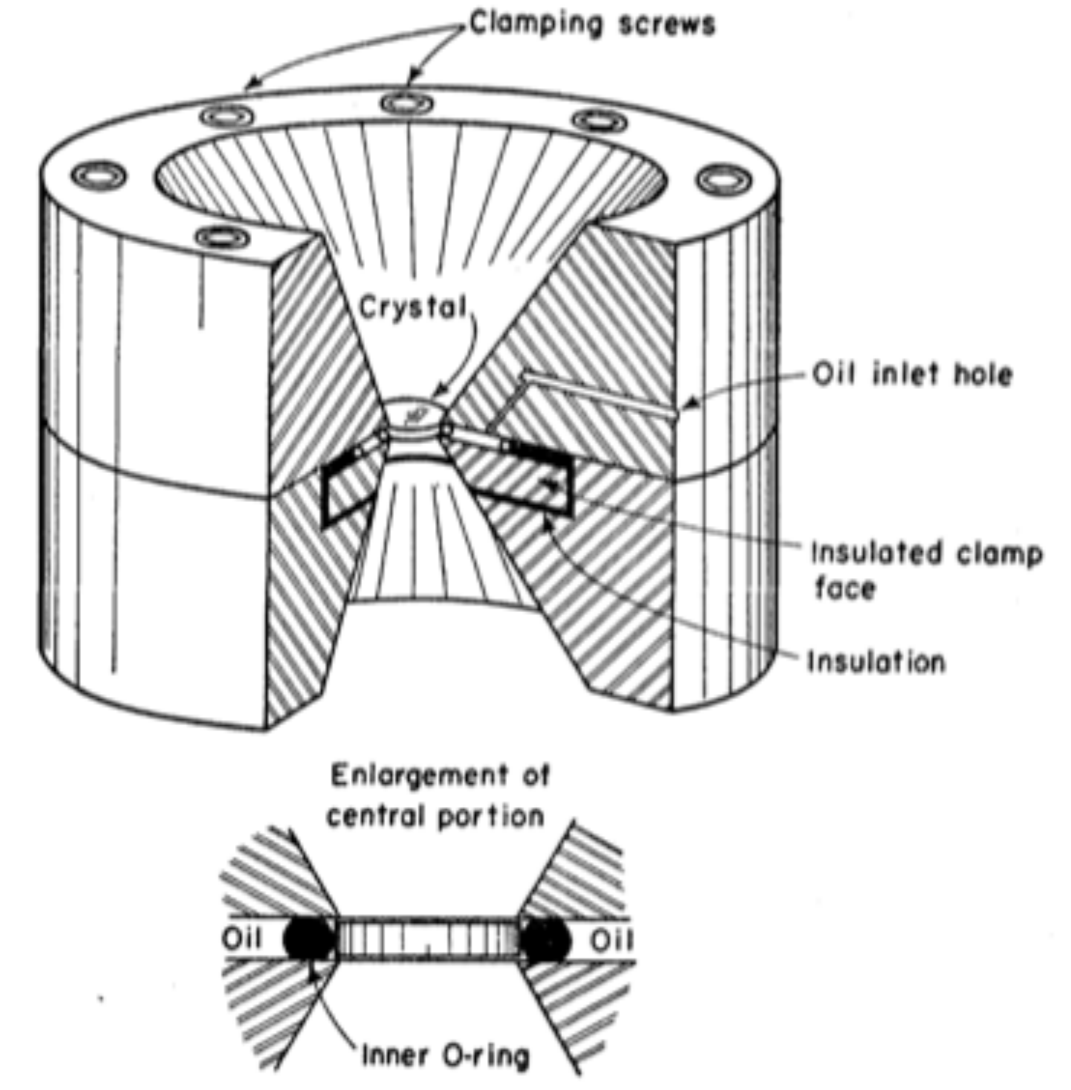
  - **Ability to Turn on Ferromagnetism in $EuTiO_3$ with *E***
  - **Ability to Turn on Ferroelectricity in $EuTiO_3$ with *B***

C.J. Fennie and K.M. Rabe, *Phys. Rev. Lett.* **97**, 267602 (2007).

  - **Effect of Strain on Band Gap of $SrTiO_3$**

R.F. Berger, C.J. Fennie, and J.B. Neaton, *Phys. Rev. Lett.* **107**, 146804 (2011).

Effect of Biaxial Strain on $BaTiO_3$



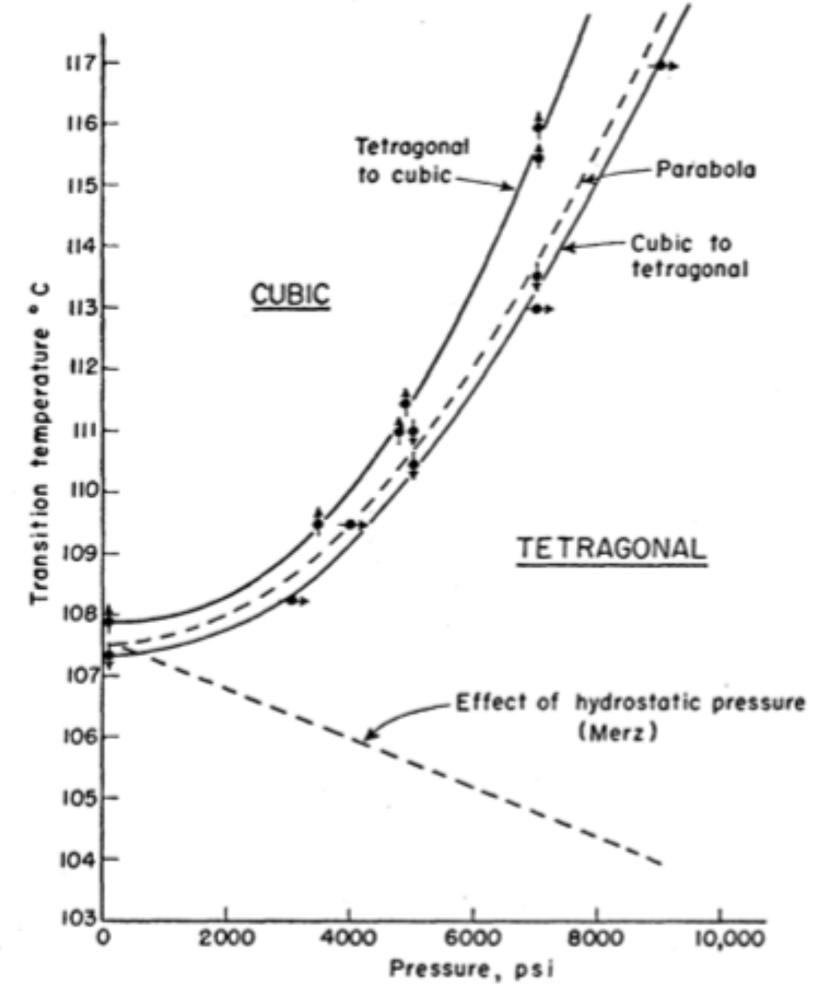


FIG. 2. Effect of two-dimensional pressure on the Curie transition in barium titanate.

P.W. Forsbergh, Jr., "Effect of a Two-Dimensional Pressure on the Curie Point of Barium Titanate," *Physical Review* **93**, 686 (1954).

Strained Silicon in MOSFETs

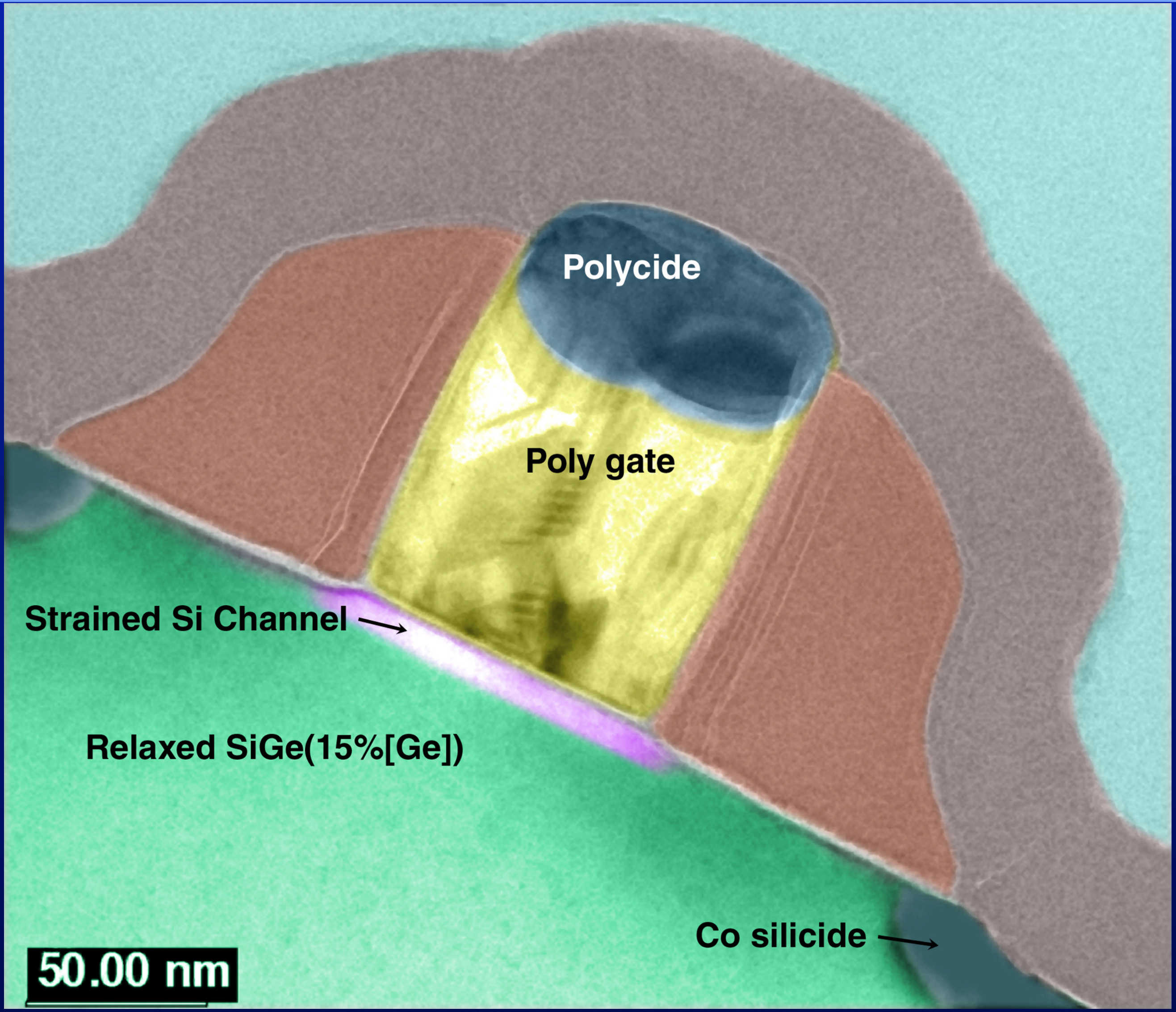
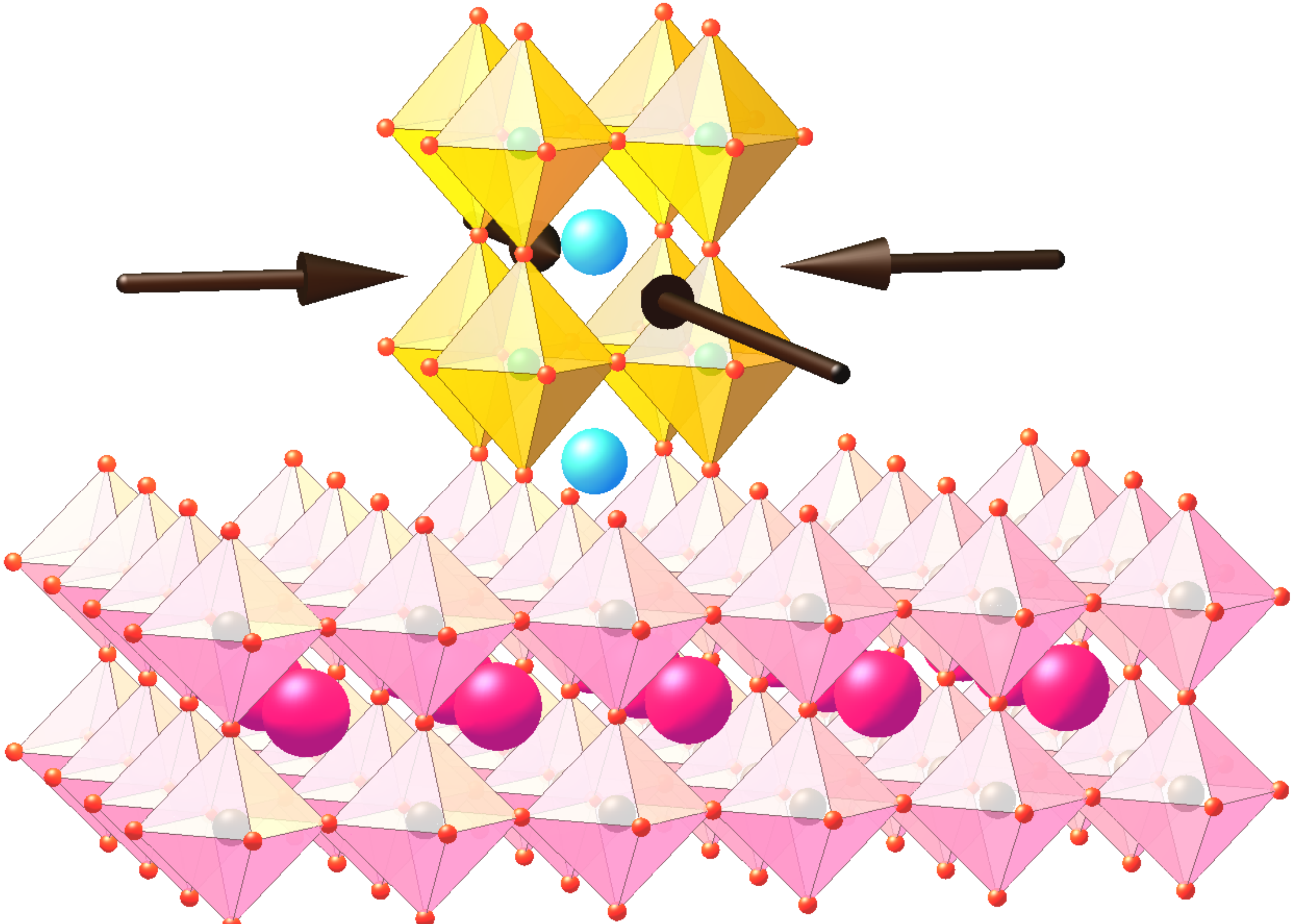


Photo: IBM Corporation (http://www.research.ibm.com/resources/press/strainedsilicon/)

Biaxial Strain via Epitaxy



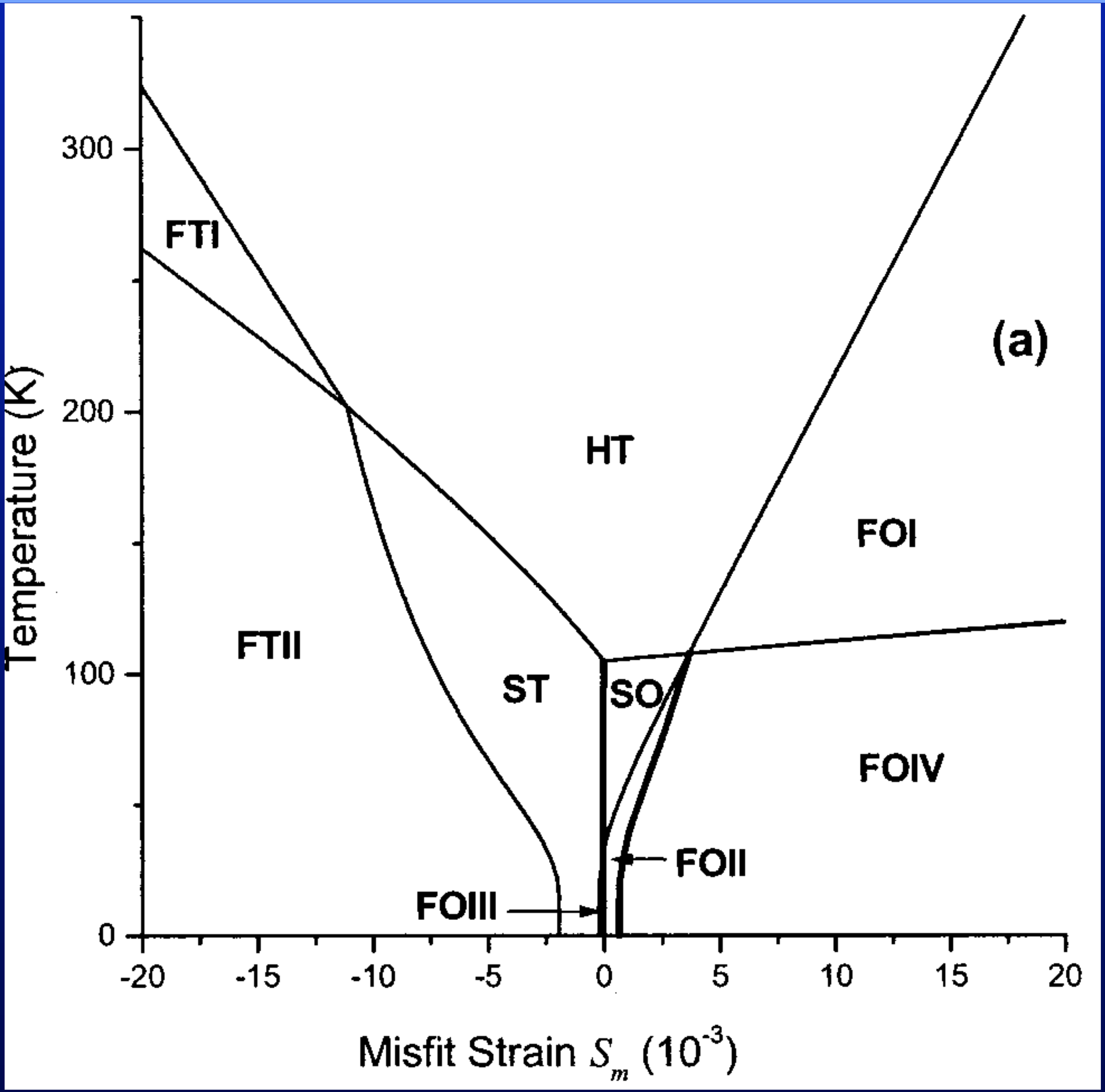
Outline

- Introduction
- **Turning a Dielectric into a Ferroelectric— Strained $SrTiO_3$**
- **Turning a Dielectric into a Multiferroic— Strained $EuTiO_3$**
- **Conclusions**
- **Future Directions**

In Collaboration with the Groups of:

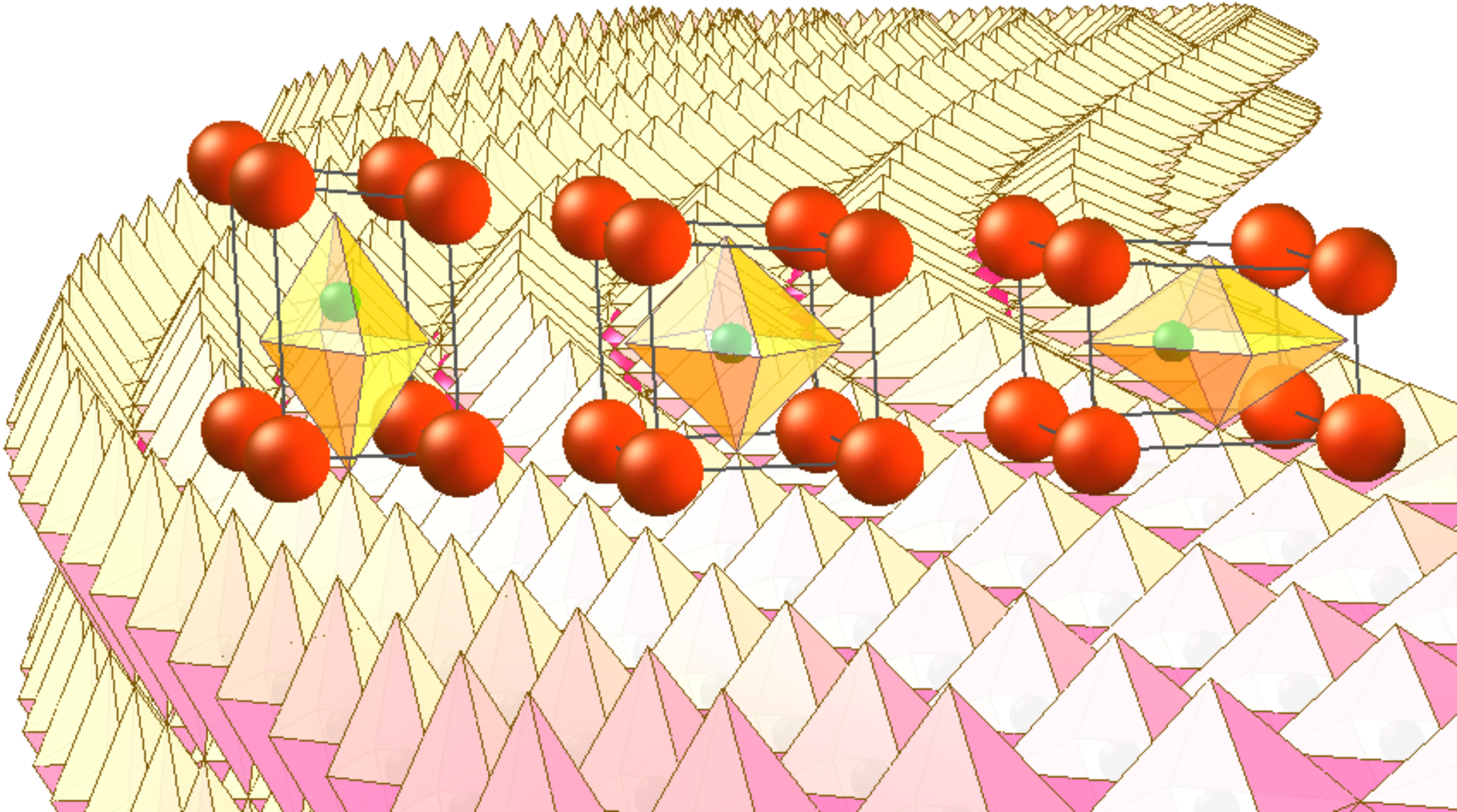
Craig J. Fennie—*Cornell University*
Karin M. Rabe—*Rutgers University*
Long-Qing Chen—*Penn State University*
David A. Muller—*Cornell University*
Kyle M. Shen—*Cornell University*
Venkatraman Gopalan—*Penn State University*
Susan Trolier-McKinstry—*Penn State University*
Peter Schiffer—*University of Illinois*
Ezekiel Johnston-Halperin—*Ohio State University*
Chris Hammel—*Ohio State University*
Xiaoqing Pan—*University of Michigan*
Jeremy Levy—*University of Pittsburgh*
Steven W. Kirchoefer—*Naval Research Laboratory*
Stanislav Kamba—*Institute of Physics, Czech Republic*
John Freeland—*Argonne National Laboratory*
Phil Ryan—*Argonne National Laboratory*
Jürgen Schubert—*Forschungszentrum Jülich GmbH*
Jochen Mannhart—*Max-Planck-Institute für Festkörperforschung*
Reinhard Uecker—*Leibniz Institute für Kristallzüchtung*

Effect of Strain on $SrTiO_3$—Theory

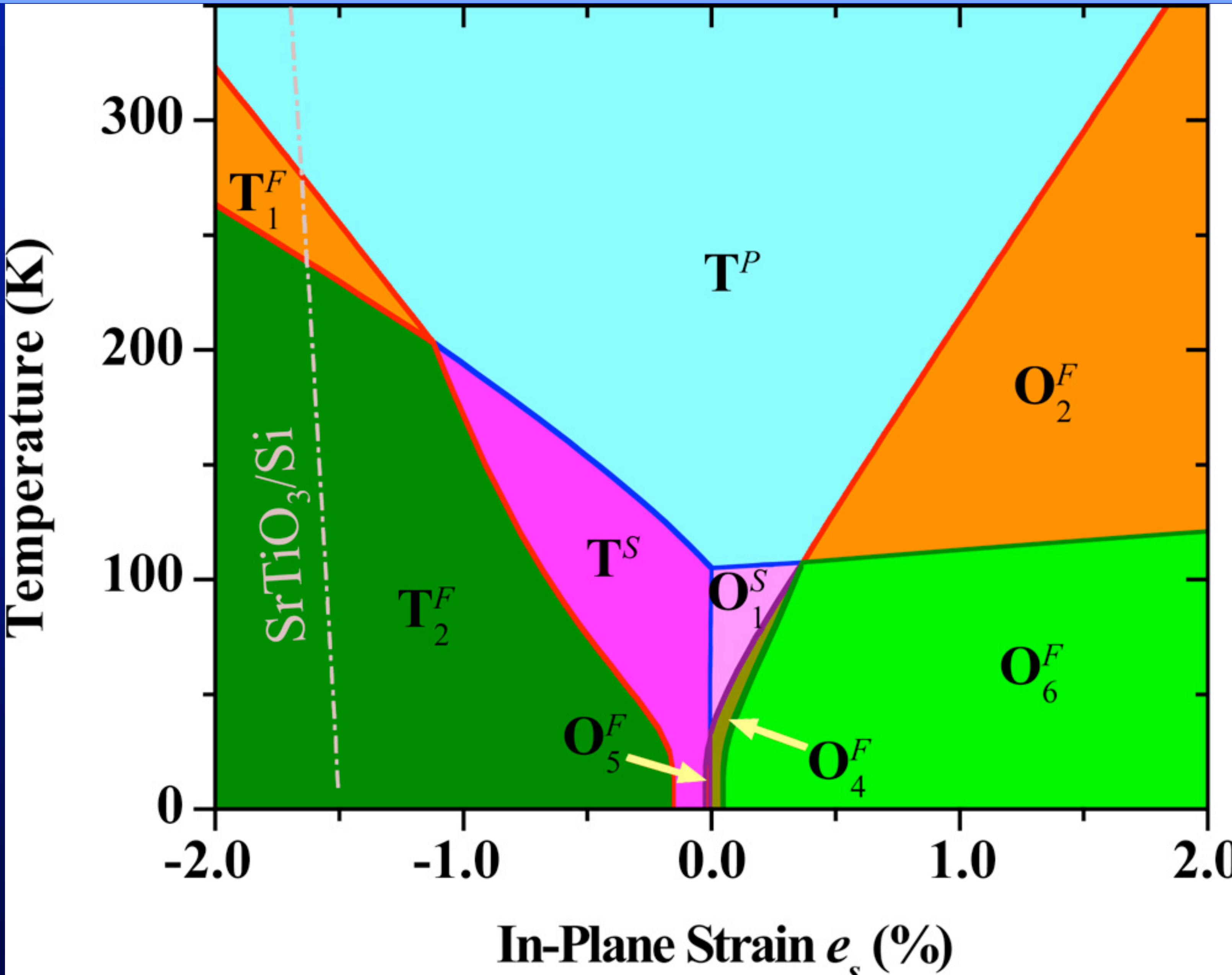


N.A. Pertsev, A.K. Tagantsev, and N. Setter, "Phase Transitions and Strain-Induced Ferroelectricity in $SrTiO_3$ Epitaxial Thin Films," *Physical Review* **61** (2000) 825-829.

Effect of *Strain* on $SrTiO_3$

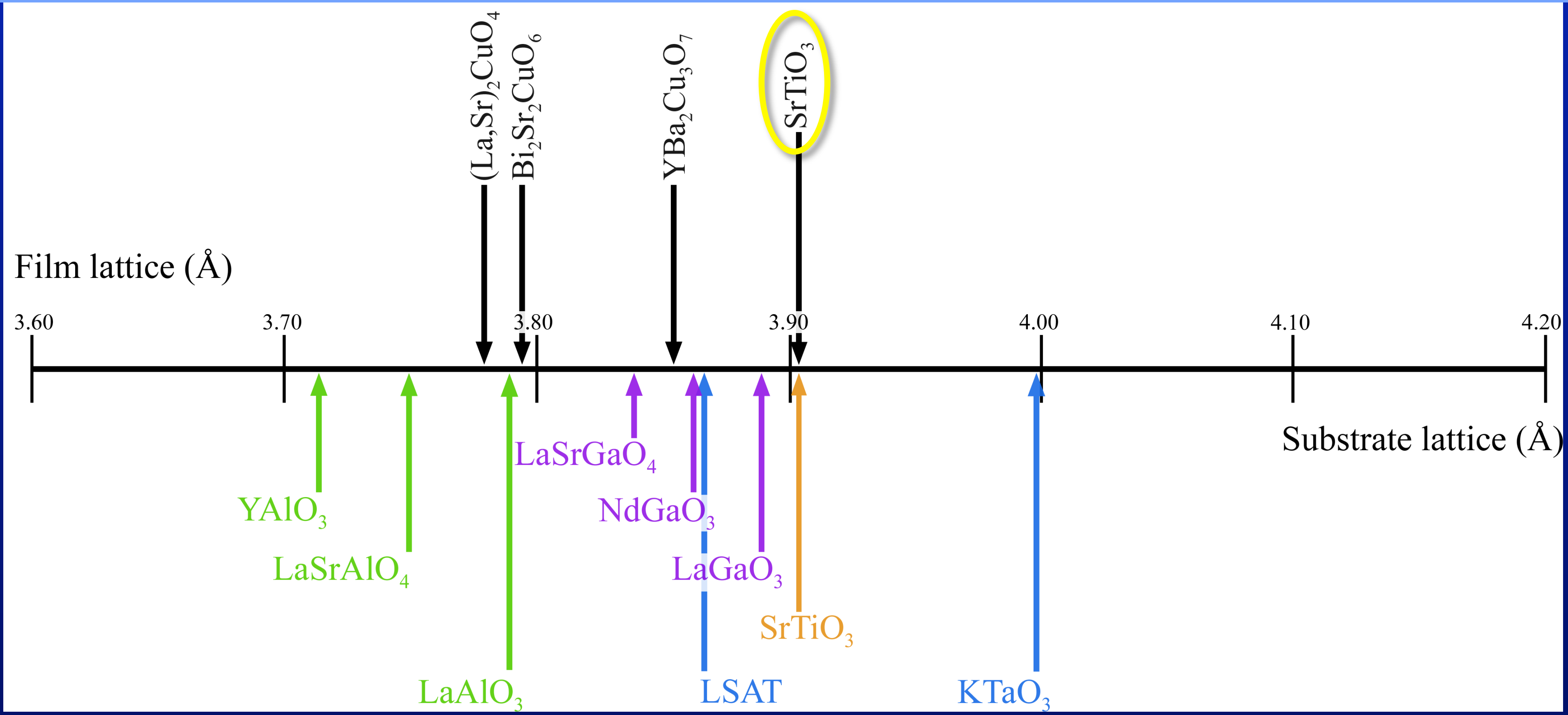


Effect of Strain on $SrTiO_3$ — Theory



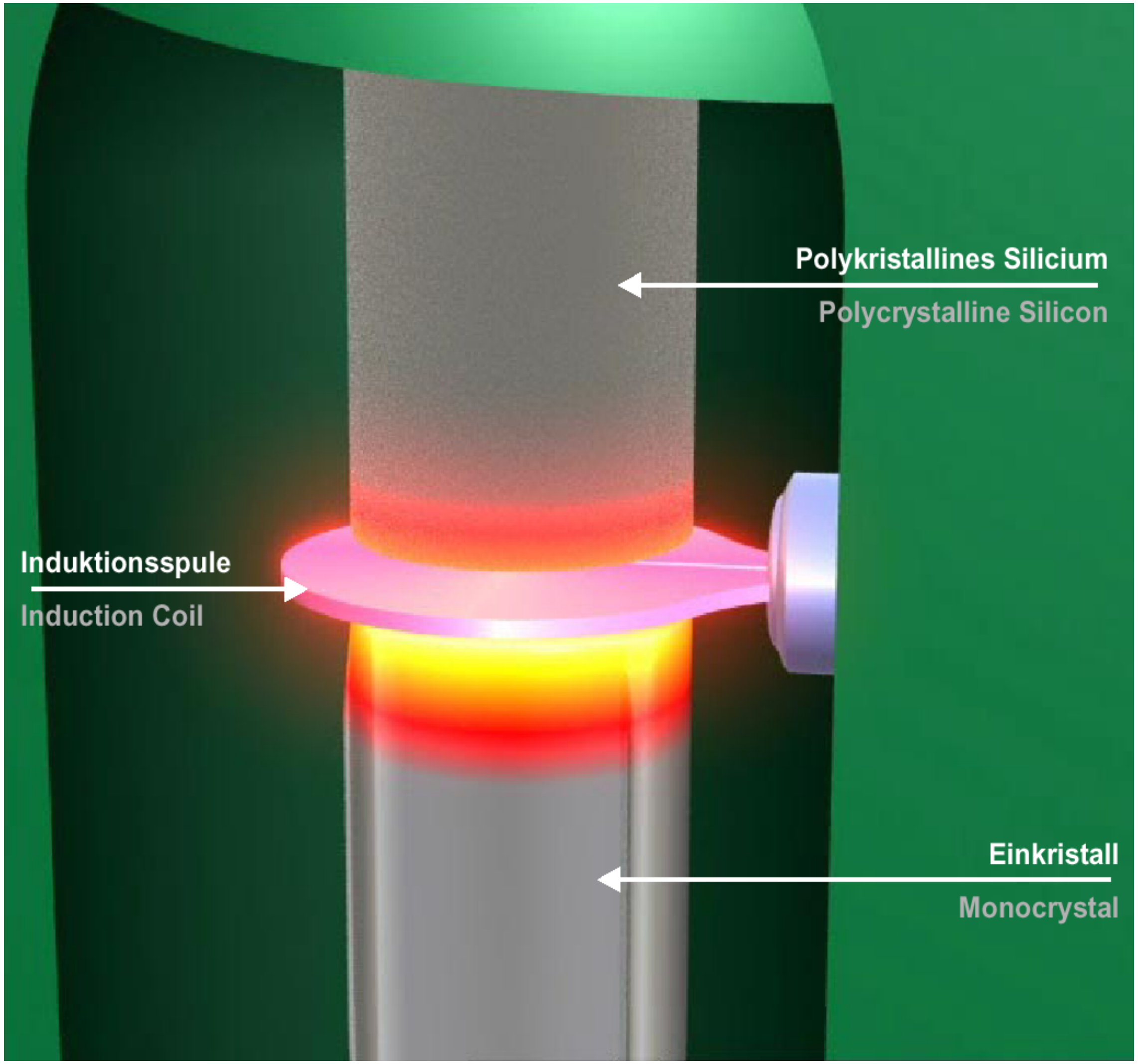
Substrates are Key

Commercial Perovskite Substrates



FLOATING ZONE (FZ) CRYSTAL GROWTH

Courtesy to Institute of Crystal Growth, Berlin



W.G. Pfann, 1951

FIRST 200 mm FZ CRYSTAL

Floating-Zone Growth of *Re*ScO_3

- **Grew Single Crystals of**

  $DyScO_3$ ($a \approx 3.94$ Å)

  $GdScO_3$ ($a \approx 3.97$ Å)

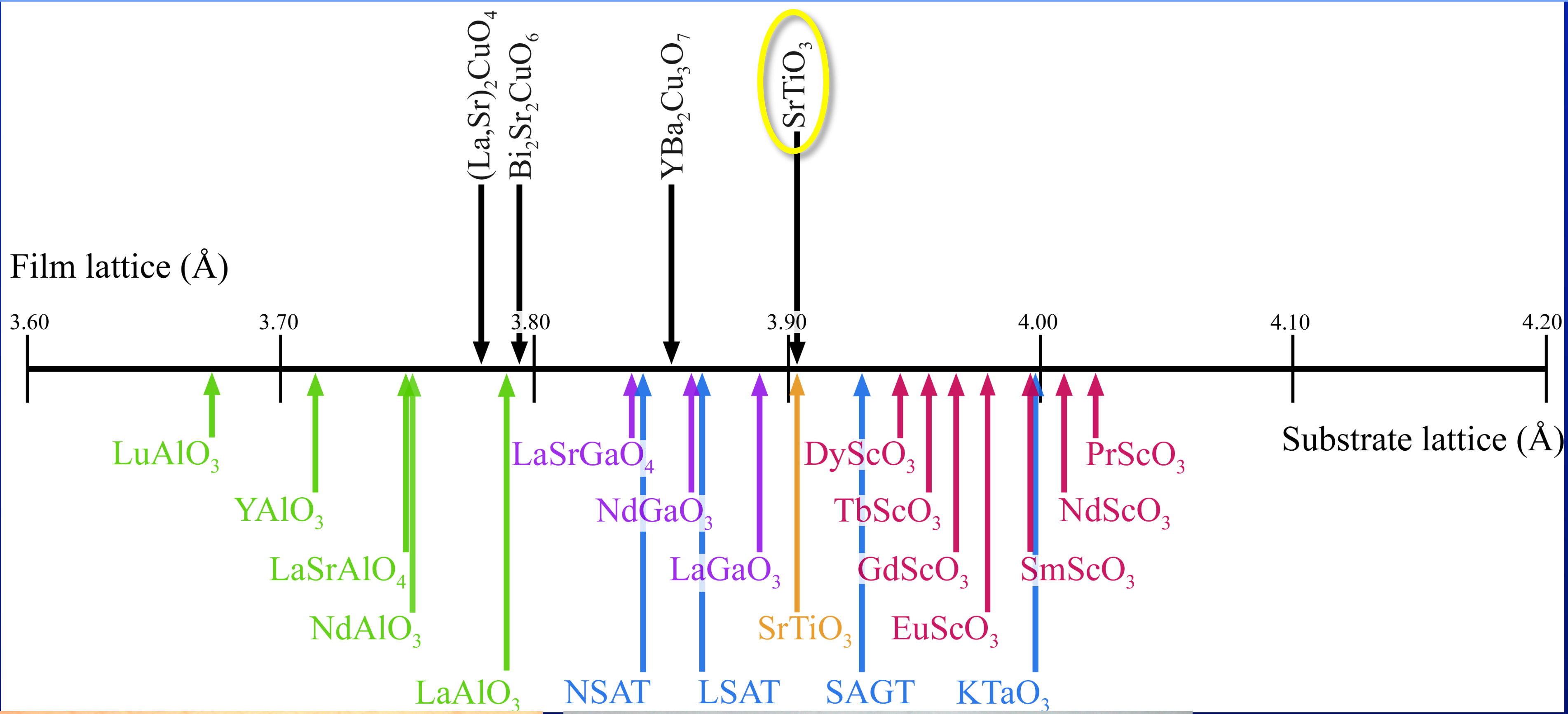
  $SmScO_3$ ($a \approx 3.99$ Å)

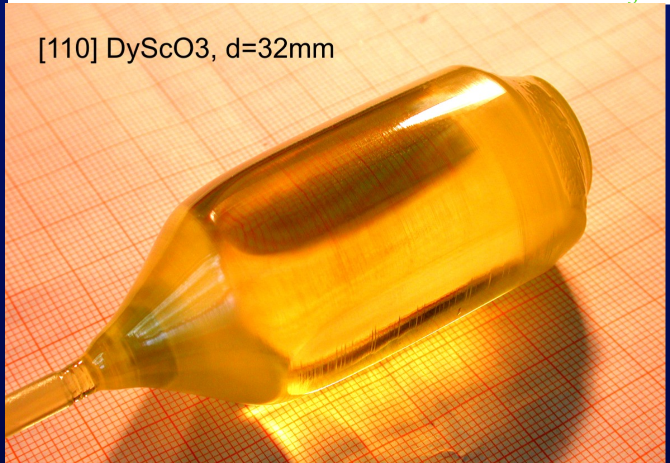
  $NdScO_3$ ($a \approx 4.01$ Å)

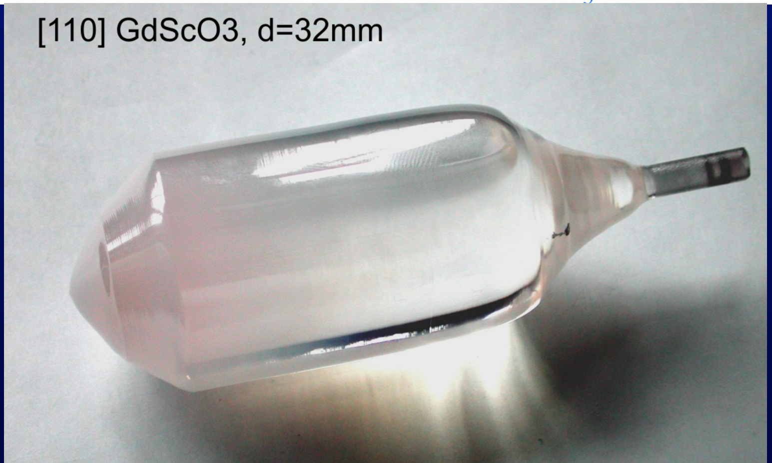
- **All Melt Congruently**
  $T_m \sim 2100$ °C

Jochen Mannhart's Group
University of Augsburg

Commercial Perovskite Substrates





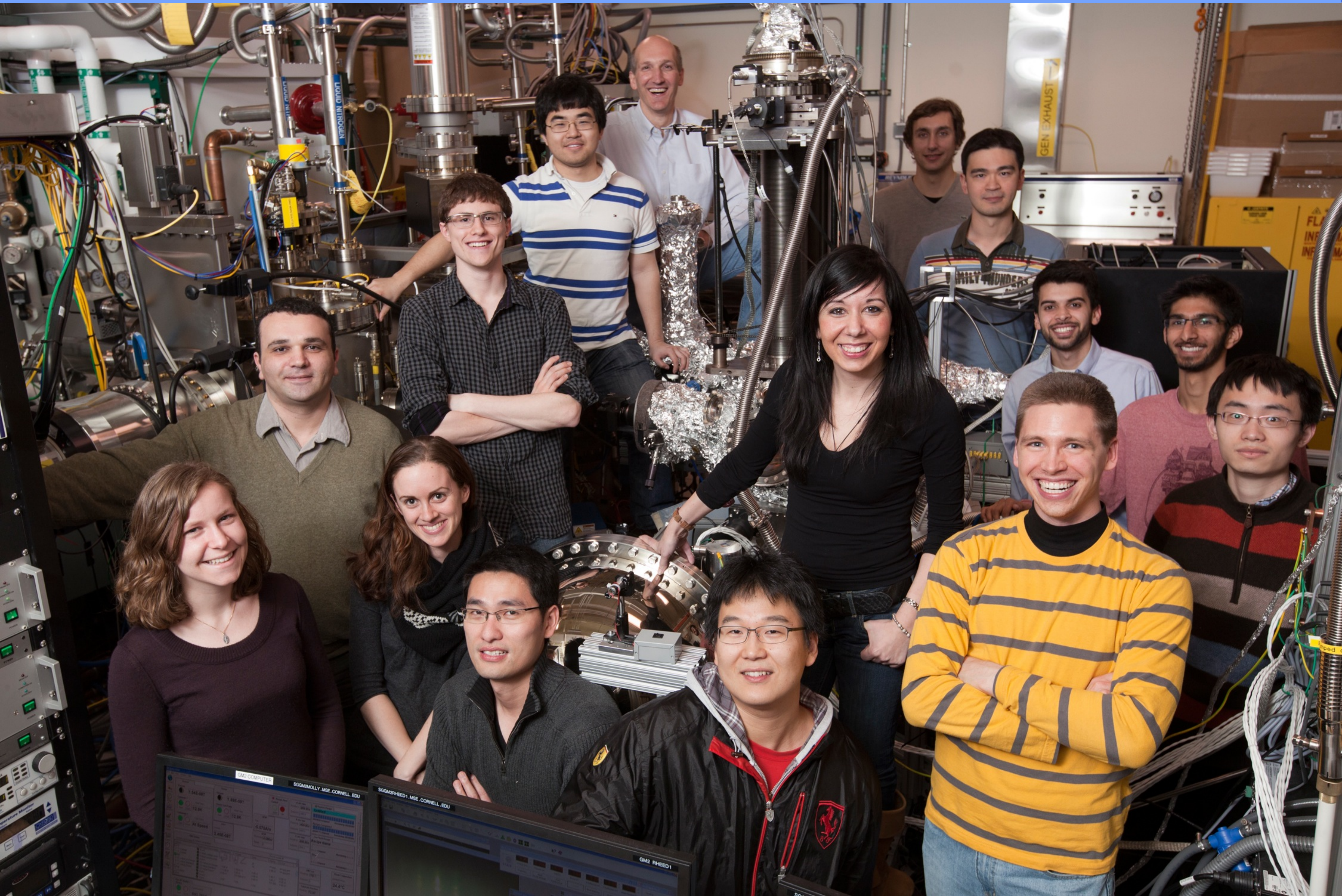


Reinhard Uecker's Group
Leibniz Institute
for Crystal Growth
Berlin, Germany

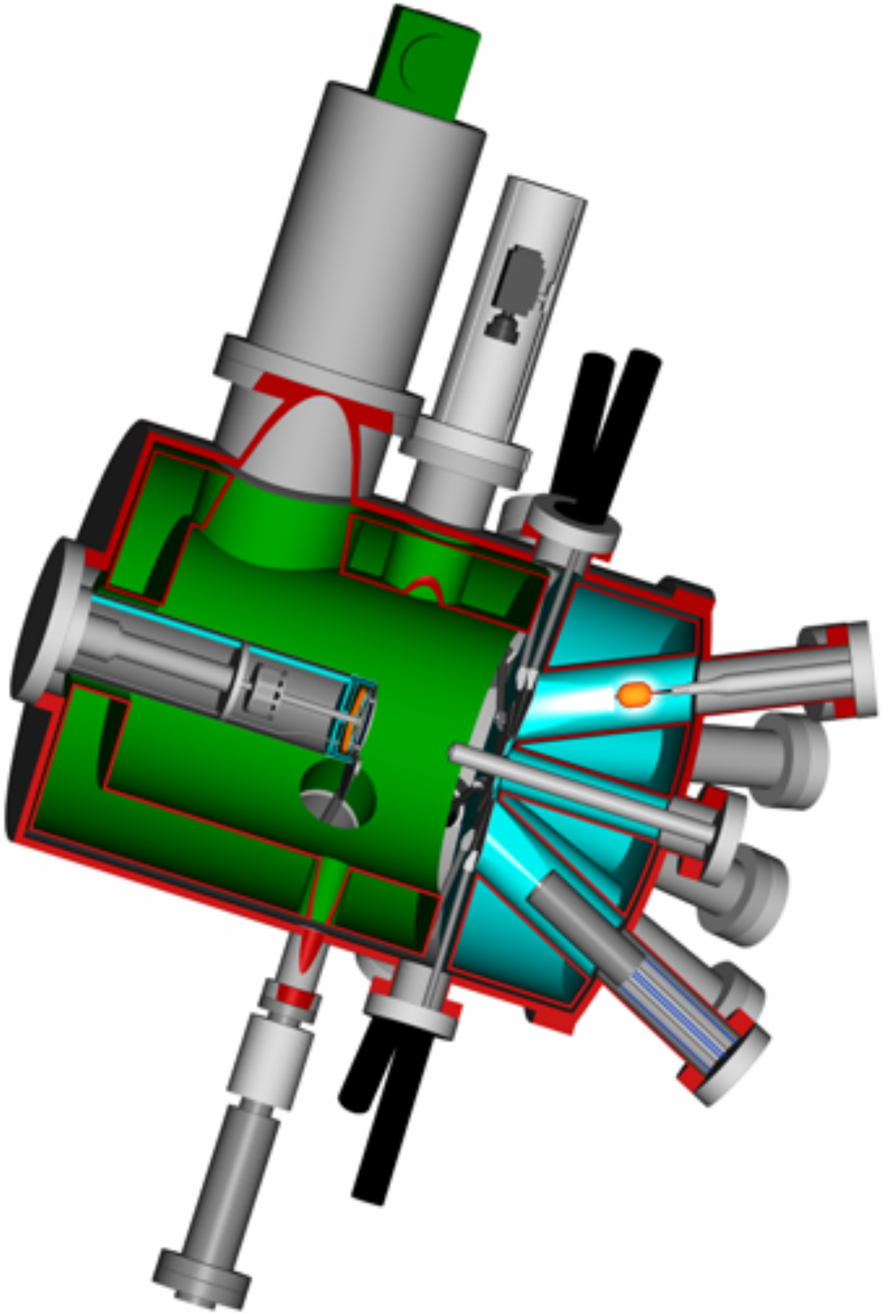
The Sorcerer's Apprentice

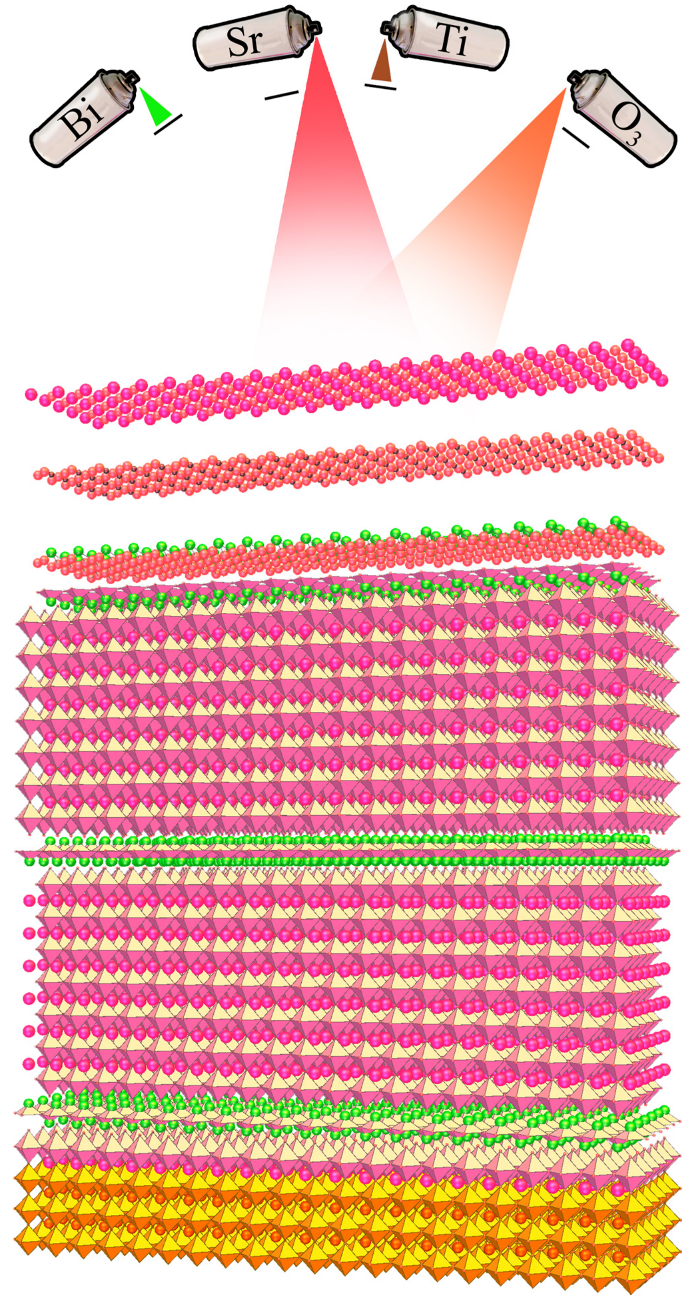
RHEED, QCM, MOSS, BandiT + ARPES, XPS, LEED

Oxide MBE Group

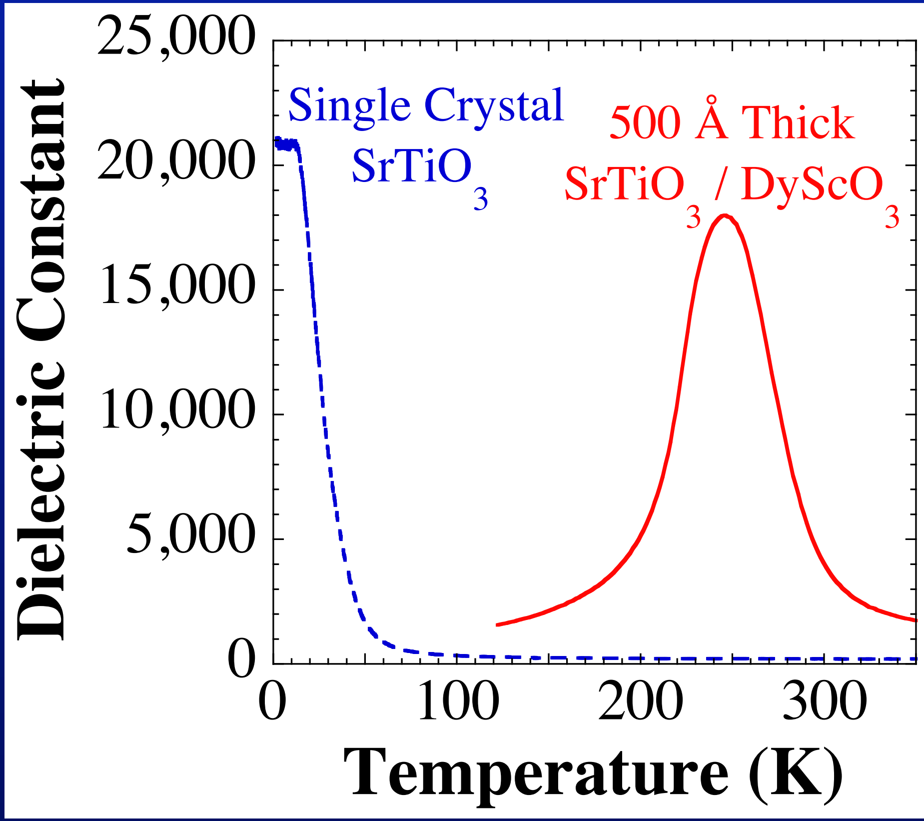


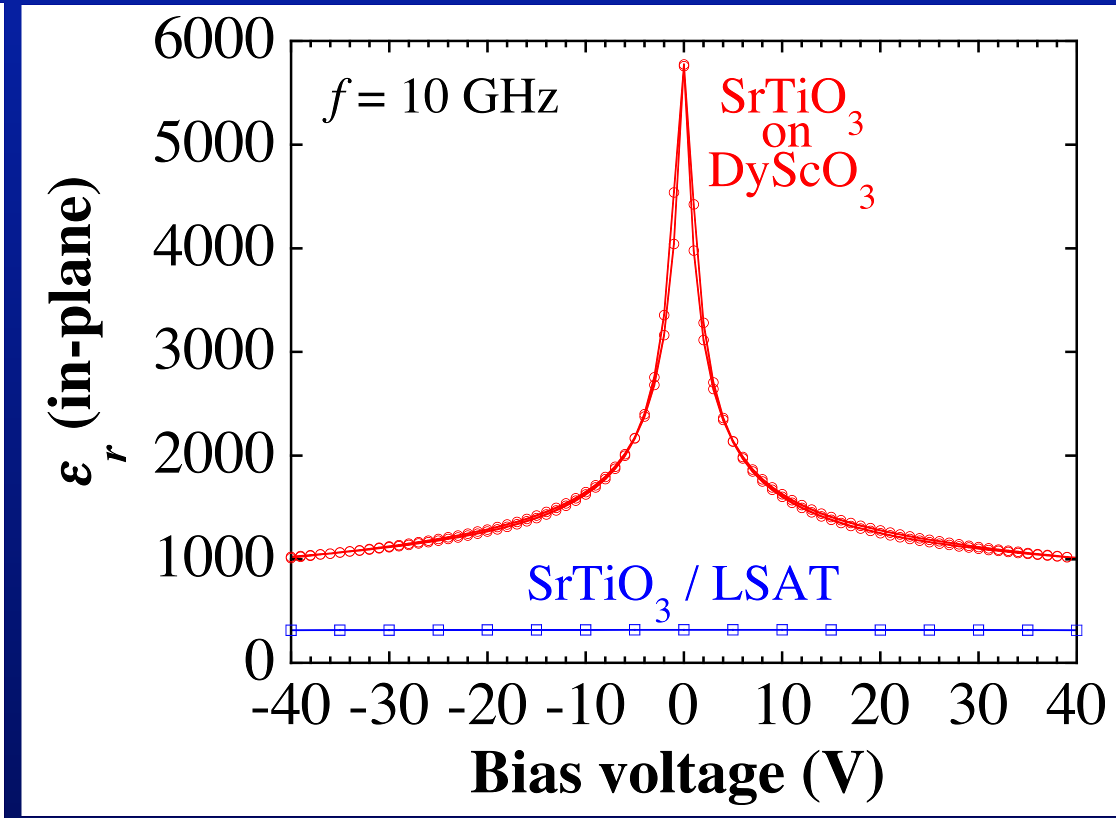
MBE ≈ Atomic Spray Painting





Strain-Enhanced $SrTiO_3$



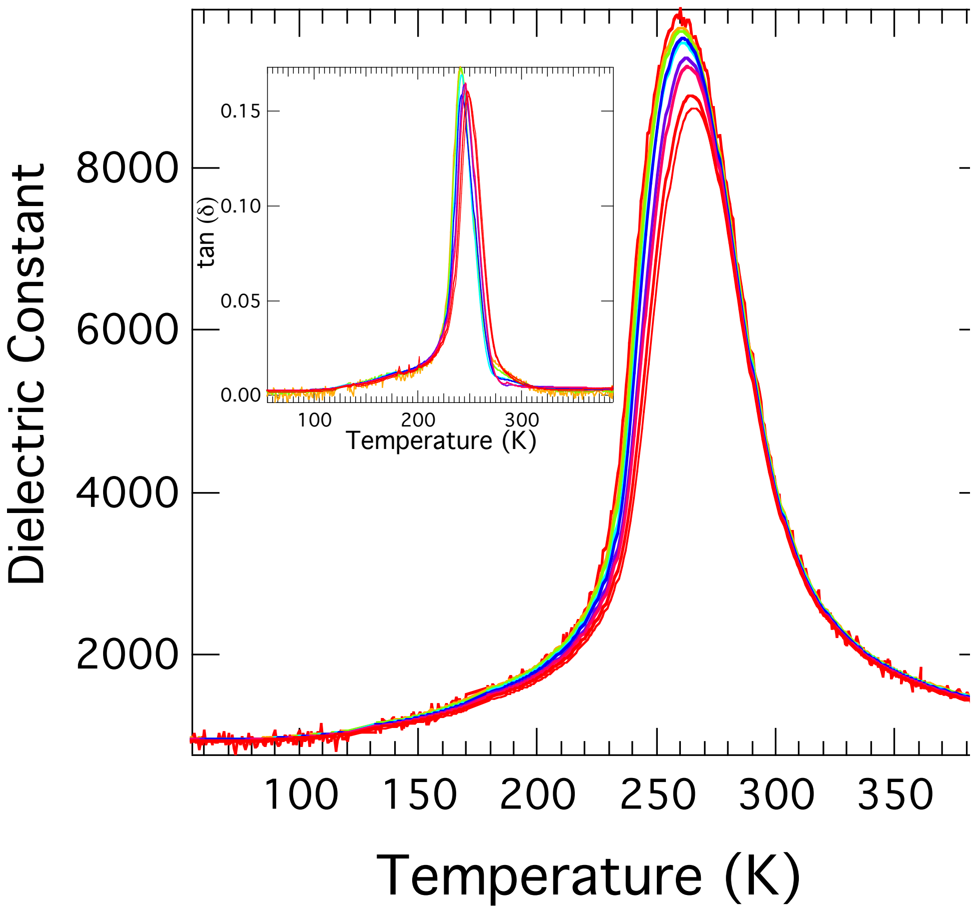


M.D. Biegalski, Y. Jia, D.G. Schlom, S. Trolier-McKinstry, S.K. Streiffer, V. Sherman, R. Uecker, and P. Reiche, *Applied Physics Letters* **88** (2006) 192907.

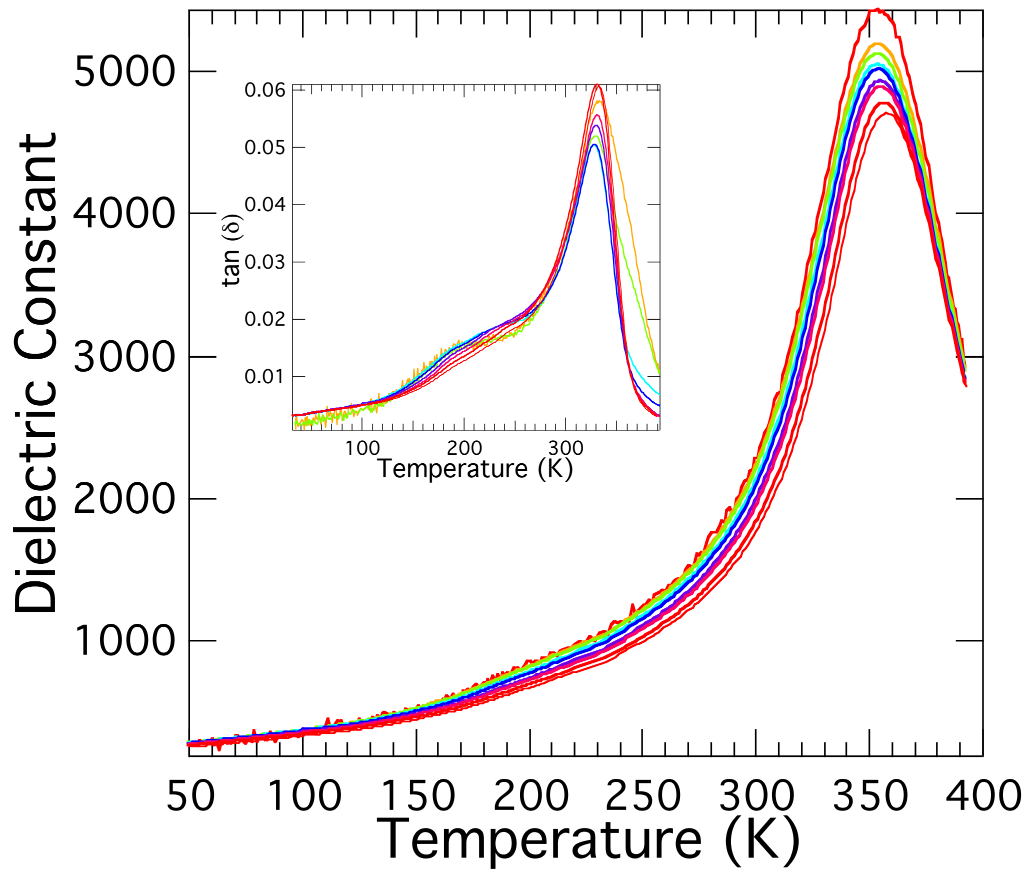
J.H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y.L. Li, S. Choudhury, W. Tian, M.E. Hawley, B. Craigo, A.K. Tagantsev, X.Q. Pan, S.K. Streiffer, L.Q. Chen, S.W. Kirchoefer, J. Levy, and D.G. Schlom, *Nature* **430** (2004) 758-761.

250 Å $SrTiO_3$ on (110) $DyScO_3$ vs. $GdScO_3$

$SrTiO_3$ / $DyScO_3$ ~ 1.0%



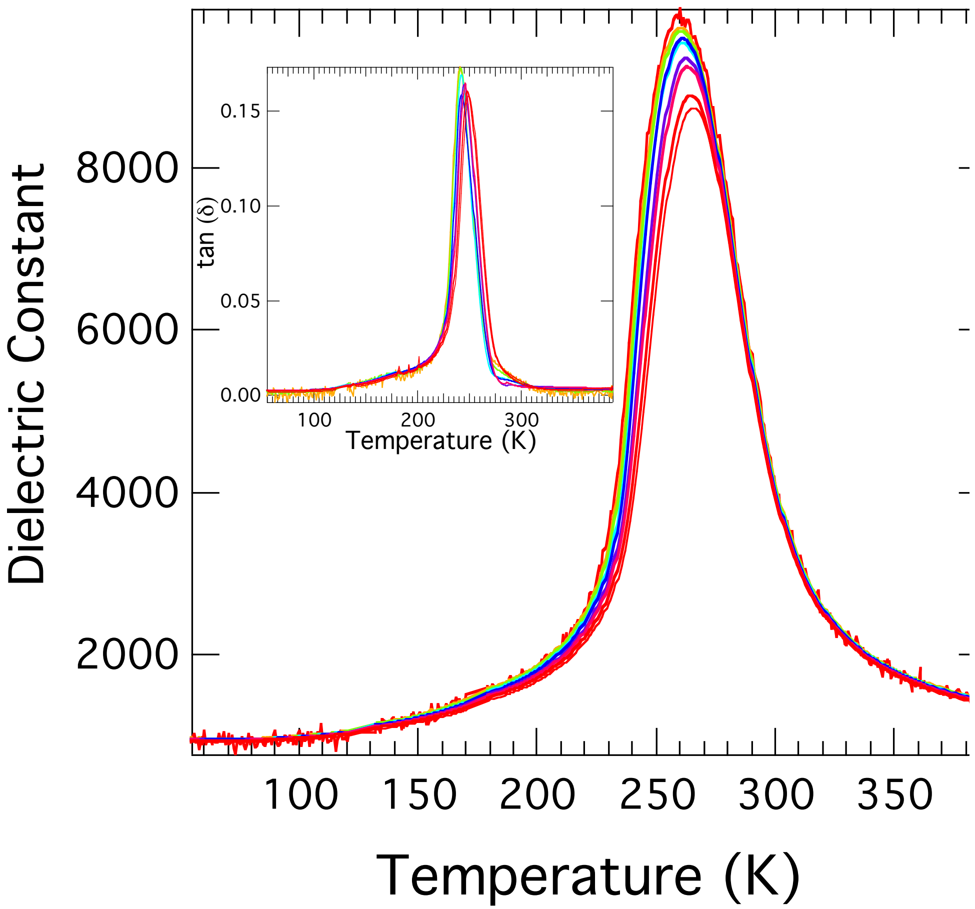
$SrTiO_3$ / $GdScO_3$ ~ 1.6%



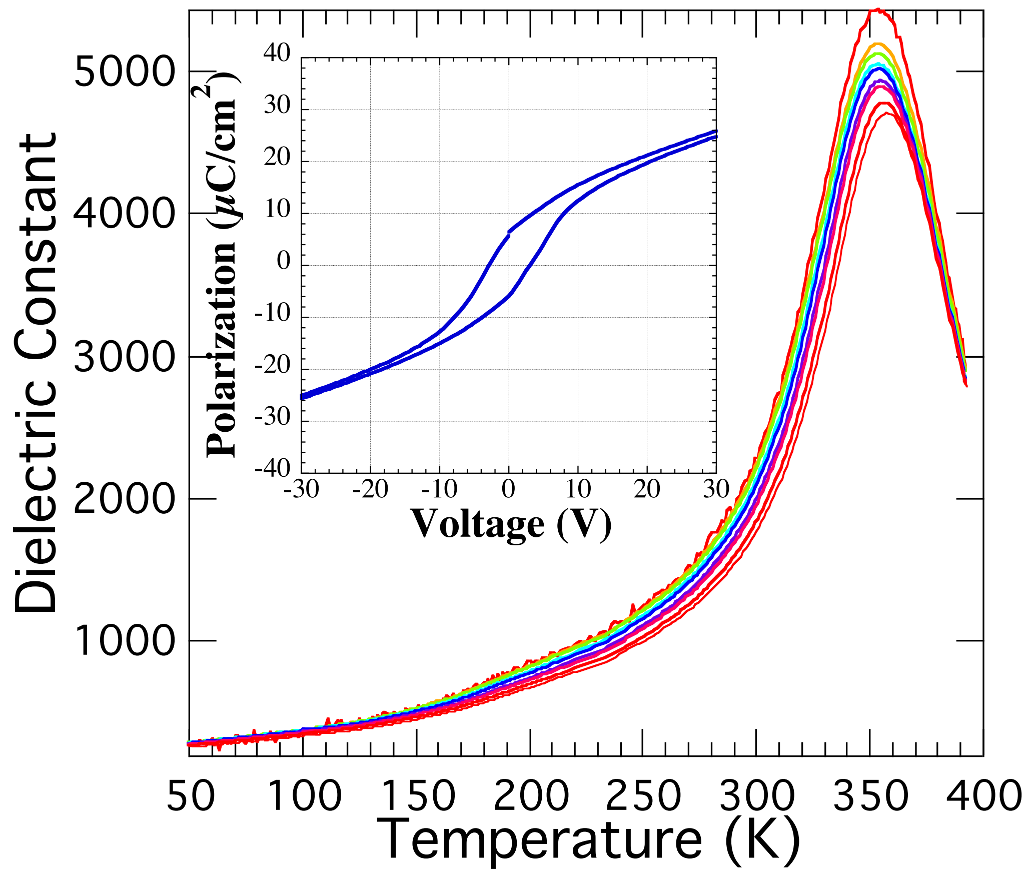
Strain shifts T_C

250 Å $SrTiO_3$ on (110) $DyScO_3$ vs. $GdScO_3$

$SrTiO_3$ / $DyScO_3$ ~ 1.0%

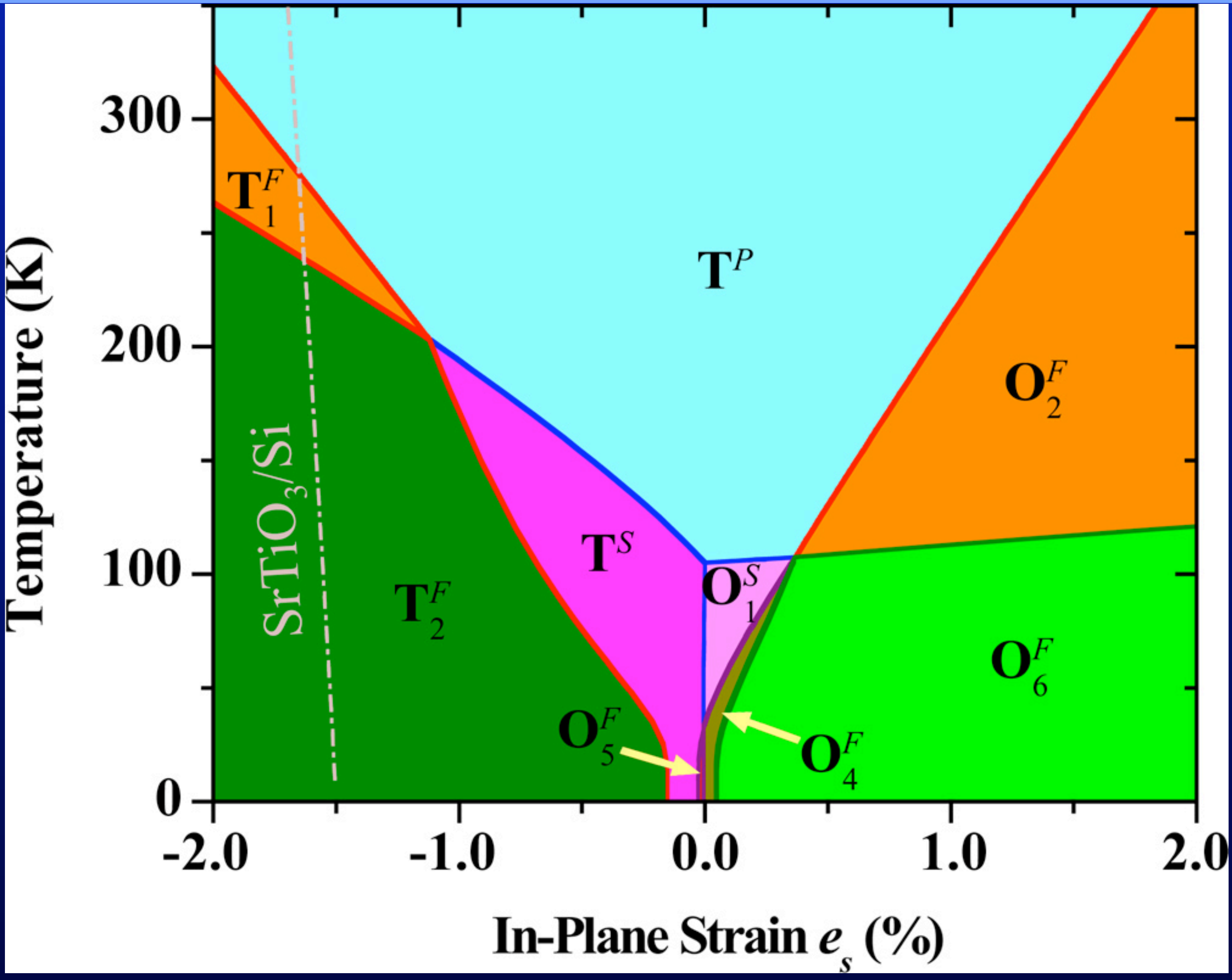


$SrTiO_3$ / $GdScO_3$ ~ 1.6%



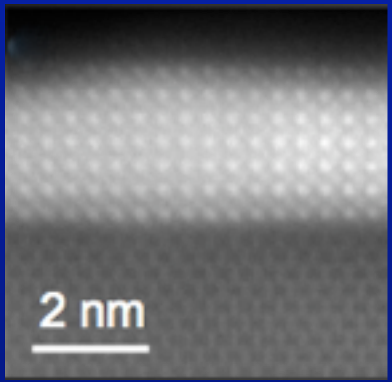
Strain shifts T_C

Effect of Strain on $SrTiO_3$ — Theory

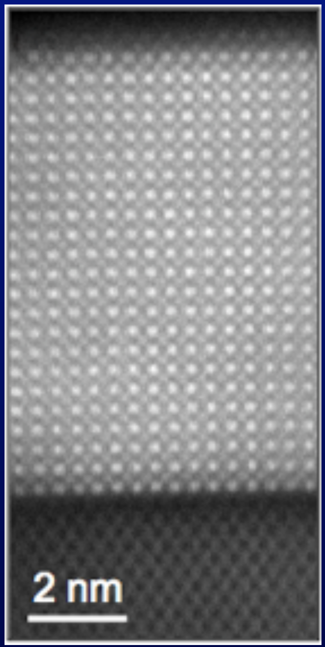


Commensurate when Thin (<~10 ML)

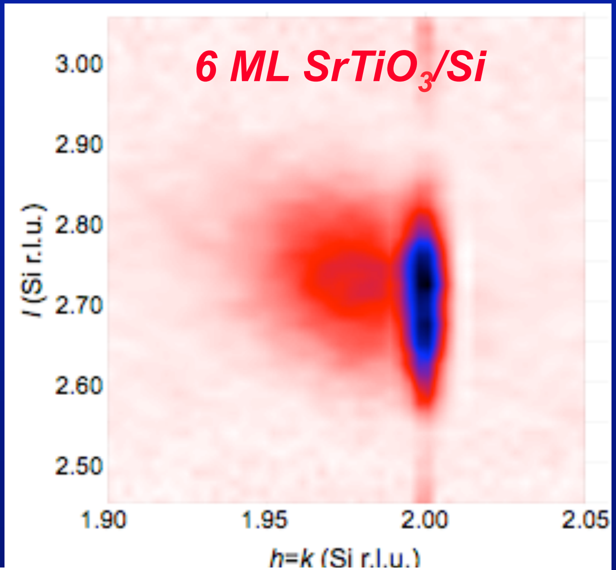
5 ML $SrTiO_3$/Si

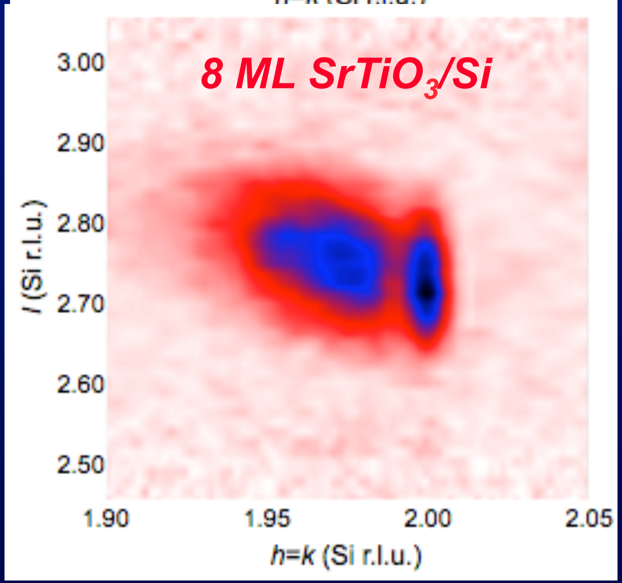


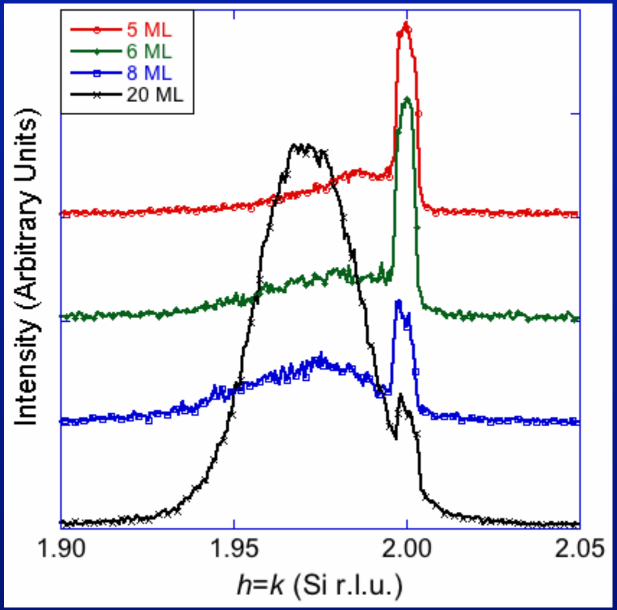
20 ML $SrTiO_3$/Si



$SrTiO_3$ 202 reflection





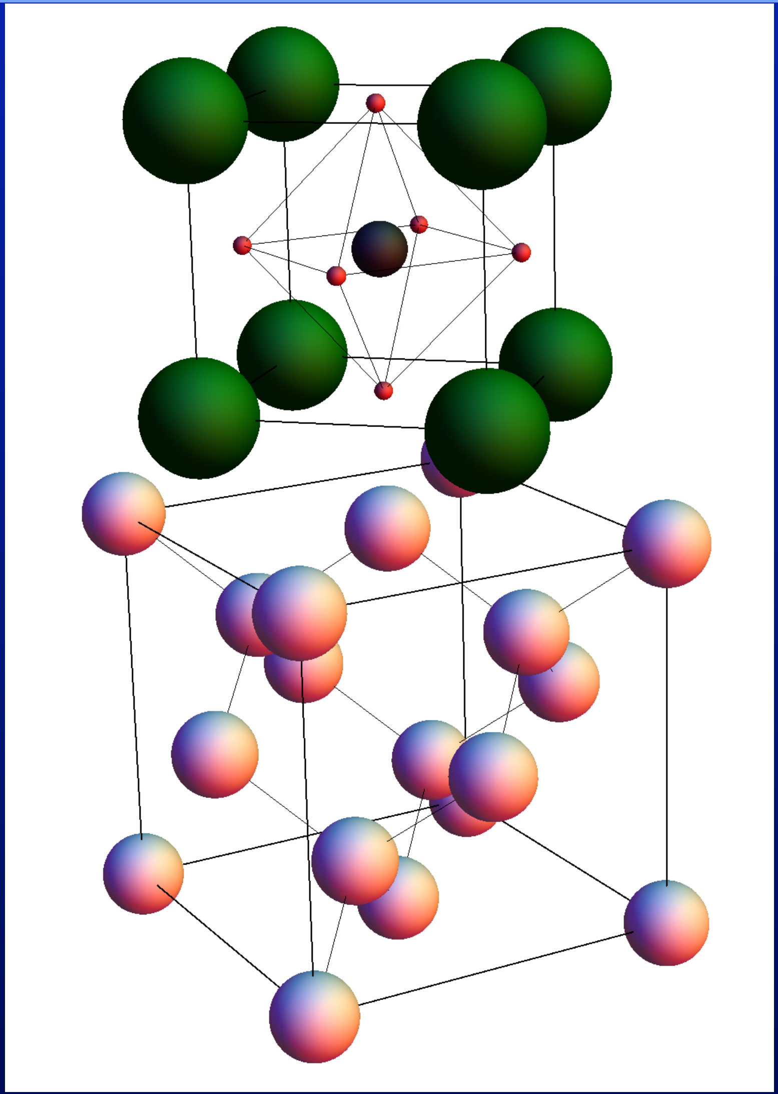


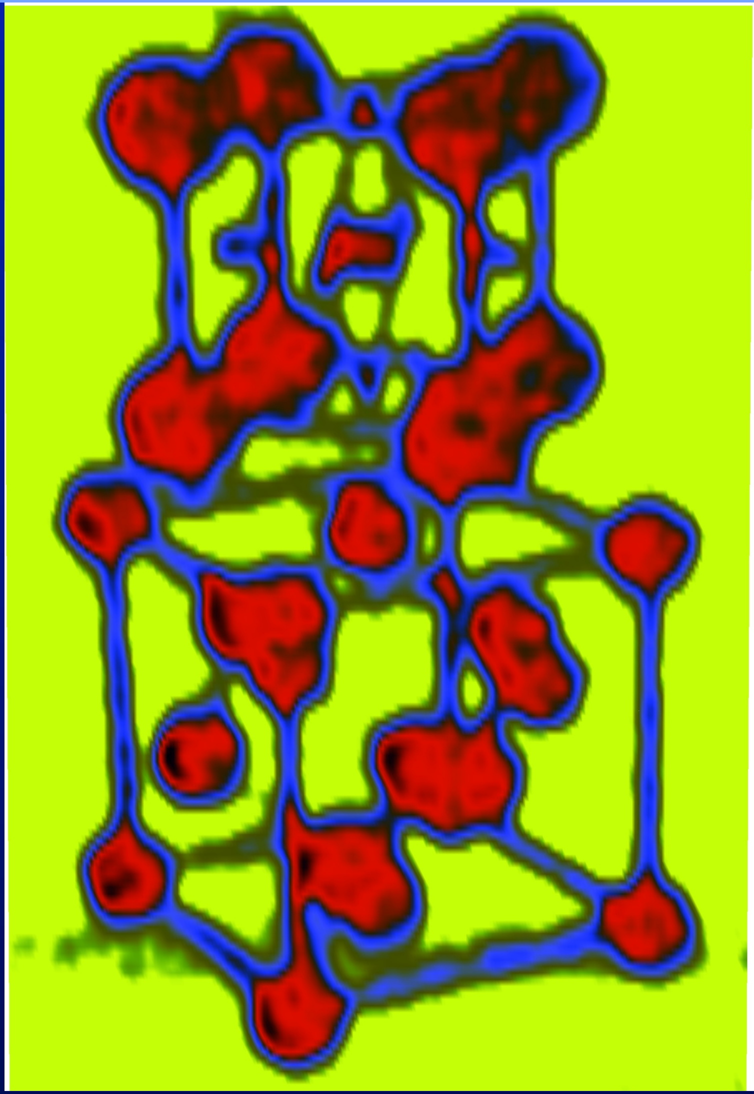
M.P. Warusawithana, C. Cen, C.R. Sleasman, J.C. Woicik, Y.L. Li, L. Fitting Kourkoutis, J.A. Klug, H. Li, P. Ryan, L-P. Wang, M. Bedzyk, D.A. Muller, L.Q. Chen, J. Levy, and D.G. Schlom, "A Ferroelectric Oxide Made Directly on Silicon," *Science* **324** (2009) 367-370.

David Muller—*Cornell University*

Joseph Woicik—*NIST*

20 Å Thick $SrTiO_3$ / (100) Si





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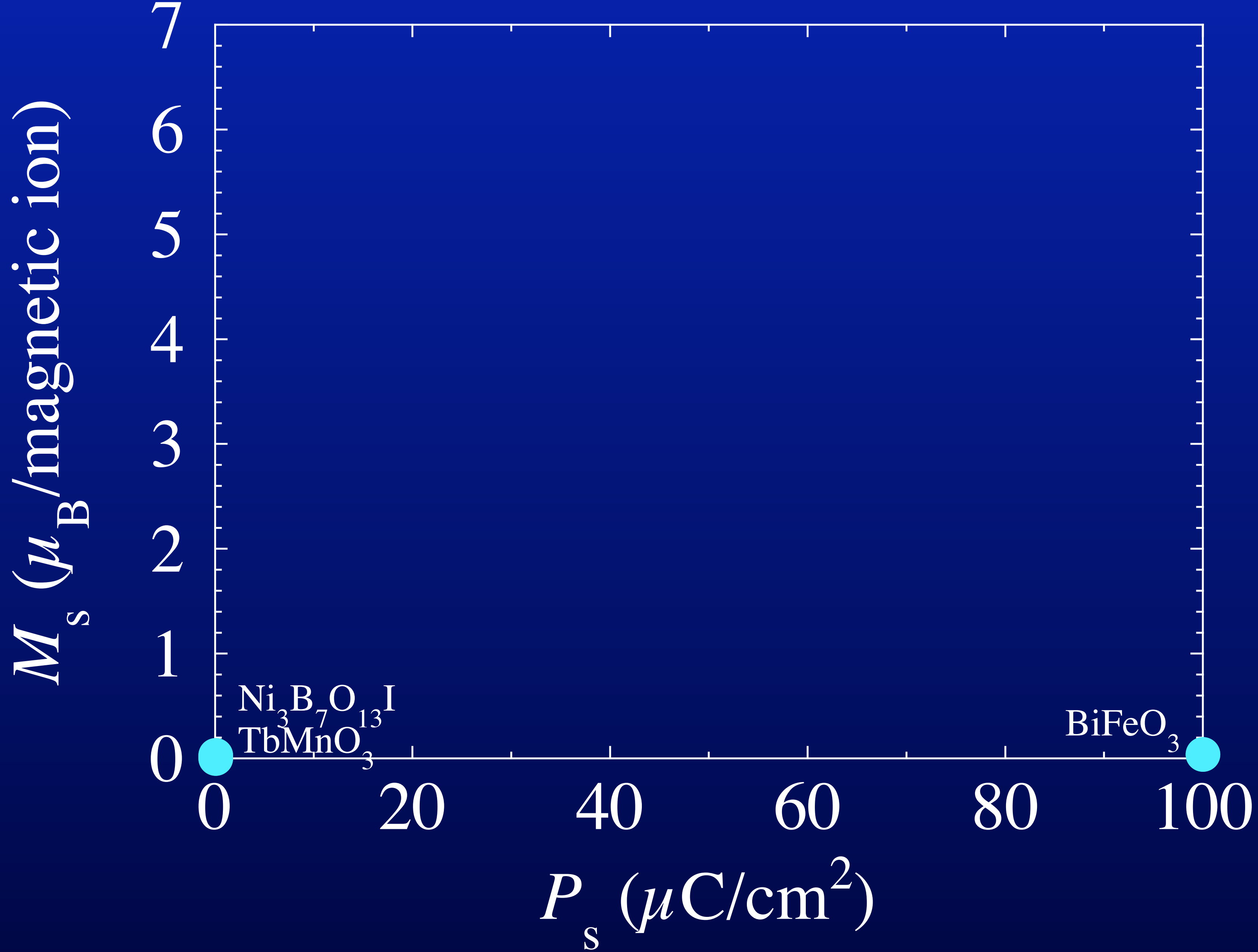
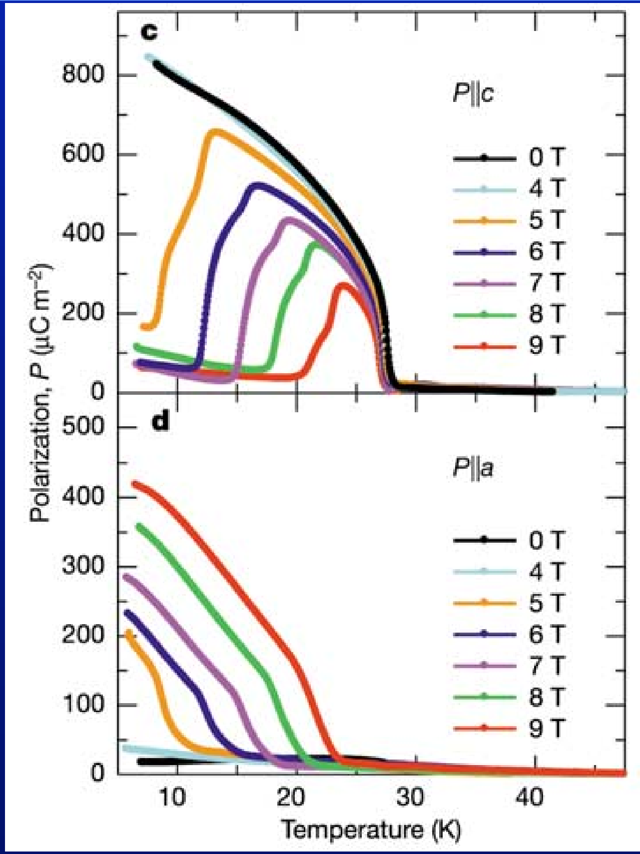
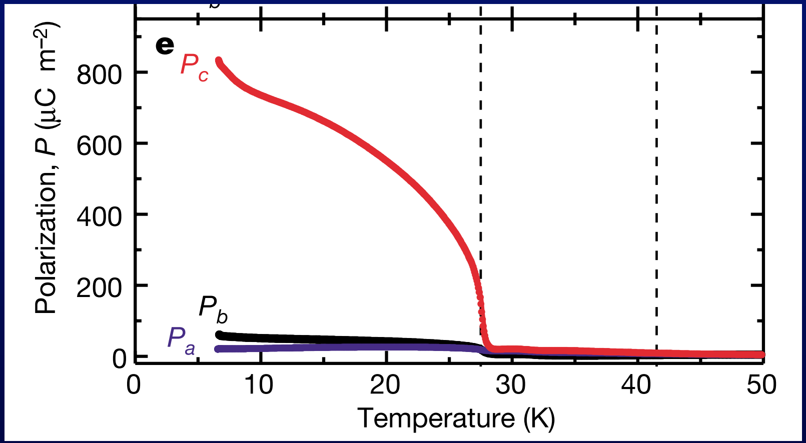
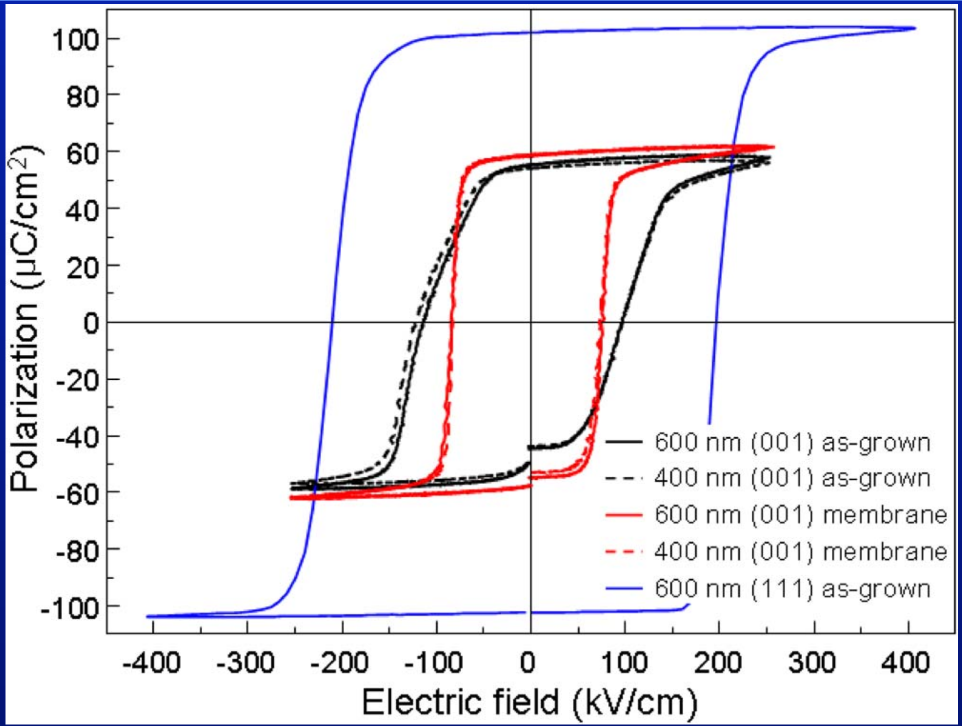
Ferromagnetic Ferroelectrics



Mind the Units!



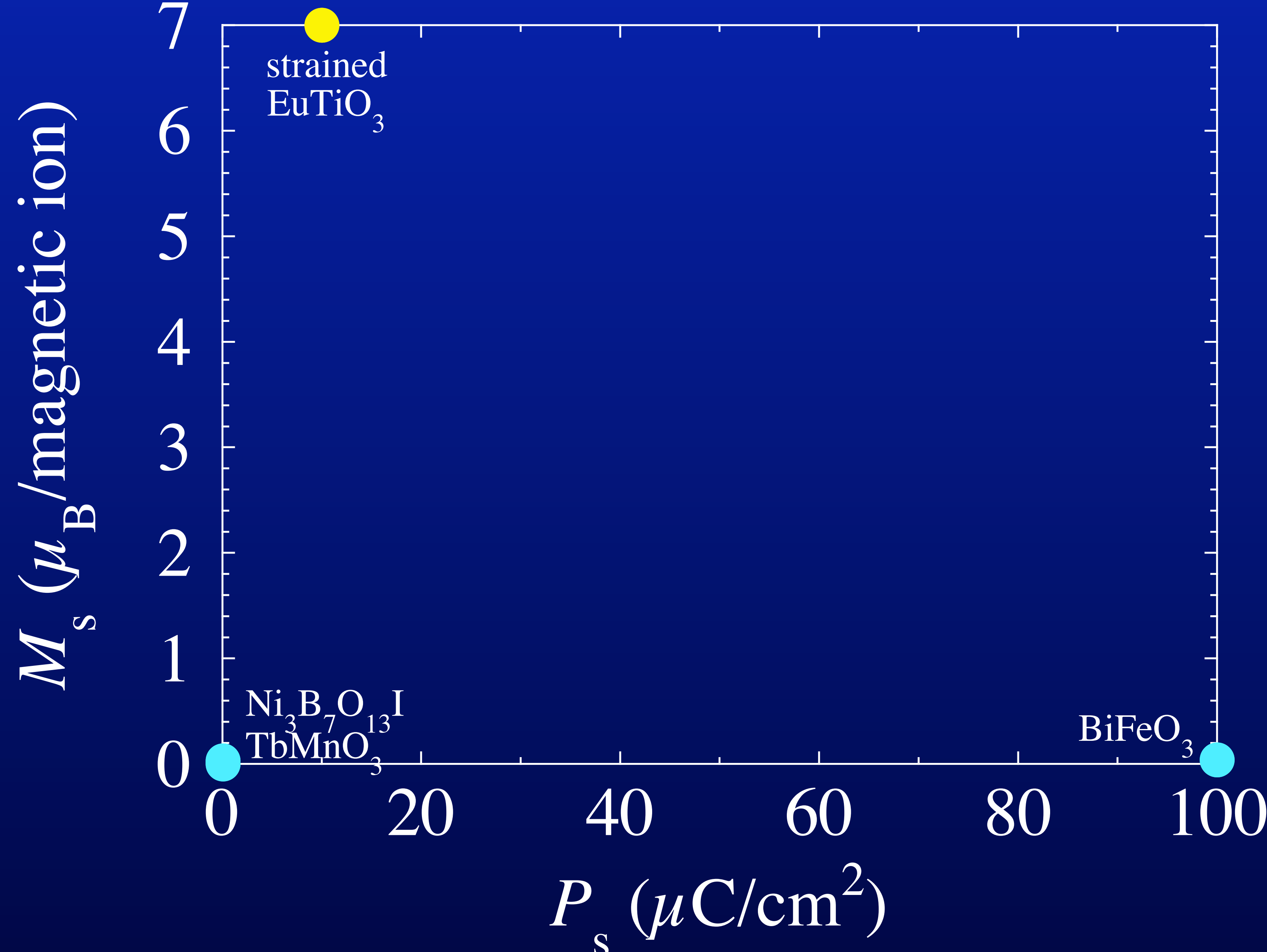




H.W. Jang, S.H. Baek, D. Ortiz, C.M. Folkman, C.B. Eom, Y.H. Chu, P. Shafer, R. Ramesh, V. Vaithyanathan, and D.G. Schlom, "Epitaxial (001) $BiFeO_3$ Membranes with Substantially Reduced Fatigue and Leakage," *Applied Physics Letters* **92** (2008) 062910

T. Kimura, T. Goto, H. Shintani, K. Ishizaka1, T. Arima, and Y. Tokura, "Magnetic Control of Ferroelectric Polarization," *Nature* **426** (2003) 55-58.

Ferromagnetic Ferroelectrics



Spin-Phonon Coupling—Route to Phase Control

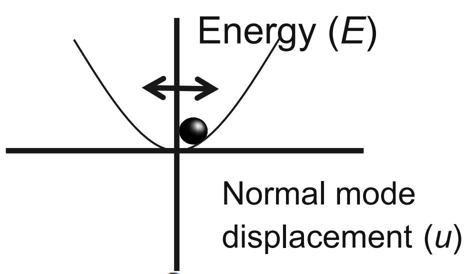
$$\Rightarrow \quad \omega^2 \propto \omega_0^2 - \partial^2 J/\partial u^2 \langle S_i \cdot S_j \rangle$$

renormalized phonon | bare phonon | magnetic contribution

With control parameter take $\omega_0 = 0 \quad \Rightarrow \quad \omega^2 \propto -\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$

AFM $\rightarrow \langle S_i \cdot S_j \rangle = -1$

Stable phonon

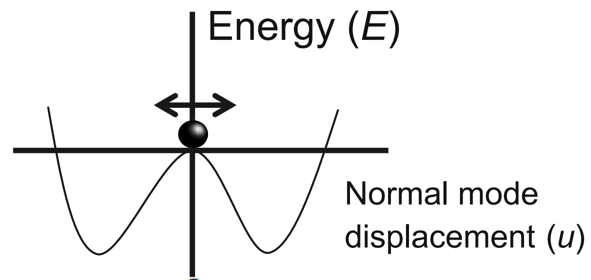


$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} > 0$$

→ Antiferromagnetic, Paraelectric

FM $\rightarrow \langle S_i \cdot S_j \rangle = +1$

Unstable phonon



$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} < 0$$

→ Ferromagnetic, Ferroelectric

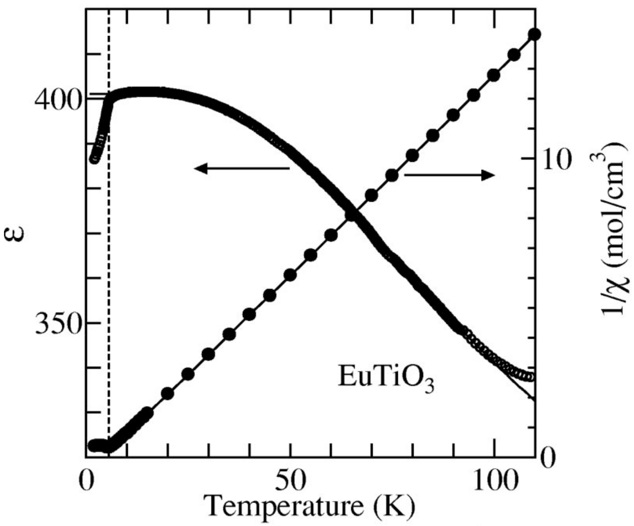
Leads to a FM-FE state competing with the AFM-PE ground state

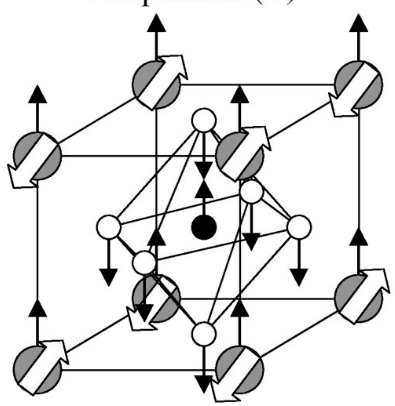
Bulk $EuTiO_3$ (unstrained)

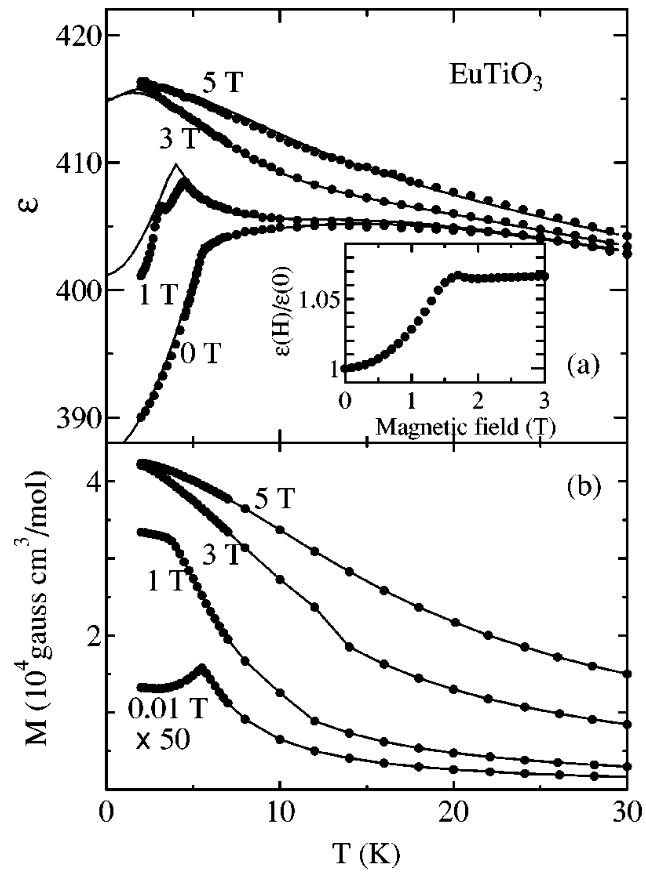
PHYSICAL REVIEW B, VOLUME 64, 054415

Coupling between magnetism and dielectric properties in quantum paraelectric $EuTiO_3$

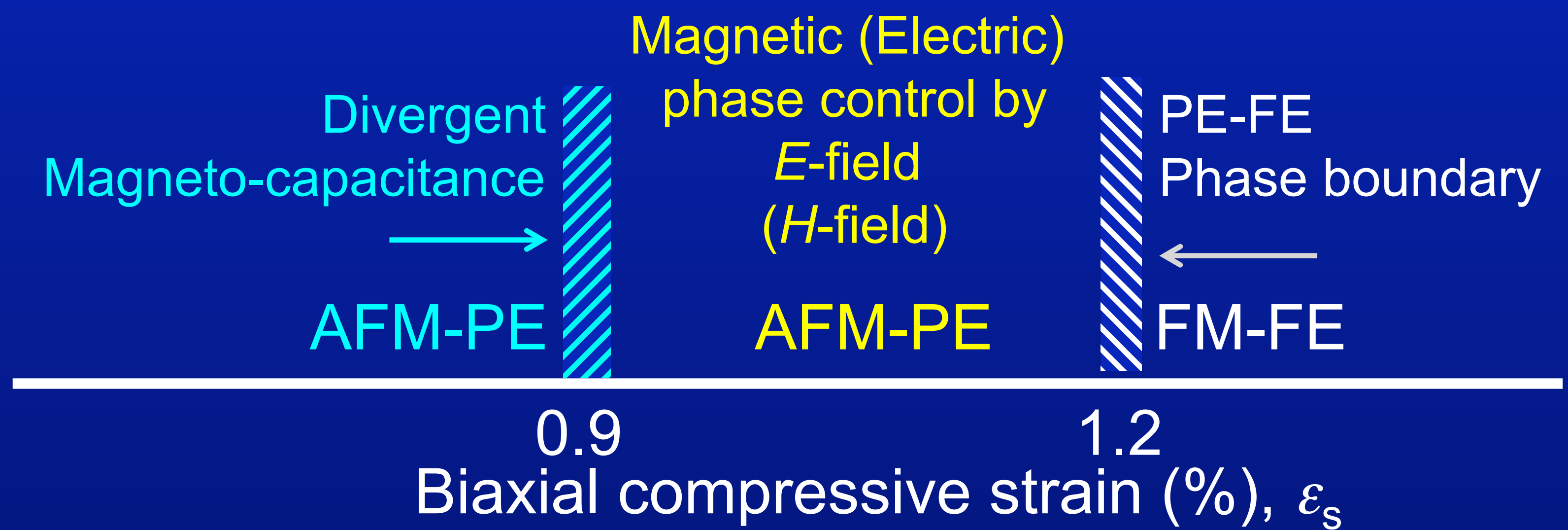
T. Katsufuji and H. Takagi
Department of Advanced Materials Science, University of Tokyo, Tokyo 113-8656, Japan
and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Corporation, Japan

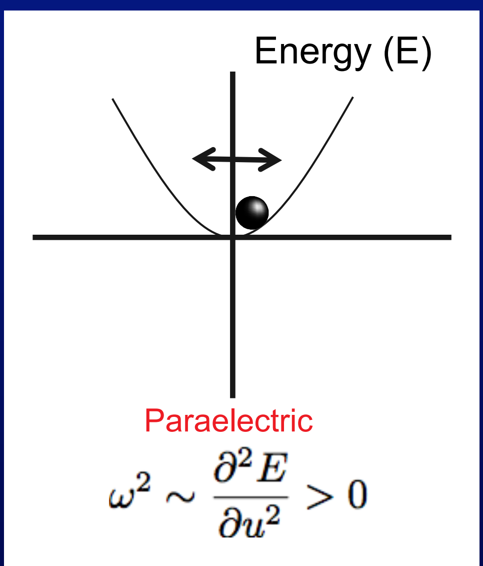


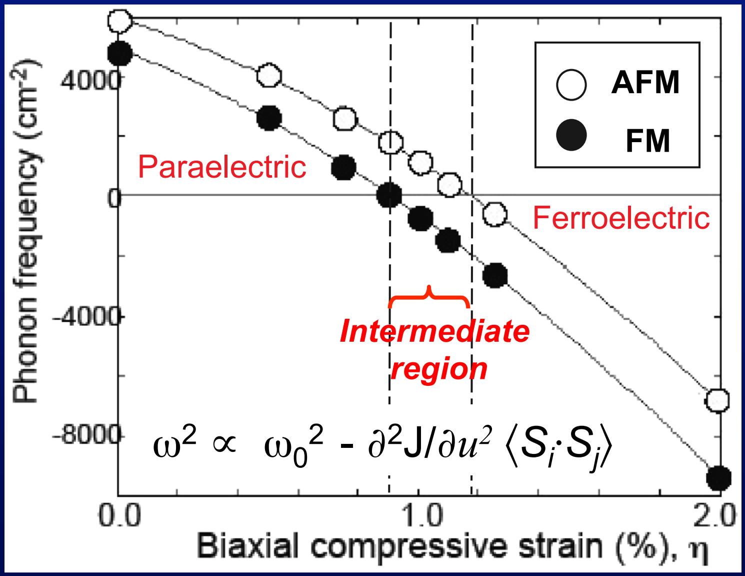


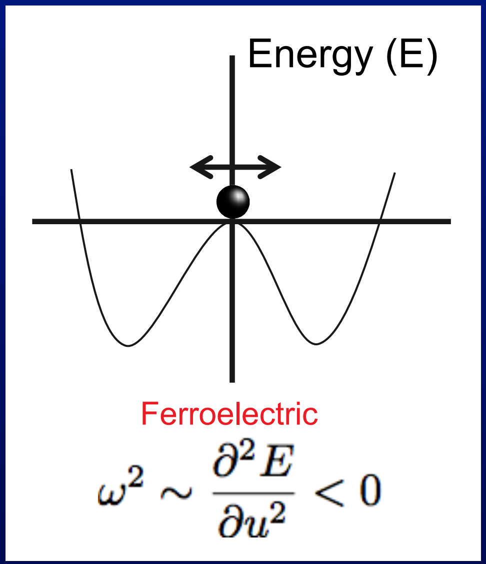


Strained $EuTiO_3$—a Ferroelectric Ferromagnet?



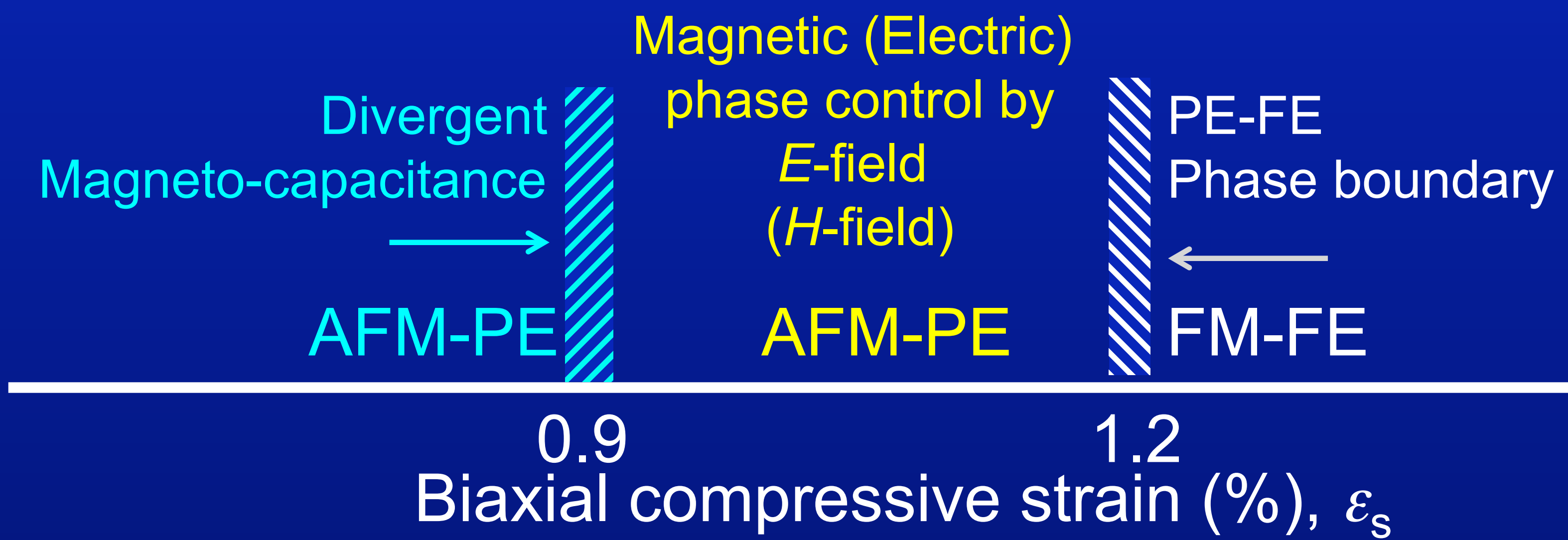


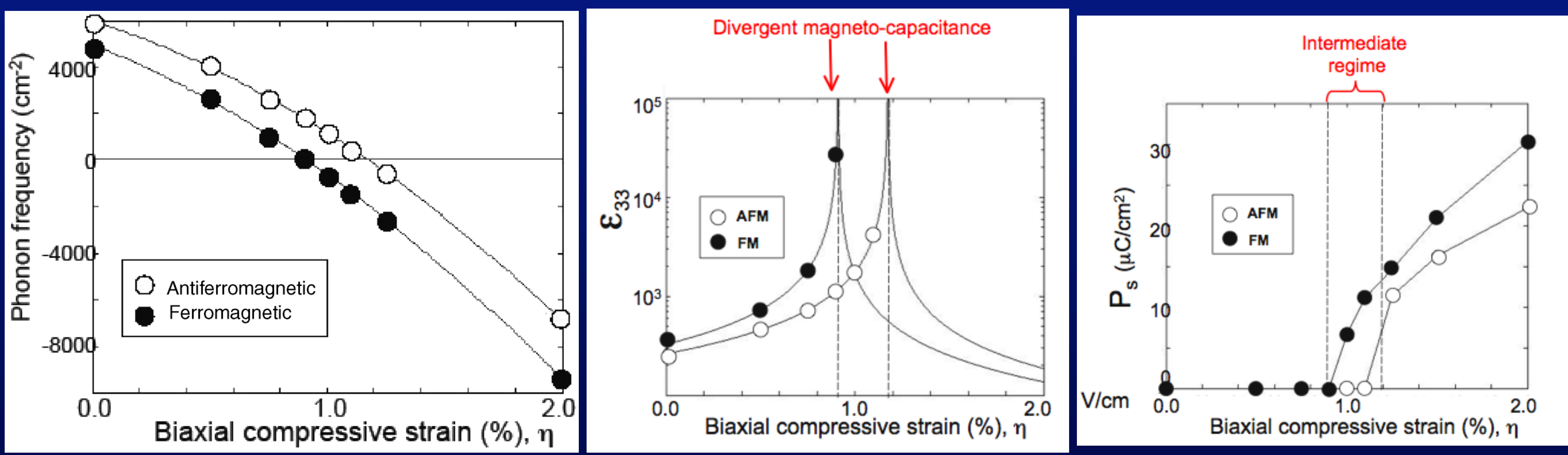




C.J. Fennie and K.M. Rabe, "Magnetic and Electric Phase Control in Epitaxial $EuTiO_3$ from First Principles," *Physical Review Letters* **97** (2006) 267602.

Strained $EuTiO_3$—a Ferroelectric Ferromagnet?





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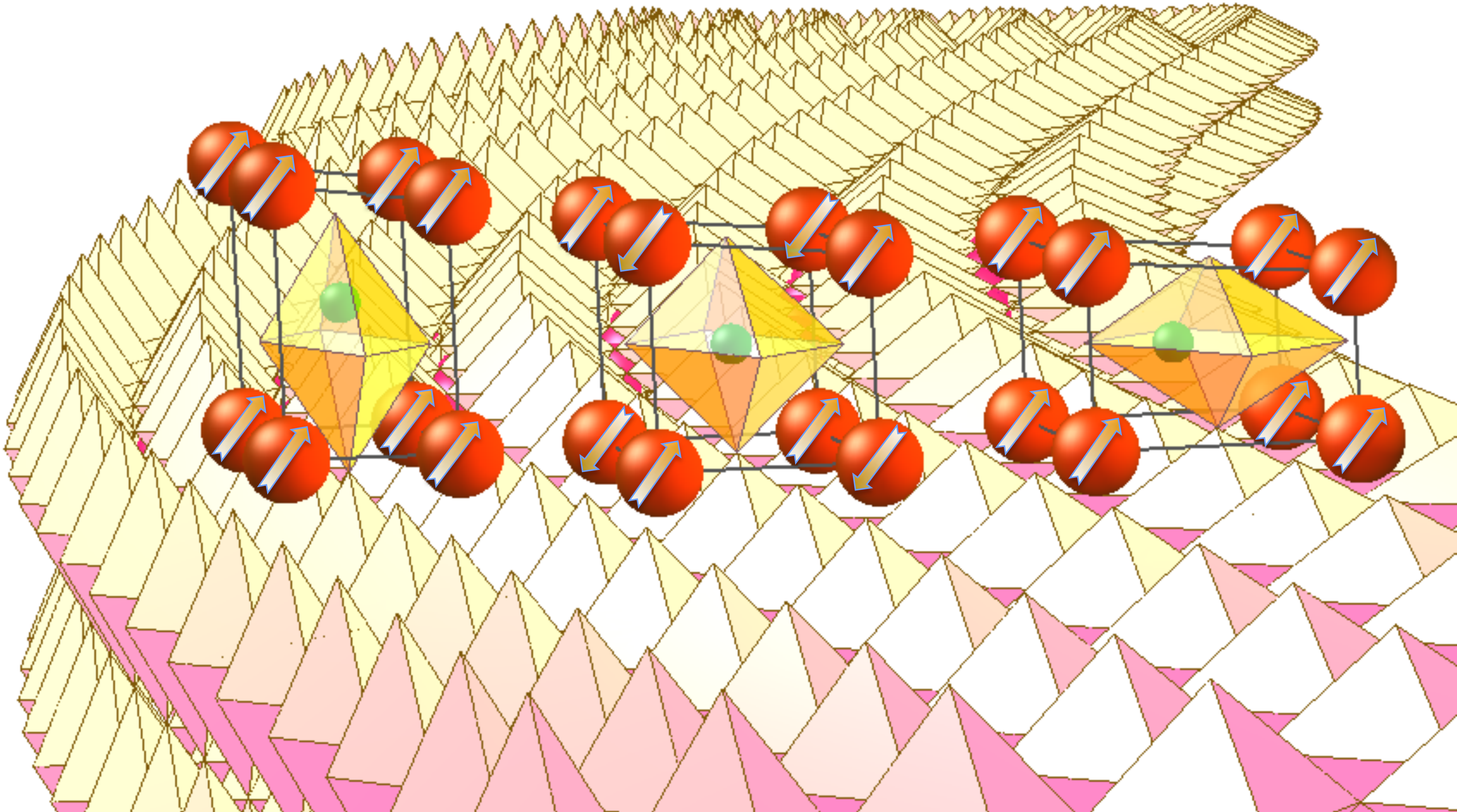
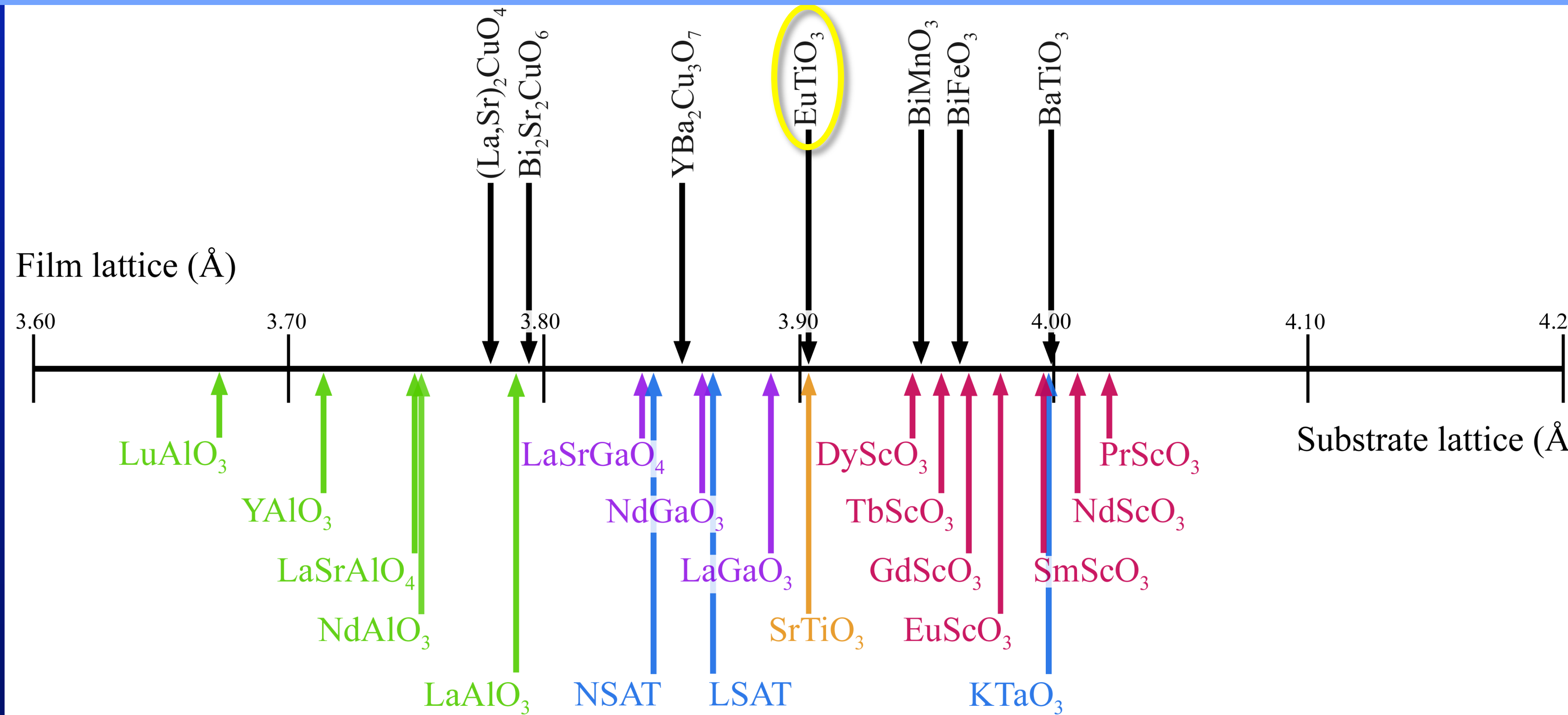
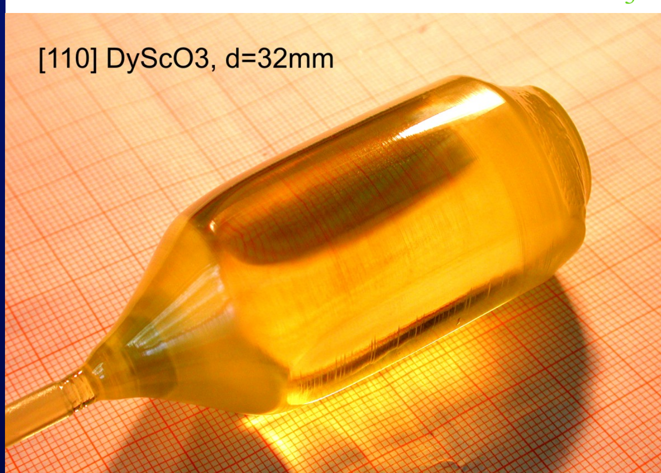
Effect of *Strain* on $EuTiO_3$



Commercial Perovskite Substrates





Reinhard Uecker's Group
Leibniz Institute
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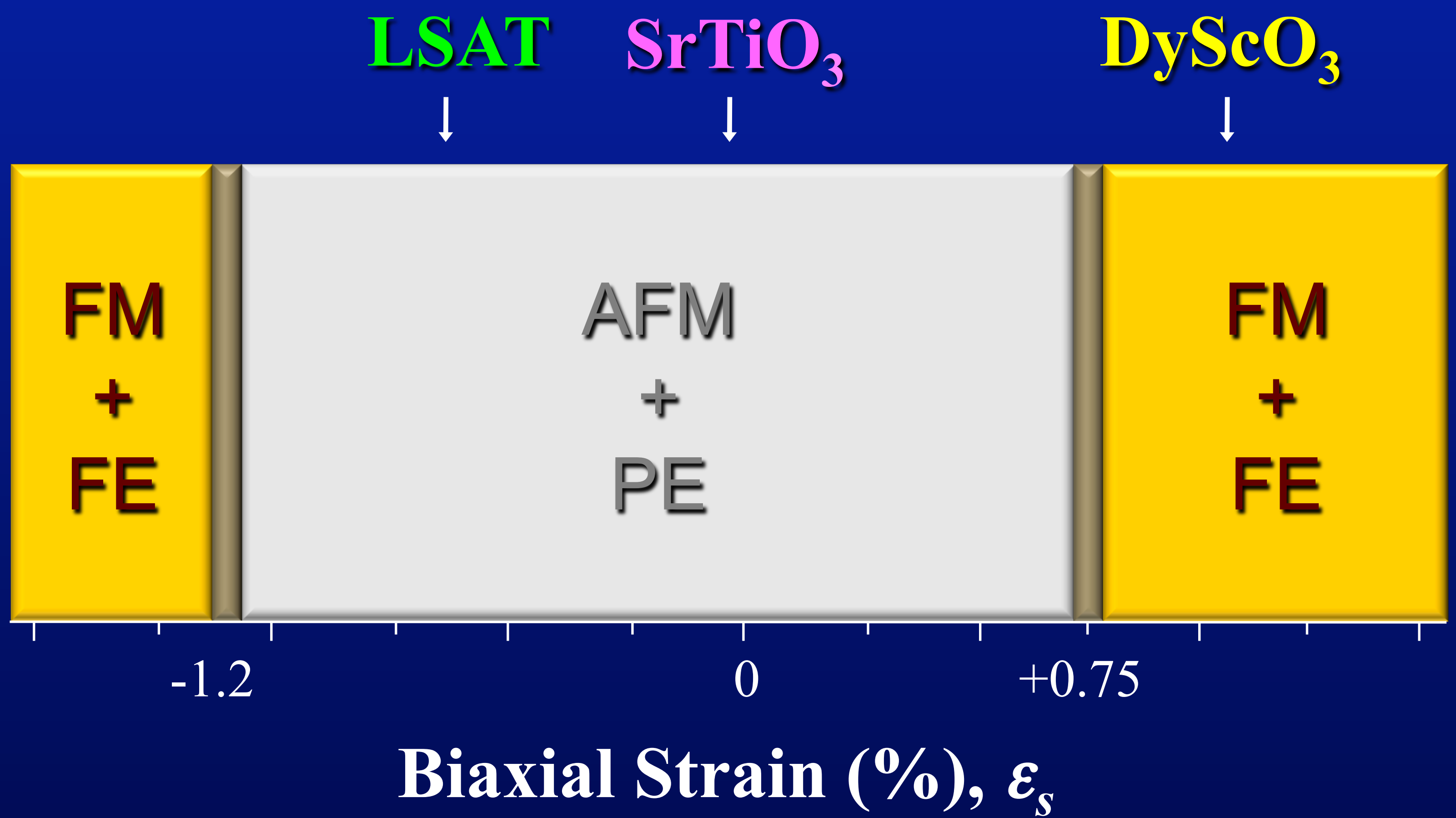
First Principles Epitaxial Phase Diagram of Strained $EuTiO_3$ (at $T = 0$ K)



EuTiO$_3$ / SrTiO$_3$ by PLD shows Expanded Lattice Constant

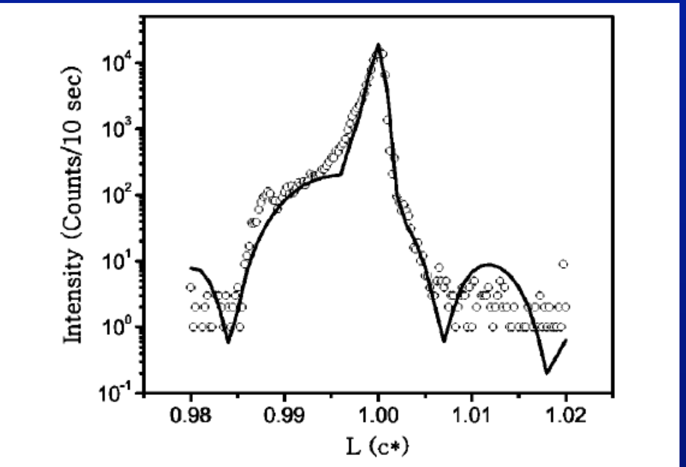


FIG. 4. Rod scan through the (001) Bragg peak of SrTiO$_3$ and finite-thickness broadened thin-film "Bragg" peak. Solid line is a simple model calculation consisting of a resolution-limited STO Bragg peak and a simple finite-size line shape for the ETO film.

H.-H. Wang, A. Fleet, J.D. Brock, D. Dale, and Y. Suzuki, *J. Appl. Phys.* **96**, 5324 (2004).

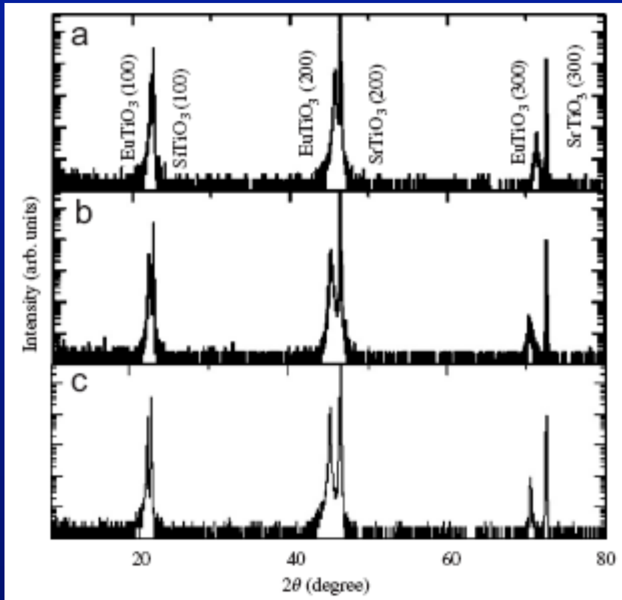


Fig. 2. Out-of-plane XRD patterns for thin films grown under $P_{O2} = 1.0 \times 10^{-4}$ Pa (a), 1.0×10^{-5} Pa (b), and 1.0×10^{-6} Pa (c).

K. Kugimiya, K. Fujita, K. Tanaka, and K. Hirao, *J. Magn. Magn. Mater.* **310**, 2268 (2007).

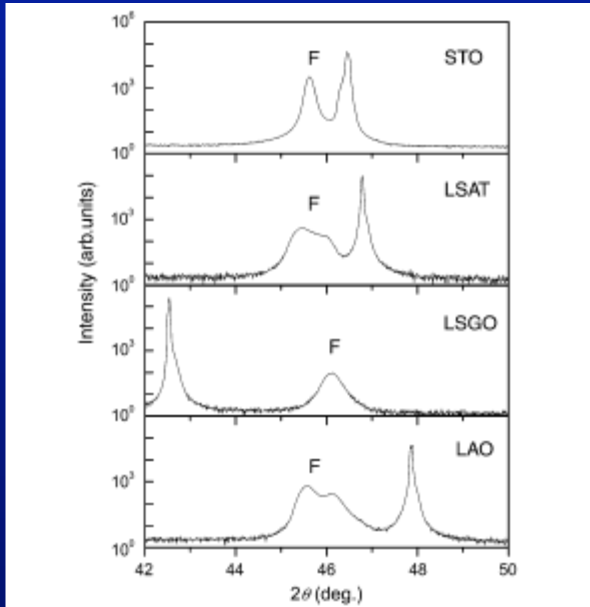


Fig. 3 X-ray diffraction pattern of EuTiO$_3$ thin films grown on SrTiO$_3$ (001), LSAT (001), LaSrGaO$_4$ (001), and LaAlO$_3$ (001) single-crystal substrates

S. C. Chae, Y. J. Chang, D.-W. Kim, B. W. Lee, I. Choi, and C. U. Jung, *J. Electroceram.* **22**, 216 (2009).

But EuTiO$_3$ and SrTiO$_3$ are perfectly lattice-matched, so no expanded out-of-plane lattice constant expected!

EuTiO$_3$ / SrTiO$_3$ by PLD shows Ferromagnetism

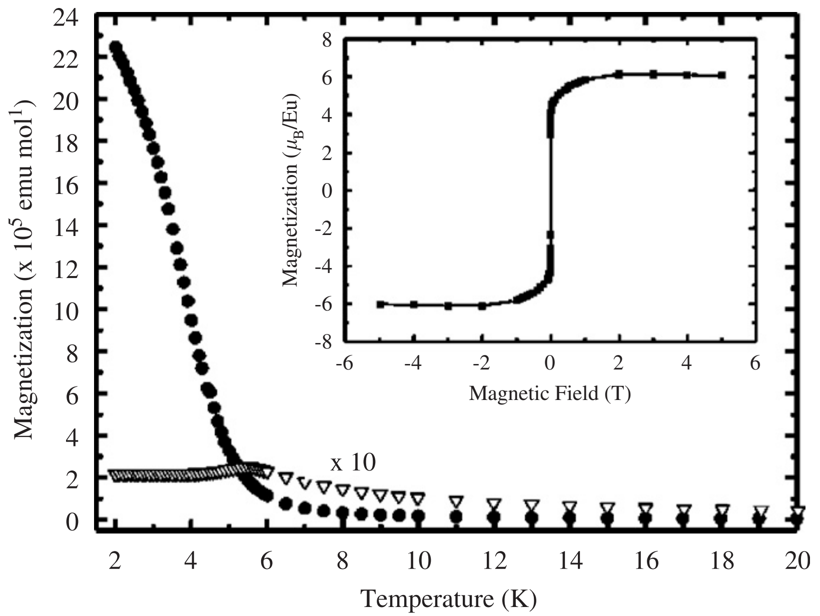
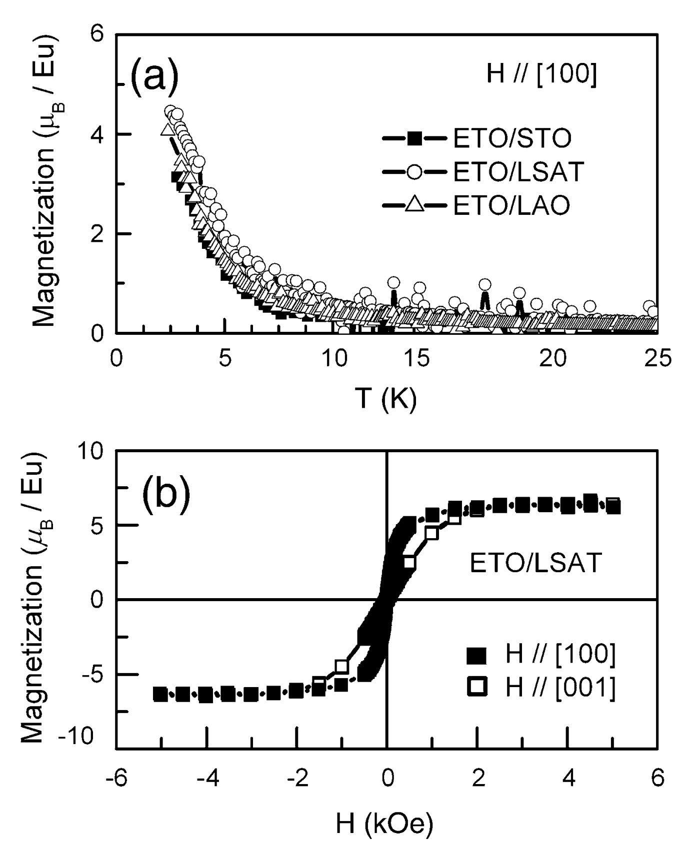


Fig. 3. Temperature dependence of magnetization for the film grown under $P_{O2} = 1.0 \times 10^{-6}$ Pa (closed circles). For comparison, data for bulk EuTiO$_3$ specimen prepared by solid-state reaction, which are magnified by a factor of 10, are also shown (open triangles). The inset shows the dependence of magnetization at 2 K on external magnetic field.



K. Kugimiya, K. Fujita, K. Tanaka, and K. Hirao, *J. Magn. Magn. Mater.* **310**, 2268 (2007).

S. C. Chae, Y. J. Chang, D.-W. Kim, B. W. Lee, I. Choi, and C. U. Jung, *J. Electroceram.* **22**, 216 (2009).

But EuTiO$_3$ and SrTiO$_3$ are perfectly lattice-matched, so no expanded lattice constants or ferromagnetism are expected!

SrTiO$_3$ / SrTiO$_3$ by PLD shows Expanded Lattice and Ferroelectricity

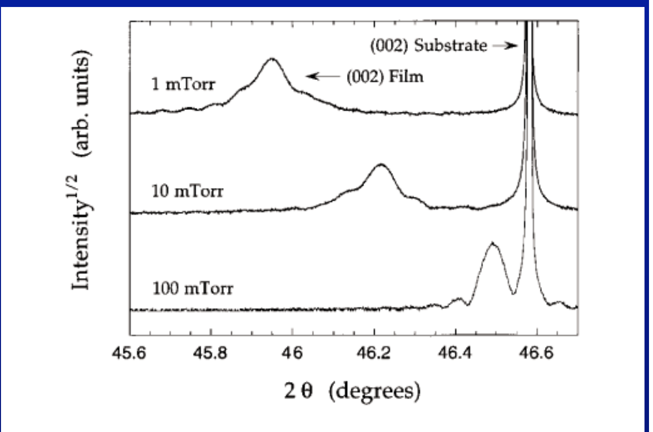
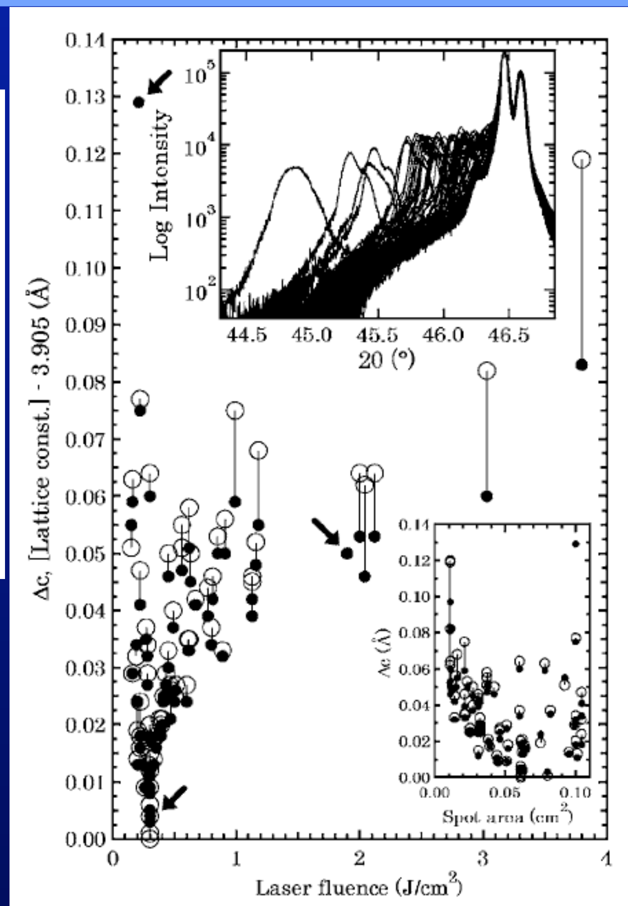


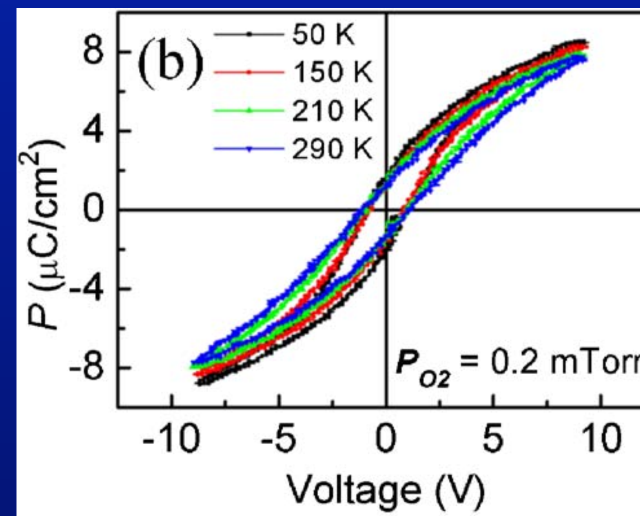
FIG. 3. X-ray ω-2θ scans for ~1400 Å thick homoepitaxial SrTiO$_3$ layers grown with background oxygen pressures of 100, 10, and 1 mTorr.

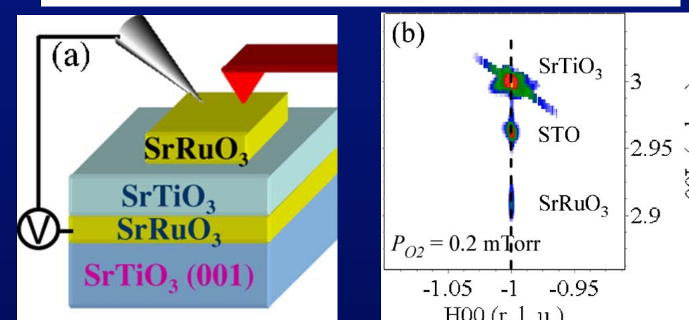
E.J. Tarsa, E.A. Hachfeld, F.T. Quinlan, J.S. Speck, and M. Eddy, *Appl. Phys. Lett.* **68**, 490 (1996).



T. Ohnishi, M. Lippmaa, T. Yamamoto, S. Meguro, and H. Koinuma, *Appl. Phys. Lett.* **87**, 2419191 (2005).

Ferroelectric!

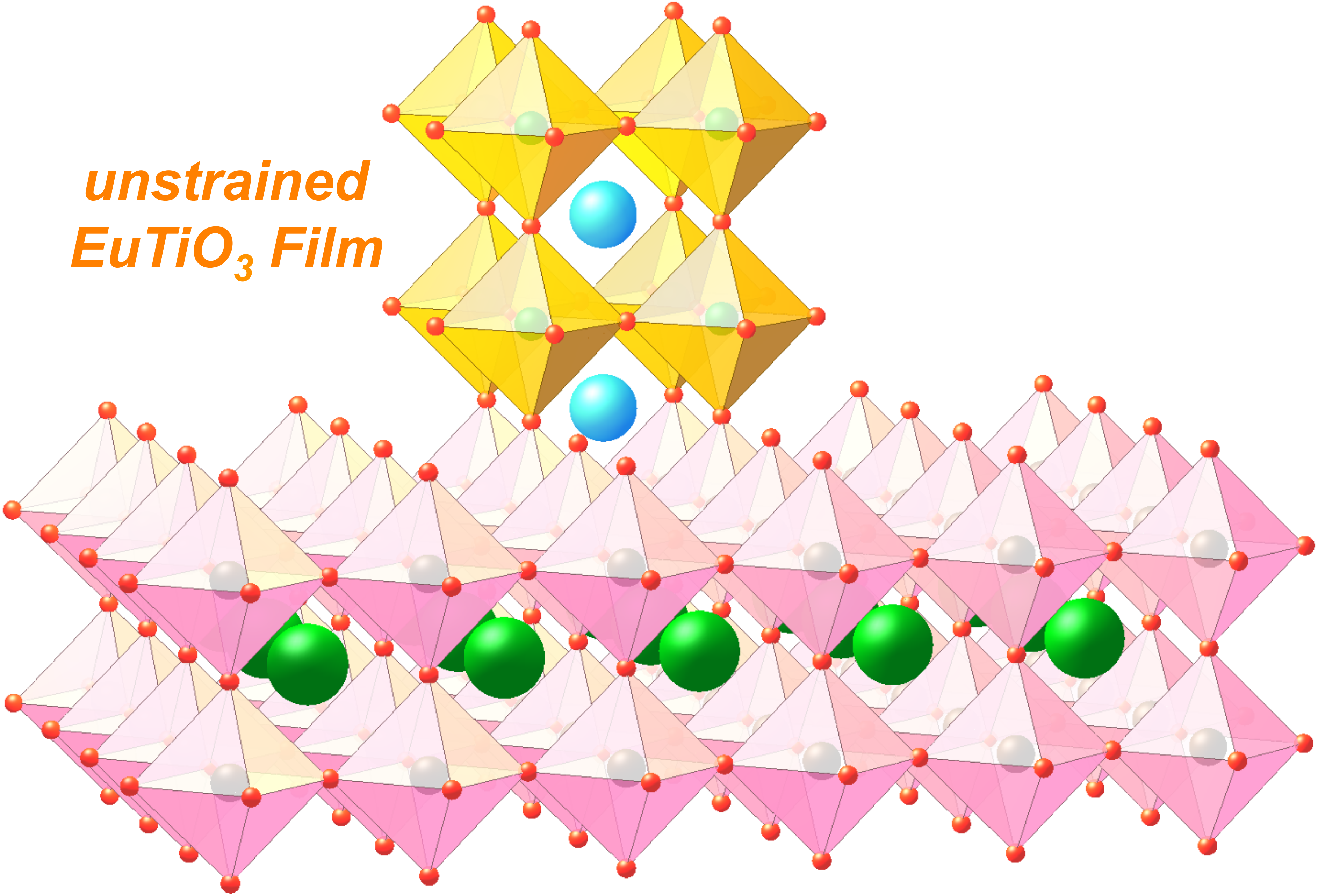




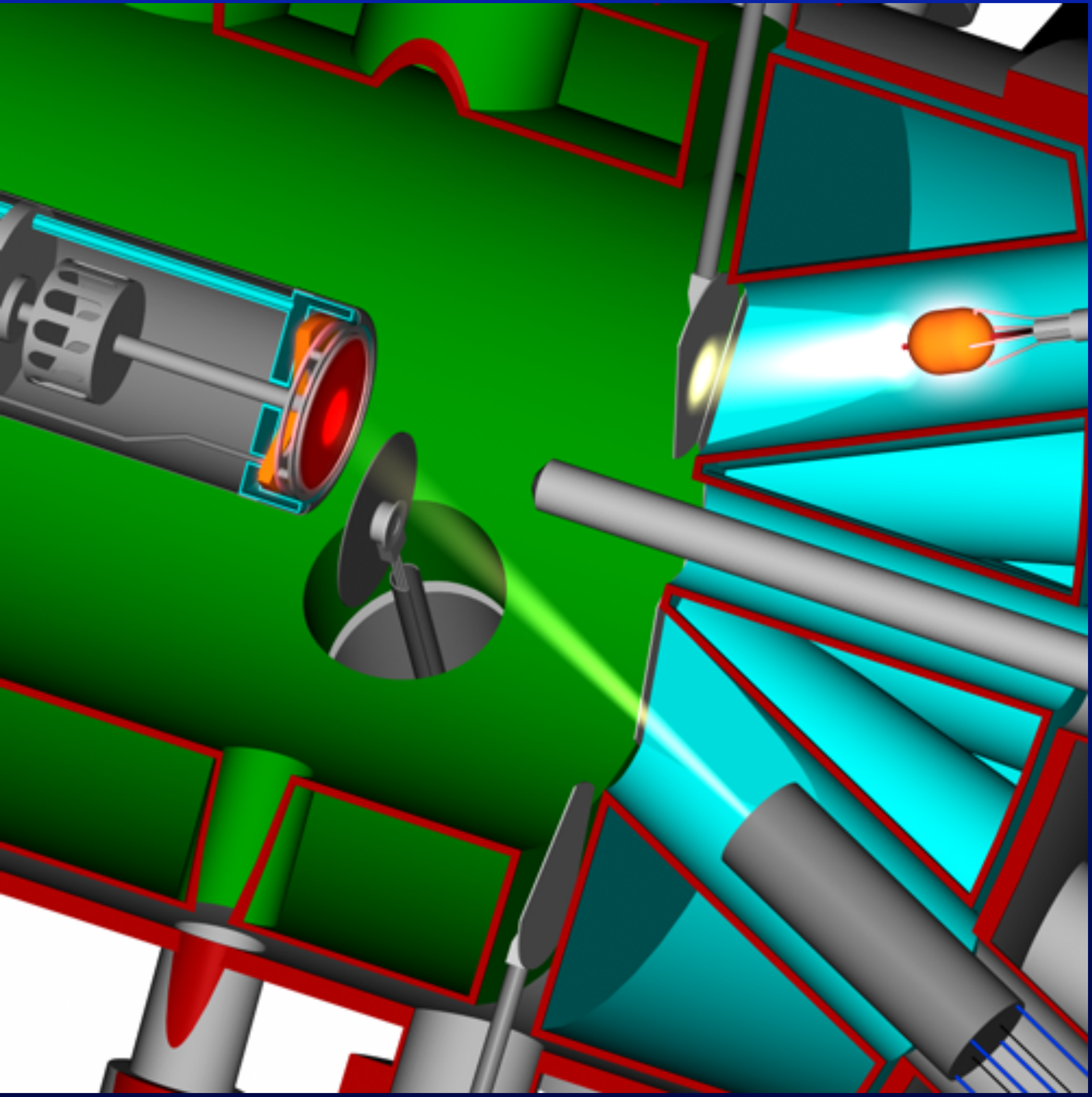
Y. S. Kim, D.J. Kim, T.H. Kim, T.W. Noh, J.S. Choi ,B.H. Park, and J.-G. Yoon, *Appl. Phys. Lett.* **91**, 042908 (2007).

But homoepitaxial SrTiO$_3$ is perfectly lattice-matched, so no extended lattice constants or ferroelectricity are expected!

Unstrained $EuTiO_3$ Control Samples

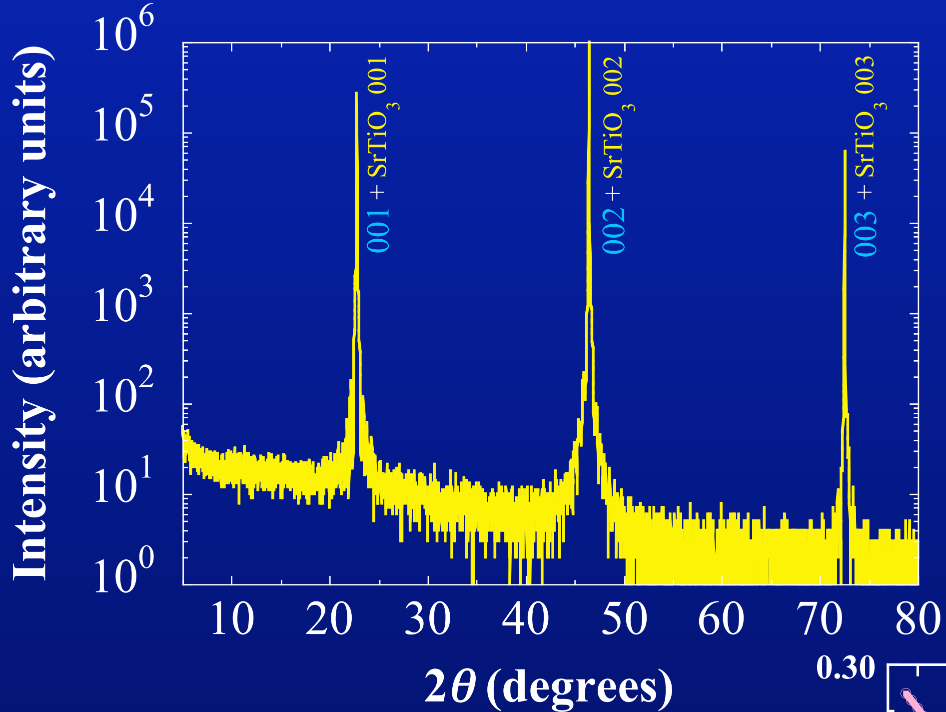


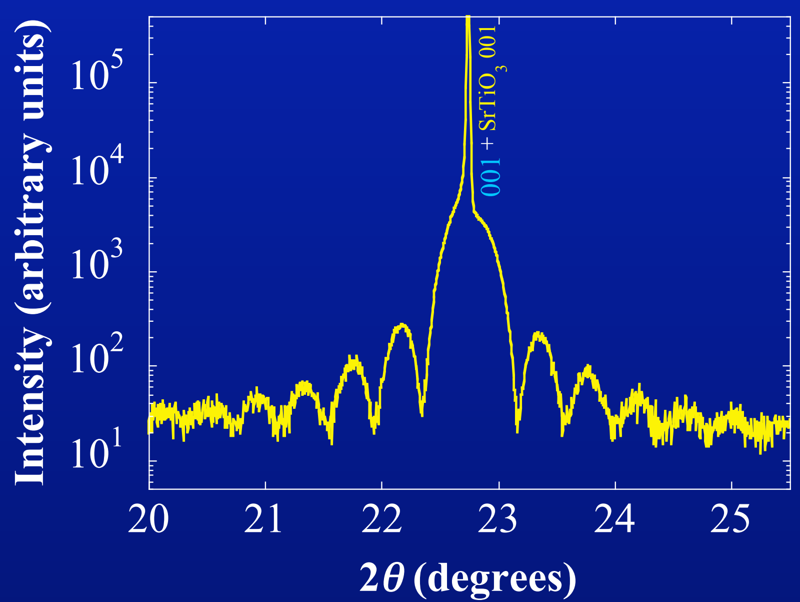
Reactive Molecular-Beam Epitaxy

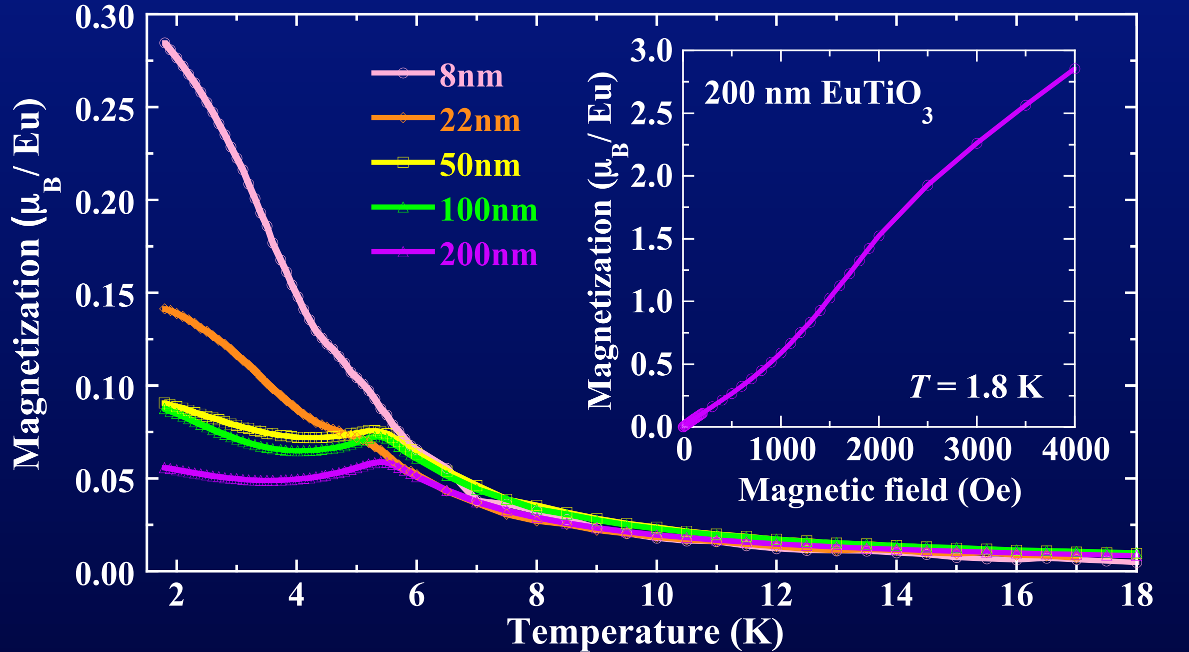


- Sources: Eu metal
  Ti metal
  O_2 gas
- $T_{sub} \approx 650$ °C
- $P_{O_2} \approx 3\times10^{-8}$ Torr
- $\upsilon_{growth} \approx 0.1$ Å/s

$EuTiO_3$ / (001) $SrTiO_3$ by MBE is ~Intrinsic

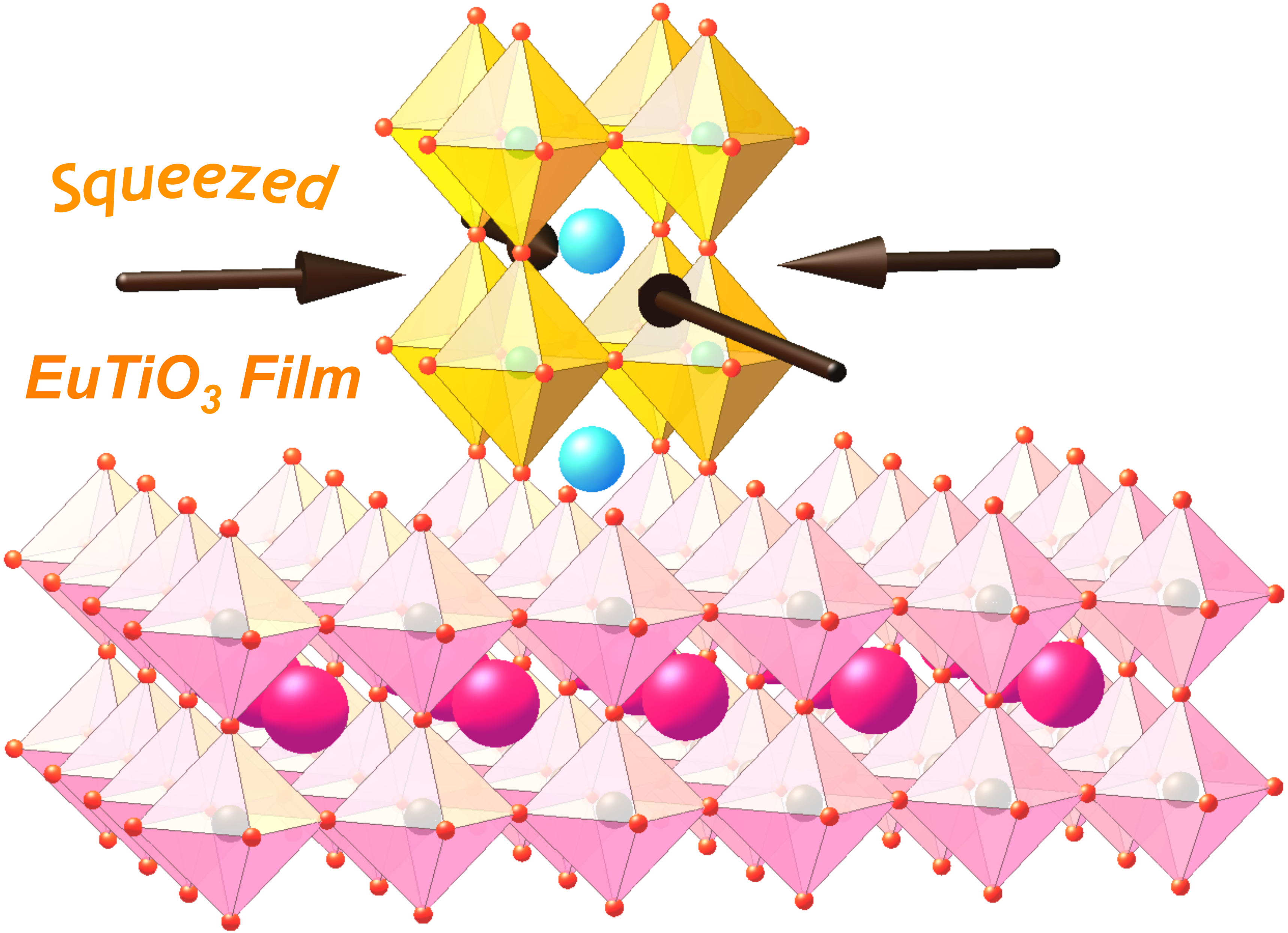




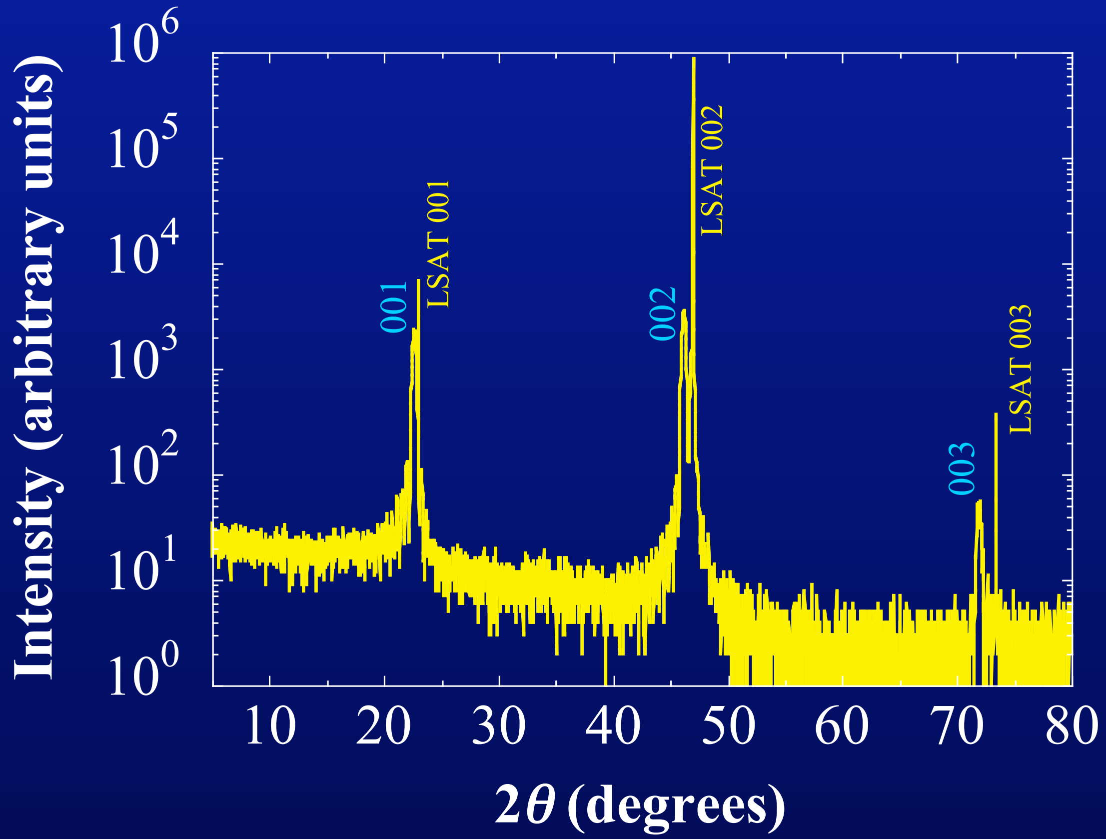


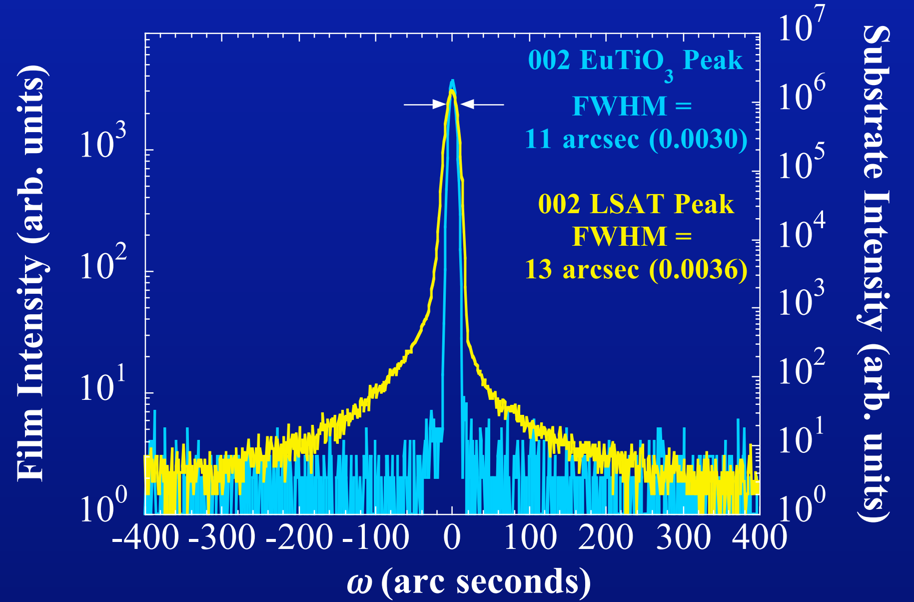
J.H. Lee, X. Ke, N.J. Podraza, L. Fitting Kourkoutis, T. Heeg, M. Roeckerath, J.W. Freeland, C.J. Fennie, J. Schubert, D.A. Muller, P. Schiffer, and D.G. Schlom, *Appl. Phys. Lett.* **94** (2009) 212509.

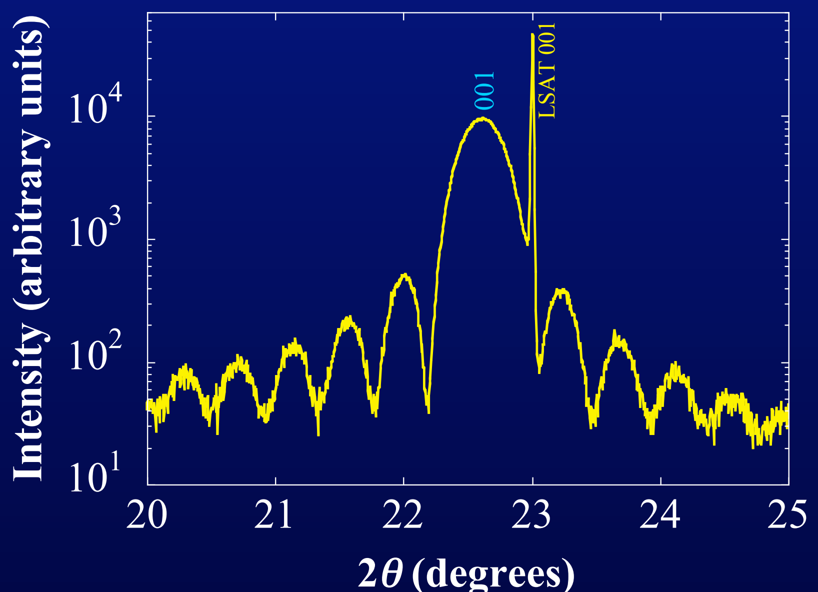
Biaxial Strain via Epitaxy



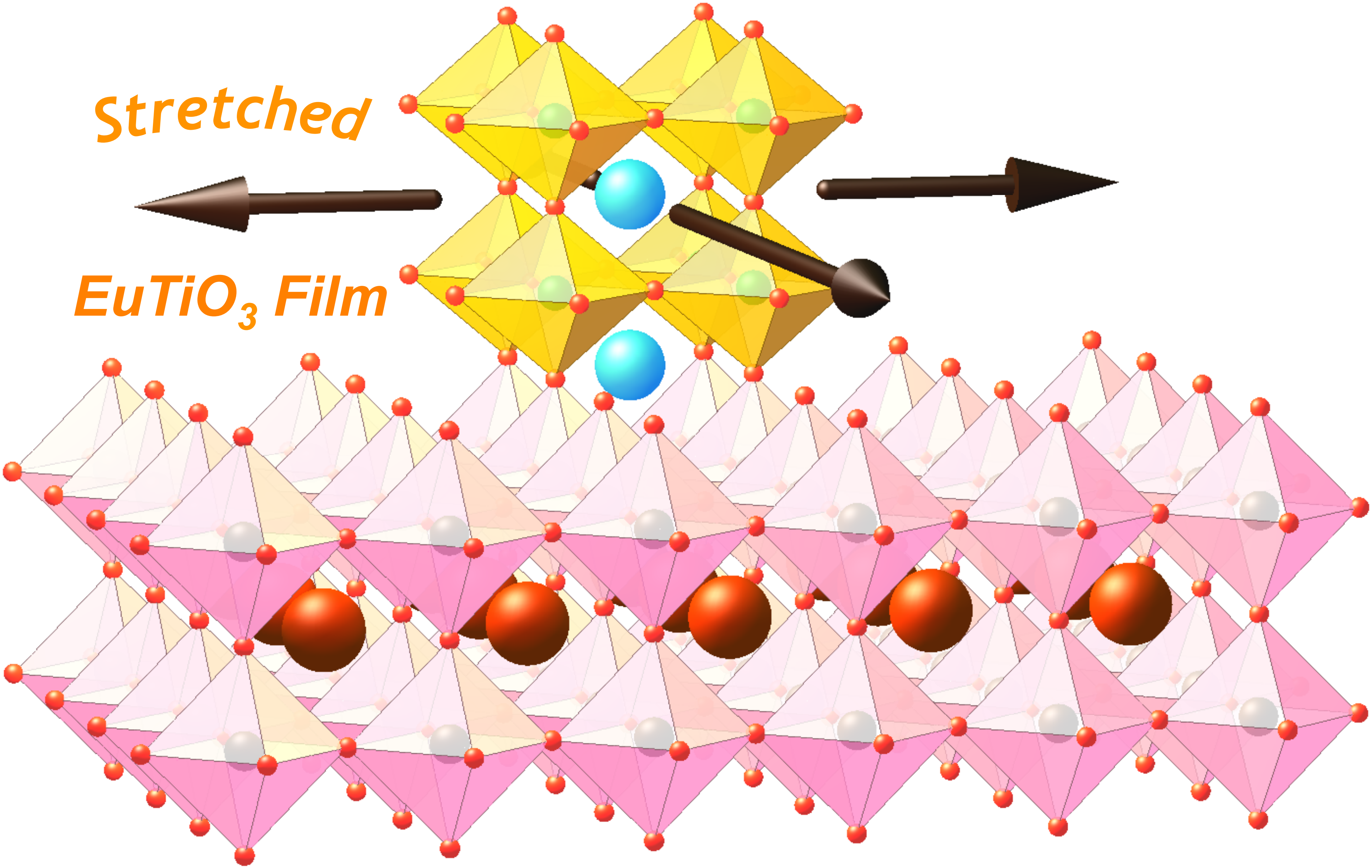
22 nm Thick (001) $EuTiO_3$ / (001) LSAT



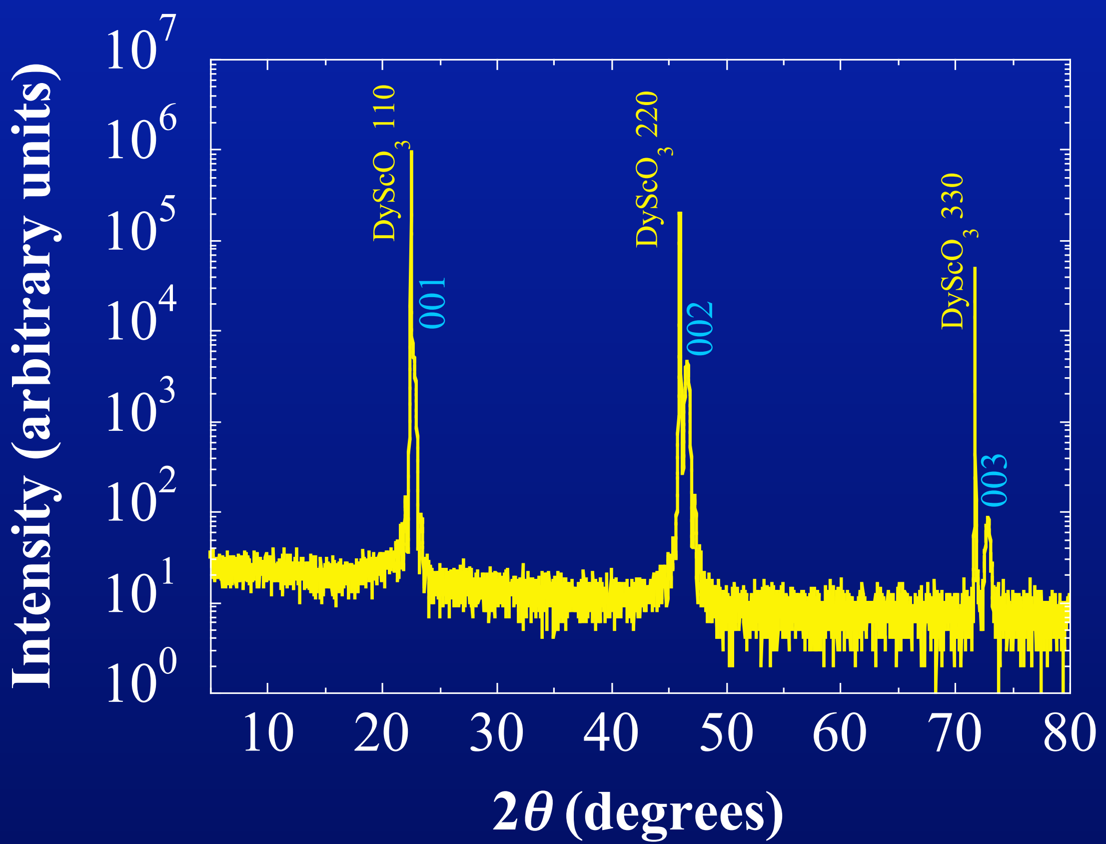


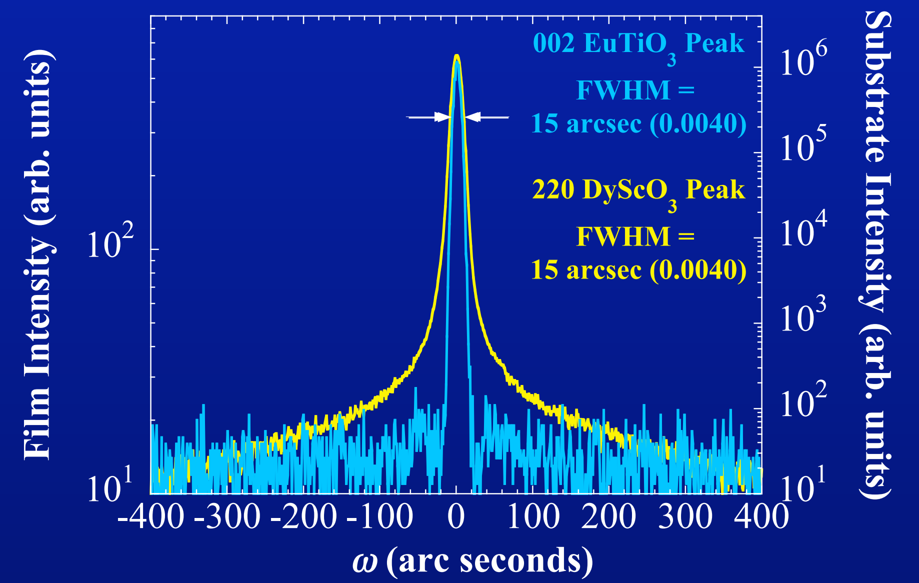


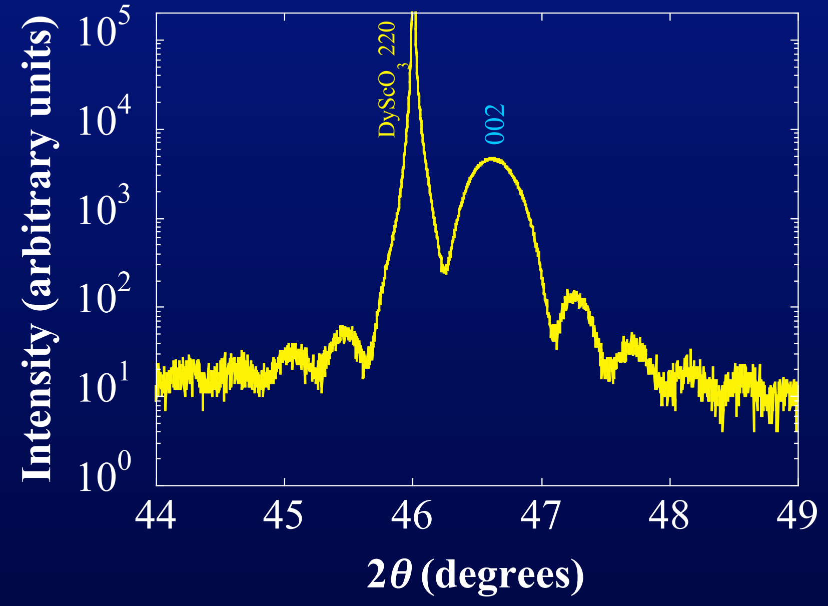
Biaxial Strain via Epitaxy



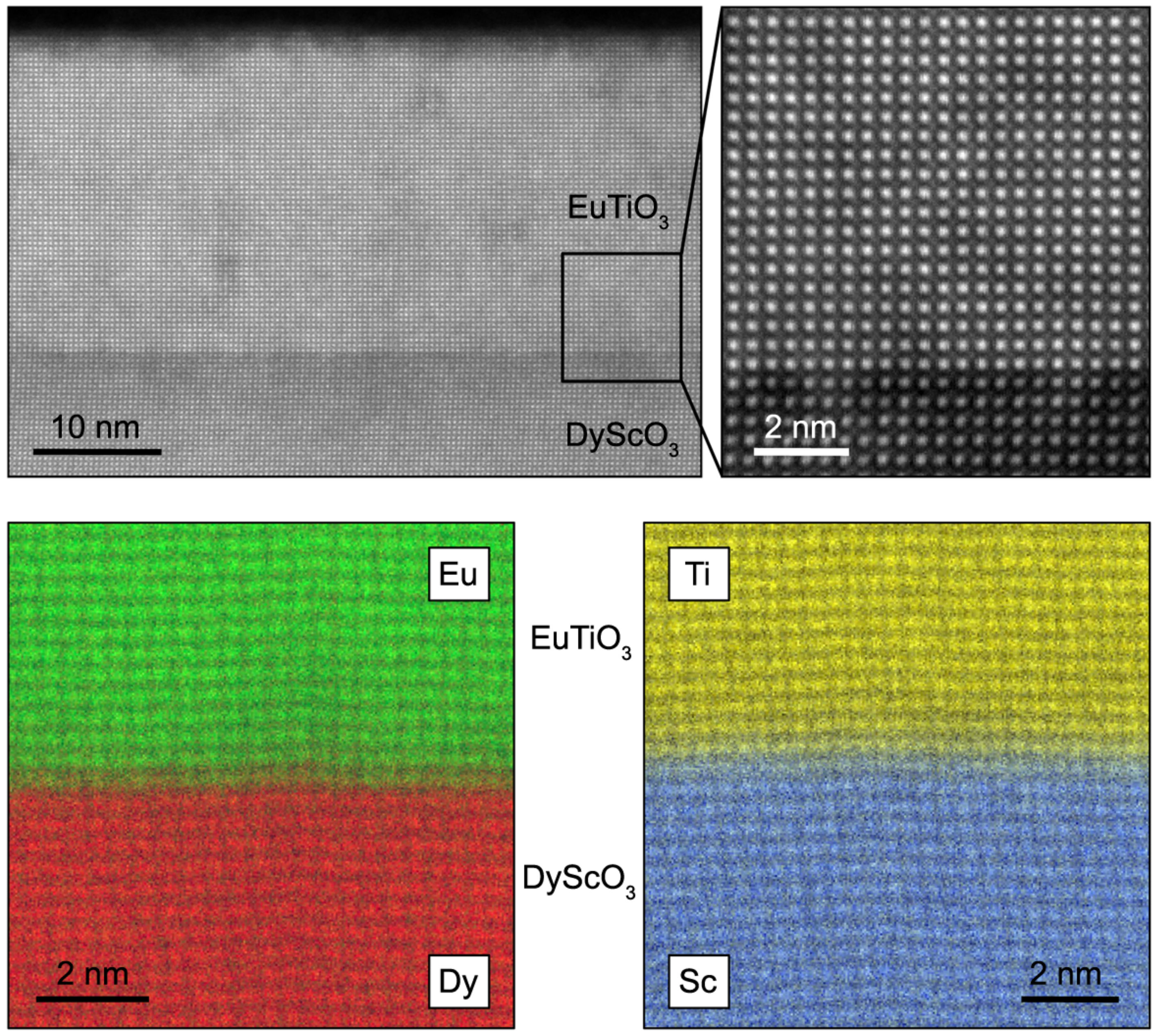
22 nm Thick (001) $EuTiO_3$ / (110) $DyScO_3$



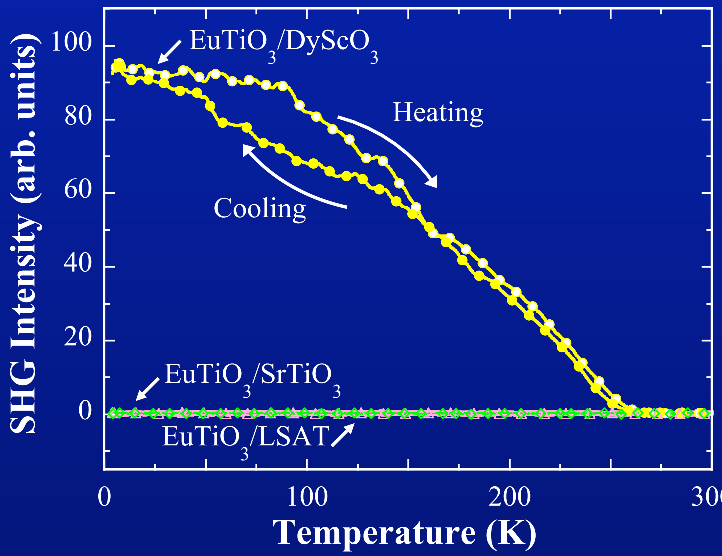


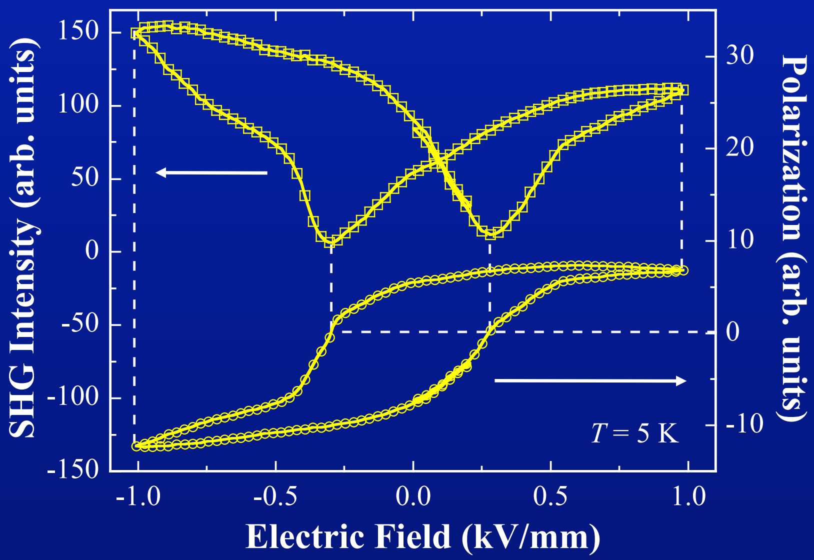


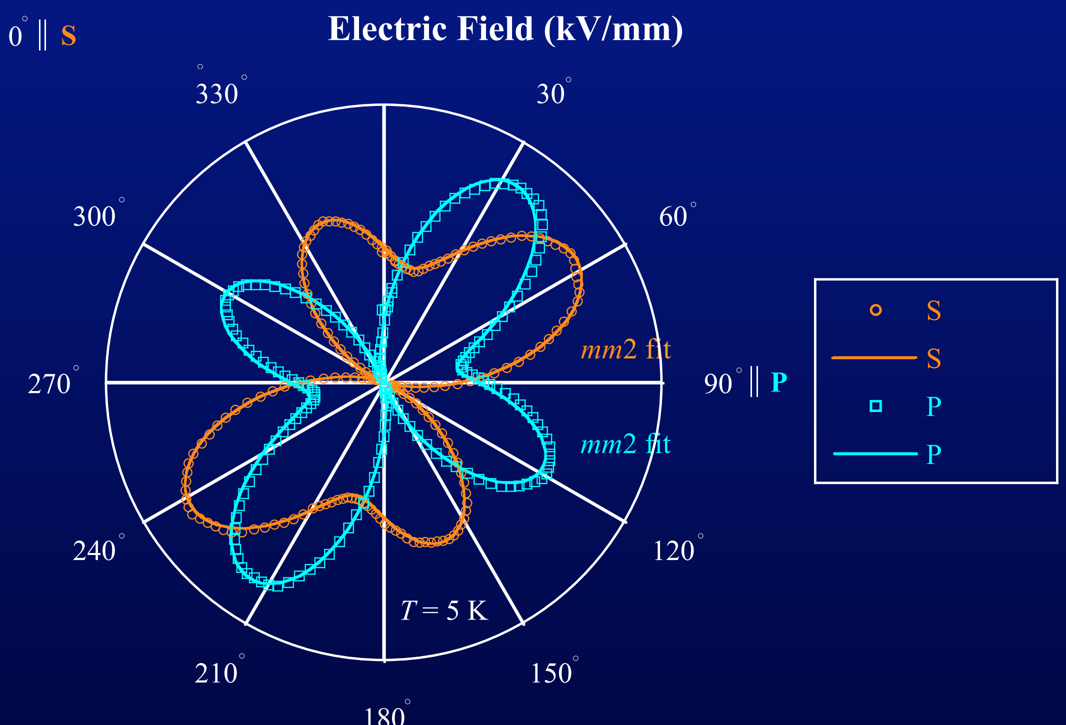
STEM of 22 nm $EuTiO_3$ / $DyScO_3$



SHG of Strained $EuTiO_3$ / (110) $DyScO_3$



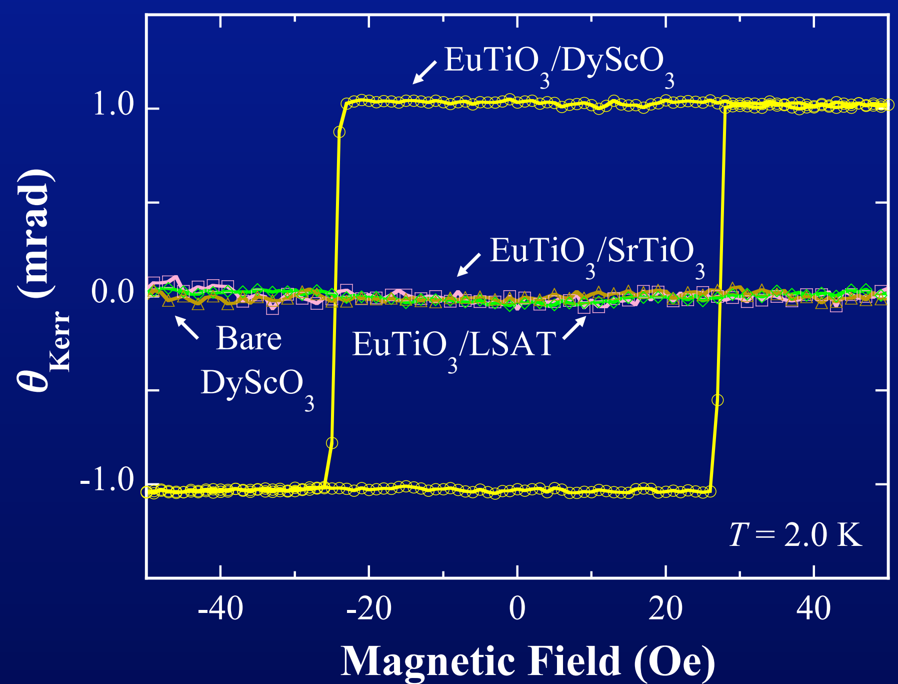




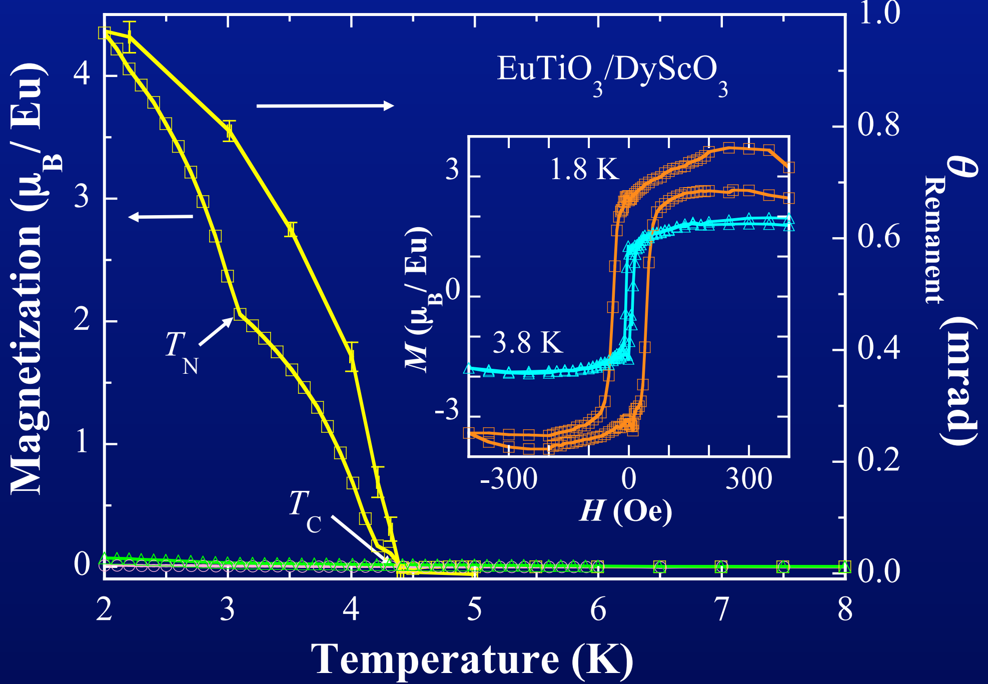
J.H. Lee, L. Fang, E. Vlahos, X. Ke, Y.W. Jung, L. Fitting Kourkoutis, J-W. Kim, P.J. Ryan, T. Heeg, M. Roeckerath, V. Goian, M. Bernhagen, R. Uecker, P.C. Hammel, K.M. Rabe, S. Kamba, J. Schubert, J.W. Freeland, D.A. Muller, C.J. Fennie, P. Schiffer, V. Gopalan, E. Johnston-Halperin, and D.G. Schlom, *Nature* **466** (2010) 954-958.

Magnetic Properties of Strained $EuTiO_3$ / (110) $DyScO_3$

MOKE

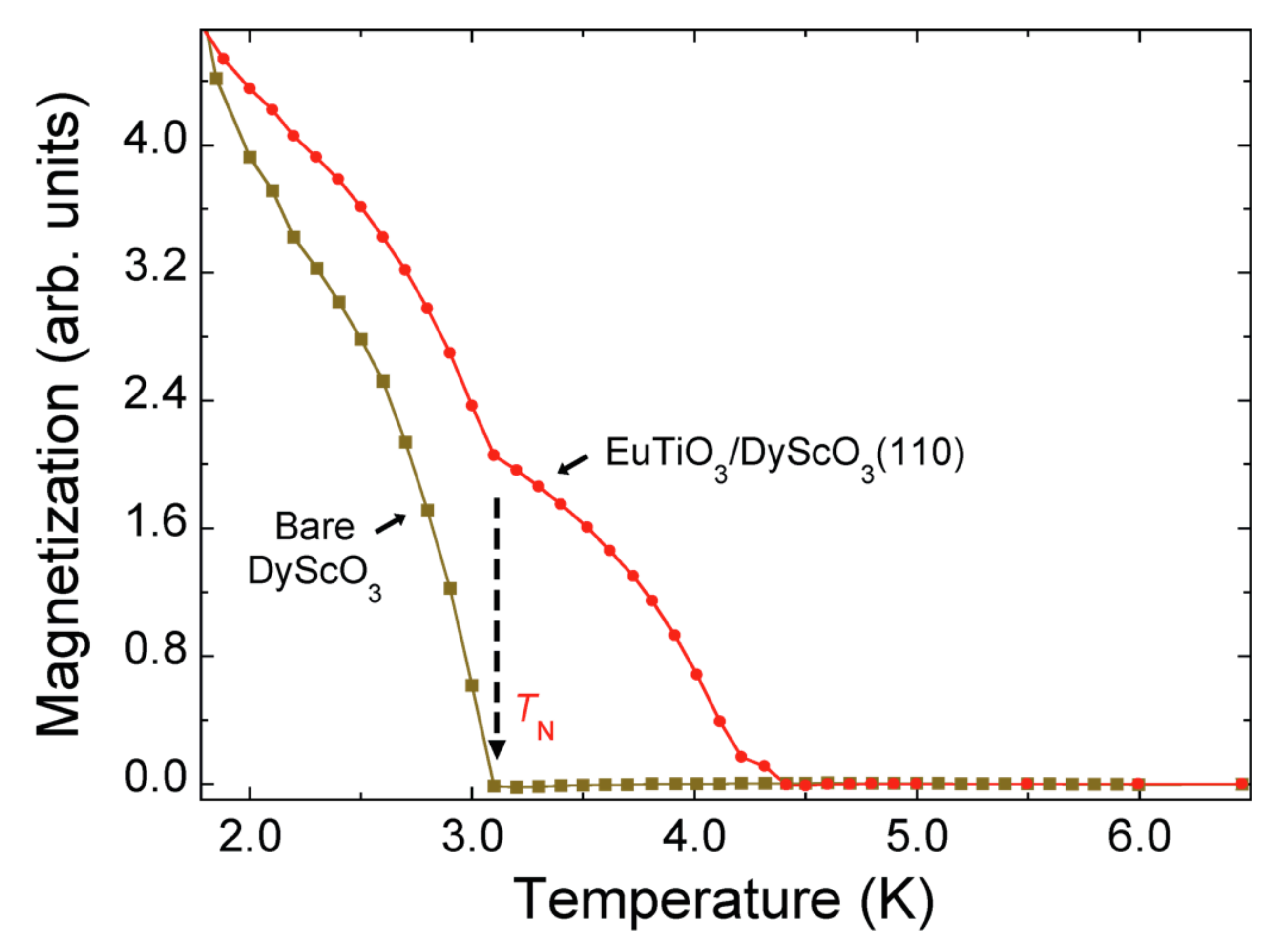


MOKE + SQUID



J.H. Lee, L. Fang, E. Vlahos, X. Ke, Y.W. Jung, L. Fitting Kourkoutis, J-W. Kim, P.J. Ryan, T. Heeg, M. Roeckerath, V. Goian, M. Bernhagen, R. Uecker, P.C. Hammel, K.M. Rabe, S. Kamba, J. Schubert, J.W. Freeland, D.A. Muller, C.J. Fennie, P. Schiffer, V. Gopalan, E. Johnston-Halperin, and D.G. Schlom, *Nature* **466** (2010) 954-958.

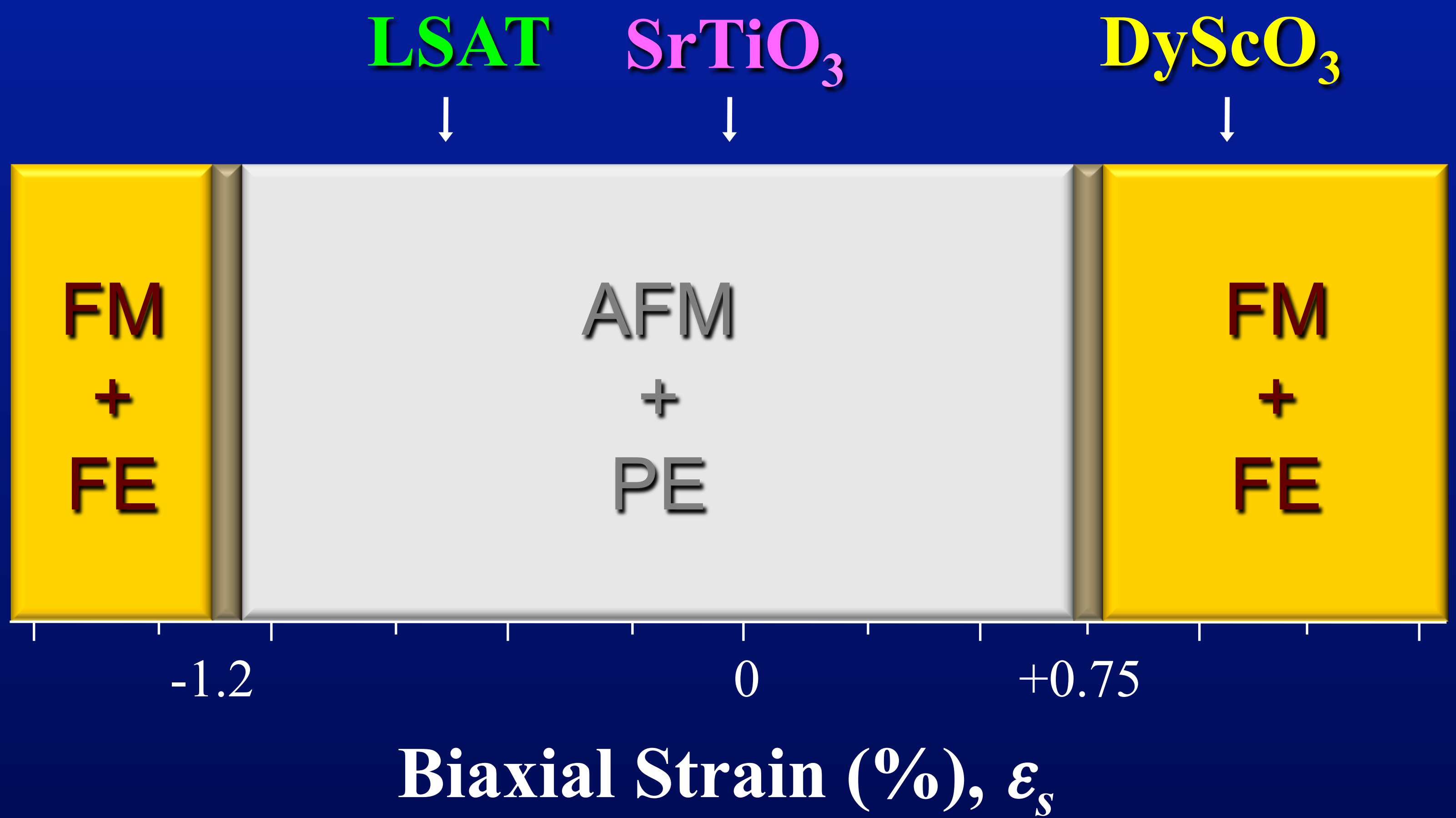
Magnetic Properties of Strained $EuTiO_3/DyScO_3$ vs. $DyScO_3$



SQUID

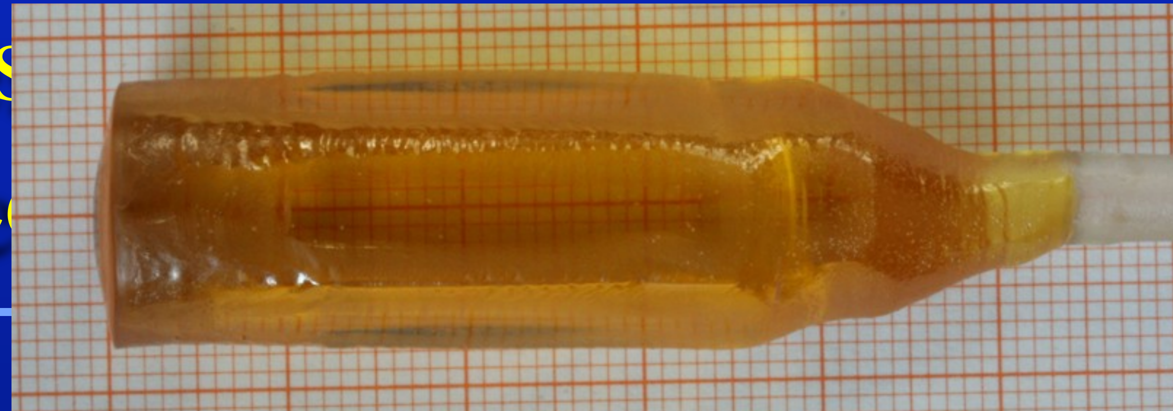
Peter Schiffer—*Penn State University (now University of Illinois)*

First Principles Epitaxial Phase Diagram of Strained $EuTiO_3$ (at $T = 0$ K)

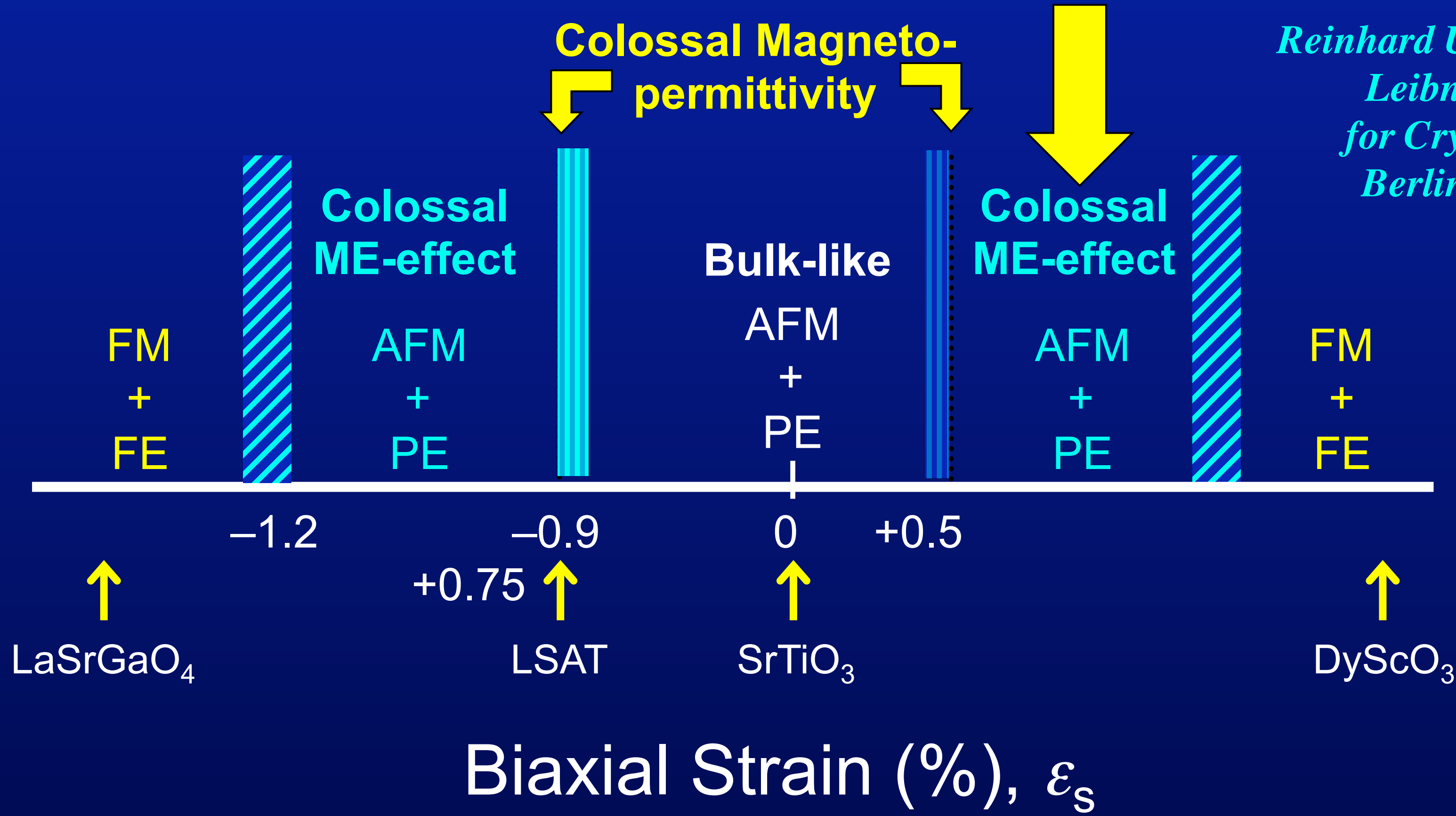


J.H. Lee, L. Fang, E. Vlahos, X. Ke, Y.W. Jung, L. Fitting Kourkoutis, J-W. Kim, P.J. Ryan, T. Heeg, M. Roeckerath, V. Goian, M. Bernhagen, R. Uecker, P.C. Hammel, K.M. Rabe, S. Kamba, J. Schubert, J.W. Freeland, D.A. Muller, C.J. Fennie, P. Schiffer, V. Gopalan, E. Johnston-Halperin, and D.G. Schlom, *Nature* **466** (2010) 954-958.

First Principles n
of Straine



Reinhard Uecker's Group
Leibniz Institute
for Crystal Growth
Berlin, Germany



$EuTiO_3$ Conclusions

- **Strained $EuTiO_3$ Results vs. Theory**
  - **Unstrained $EuTiO_3$ has Intrinsic Properties ✔**
  - **Effect of Strain and Magnetic Field on Soft Modes ✔**
  - **Ferroelectricity ✔**
  - **Ferromagnetism ✔**
  - **Ability to Turn on *M* with *E***
  - **Ability to Turn on *P* with *H***

Conclusions

- **The Properties of Oxides can be Enhanced using Strain**
  - **Enhance Ferroelectric T_C**
  - **Enhance Ferroelectric P_s**
  - **Turn on Ferroelectricity and Ferromagnetism**
  - **Alter Bandgap and Band Lineup of Photocatalysts**
  - **Create Tunable Dielectrics with Highest Figure of Merit of any Known Material in GHz Regime**