Thin-Film Alchemy: Using Epitaxial Engineering to Unleash the Hidden Properties of Oxides

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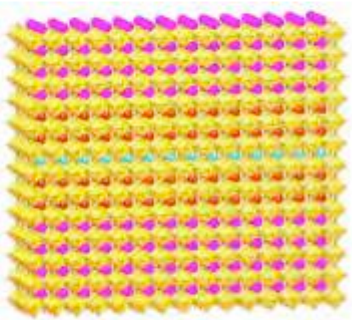
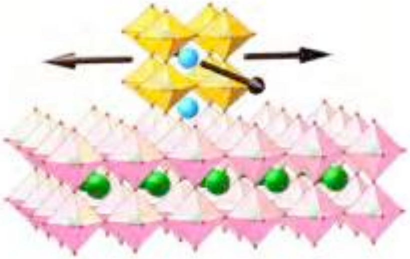
Kavli Institute at Cornell for Nanoscale Science

Unleashing Hidden Properties

Interface Engineering

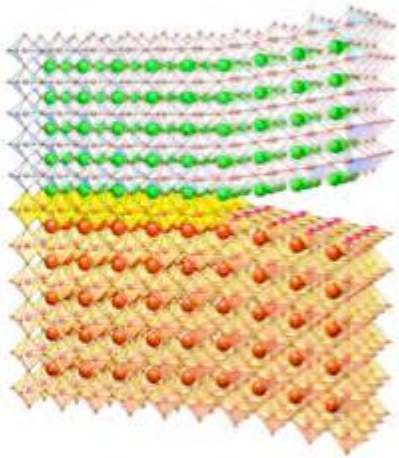


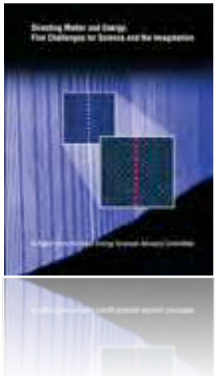
$(LaMnO_3)_{2n}$ / $(SrMnO_3)_n$



Strain Engineering

FeSe / $SrTiO_3$

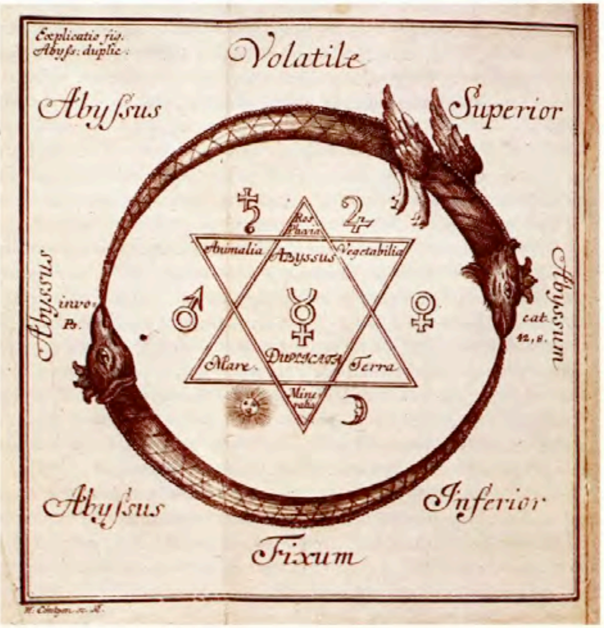


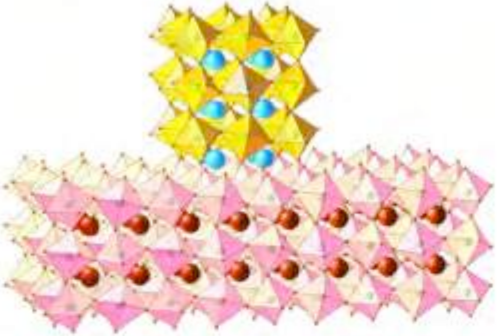


$LaAlO_3$ / $SrTiO_3$

Bi_2Se_3 / EuS

Polarization Doping & Proximity Effects
(from juxtaposed competing ground states)





Epitaxial Stabilization

$BaRuO_3$ / $SrTiO_3$

Ba_2RuO_4 / $GdScO_3$

Dimensional Confinement

$A_{n+1}B_nO_{3n+1}$: $(La,Sr)_2CuO_4$, Sr_2RuO_4, Sr_2IrO_4

Unleashing Hidden Properties

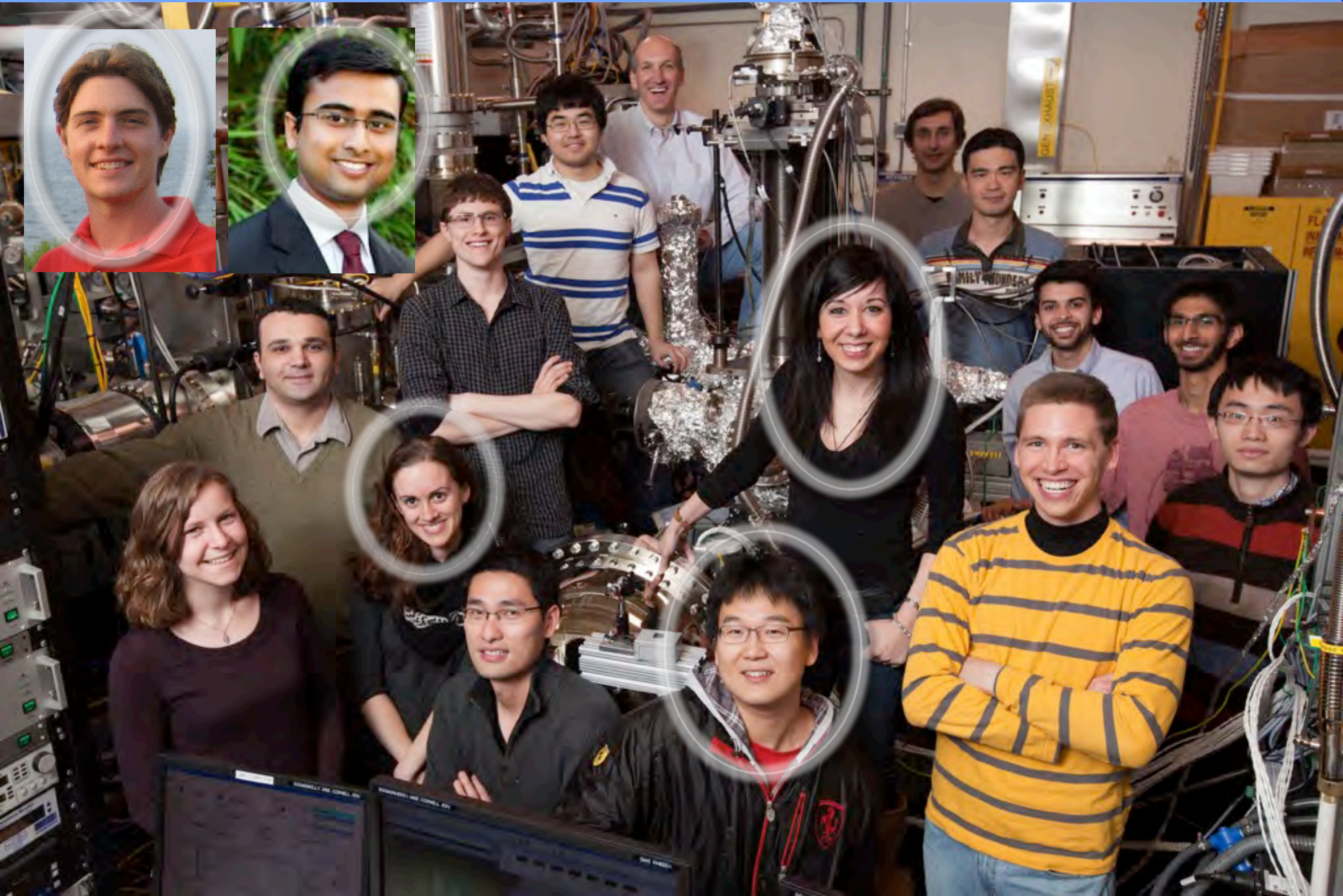
- Toolkit Enabling Materials-by-Design of Oxide Thin Films
- Ruthenates—$BaRuO_3$, $(Ca,Sr,Ba)_2RuO_4$
  altering band structure and properties
- $EuTiO_3$
  strongest ferromagnetic ferroelectric
- $(LuFeO_3)_9$ / $(LuFe_2O_4)_1$ Superlattices
  strongest ferromagnetic ferroelectric at room temperature

The Sorcerers

Craig Fennie
(Cornell)

Karin Rabe (Rutgers)

The Sorcerer’s Apprentices



In Collaboration with the Groups of:

Craig J. Fennie—*Cornell University*
Karin M. Rabe—*Rutgers University*
Kyle M. Shen—*Cornell University*
David A. Muller—*Cornell University*
Lena F. Kourkoutis—*Cornell University*
Peter Schiffer—*University of Illinois*
Ramamoorthy Ramesh—*University of California, Berkeley*
Andreas Scholl—*Lawrence Berkeley National Laboratory*
Elke Arenholz—*Lawrence Berkeley National Laboratory*
Ezekiel Johnston-Halperin—*Ohio State University*
Venkatraman Gopalan—*Penn State University*
Stanislav Kamba—*Institute of Physics, Czech Republic*
Julie A. Borchers—*NIST*
William D. Ratcliff—*NIST*
Jürgen Schubert—*Forschungszentrum Jülich GmbH*
Reinhard Uecker—*Leibniz Institute für Kristallzüchtung*

Important Synthesis Rules

- Gibbs' Rule
  $\Delta G < 0$ to form stable phases

- Matthias's Rules for Superconductors
  … "Stay away from Theorists"

- Pauling's Rules for Crystal Structures
  Radius ratio criteria for stability

Rules for QM Synthesis

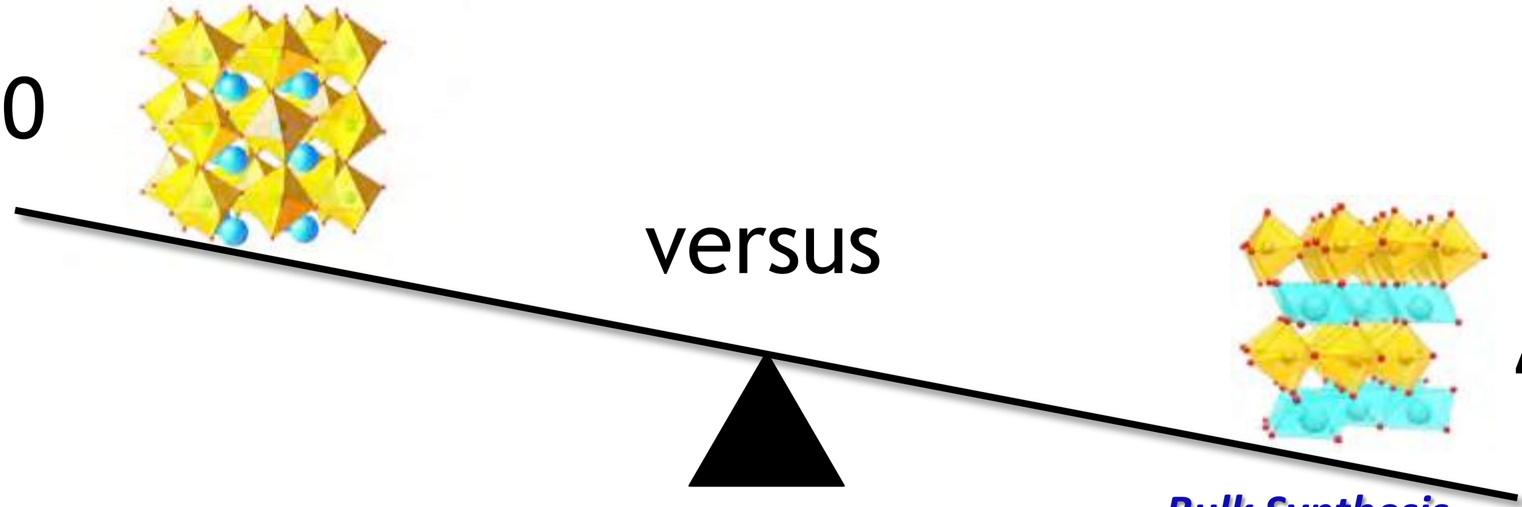
- Gibbs' Rule
  $\Delta G < 0$ to form stable phases
- Matthias's Rules for Superconductors
  … "Stay away from Theorists"
- Pauling's Rules for Crystal Structures
  Radius ratio criteria for stability

BREAK THE RULES!

BREAK THE RULES

- Gibbs’ Rule
  $\Delta G < 0$ to form stable phases

Gibbs' Rule



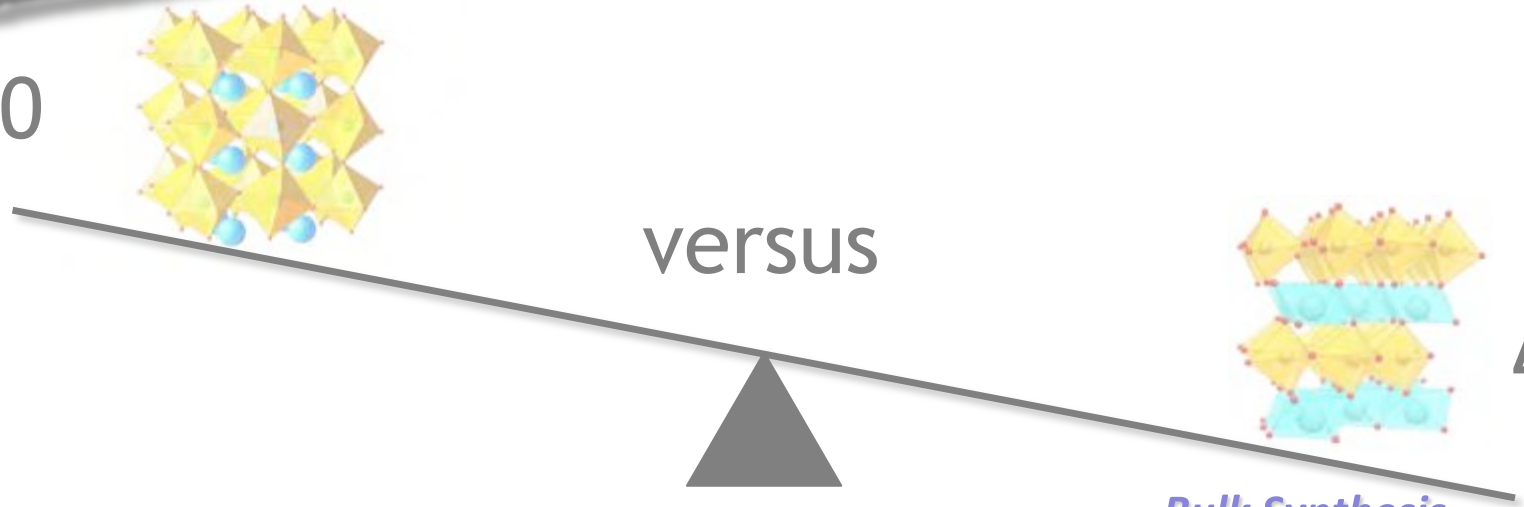
$\Delta G > 0$

versus

$\Delta G < 0$

Bulk Synthesis

BREAK Gibbs' Rule



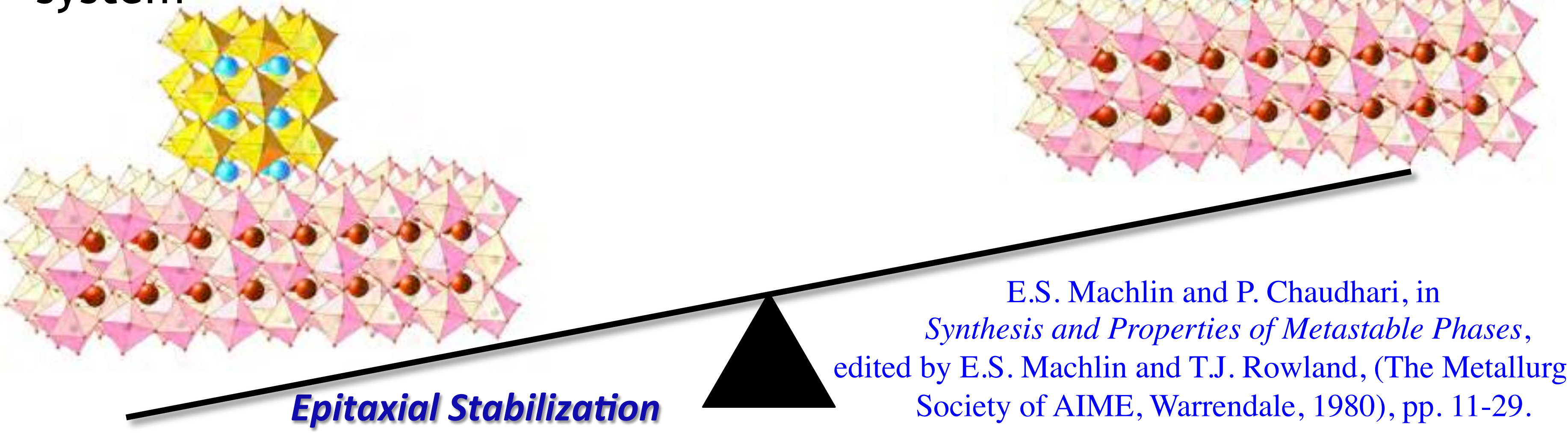
$\Delta G > 0$

versus

$\Delta G < 0$

Bulk Synthesis

Stable if free energy difference overcome by
Δ(interface energy) + Δ(strain energy) + Δ(surface energy)



$\Delta G_{\text{system}} > 0$

$\Delta G_{\text{system}} < 0$

Epitaxial Stabilization

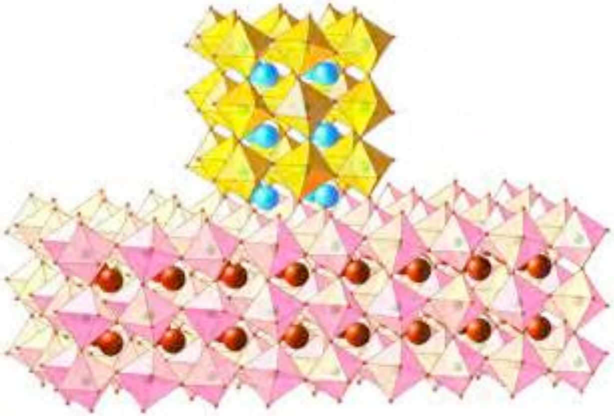
E.S. Machlin and P. Chaudhari, in *Synthesis and Properties of Metastable Phases*, edited by E.S. Machlin and T.J. Rowland, (The Metallurgical Society of AIME, Warrendale, 1980), pp. 11-29.

BREAK THE RULES

- Gibbs’ Rule
  $\Delta G < 0$ to form stable phases
  Exploit interfacial energy from substrate

Substrates are Important

“Indeed, to achieve the objective of ‘psuedomorphic stabilization,’ the researcher should make the attempt to choose the substrate …”



Epitaxial Stabilization

E.S. Machlin and P. Chaudhari,
“Theory of ‘Pseudomorphic Stabilization’ of
Metastable Phases in Thin Film Form,” in
Synthesis and Properties of Metastable Phases,
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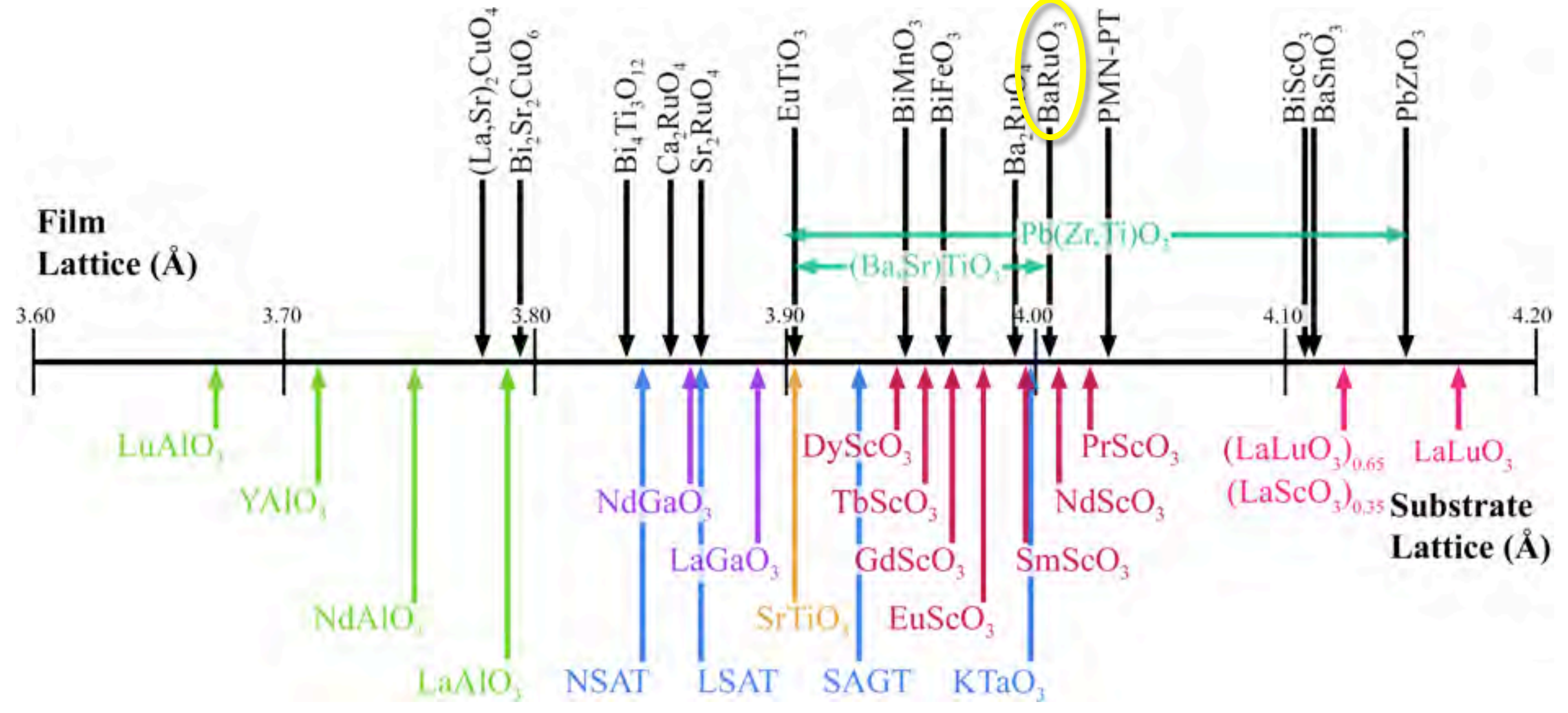
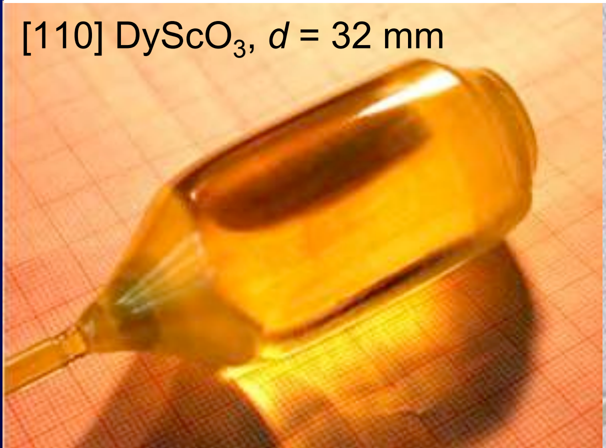
Commercial Perovskite Substrates

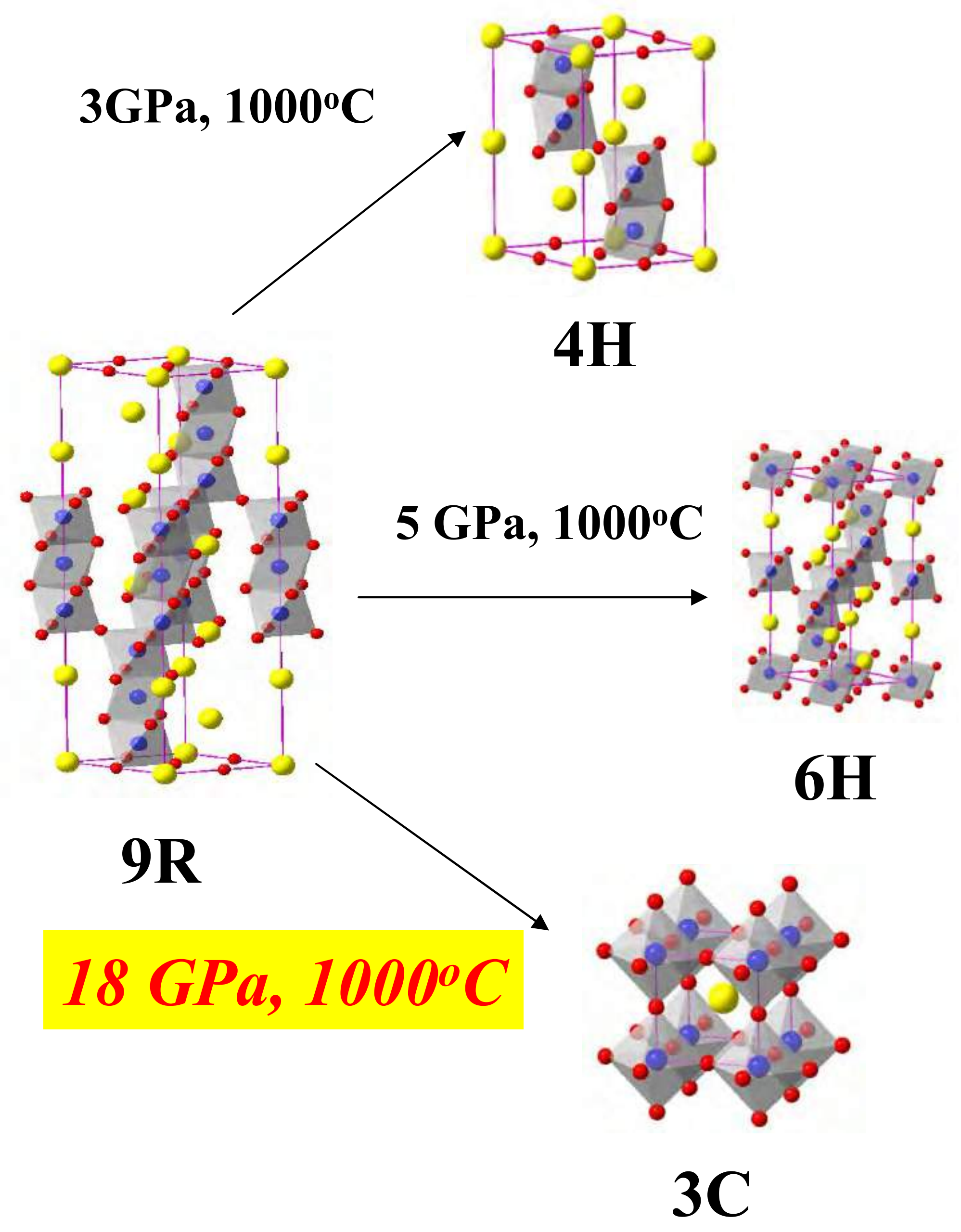



[110] $DyScO_3$, *d* = 32 mm


[110] $GdScO_3$, *d* = 32 mm

D.G. Schlom, L.Q. Chen, C.J. Fennie, V. Gopalan, D.A. Muller, X.Q. Pan, R. Ramesh, and R. Uecker, "Elastic Strain Engineering of Ferroic Oxides," *MRS Bulletin* **39** (2014) 118-130.

BaRuO$_3$ Polymorphs



3GPa, 1000°C

4H

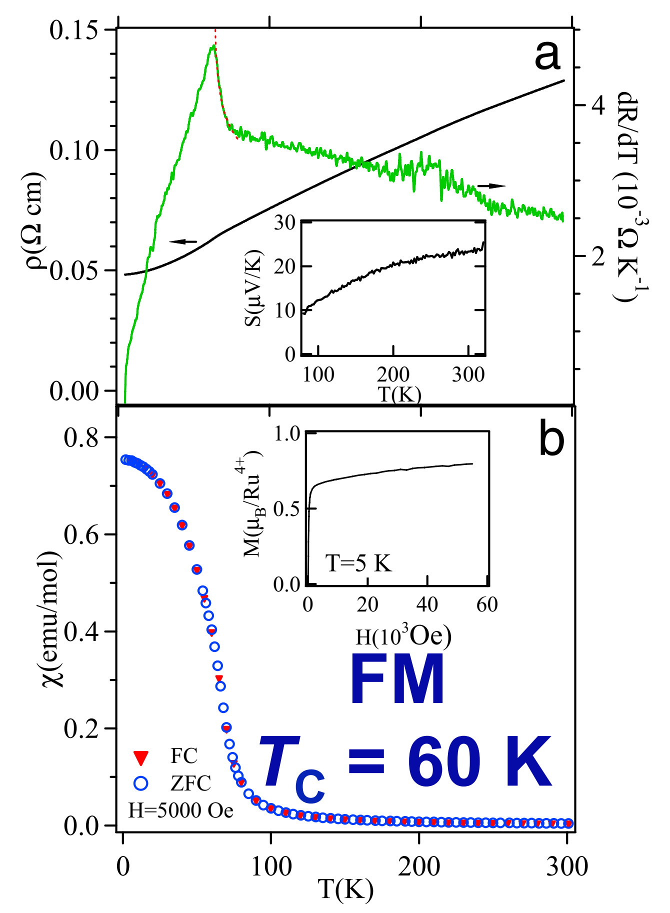
5 GPa, 1000°C

6H

9R

18 GPa, 1000°C

3C



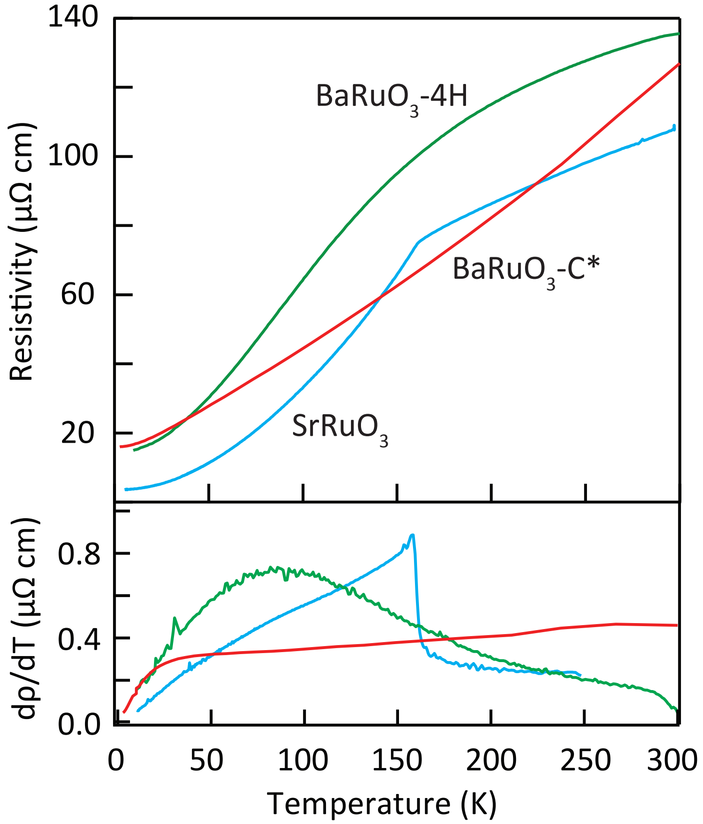
FM

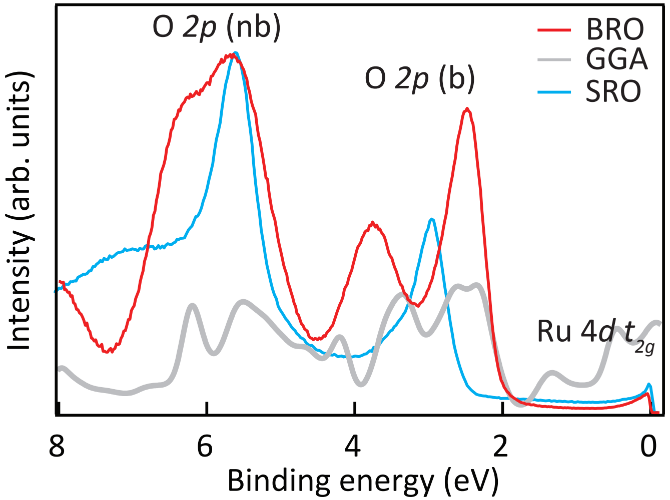
T_C = 60 K

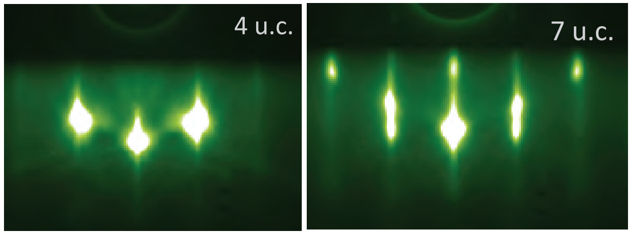
C.Q. Jin, J.S. Zhou, J.B. Goodenough, Q.Q. Liu, J.G. Zhao, L.X. Yang, Y. Yu, R.C. Yu, T. Katsura, A. Shatskiy, and E. Ito, "High-Pressure Synthesis of the Cubic Perovskite BaRuO$_3$ and Evolution of Ferromagnetism in *A*RuO$_3$ (*A* = Ca, Sr, Ba) Ruthenates," *PNAS* **105** (2008) 7115–7119.

Example — $BaRuO_3$ / $SrTiO_3$

- Epitaxially stabilized for ≤ 5 unit cells
- No octahedral rotations
  (2.5% compressive strain ➔ tetragonal)
- $$\frac{\rho_{300\ K}}{\rho_{4\ K}} = 7$$
- No FM



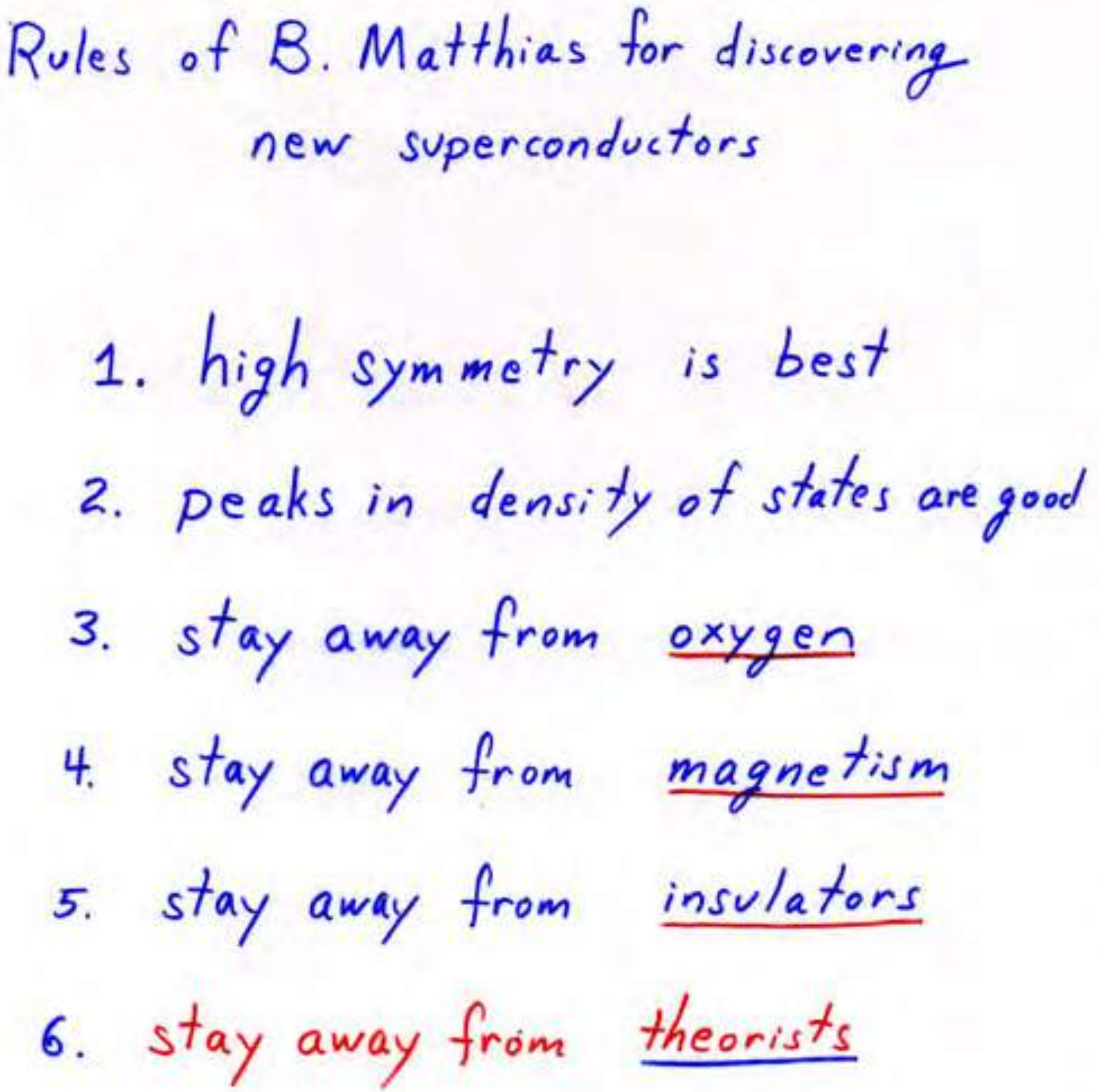




BREAK THE RULES

- Gibbs' Rule
  $\Delta G < 0$ to form stable phases
  Exploit interfacial energy from substrate

- Matthias's Rules for Superconductors
  … "Stay away from Theorists"



Rules of B. Matthias for discovering new superconductors

1. high symmetry is best
2. peaks in density of states are good
3. stay away from oxygen
4. stay away from magnetism
5. stay away from insulators
6. stay away from theorists

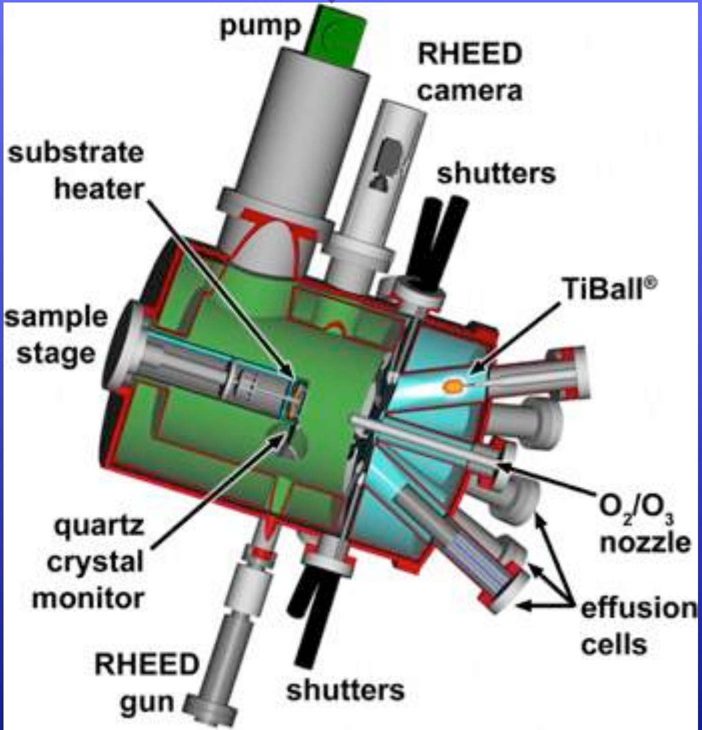
Scanned at the American Institute of Physics

From Steve Girvin's lecture (Boulder Summer School 2000) courtesy of Mike Norman via Matthew Fisher

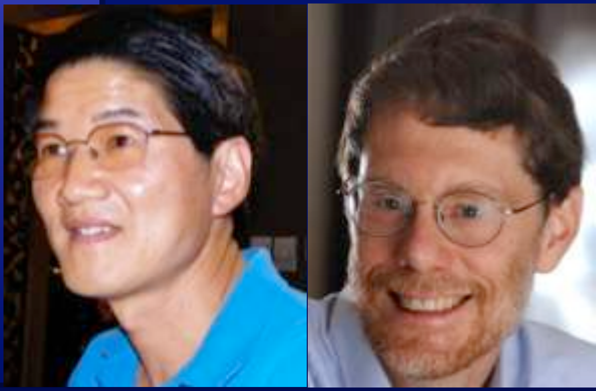
BREAK

Matthias' Rule

Team up with Theorists

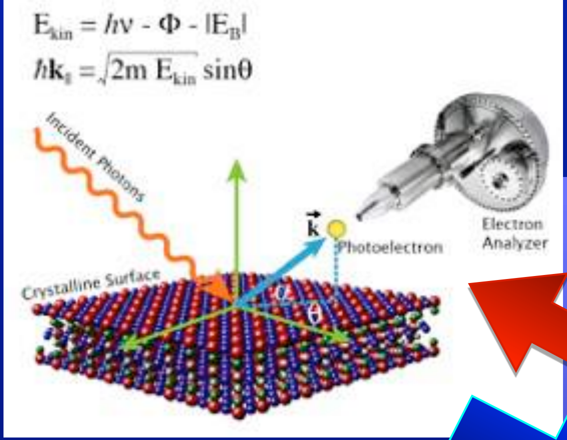


Thin-Film Synthesis

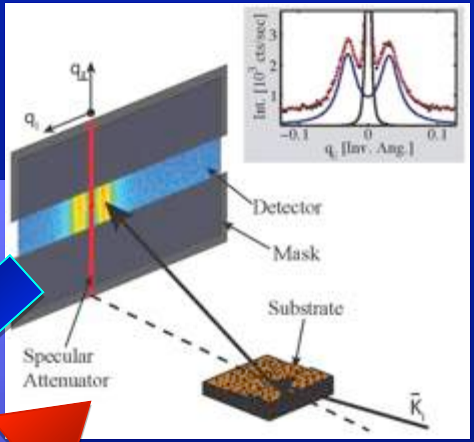


Provide useful Feedback to Theory

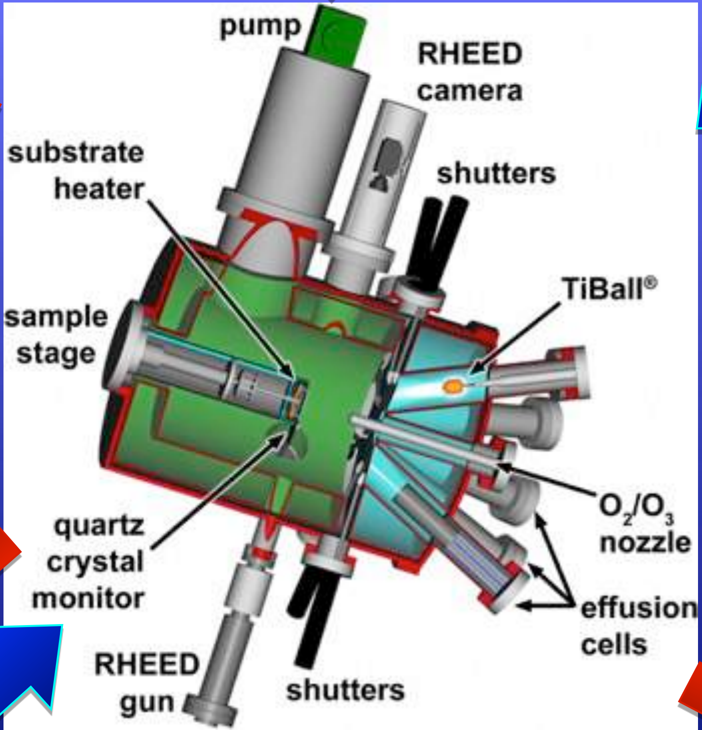
Theory



Photoemission Spectroscopy

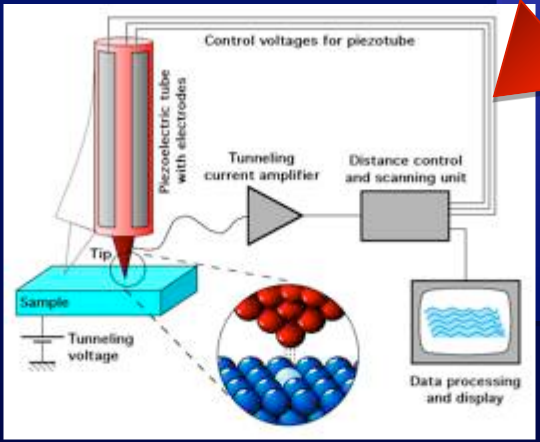


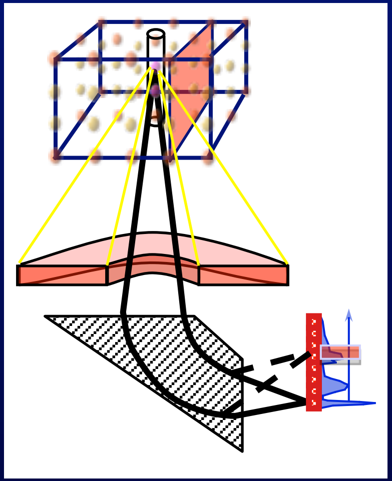
Synchrotron X-ray Diffraction



Thin-Film Synthesis

Scanning Tunneling Microscopy





Transmission Electron Microscopy

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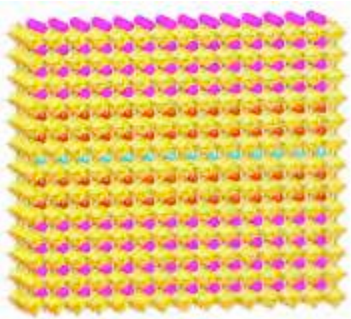
- Matthias's Rules for Superconductors
  … "Stay away from Theorists"
  Team up with theorists
  (and provide them with useful feedback
  e.g., Thin-Film Synthesis + ARPES)

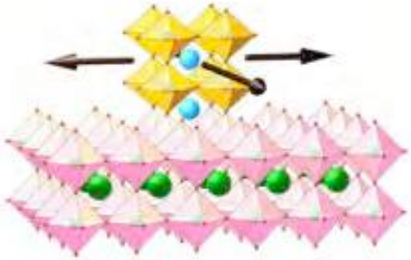
Why Thin-Film Synthesis + ARPES ?

“Artificial” Quantum Materials

Interface Engineering

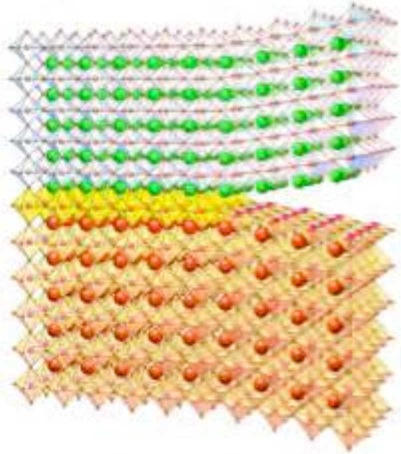


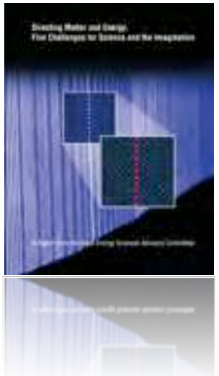
$(LaMnO_3)_{2n}$ / $(SrMnO_3)_n$



Strain Engineering

FeSe / $SrTiO_3$

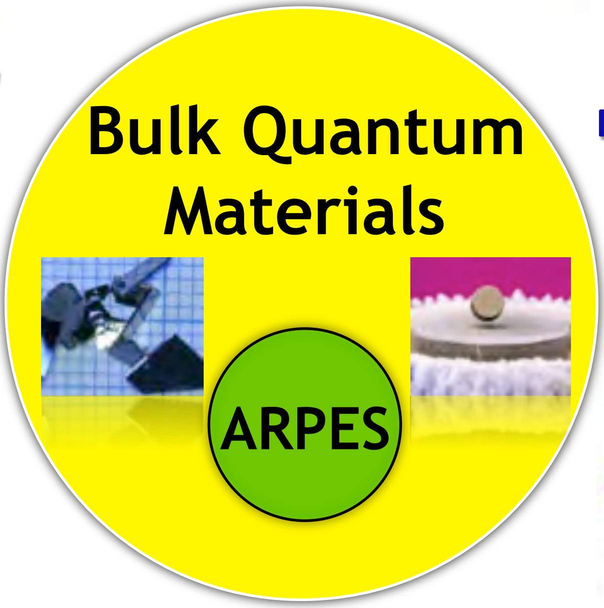




$LaAlO_3$ / $SrTiO_3$

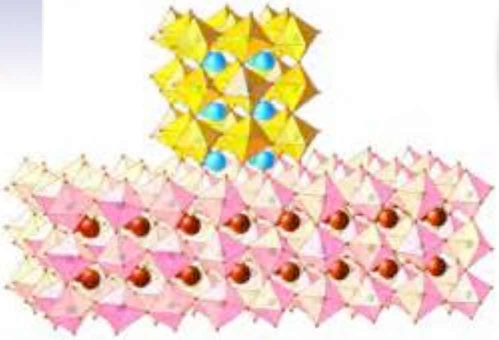
Bi_2Se_3 / EuS

Polarization Doping & Proximity Effects (from juxtaposed competing ground states)



Bulk Quantum Materials

ARPES



Epitaxial Stabilization

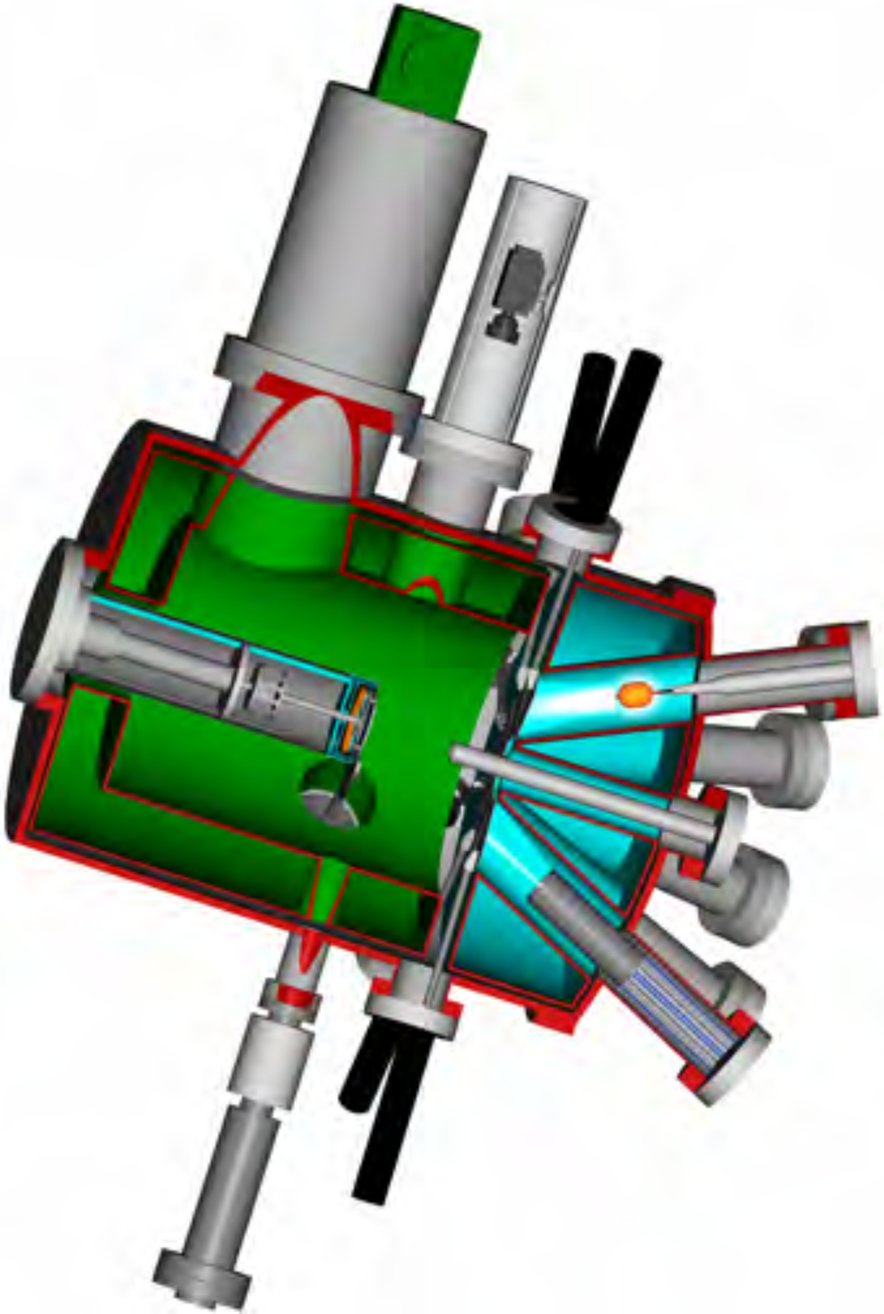
$BaRuO_3$ / $SrTiO_3$

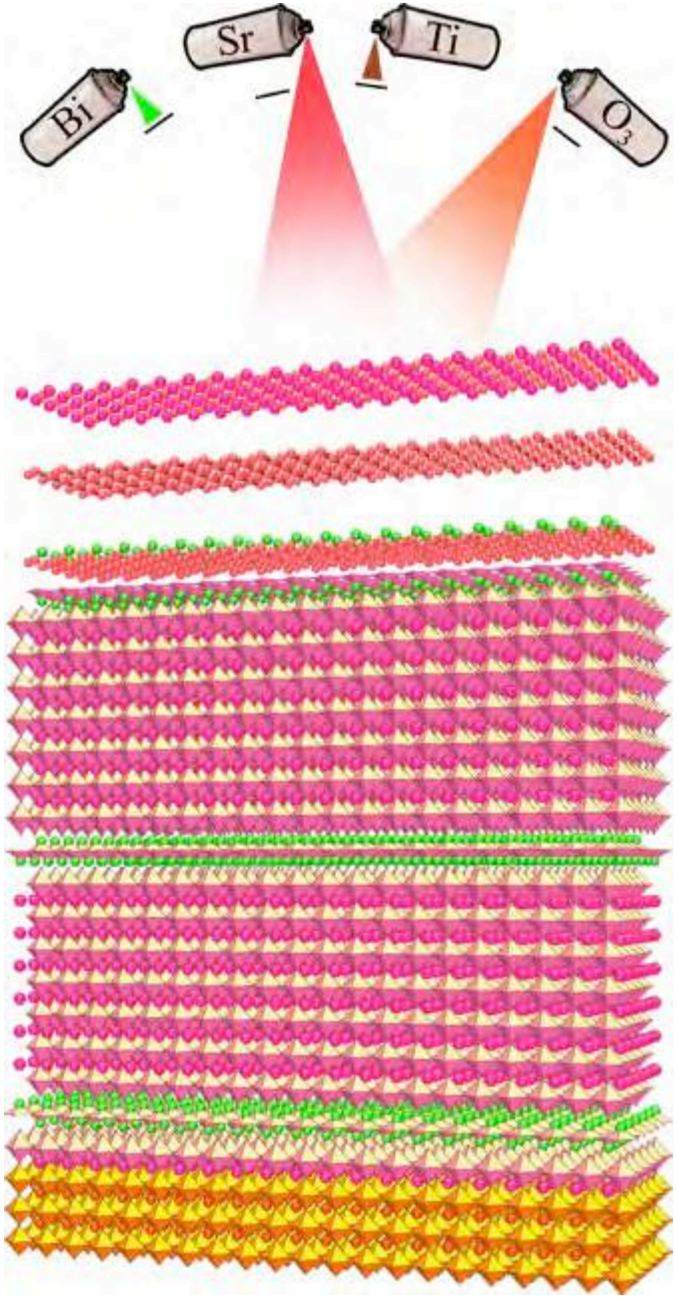
Ba_2RuO_4 / $GdScO_3$

Dimensional Confinement

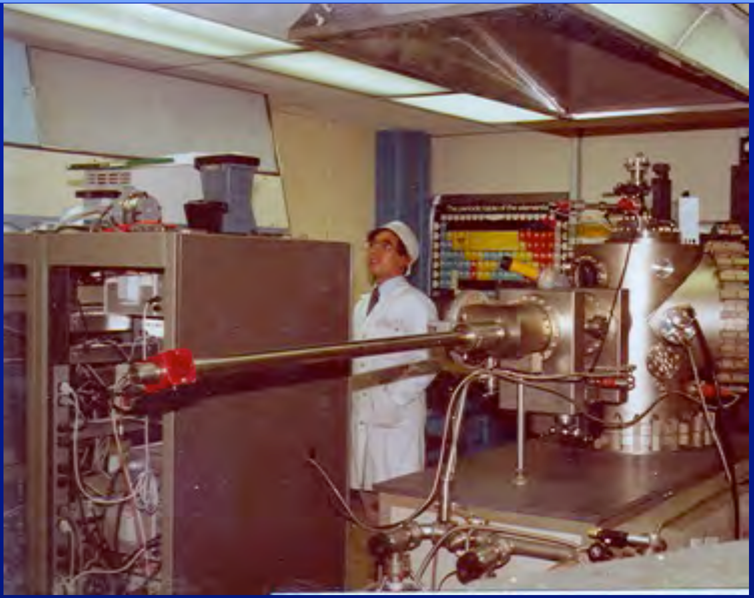
$A_{n+1}B_nO_{3n+1}$: $(La,Sr)_2CuO_4$, Sr_2RuO_4, Sr_2IrO_4

MBE ≈ Atomic Spray Painting

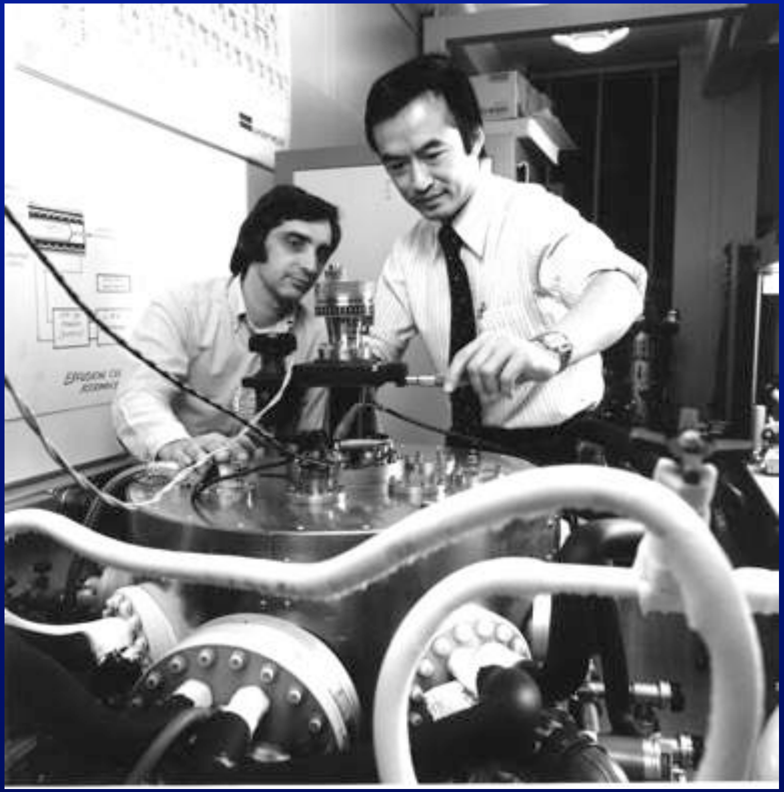




Evolution of MBE



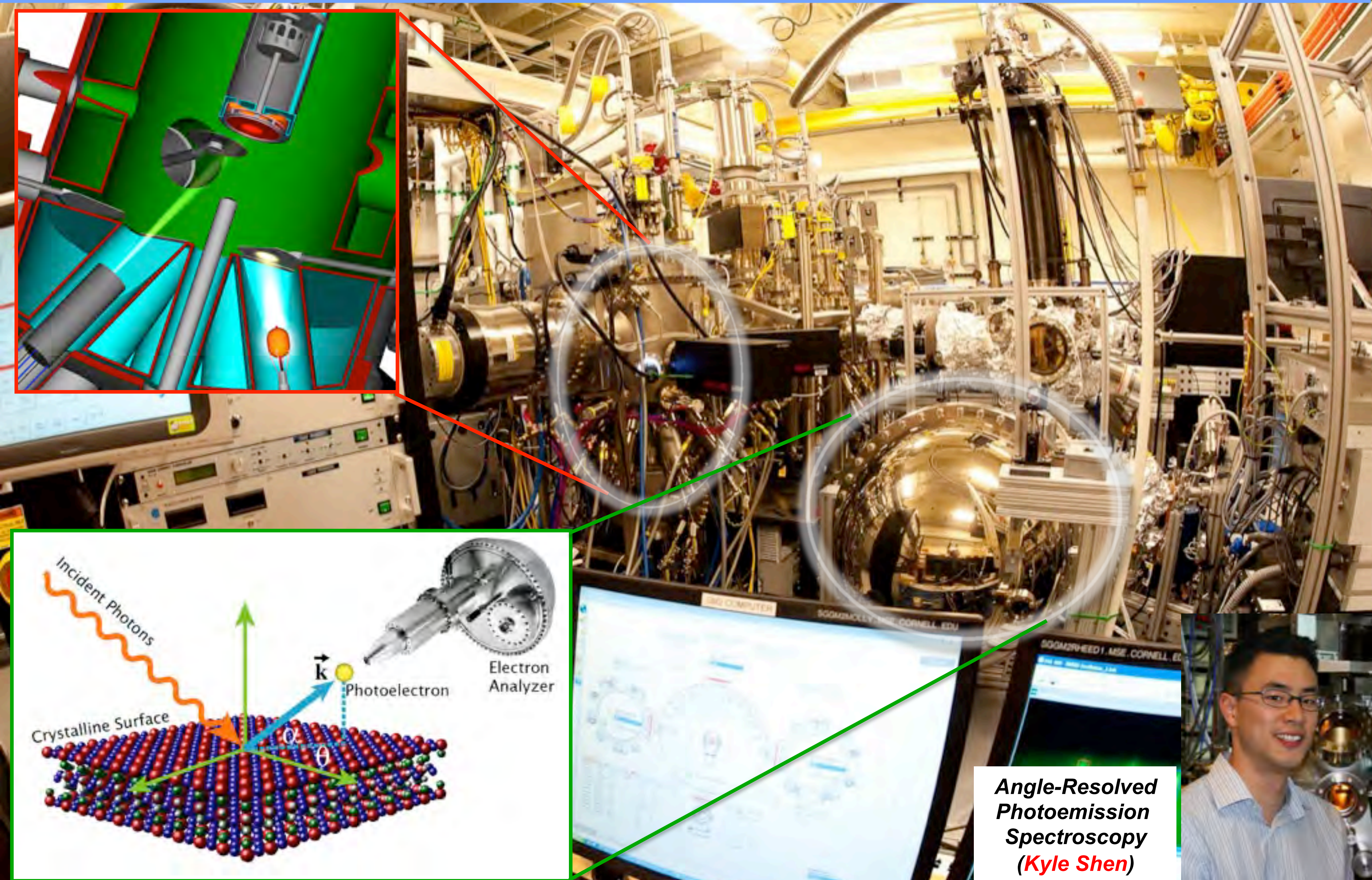
1st University MBE Cornell, 1978



1st MBE
Al Cho at Bell Labs, 1972

Production MBE Today
(courtesy of TRW)

Oxide MBE + ARPES



***Angle-Resolved Photoemission Spectroscopy* (*Kyle Shen*)**

MBE + ARPES

Titanates
$SrTiO_3$
Sr_2TiO_4
$LaTiO_3$

Vanadates
$SrVO_3$
$LaVO_3$
$SrVO_3$ / $LaVO_3$

Manganites
$La_{1-x}Sr_xMnO_3$
$SrMnO_3$
$LaMnO_3$ / $SrMnO_3$

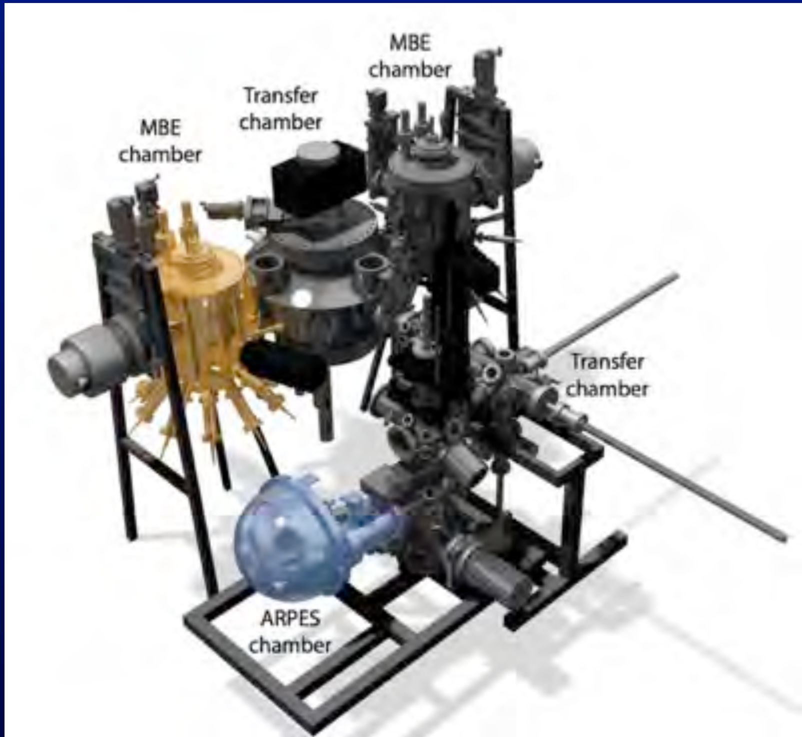
Nickelates
$LaNiO_3$

Cuprates
La_2CuO_4 *T’*
$Sr_{1-x}La_xCuO_2$

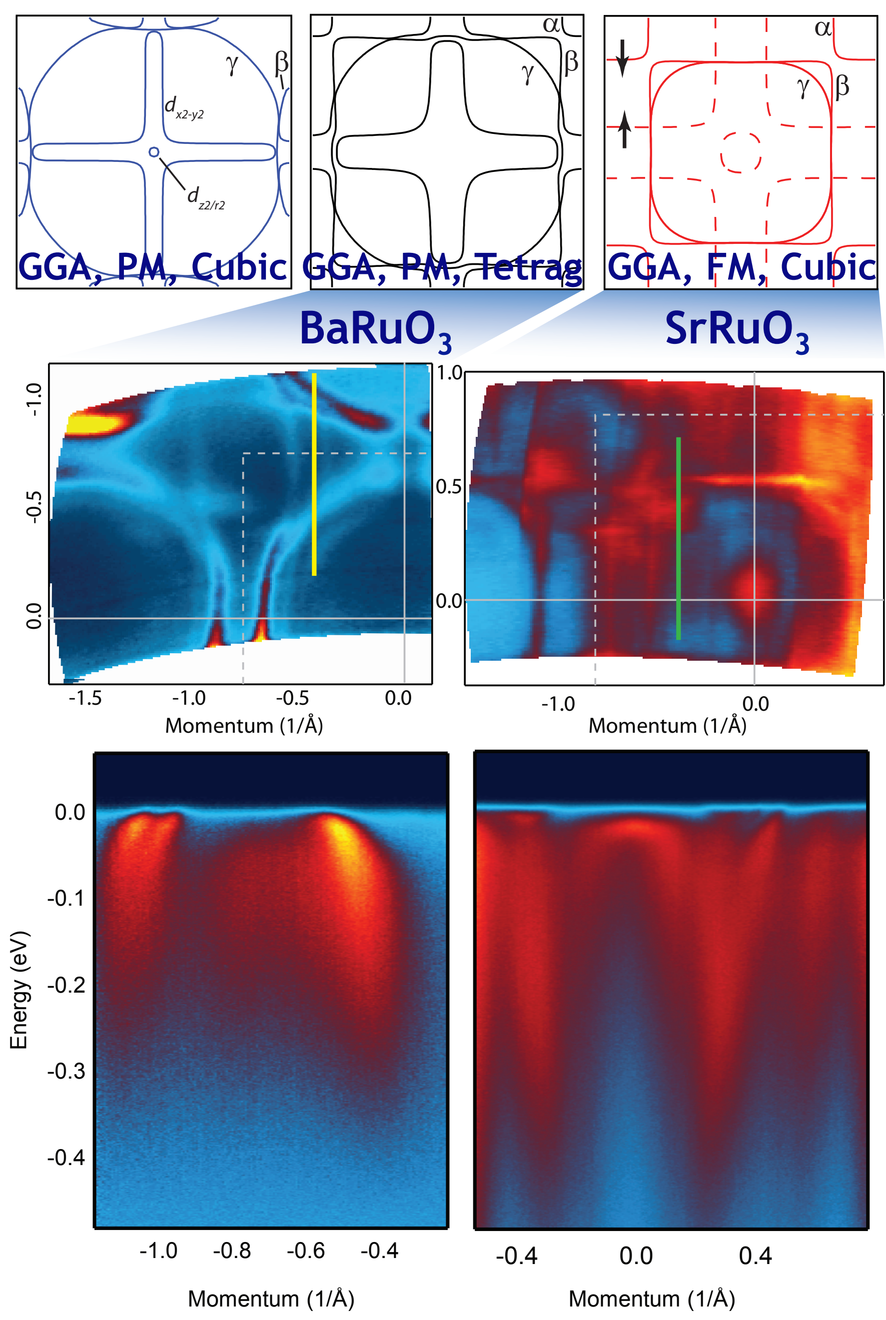
Ruthenates
RuO_2
$SrRuO_3$
Sr_2RuO_4
$BaRuO_3$
Ba_2RuO_4
$CaRuO_3$
Ca_2RuO_4
$Pb_2Ru_2O_{6.5}$

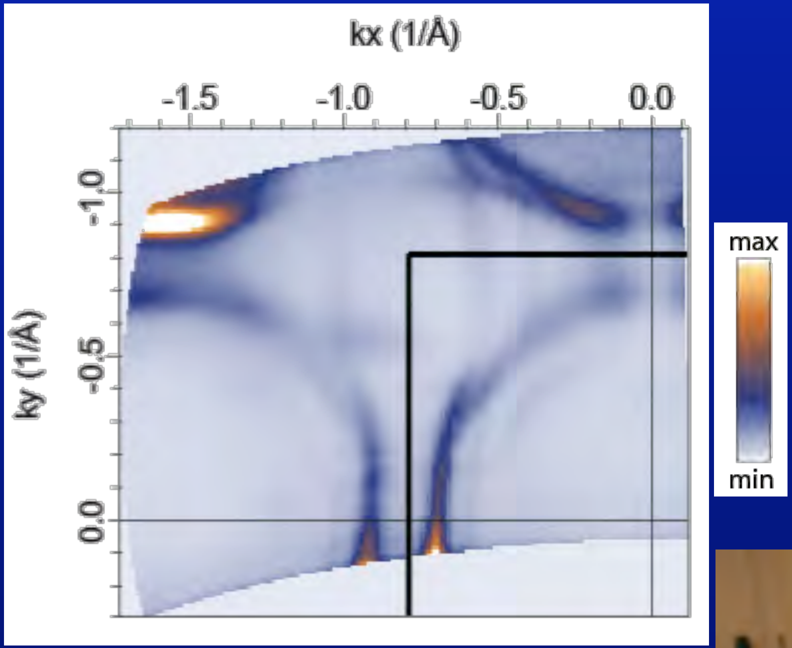
Iridates
IrO_2
IrO_2 / TiO_2
$SrIrO_3$
Sr_2IrO_4
Ba_2IrO_4
$Bi_2Ir_2O_7$

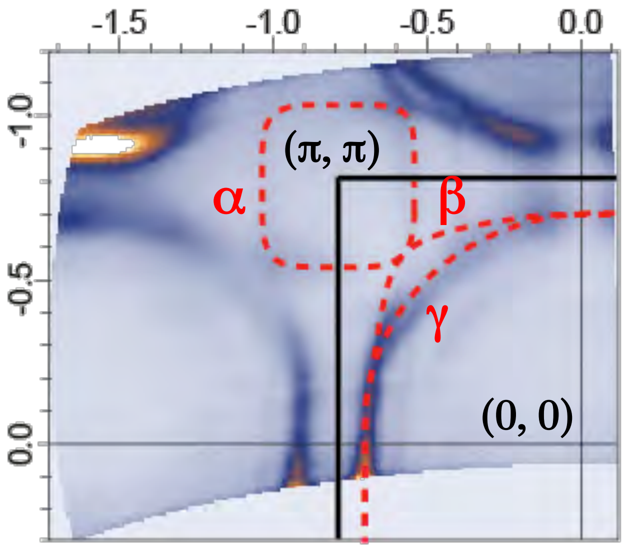
Other Materials
$YbAl_3$
$LuAl_3$
$YbAl_3$ / $LuAl_3$
$BaBiO_3$
$BaSnO_3$
$BaPbO_3$
FeSe

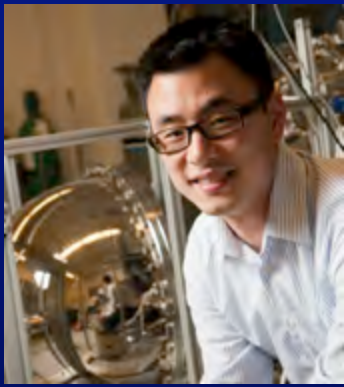


ARPES of $BaRuO_3$ / $SrTiO_3$





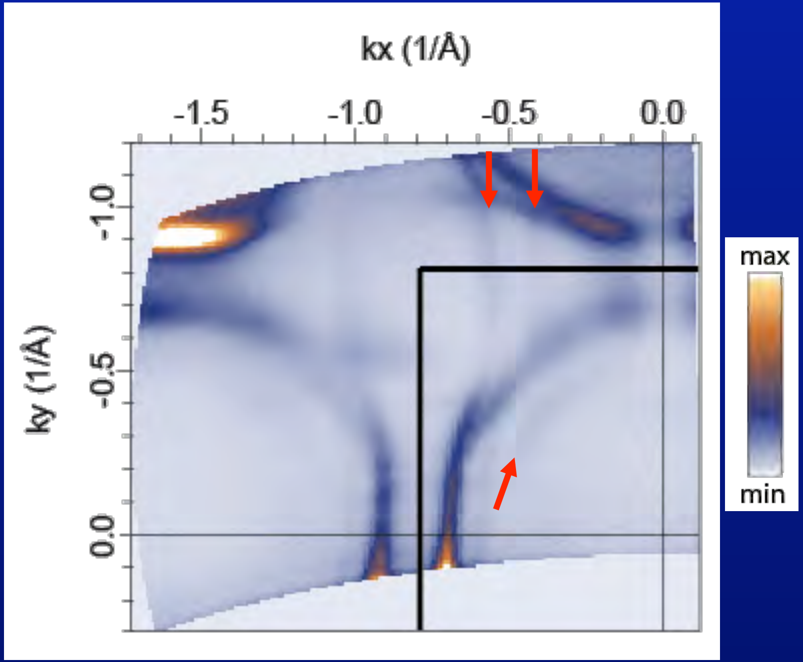


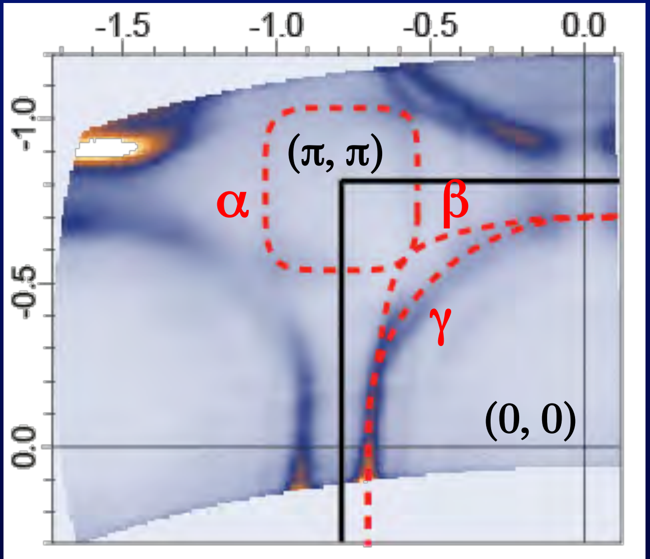


Kyle Shen

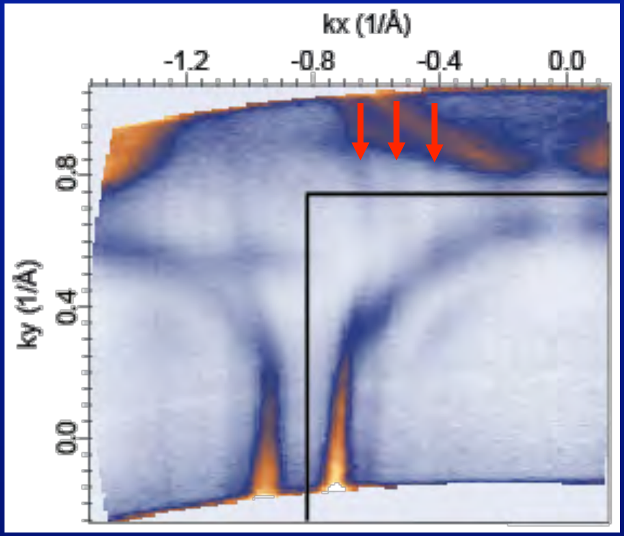
Quantum Well States in BaRuO$_3$

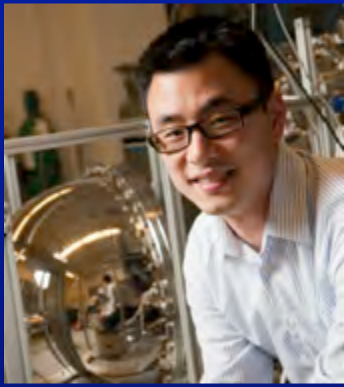
Thickness 3 unit cells





Thickness 4 unit cells

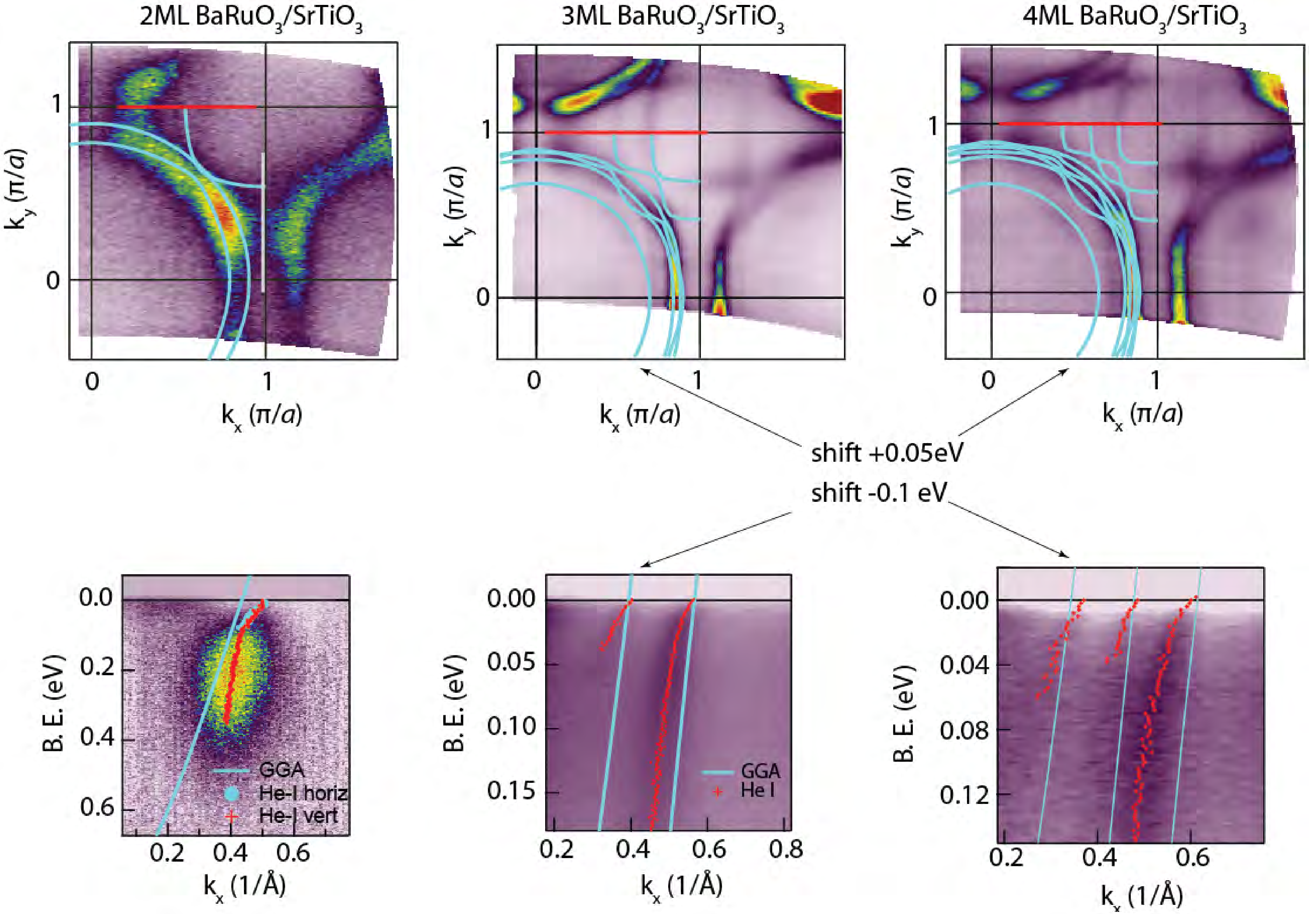




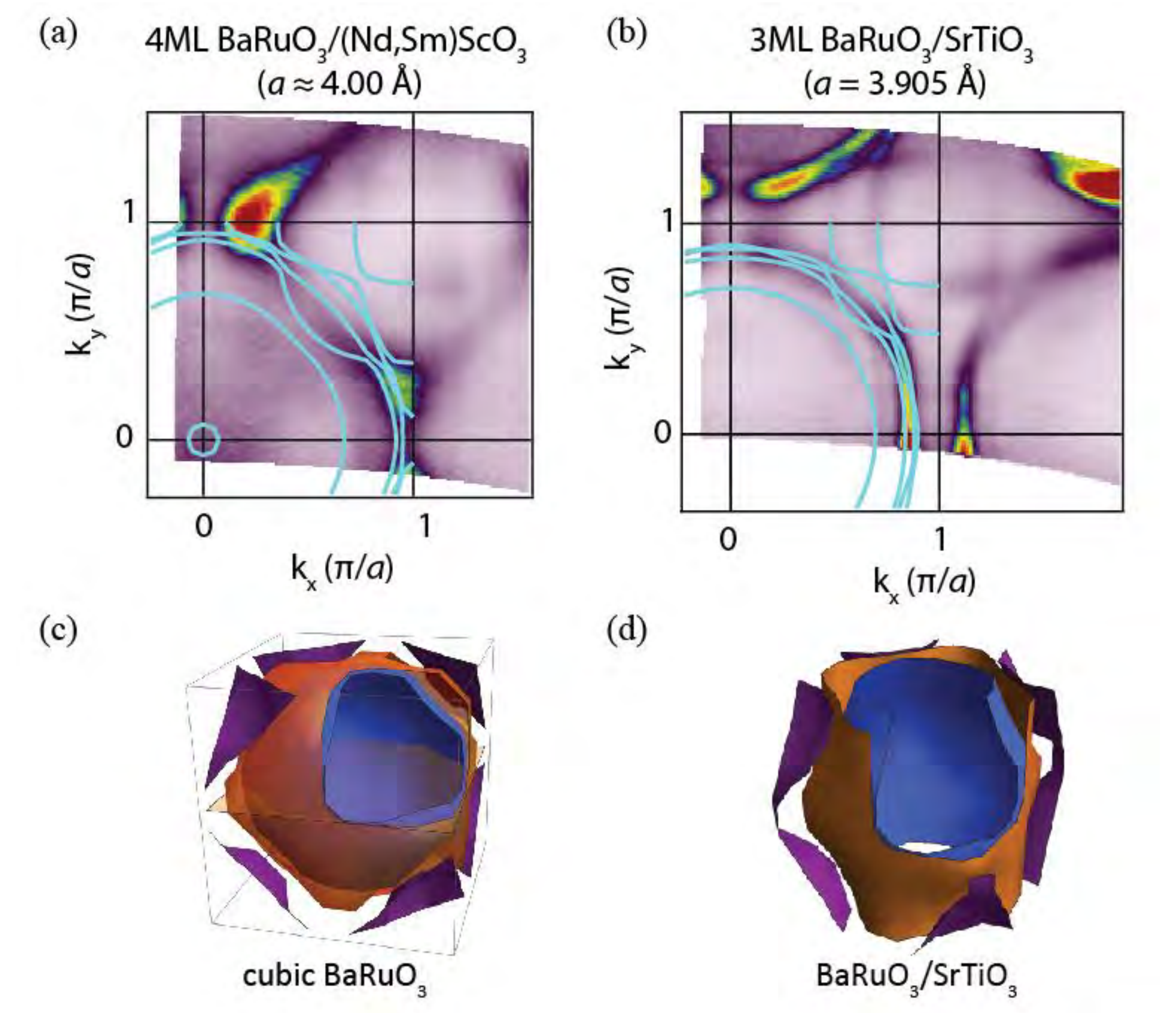
Kyle Shen

- FM suppressed because of finite thickness?
- Or tetragonal distortion?

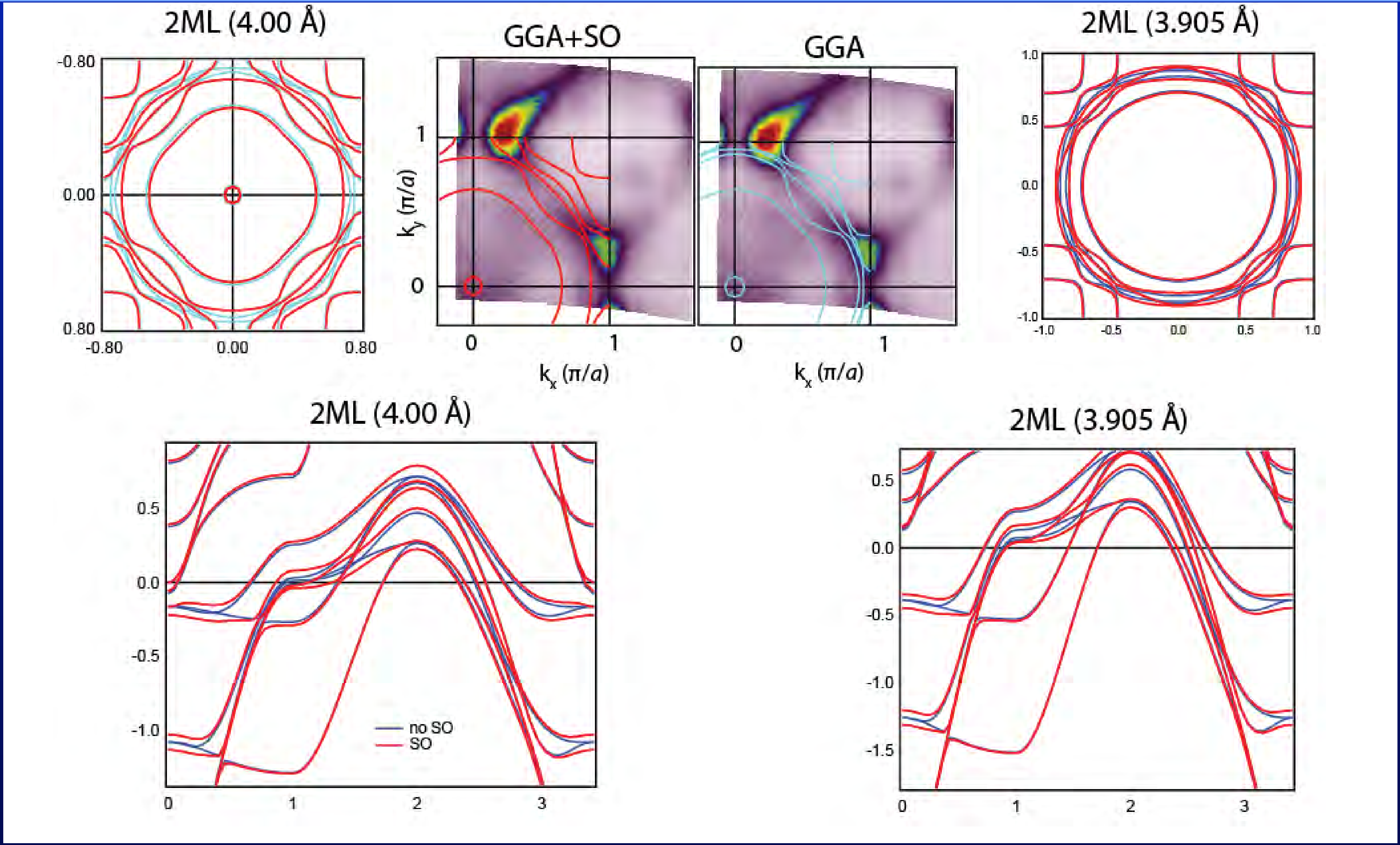
Thickness Dependence



Strain Dependence



Effect of Spin-Orbit (2 ML Cubic)



Spin-Orbit makes little difference except near (π,0)

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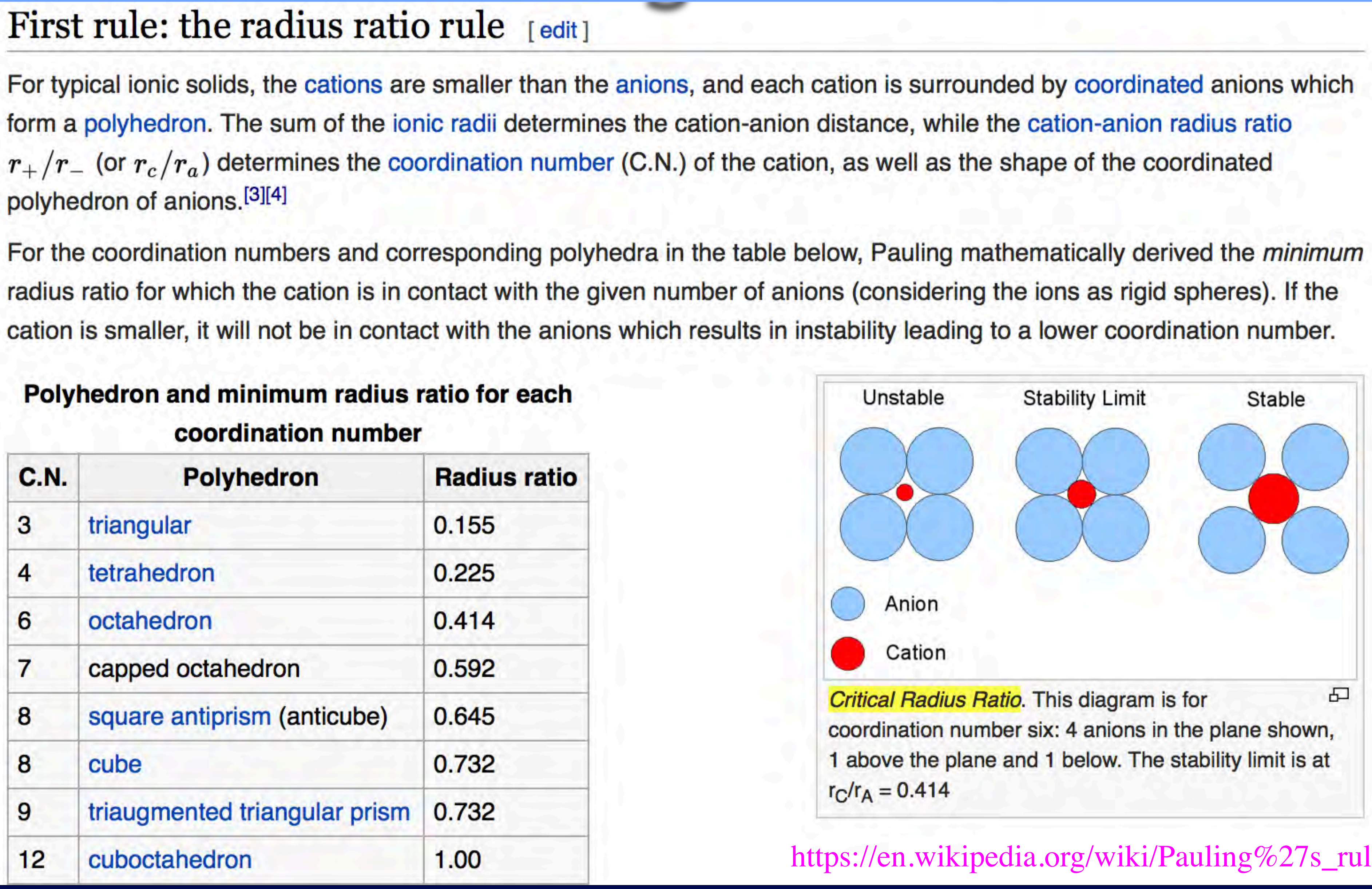
  Radius ratio criteria for stability

Pauling's Rules



First rule: the radius ratio rule [edit]

For typical ionic solids, the cations are smaller than the anions, and each cation is surrounded by coordinated anions which form a polyhedron. The sum of the ionic radii determines the cation-anion distance, while the cation-anion radius ratio r_+/r_- (or r_c/r_a) determines the coordination number (C.N.) of the cation, as well as the shape of the coordinated polyhedron of anions.[3][4]

For the coordination numbers and corresponding polyhedra in the table below, Pauling mathematically derived the *minimum* radius ratio for which the cation is in contact with the given number of anions (considering the ions as rigid spheres). If the cation is smaller, it will not be in contact with the anions which results in instability leading to a lower coordination number.

Polyhedron and minimum radius ratio for each coordination number

C.N.	Polyhedron	Radius ratio
3	triangular	0.155
4	tetrahedron	0.225
6	octahedron	0.414
7	capped octahedron	0.592
8	square antiprism (anticube)	0.645
8	cube	0.732
9	triaugmented triangular prism	0.732
12	cuboctahedron	1.00

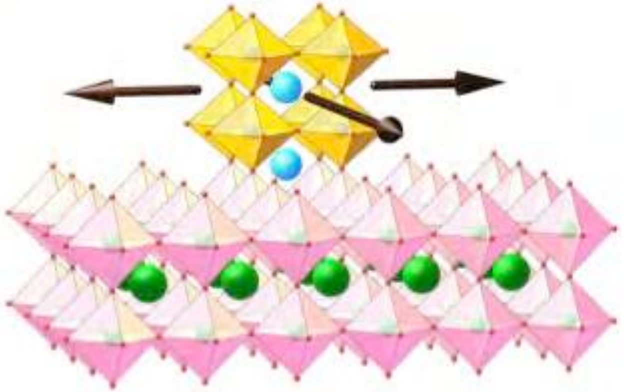
Critical Radius Ratio. This diagram is for coordination number six: 4 anions in the plane shown, 1 above the plane and 1 below. The stability limit is at $r_C/r_A = 0.414$

https://en.wikipedia.org/wiki/Pauling%27s_rules

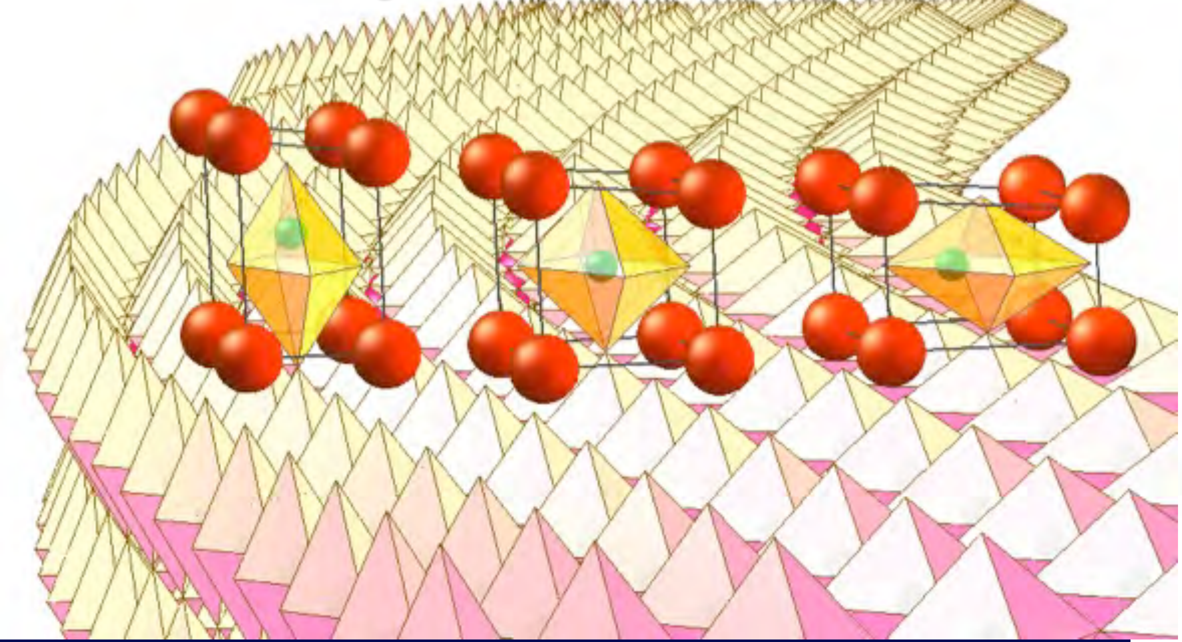
A. Magnus, "Über chemische Komplexverbindungen," *Z. Anorg. Allg. Chem.* **124** (1922) 289–321.

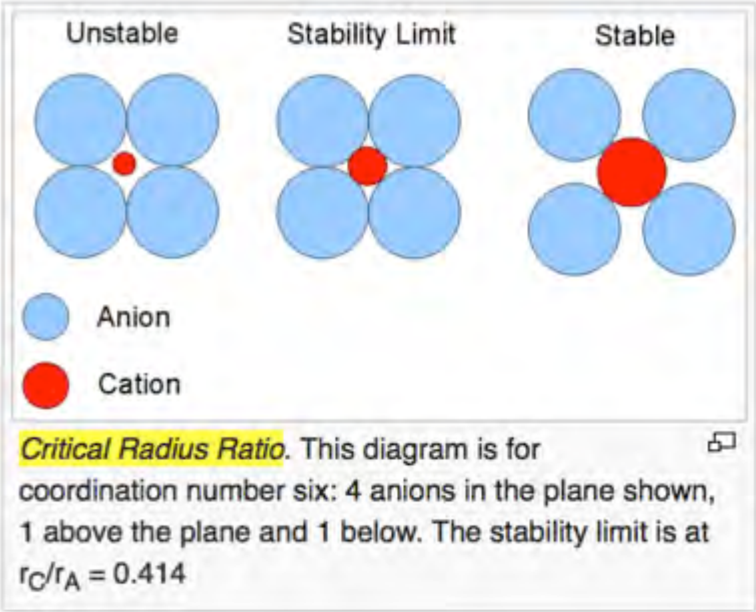
L. Pauling, "The Principles Determining the Structure of Complex Ionic Crystals," *J. Am. Chem. Soc.* **51** (1929) 1010–1026.

BREAK Pauling’s Rules



Strain Engineering





Critical Radius Ratio. This diagram is for coordination number six: 4 anions in the plane shown, 1 above the plane and 1 below. The stability limit is at $r_C/r_A = 0.414$

https://en.wikipedia.org/wiki/Pauling%27s_rules

A. Magnus, “Über chemische Komplexverbindungen,” *Z. Anorg. Allg. Chem.* **124** (1922) 289–321.

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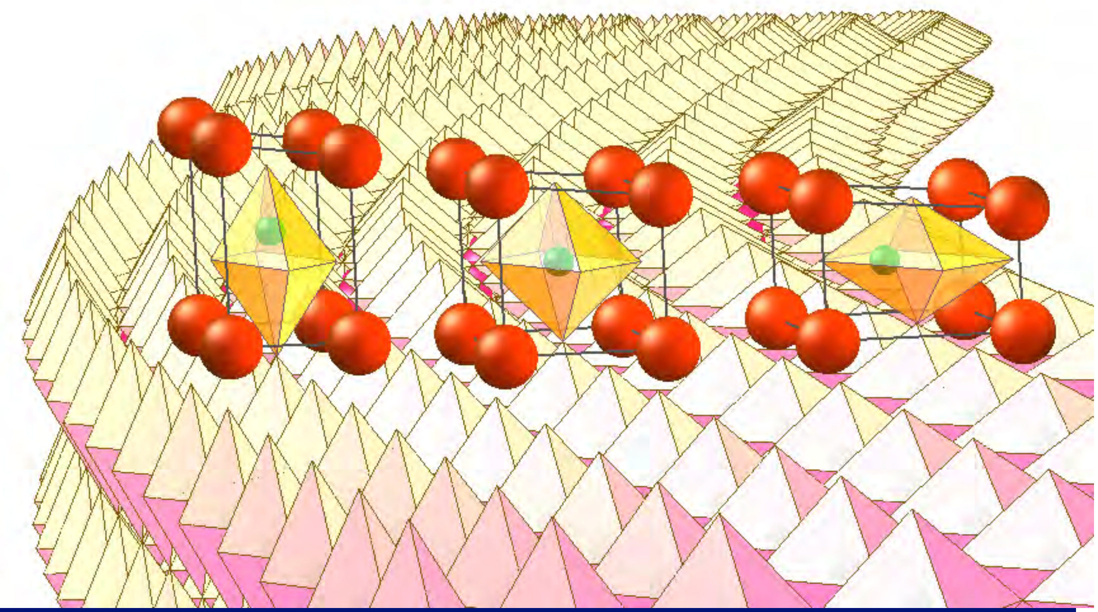
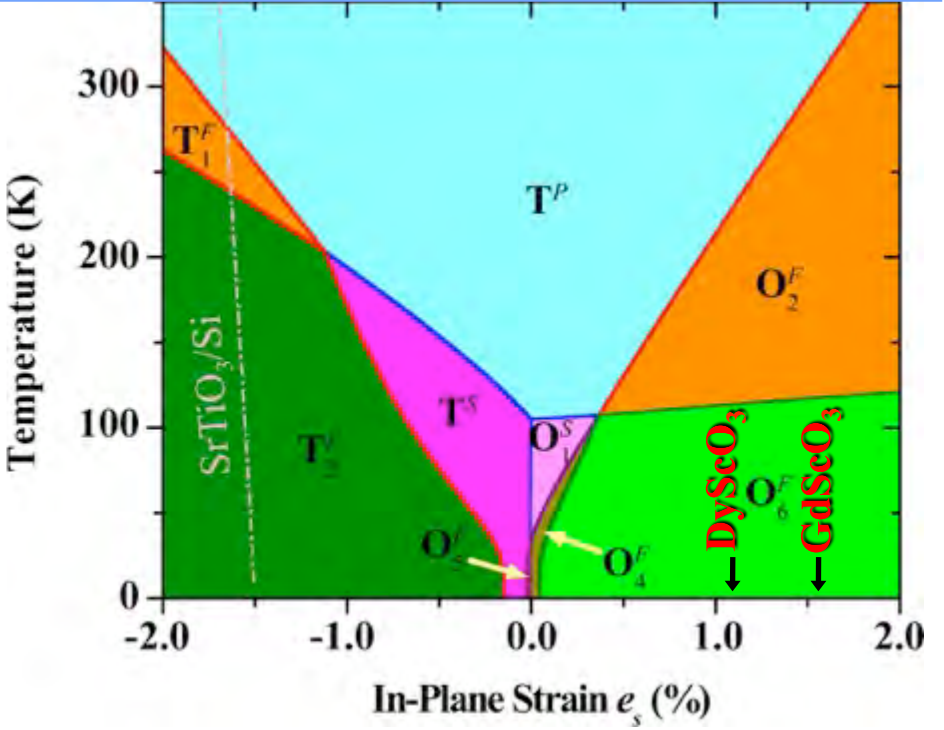
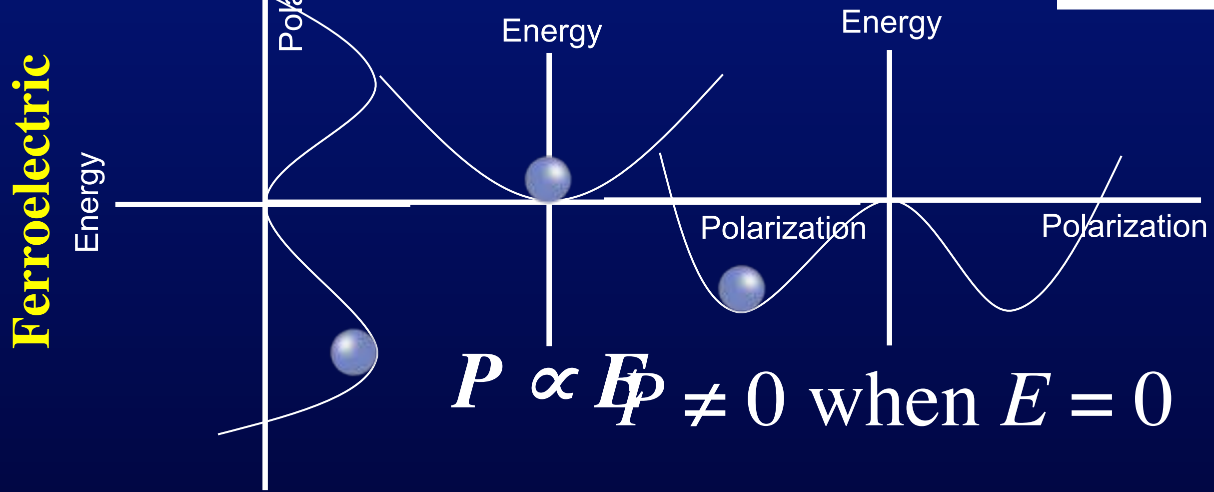
Strained SrTiO$_3$—Transmuting a Dielectric into a Ferroelectric





N.A. Pertsev, A.K. Tagantsev, and N. Setter, *Physical Review* **61** (2000) 825-829.

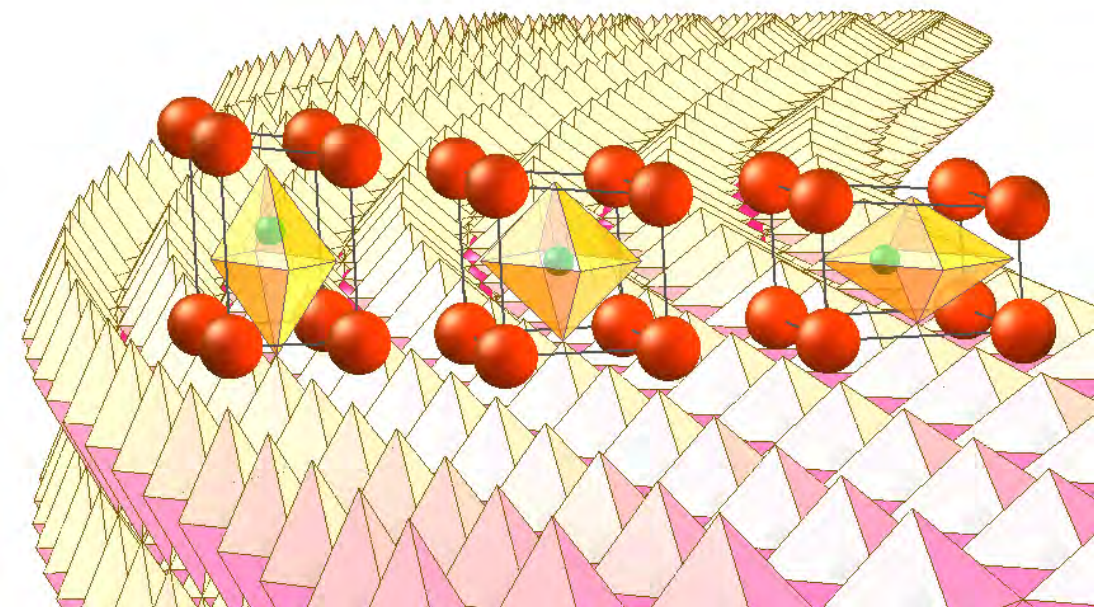
Paraelectric **Ferroelectric**

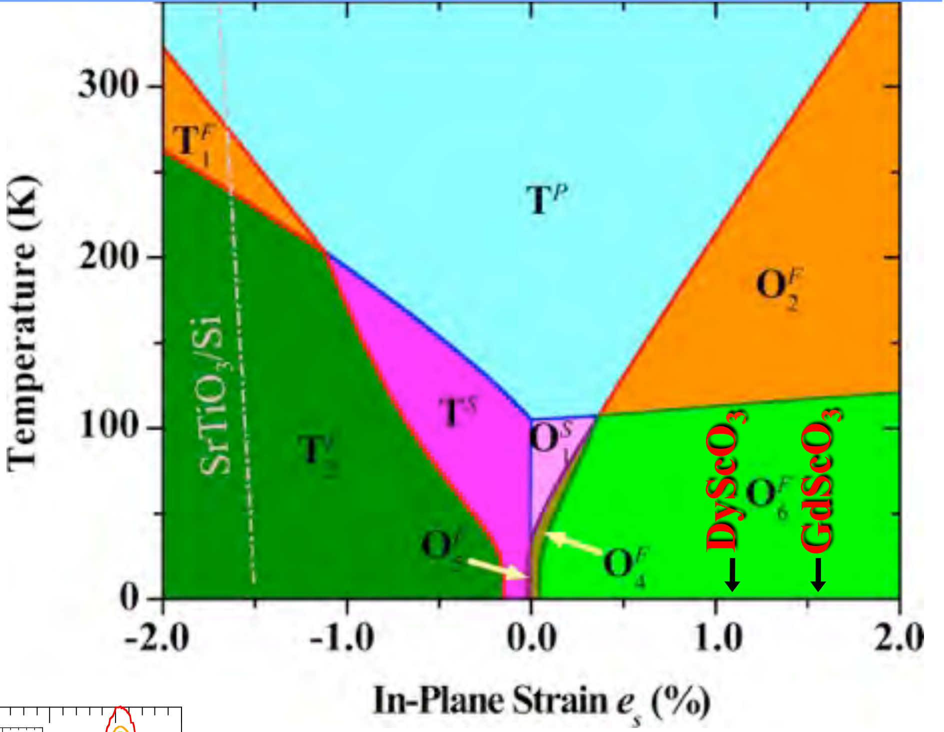


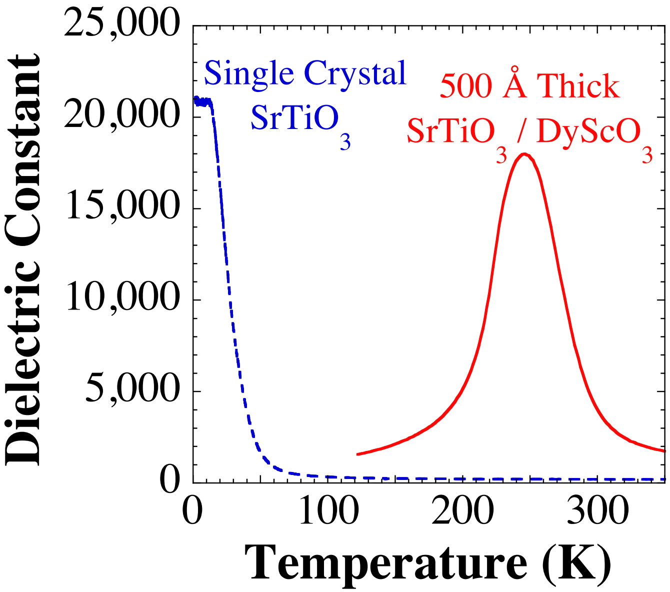
$P \propto E$

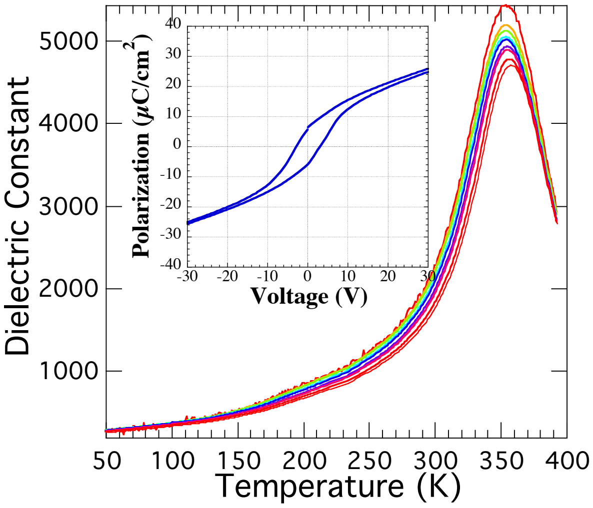
$P \neq 0$ when $E = 0$

Strained $SrTiO_3$—Transmuting a Dielectric into a Ferroelectric







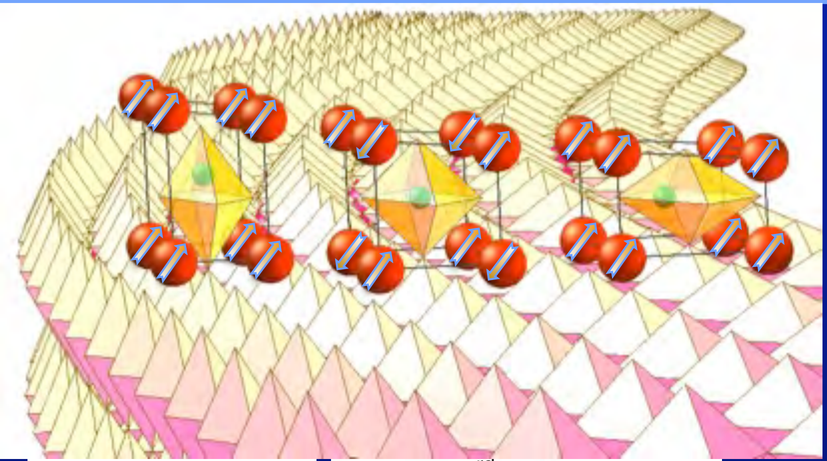


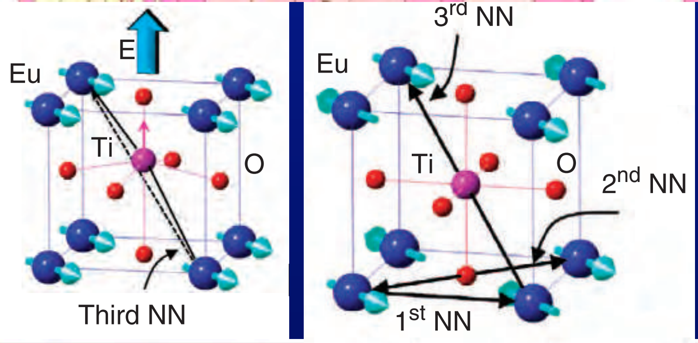
N.A. Pertsev, A.K. Tagantsev, and N. Setter, *Physical Review* **61** (2000) 825-829.

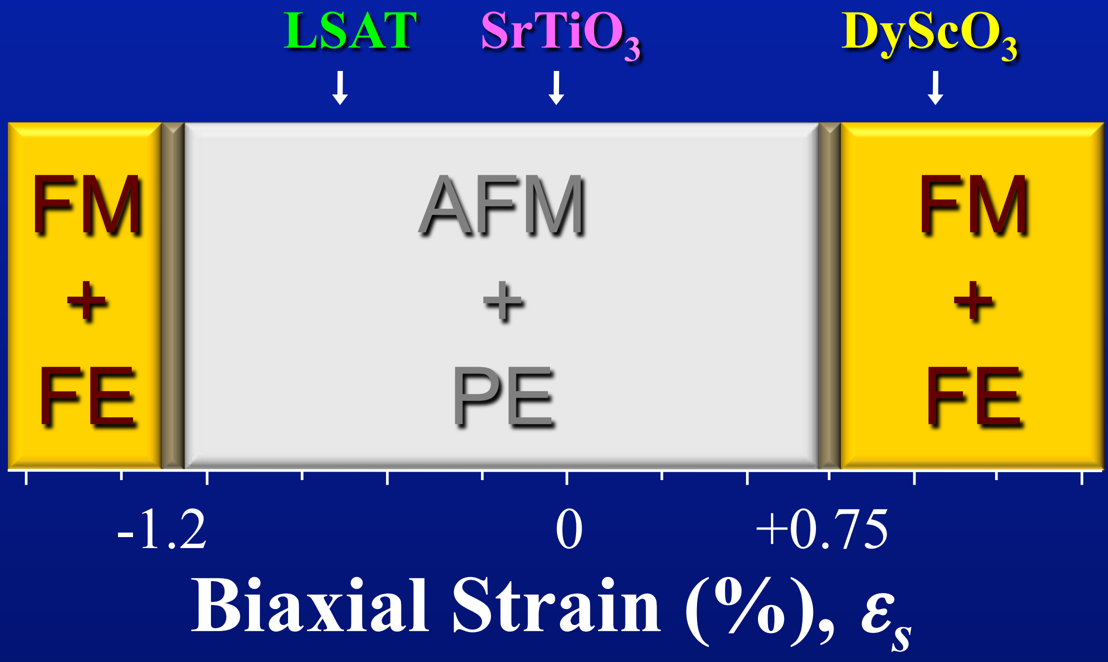
Ferroelectric at Room Temperature

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.

Strained $EuTiO_3$—Strongest Ferromagnetic Ferroelectric







C.J. Fennie and K.M. Rabe
Physical Review Letters **97** (2006)

P.J. Ryan, J.-W. Kim, T. Birol, P. Thompson, J.-H. Lee, X. Ke, P.S. Normile, E. Karapetrova, P. Schiffer, S.D. Brown, C.J. Fennie, and D.G. Schlom
Nature Communications **4** (2013) 1334.

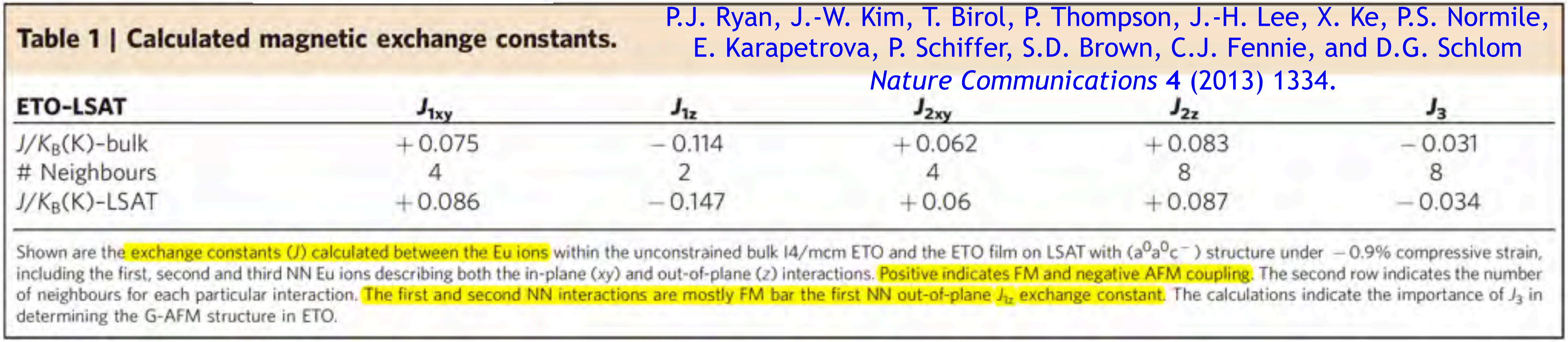
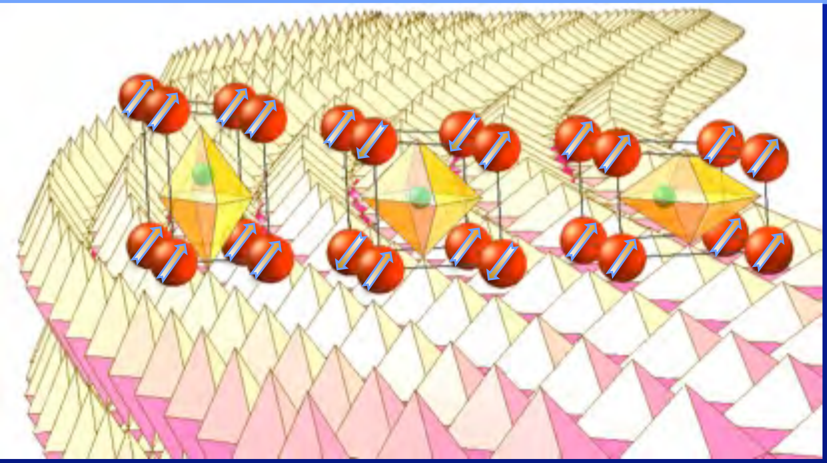


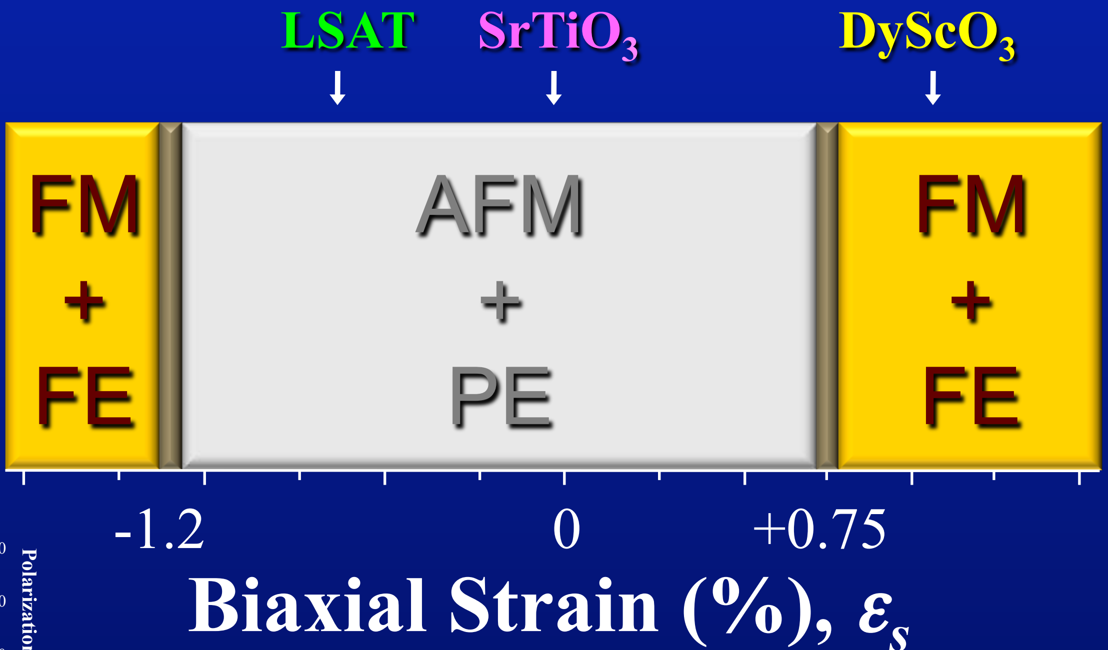
Table 1 | Calculated magnetic exchange constants.

ETO-LSAT	J_{1xy}	J_{1z}	J_{2xy}	J_{2z}	J_3
J/K_B(K)-bulk	+0.075	−0.114	+0.062	+0.083	−0.031
# Neighbours	4	2	4	8	8
J/K_B(K)-LSAT	+0.086	−0.147	+0.06	+0.087	−0.034

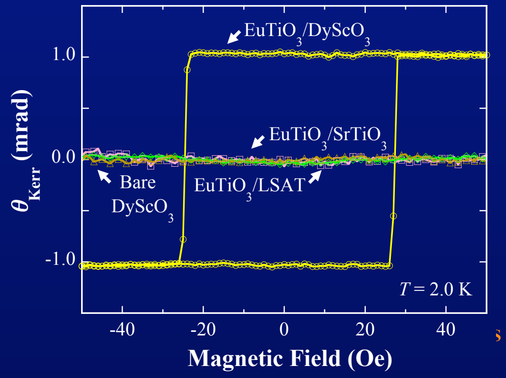
Shown are the exchange constants (J) calculated between the Eu ions within the unconstrained bulk I4/mcm ETO and the ETO film on LSAT with ($a^0a^0c^-$) structure under −0.9% compressive strain, including the first, second and third NN Eu ions describing both the in-plane (xy) and out-of-plane (z) interactions. Positive indicates FM and negative AFM coupling. The second row indicates the number of neighbours for each particular interaction. The first and second NN interactions are mostly FM bar the first NN out-of-plane J_{1z} exchange constant. The calculations indicate the importance of J_3 in determining the G-AFM structure in ETO.

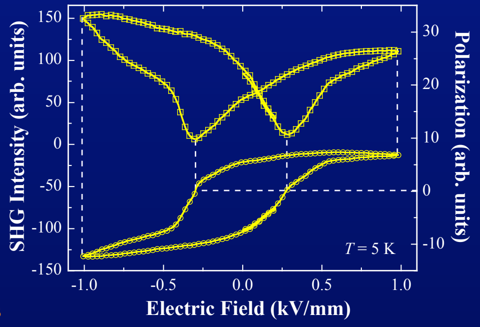
Strained $EuTiO_3$—Strongest Ferromagnetic Ferroelectric





C.J. Fennie and K.M. Rabe
Physical Review Letters **97** (2006) 267602.

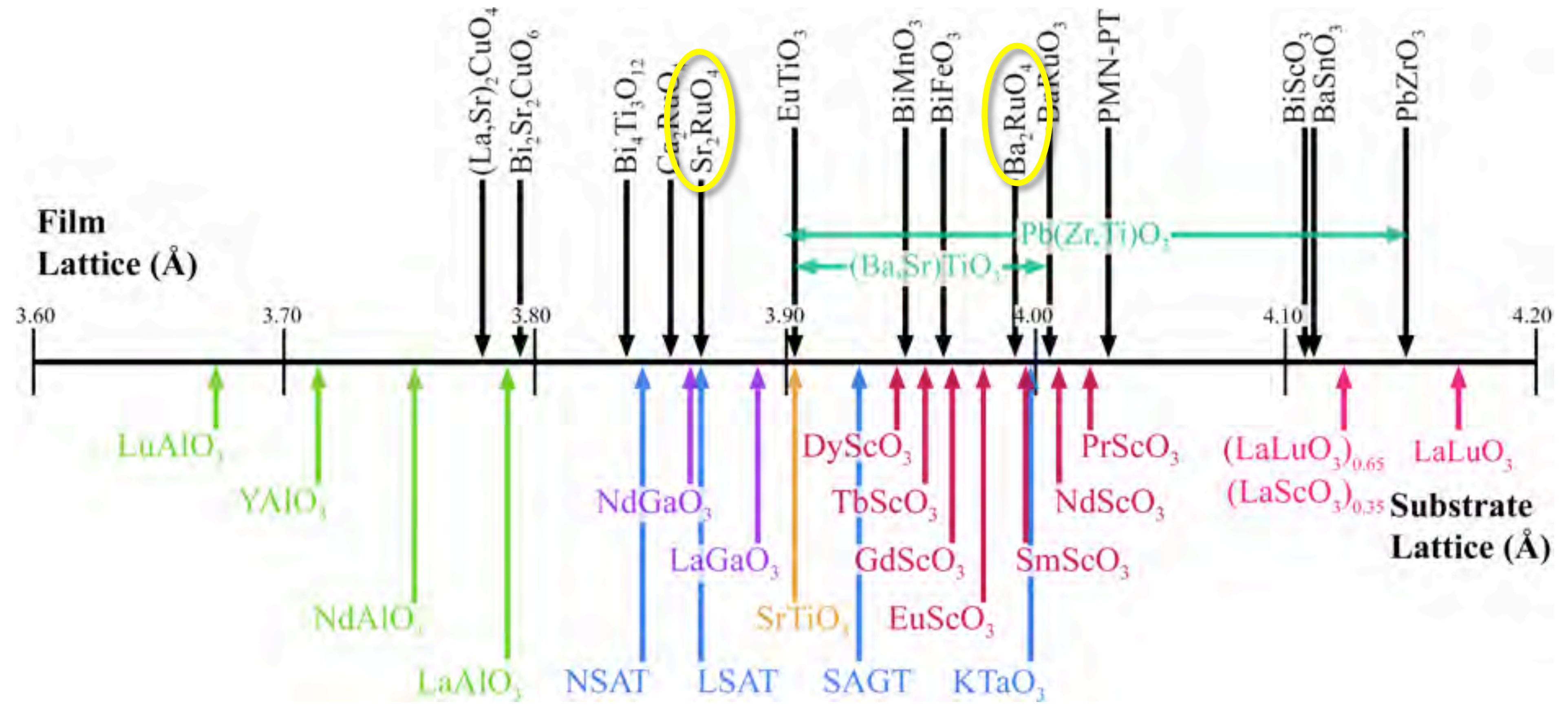


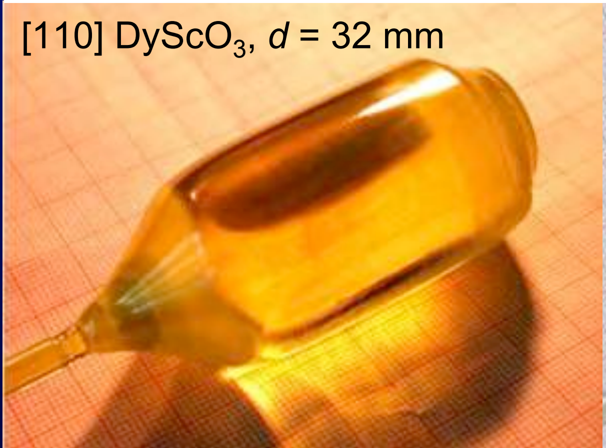


22 nm thick $EuTiO_3$ (a boring dielectric) **+ 1.1% Strain** (by growing it commensurately) **= Multiferroic** (1000× stronger than prior ferromagnetic ferroelectrics)

J.H. Lee, L. Fang, E. Vlahos, X. Ke, Y.W. Jung, L.F. 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.

Commercial Perovskite Substrates





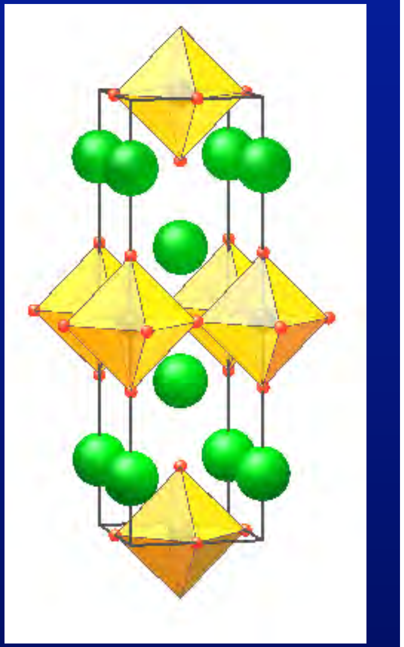
[110] $DyScO_3$, *d* = 32 mm

[110] $GdScO_3$, *d* = 32 mm

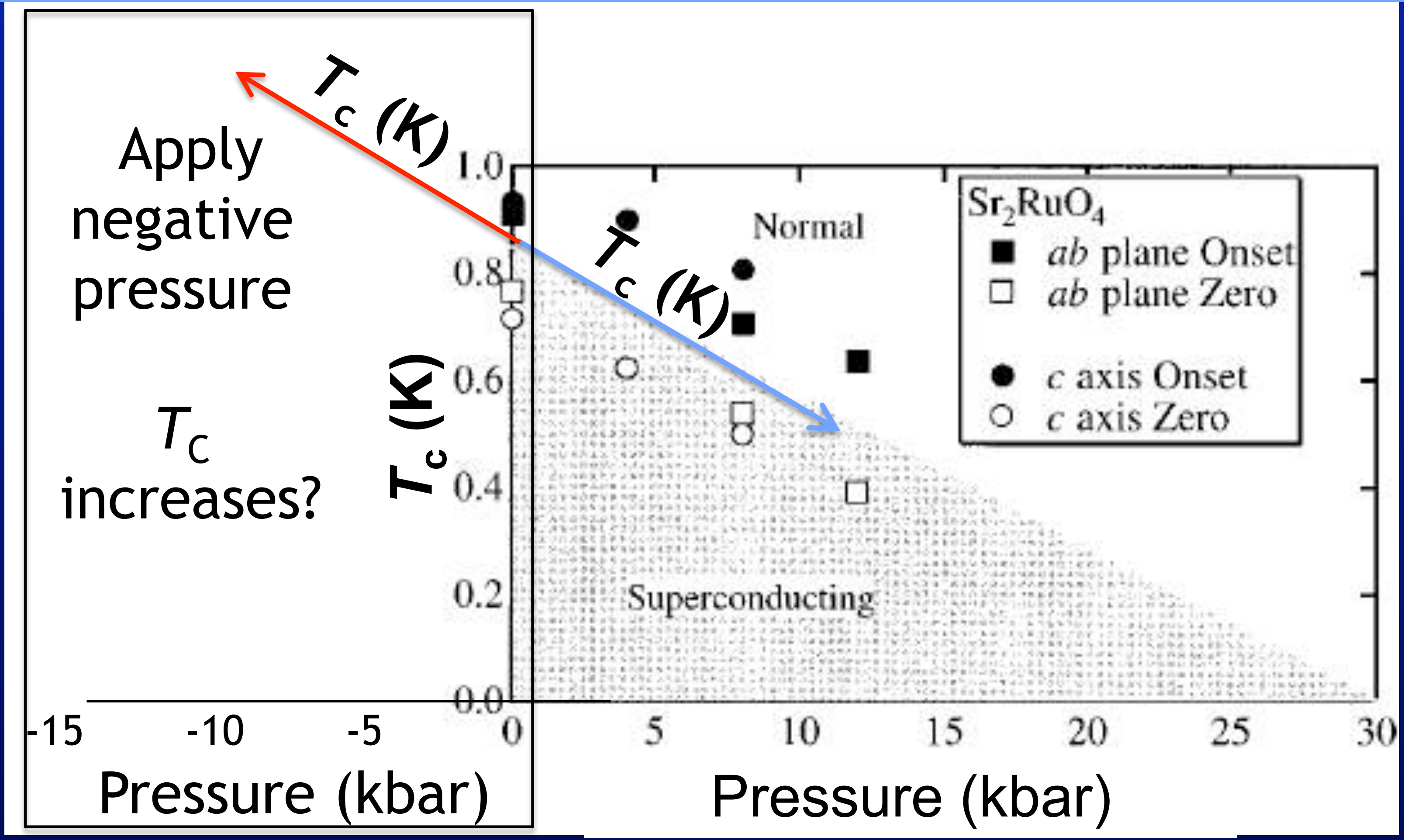
D.G. Schlom, L.Q. Chen, C.J. Fennie,
V. Gopalan, D.A. Muller, X.Q. Pan,
R. Ramesh, and R. Uecker,
"Elastic Strain Engineering
of Ferroic Oxides,"
MRS Bulletin **39** (2014) 118-130.

Effect of Strain on Sr_2RuO_4 (a spin-triplet superconductor)

Sr_2RuO_4



$n = 1$



Apply negative pressure

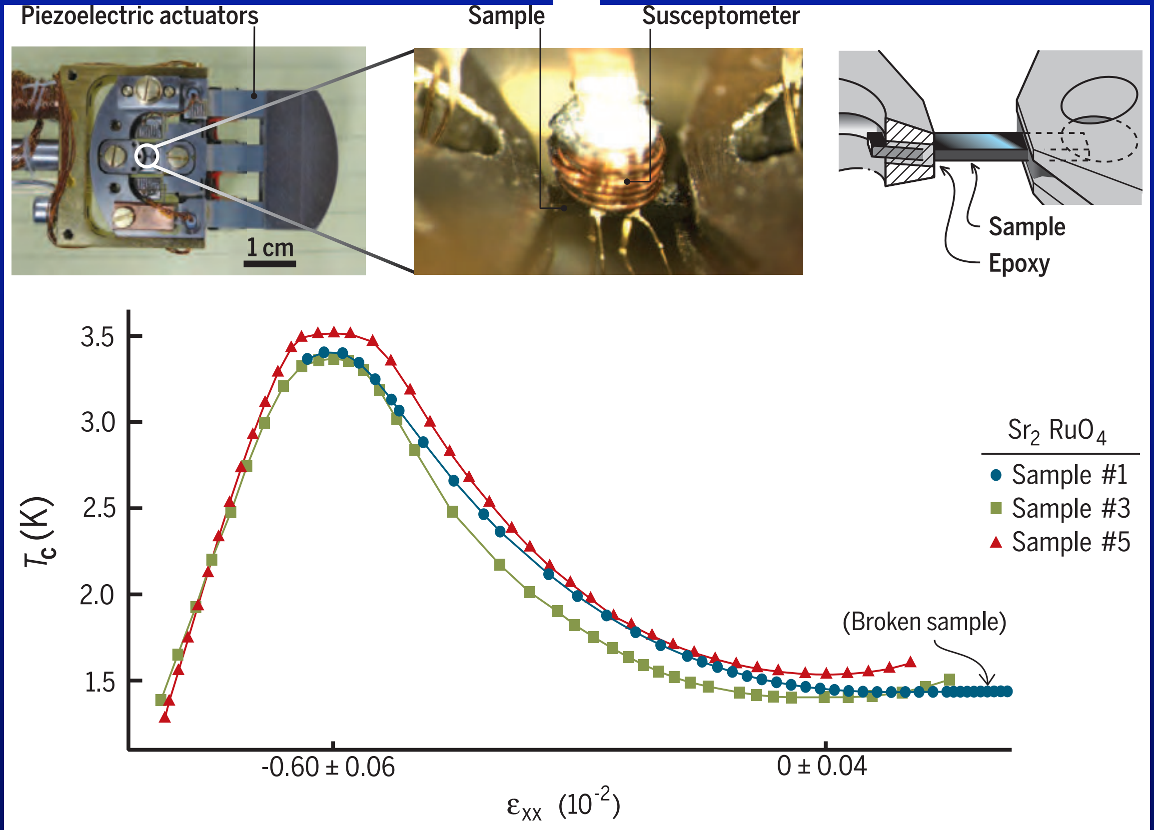
T_C increases?

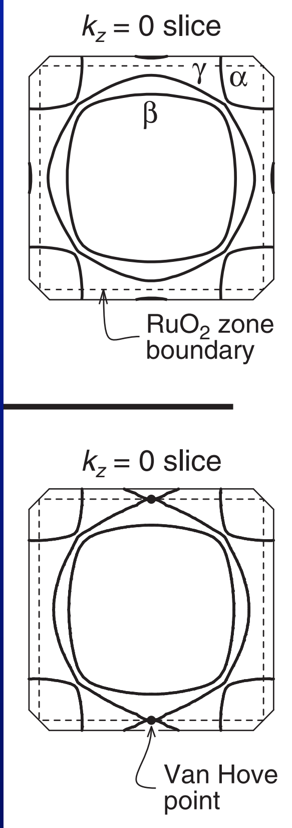
T_C goes down with increasing pressure

→ apply negative pressure

N. Shirakawa, K. Murata, S. Nishizaki, Y. Maeno, T. Fujita, *Phys. Rev. B* **56** (1997) 7890-7893.

In-plane Uniaxial Strain Dramatically Increases T_c in Sr_2RuO_4





$\varepsilon_{xx} = 0$

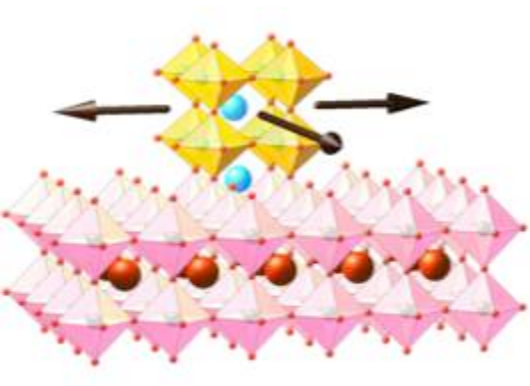
$\varepsilon_{xx} = -0.75\%$

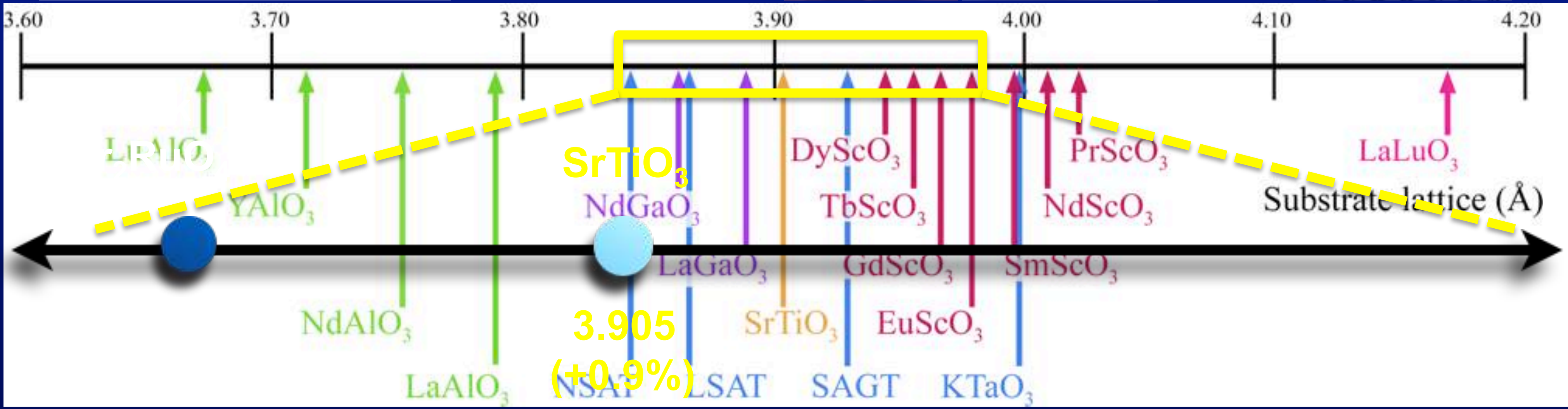
enhancements in T_c may be tied to proximity of van Hove singularity to E_F, but strains that can be applied to single crystal Sr_2RuO_4 are relatively modest (≤ 0.8%; $T_{c,max}$ of 3.4 K at 0.6% uniaxial compressive strain)

C.W. Hicks, D.O. Brodsky, E.A. Yelland, A.S. Gibbs, J.A.N. Bruin, M.E. Barber, S.D. Edkins, K. Nishimura, S. Yonezawa, Y. Maeno, and A.P. Mackenzie, *Science* **344** (2014) 283–285.

A. Steppke, L. Zhao, M.E. Barber, T. Scaffidi, F. Jerzembeck, H. Rosner, A.S. Gibbs, Y. Maeno, S.H. Simon, A.P. Mackenzie, and C.W. Hicks, *Science* **355**, 9398 (2017).

Much Larger Elastic Strains are Possible in Epitaxial Thin Films

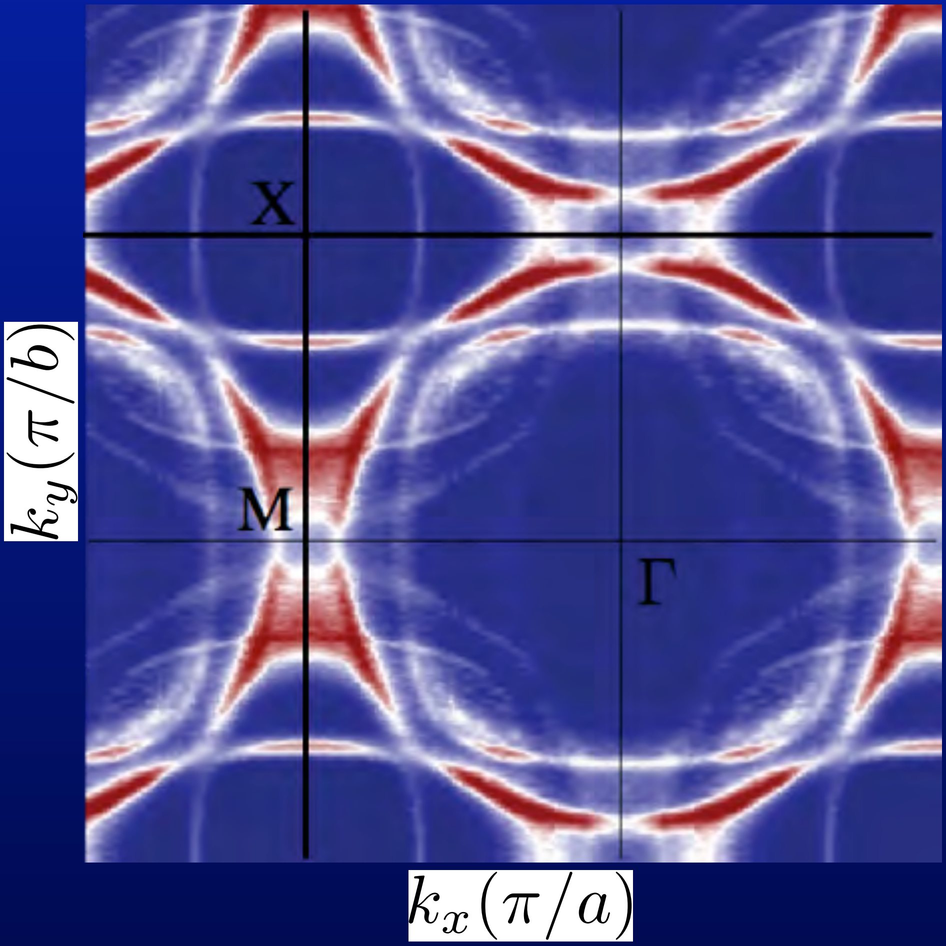




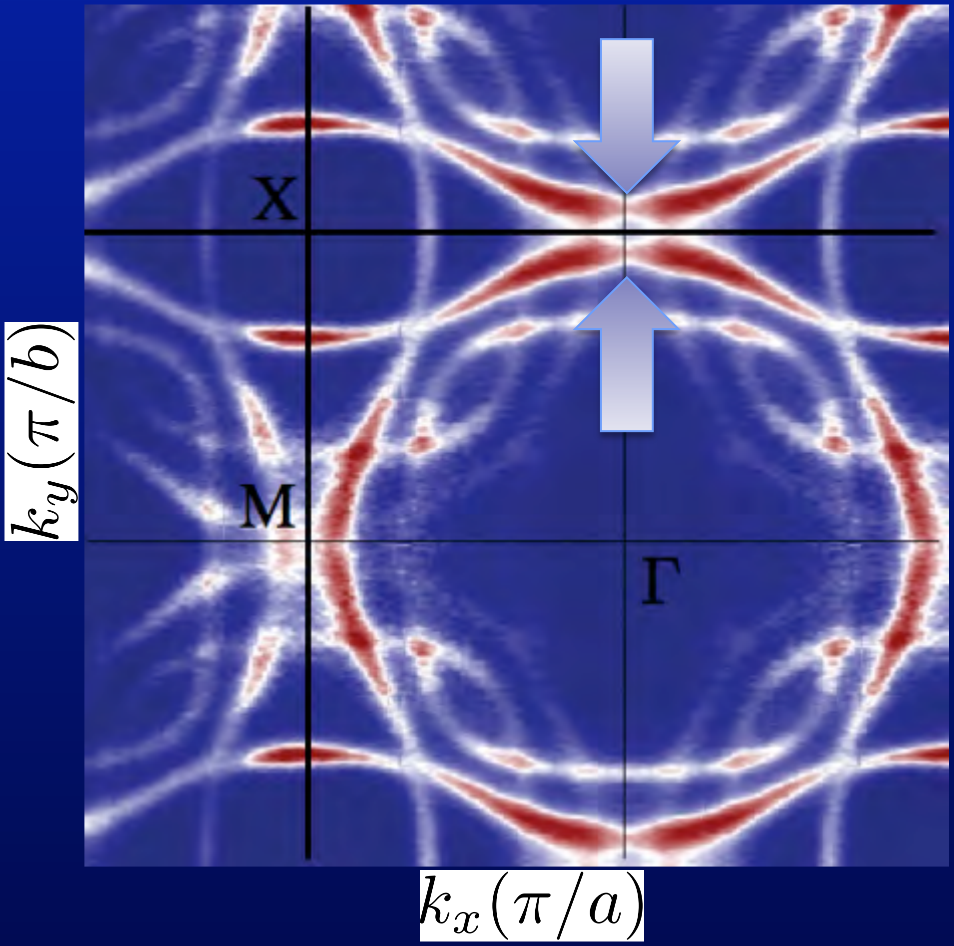
In-Plane Lattice Constant (Å)

Strain Control of Fermi Surface in Sr_2RuO_4

Unstrained Sr_2RuO_4

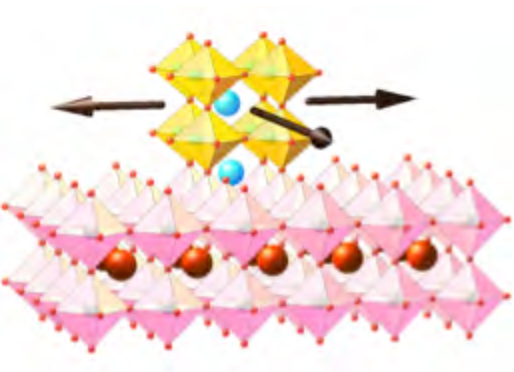


Sr_2RuO_4 on $SrTiO_3$ (+0.9%)

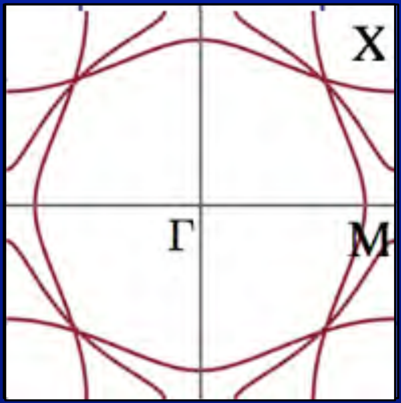


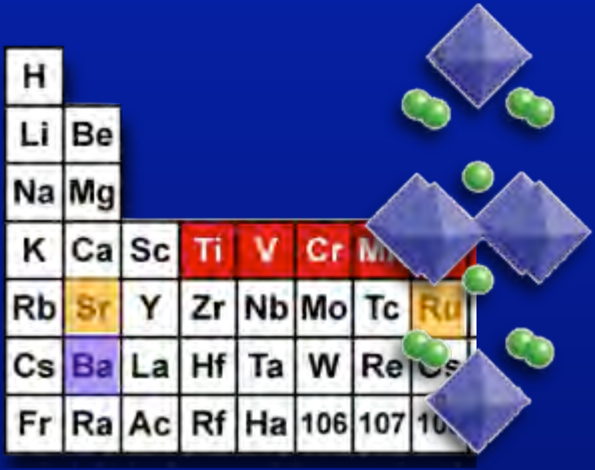
thin films still non-superconducting due to extreme sensitivity of spin-triplet SC to disorder, but low resistivities (5 μΩ·cm)

Pushing to Higher "strains" using Epitaxial Stabilization of Ba_2RuO_4



Lifshitz transition





bulk Sr_2RuO_4 — 3.860

$SrTiO_3$ — 3.905 (+0.9%)

$DyScO_3$ — 3.942 (+2.1%)

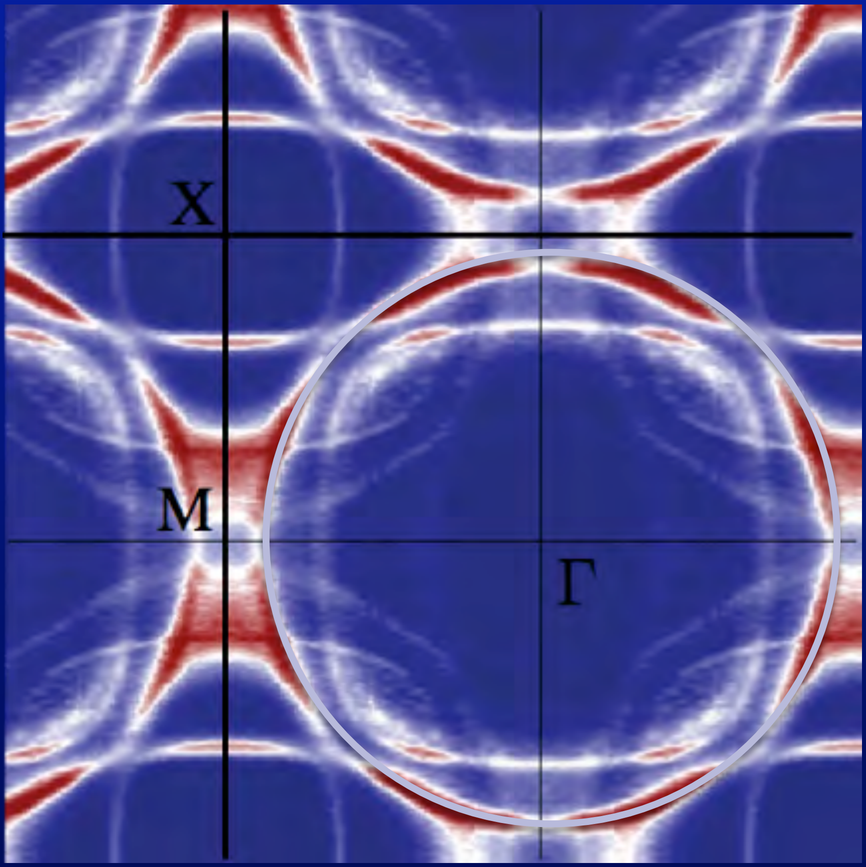
$GdScO_3$ — 3.960 (+2.6%)

In-Plane Lattice Constant (Å)

- Ba_2RuO_4 is isoelectronic and isostructural to Sr_2RuO_4
- Metastable in bulk, but can be epitaxially stabilized

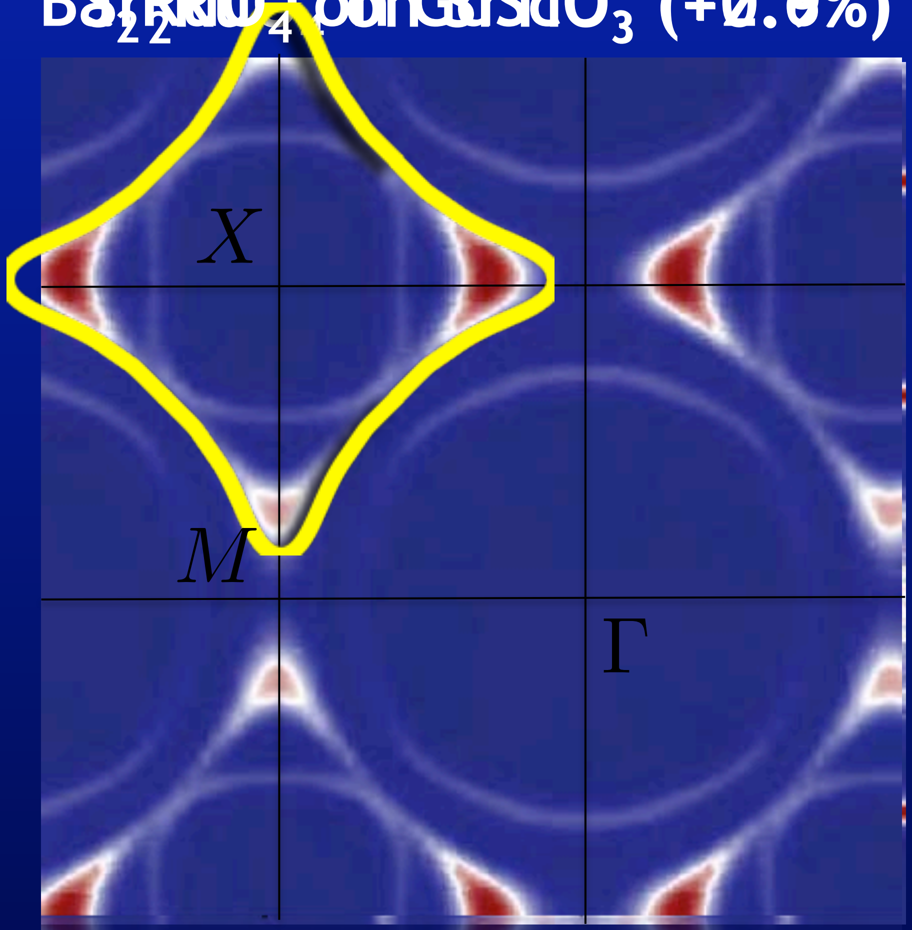
Strain Control of Fermi Surface in Sr_2RuO_4

Unstrained Sr_2RuO_4



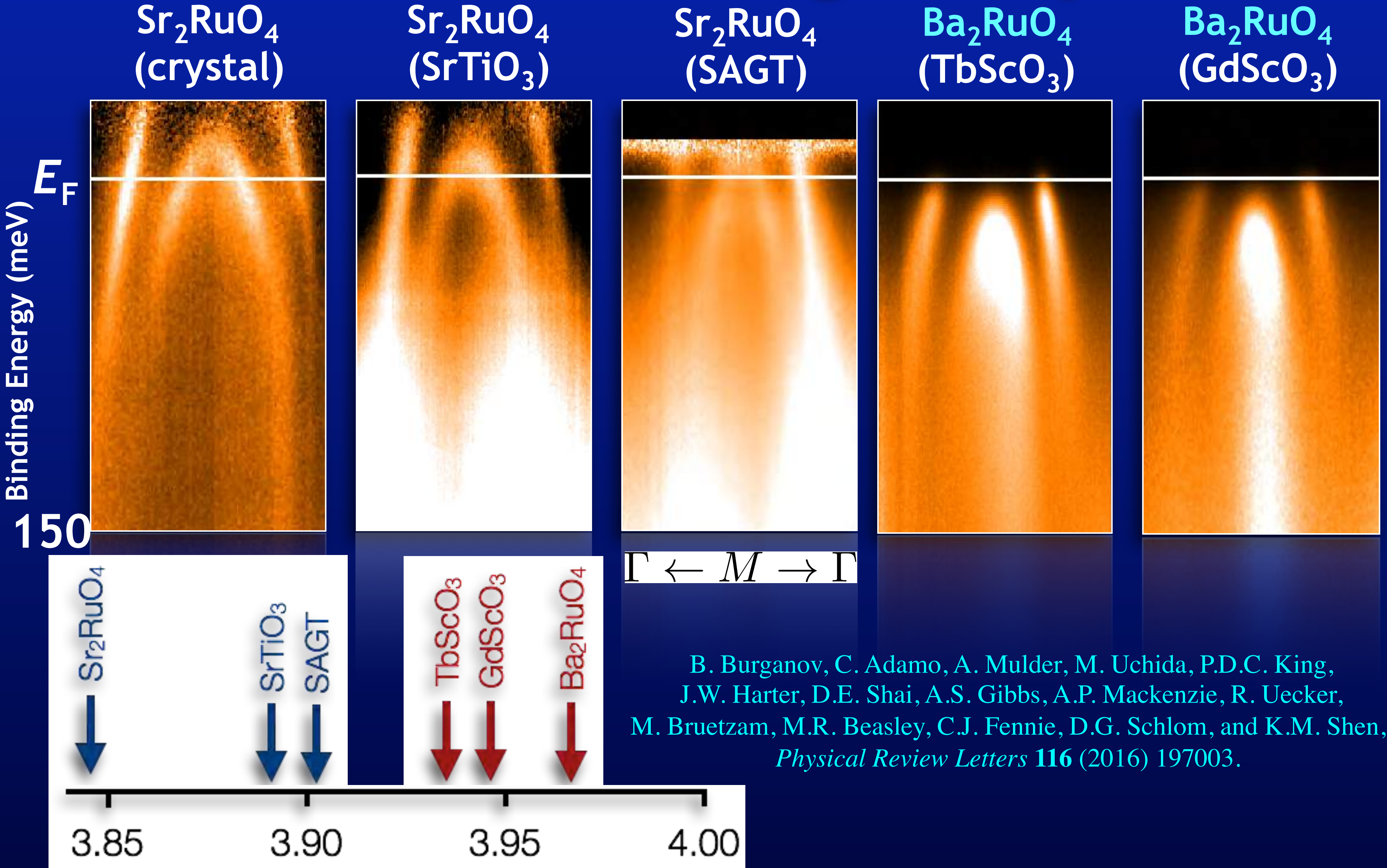
Ba_2RuO_4 on $GdScO_3$ (+2.0%)

Sr_2RuO_4 on $SrTiO_3$ (+0.6%)



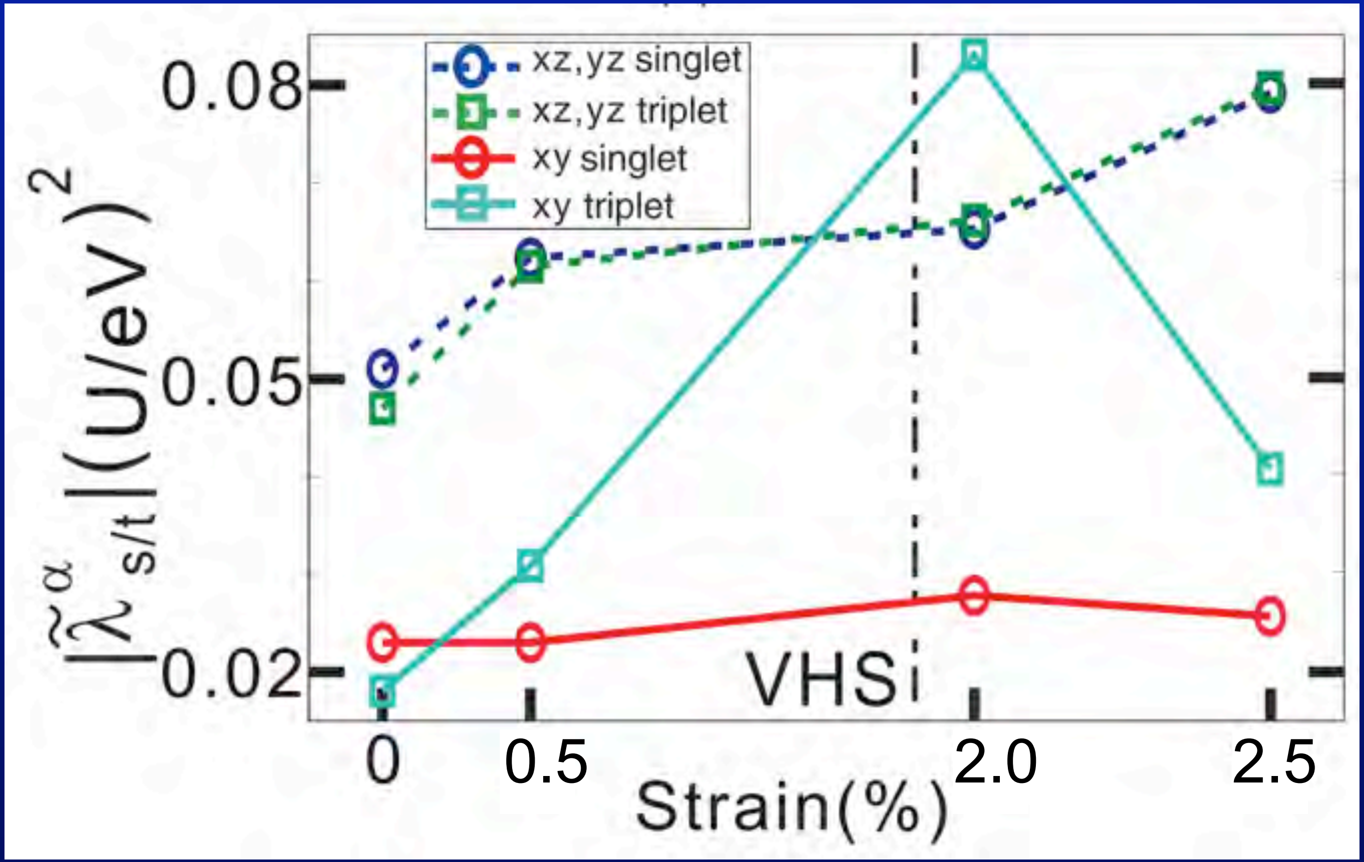
Large epitaxial strains turn the large electron-like Fermi surface closed around Γ to a hole-like Fermi surface closed around X

Strain Control of Band Structure and van Hove singularity



B. Burganov, C. Adamo, A. Mulder, M. Uchida, P.D.C. King, J.W. Harter, D.E. Shai, A.S. Gibbs, A.P. Mackenzie, R. Uecker, M. Bruetzam, M.R. Beasley, C.J. Fennie, D.G. Schlom, and K.M. Shen, *Physical Review Letters* **116** (2016) 197003.

Theory Predicts Enhancement of Spin-triplet Superconductivity

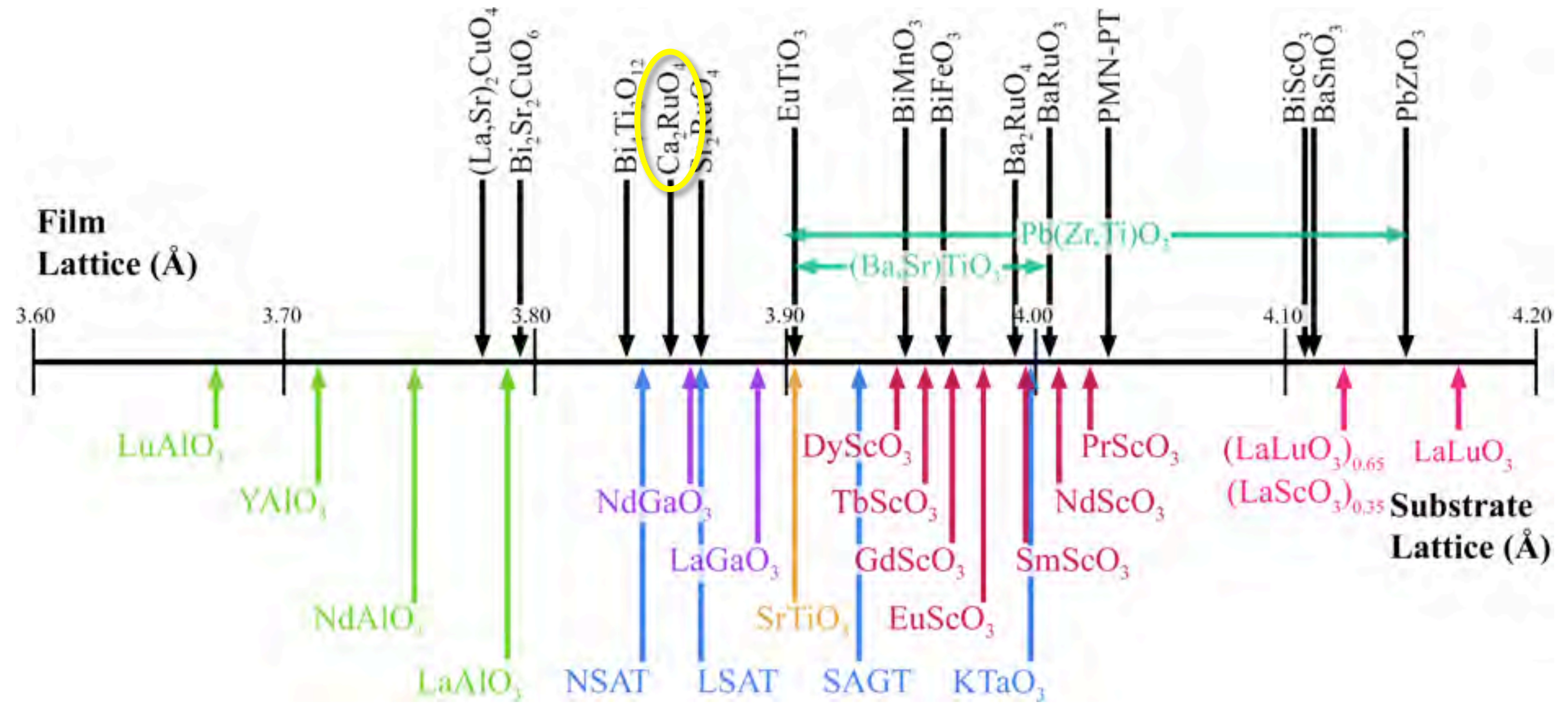


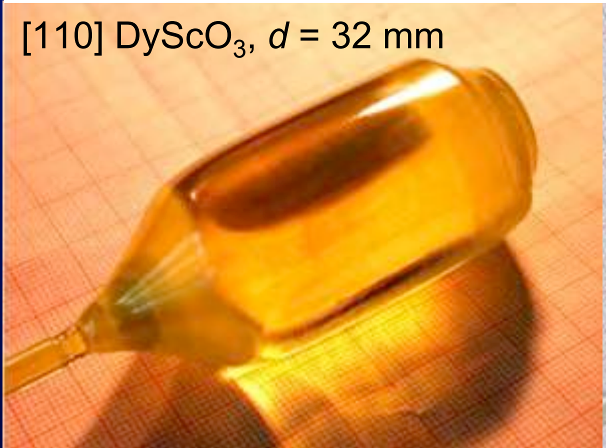
Eun-Ah Kim

Craig Fennie

Spin-triplet superconductivity is predicted to be strongly enhanced when the van Hove singularity is brought near the Fermi level (see arXiv:1604.06661)

Commercial Perovskite Substrates

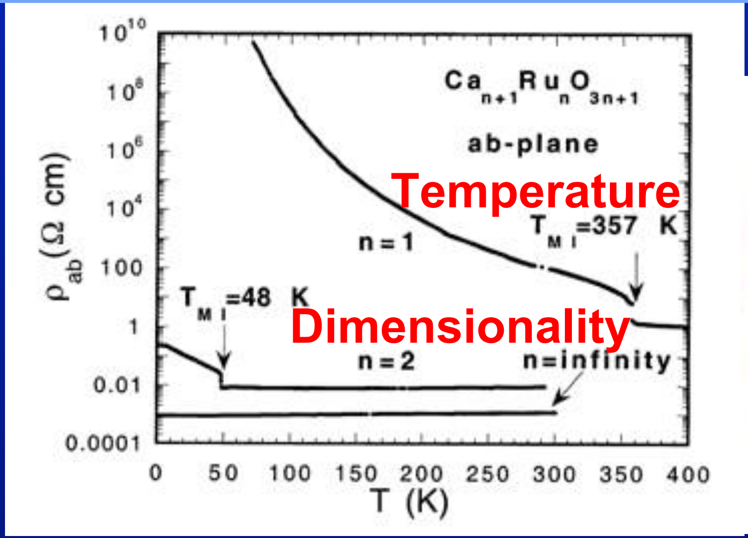



[110] $DyScO_3$, *d* = 32 mm

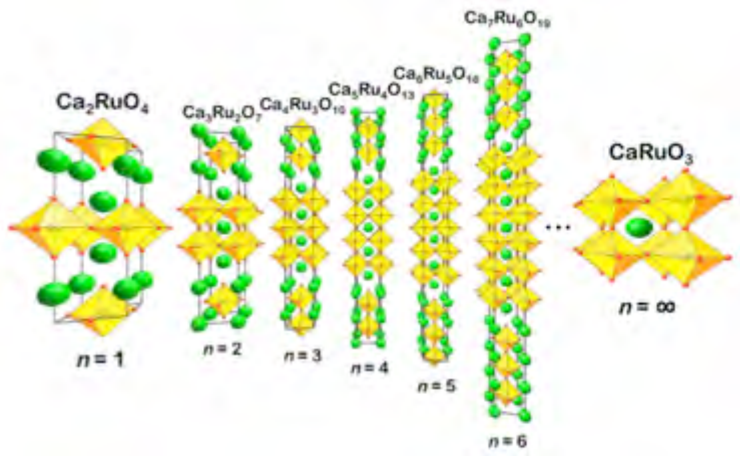

[110] $GdScO_3$, *d* = 32 mm

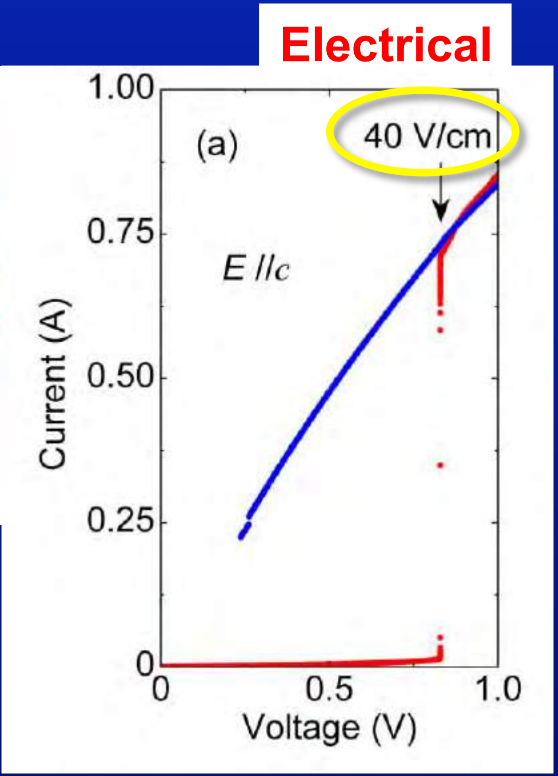
D.G. Schlom, L.Q. Chen, C.J. Fennie,
V. Gopalan, D.A. Muller, X.Q. Pan,
R. Ramesh, and R. Uecker,
"Elastic Strain Engineering
of Ferroic Oxides,"
MRS Bulletin **39** (2014) 118-130.

Ca_2RuO_4—a very Tunable System



G. Cao, C.S. Alexander, S. McCall, and
J.E. Crow, *Mater. Sci. Eng., B* **63** (1999) 76–82.

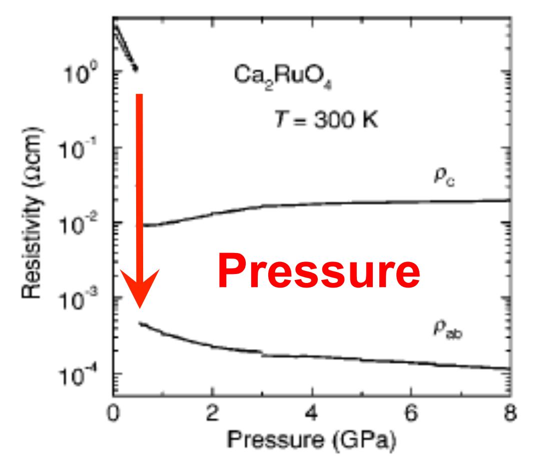




F. Nakamura, M. Sakaki,
Y. Yamanaka, S. Tamaru,
T. Suzuki, and Y. Maeno,
Sci. Rep. **3** (2013) 1–6.

Metal-Insulator Transition in Ca_2RuO_4 Triggered by

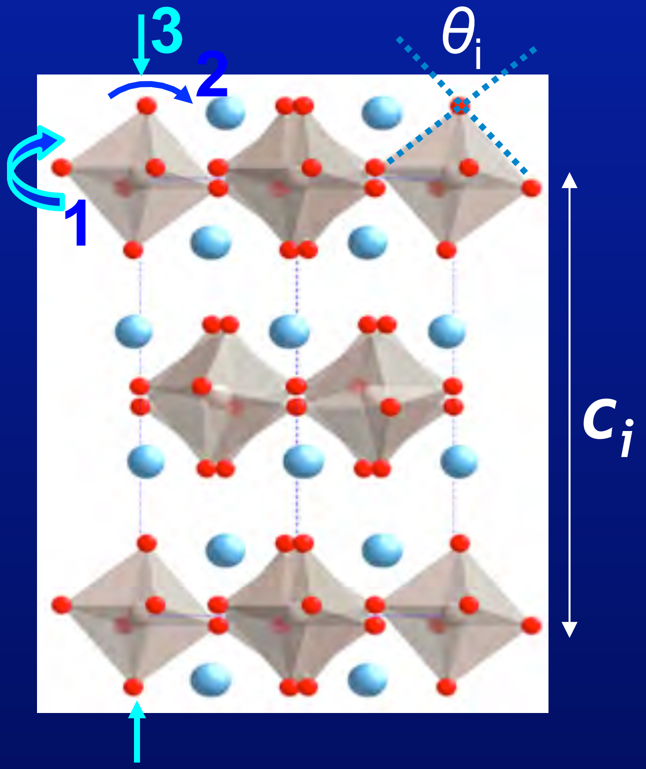
- **Temperature**
- **Dimensionality**
- **Pressure**
- **Voltage/current**



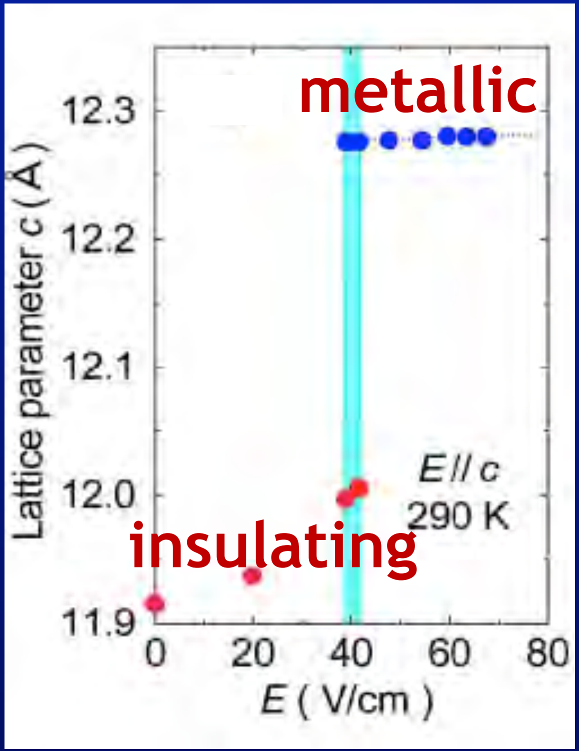
F. Nakamura, T. Goko, M. Ito, T. Fujita, S. Nakatsuji, H. Fukazawa,
Y. Maeno, P. Alireza, D. Forsythe, and S. R. Julian
Phys. Rev. B **65**, (2002) 220402.

Ca_2RuO_4—Phase Transition at T_{MIT}

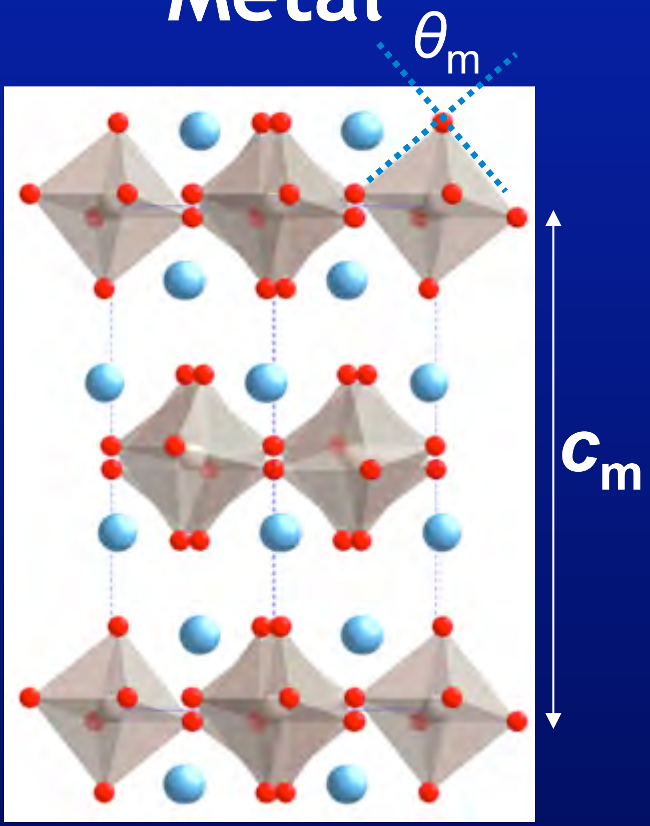
Insulator



F. Nakamura, M. Sakaki, Y. Yamanaka,
S. Tamaru, T. Suzuki, and Y. Maeno,
Sci. Rep. **3** (2013) 1–6.



Metal

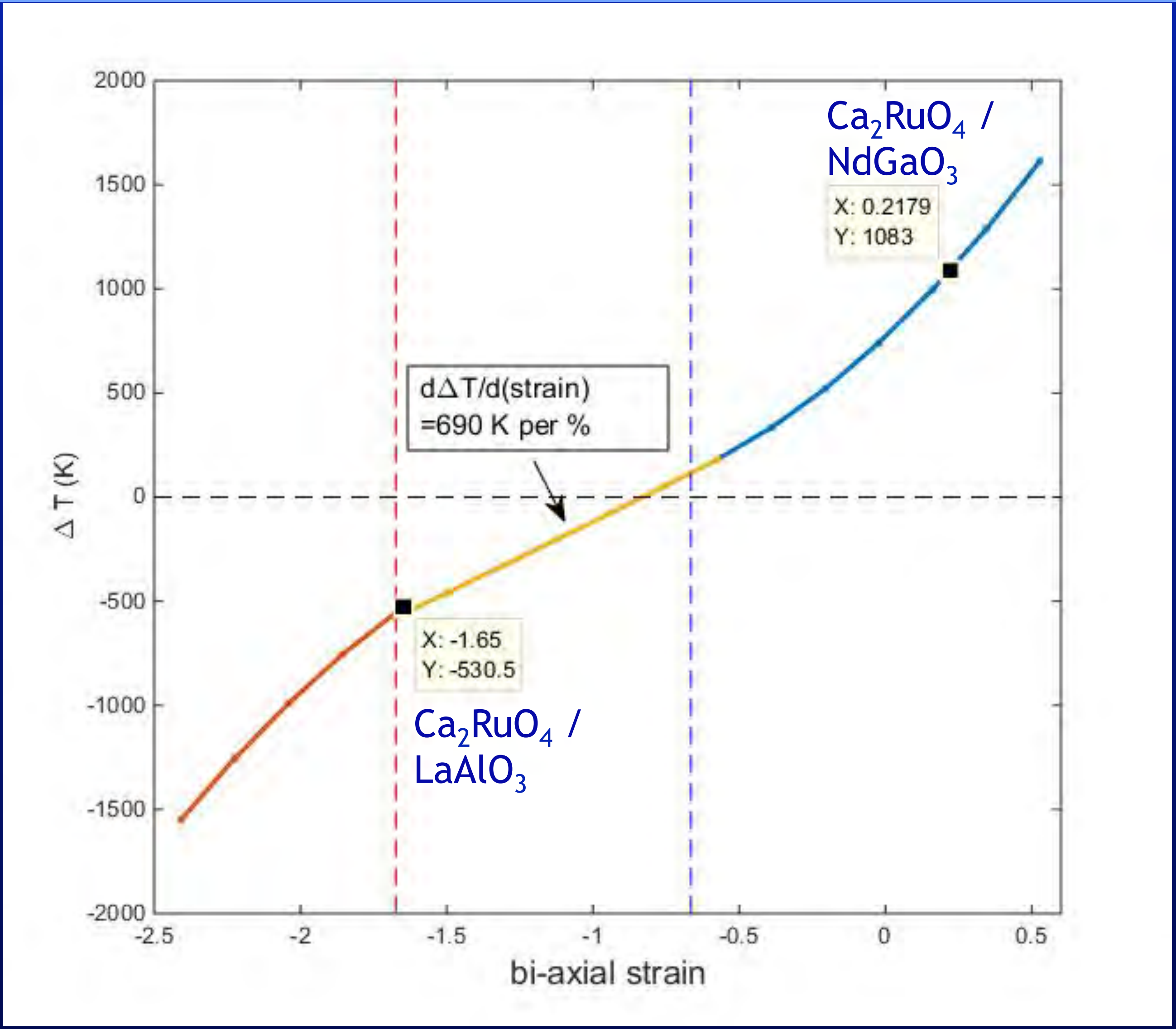


$\theta_i = 91.3^\circ$
$a = 5.410$ Å
$b = 5.492$ Å
$c = 11.96$ Å

$\theta_i > \theta_m$
$\Delta a = -0.9\%$
$\Delta b = -2.6\%$
$\Delta c = 2.5\%$

$\theta_m = 87.3^\circ$
$a = 5.361$ Å
$b = 5.351$ Å
$c = 12.26$ Å

Ca_2RuO_4—Effect of Strain on T_{MIT}

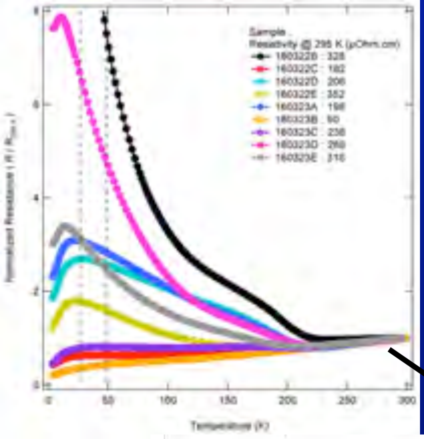


Andy Millis

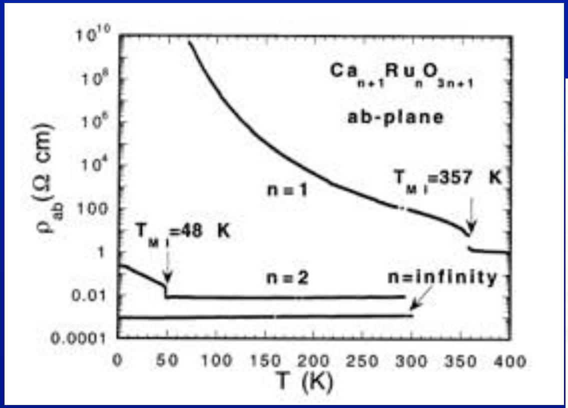
$$\frac{\partial T_{\mathrm{MIT}}}{\partial \varepsilon_{\mathrm{biaxial}}} = 69{,}000\ \mathrm{K}$$

Transport on Strained Ca_2RuO_4

Compressive

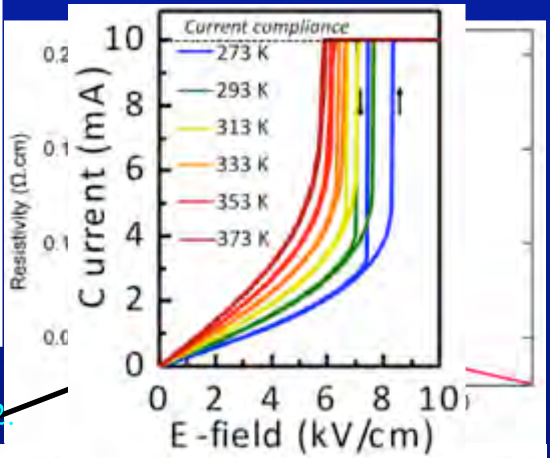


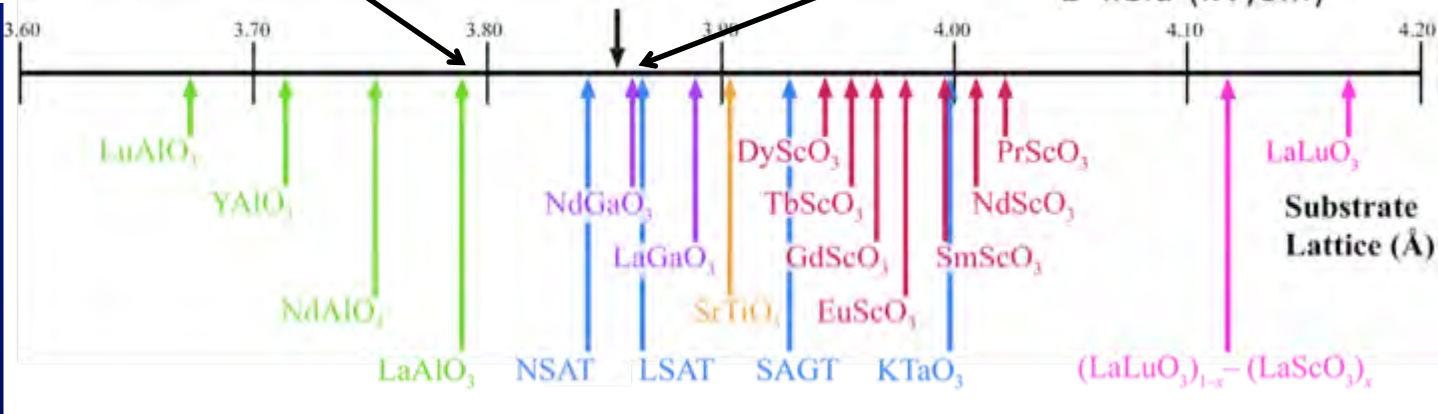
Bulk - unstrained



G. Cao, C.S. Alexander, S. McCall, and J.E. Crow, *Mater. Sci. Eng., B* **63** (1999) 76–82.

Tensile



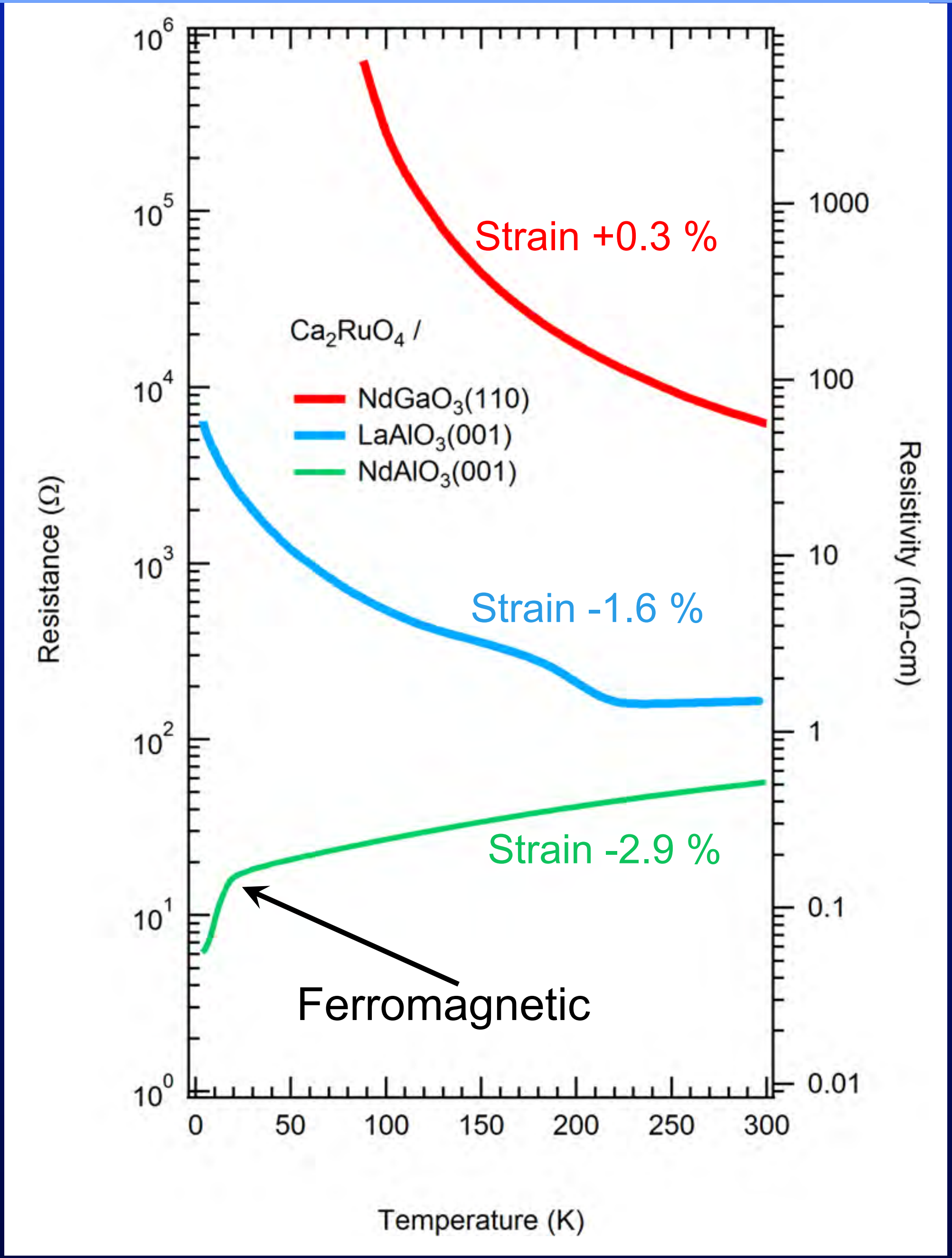


Bulk – T_{MIT} at 360 K

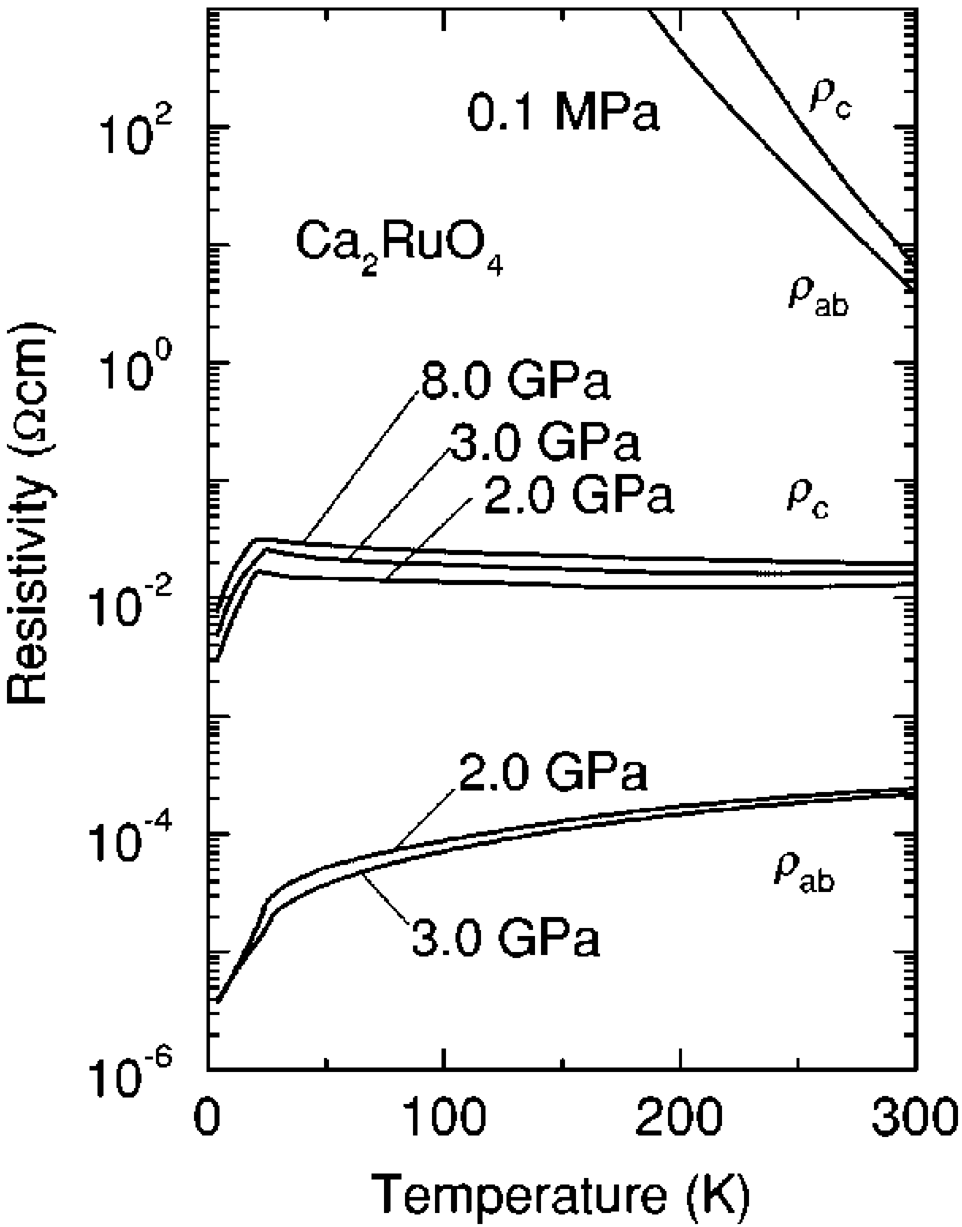
0.3% tensile – T_{MIT} above 650 K

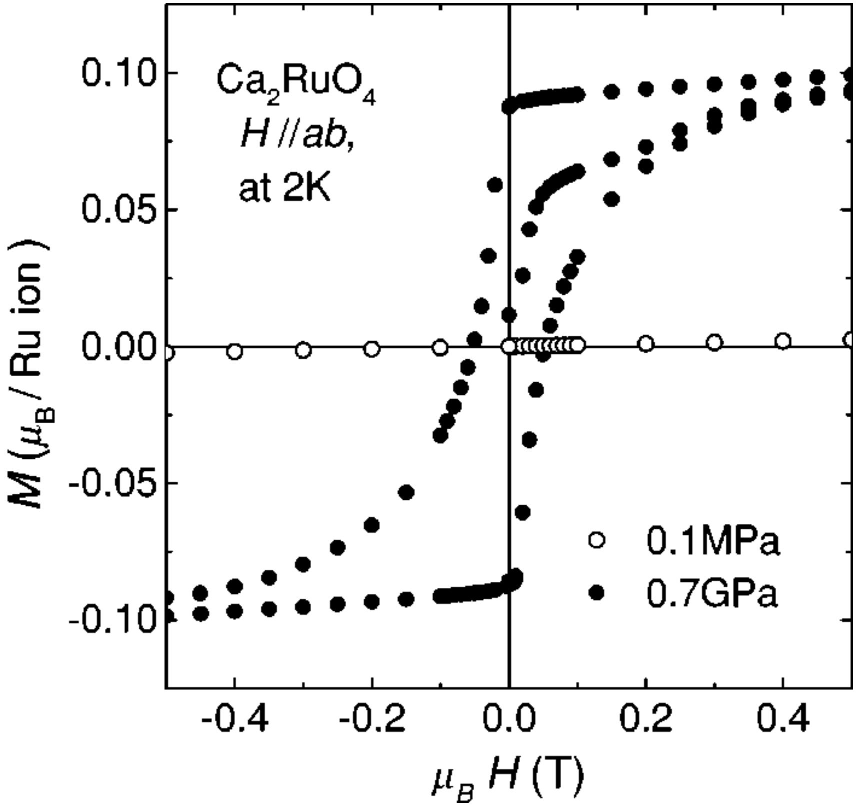
1.6% compressive – T_{MIT} suppressed or shifted to lower T

Transport on Strained Ca_2RuO_4



Ca_2RuO_4 under Hydrostatic Pressure





F. Nakamura, T. Goko, M. Ito, T. Fujita, S. Nakatsuji, H. Fukazawa, Y. Maeno, P. Alireza, D. Forsythe, and S. R. Julian, *Phys. Rev. B* **65** (2002) 220402.

Unleashing Hidden Properties

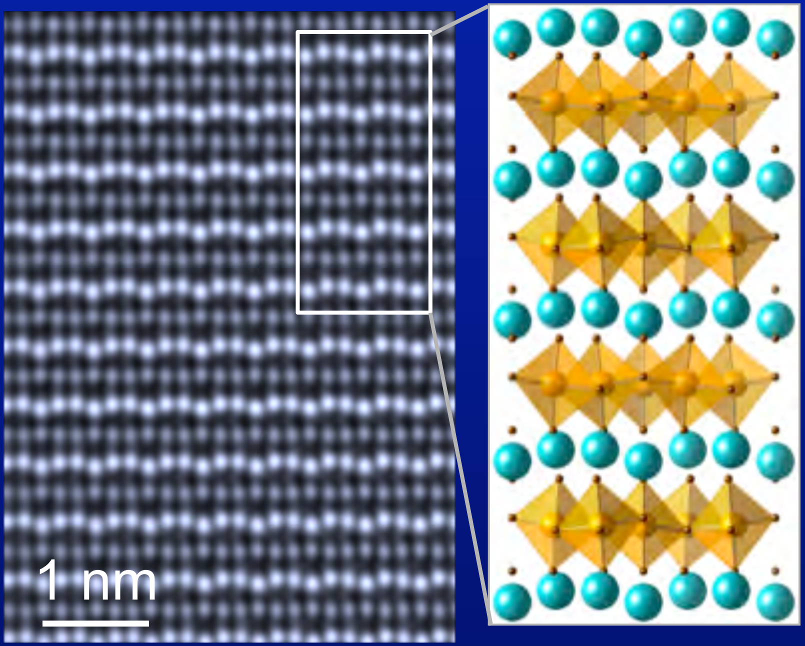
- Toolkit Enabling Materials-by-Design of Oxide Thin Films
- Ruthenates—$BaRuO_3$, $(Ca,Sr,Ba)_2RuO_4$ altering band structure and properties
- $EuTiO_3$
  strongest ferromagnetic ferroelectric
- $(LuFeO_3)_9$ / $(LuFe_2O_4)_1$ Superlattices
  strongest ferromagnetic ferroelectric at room temperature

Room-Temperature Multiferroics

Material	**M_s and P_s**	**T_N and T_C**	**Synthesis**
$BiFeO_3$	$M_s \sim 0.03\ \mu_B$/Fe $P_s \sim 95\ \mu C/cm^2$	$T_N \sim 643$ K $T_C \sim 1100$ K	
$BiCoO_3$	$M_s = 0$ (AFM) $P_{s,theory} \sim 170\ \mu C/cm^2$	$T_N \sim 470$ K $T_C > 520$ K	60,000 atm
$ScFeO_3$ (corundum polymorph)	$M_s \sim 0.01\ \mu_B$/Fe $P_{s,theory} \sim 3\ \mu C/cm^2$	$T_N \sim 356$ K $T_{C,theory} \sim 1300$ K	60,000 atm or Epitaxial Stabilization
$[(Ca_{0.6}Sr_{0.4})_{1.15}Tb_{1.85}Fe_2O_7]_{0.83}$ — $[Ca_3Ti_2O_7]_{0.17}$	$M_s \sim 0.009\ \mu_B$/Fe $P_{s,theory} \sim 10\ \mu C/cm^2$	$T_N \sim 330$ K $T_C \sim 430$ K	

The Idea: $(LuFeO_3)_m$ / $(LuFe_2O_4)_n$ Superlattices

$LuFeO_3$



Canted AFM, T_N ~ 147 K

Ferroelectric, T_C ~ 1050 K

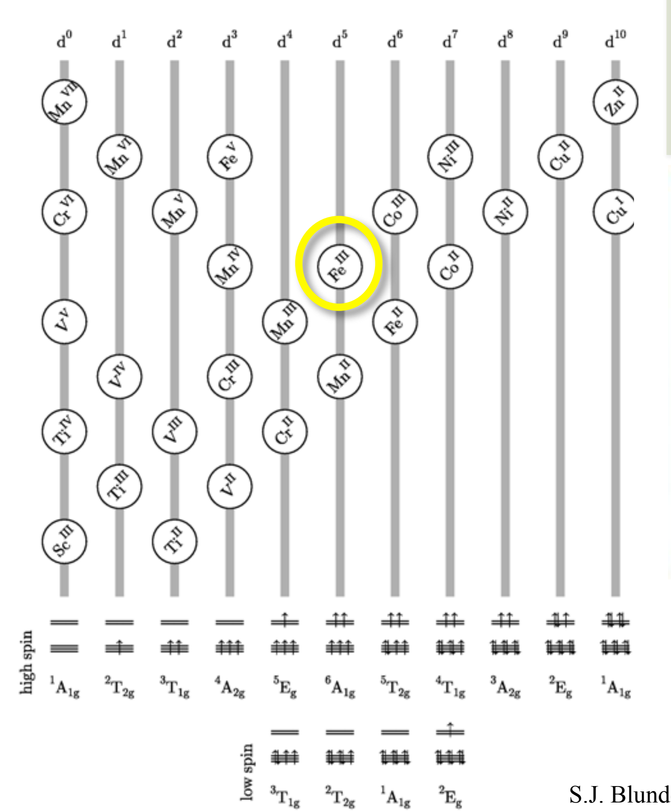
Bossak, A.A. *et al. Chem. Mater.* **16**, 1751 (2004

Wang, W. *et al. Phys. Rev. Lett.* **110,** 237601 (20

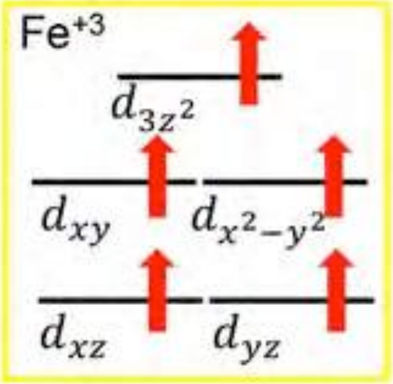
Moyer, J. A. *et al. APL Mater.* **2,** 12106 (2014).

Disseler, S. M. *et al. Phys. Rev. Lett.* **114,** 21760

H. Das, A. L. Wysocki, Y. Geng, W. Wu, and C. J. Fennie, “Bulk Magnetoelectricity in the Hexagonal Manganites and Ferrites,” *Nature Communications* 5, 2998 (2014).

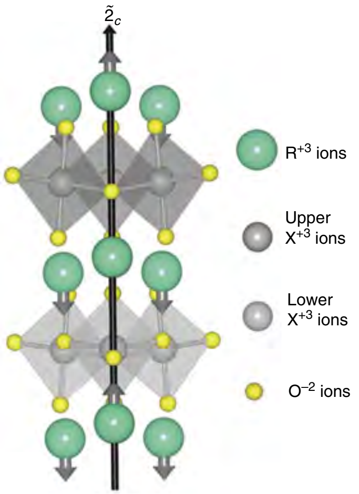


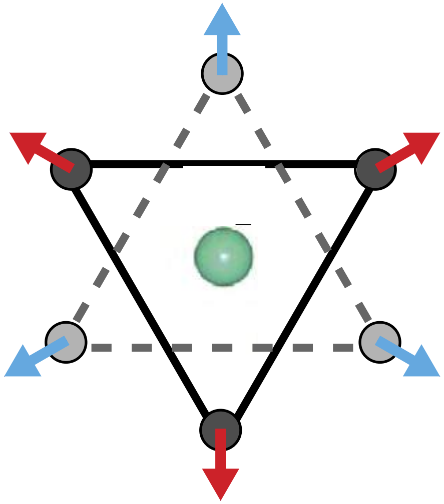
Transition metal (3d) ions



S.J. Blundell, Contemp. Phys. **48,** 275 (2007)

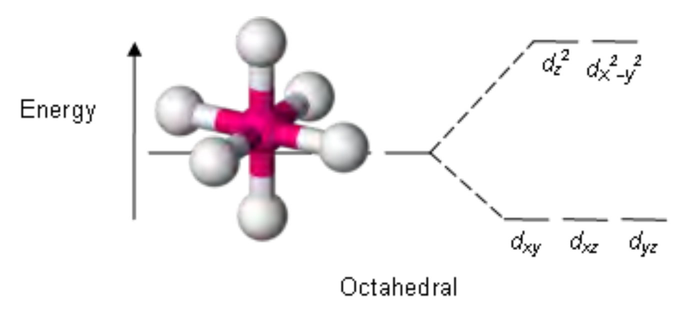
89



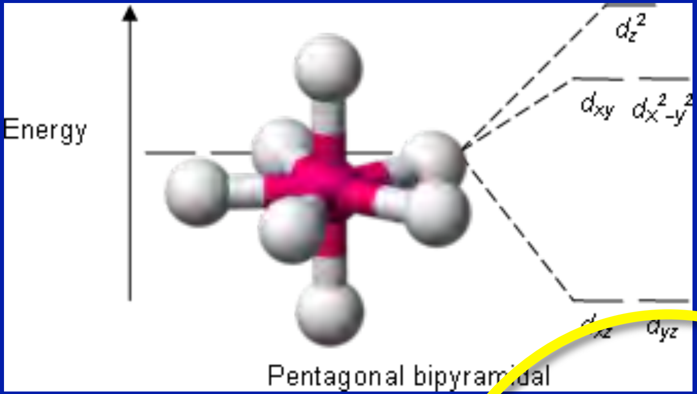


From Lecture #2

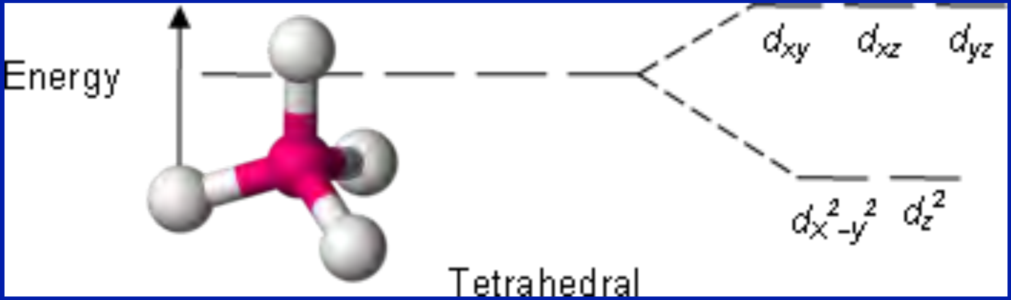
Other environments



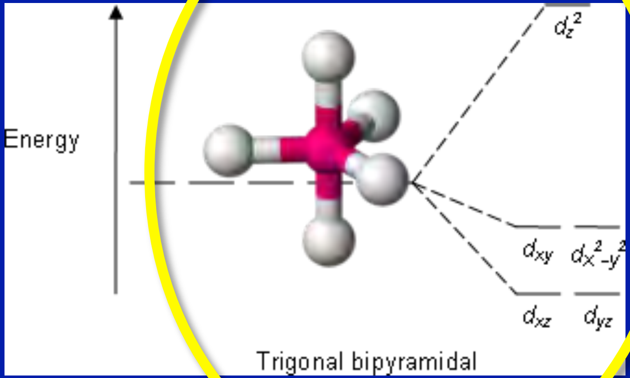
Octahedral



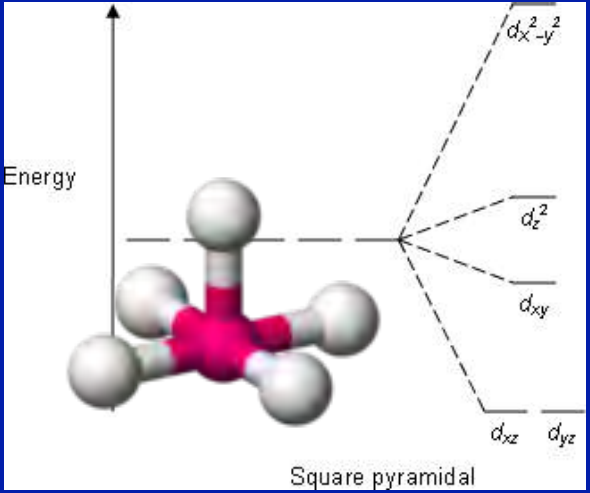
Pentagonal bipyramidal



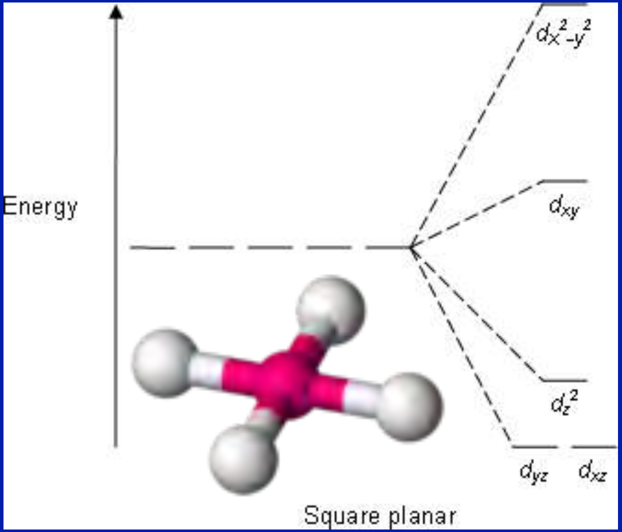
Tetrahedral



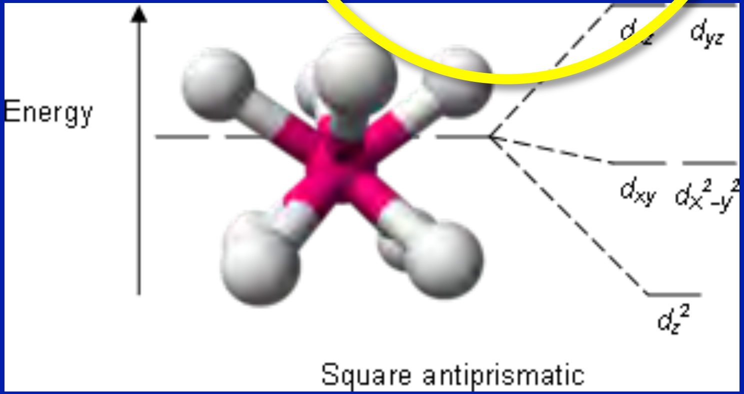
Trigonal bipyramidal



Square pyramidal



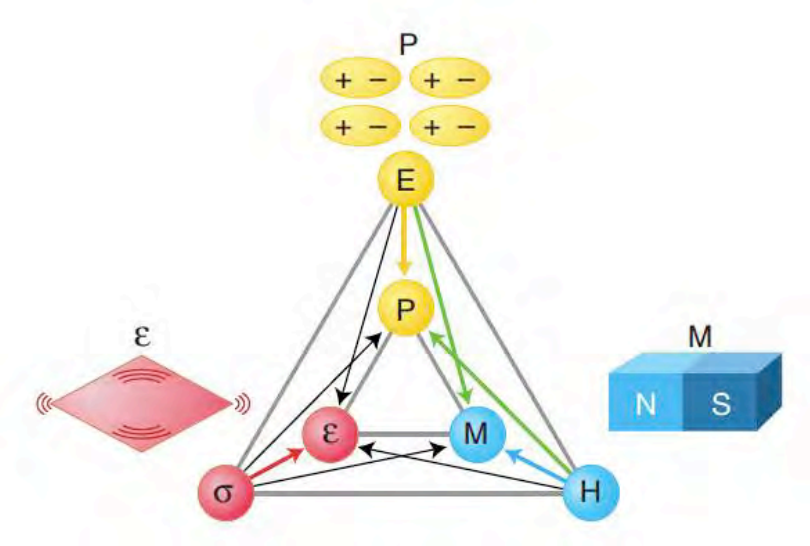
Square planar



Square antiprismatic

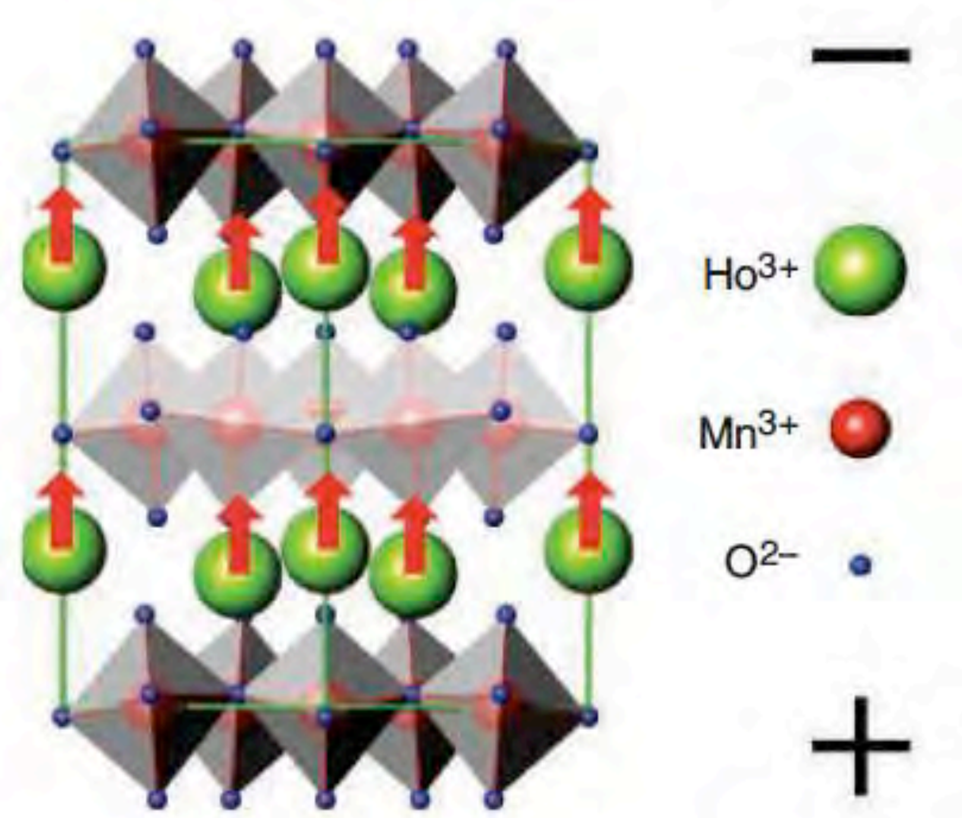
From Lecture #1

Ferroelectricity + Magnetism: *Multiferroics*



Phase control in ferroics and multiferroics. The electric field *E*, magnetic field *H*, and stress σ control the electric polarization *P*, magnetization *M*, and strain ε, respectively. In a ferroic material, *P*, *M*, or ε are spontaneously formed to produce ferromagnetism, ferroelectricity, or ferroelasticity, respectively. In a multiferroic, the coexistence of at least two ferroic forms of ordering leads to additional interactions. In a magnetoelectric multiferroic, a magnetic field may control *P* or an electric field may control *M* (green arrows).

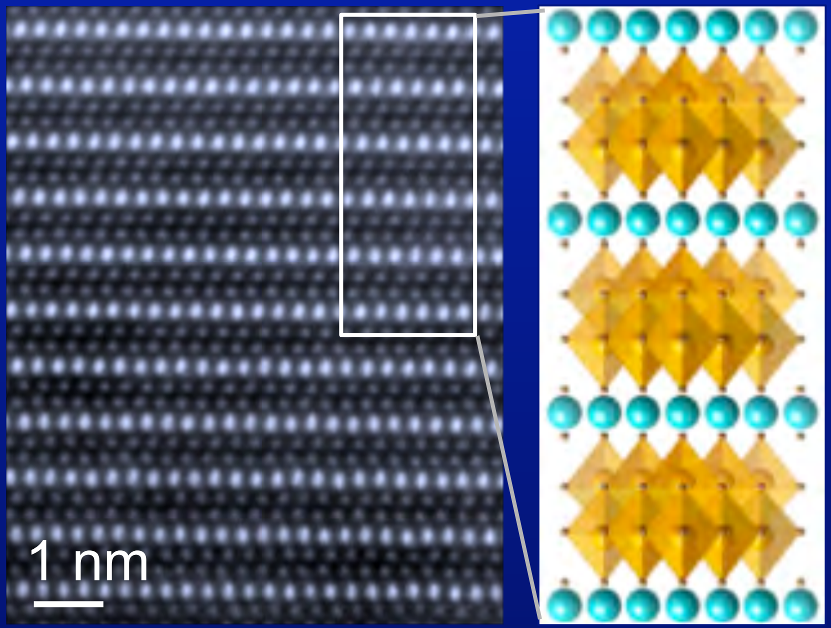
N.Spaldin, Science, 2005

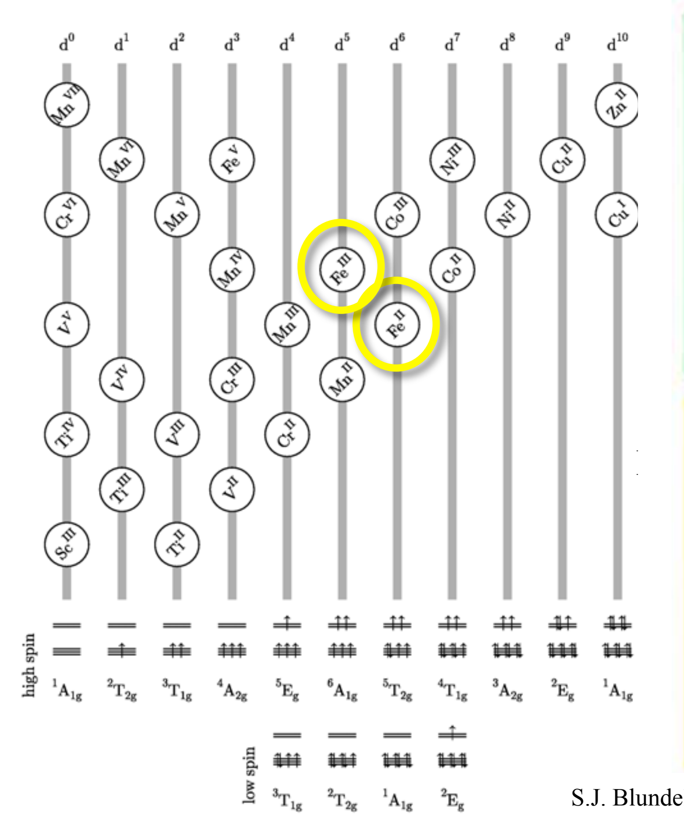


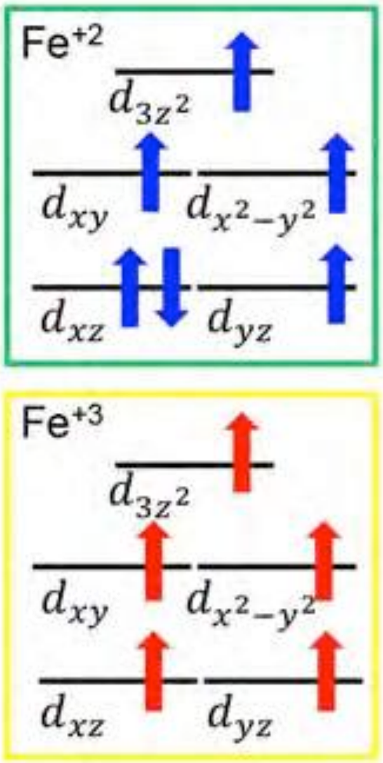
Structure of multiferroic HoMnO$_3$. Hexagonal HoMnO$_3$ is ferroelectric, because the oxygen bipyramids surrounding each Mn^{3+} ion are tilted and shifted relative to the Ho^{3+} ions. It is also magnetic, with ferromagnetic alignment of the Ho^{3+} magnetic moments combined with antiferromagnetic Mn^{3+} ordering. Therefore, hexagonal HoMnO$_3$ is multiferroic.

The Idea: $(LuFeO_3)_m$ / $(LuFe_2O_4)_n$ Superlattices

$LuFe_2O_4$







S.J. Blundell, Contemp. Phys. **48,** 275 (2007)

Ferrimagnetic, T_C ~ 240 K

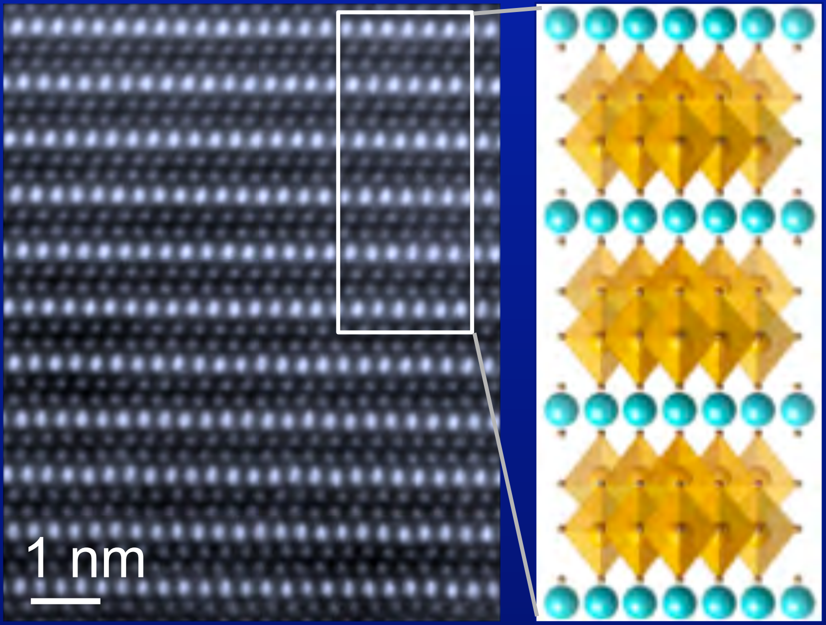
Ikeda, N. *et al. Nature* **436,** 1136–1138 (2005).
Iida, J. *et al. J. Phys. Soc. Jpn.* **62** (1993) 1723-1735.

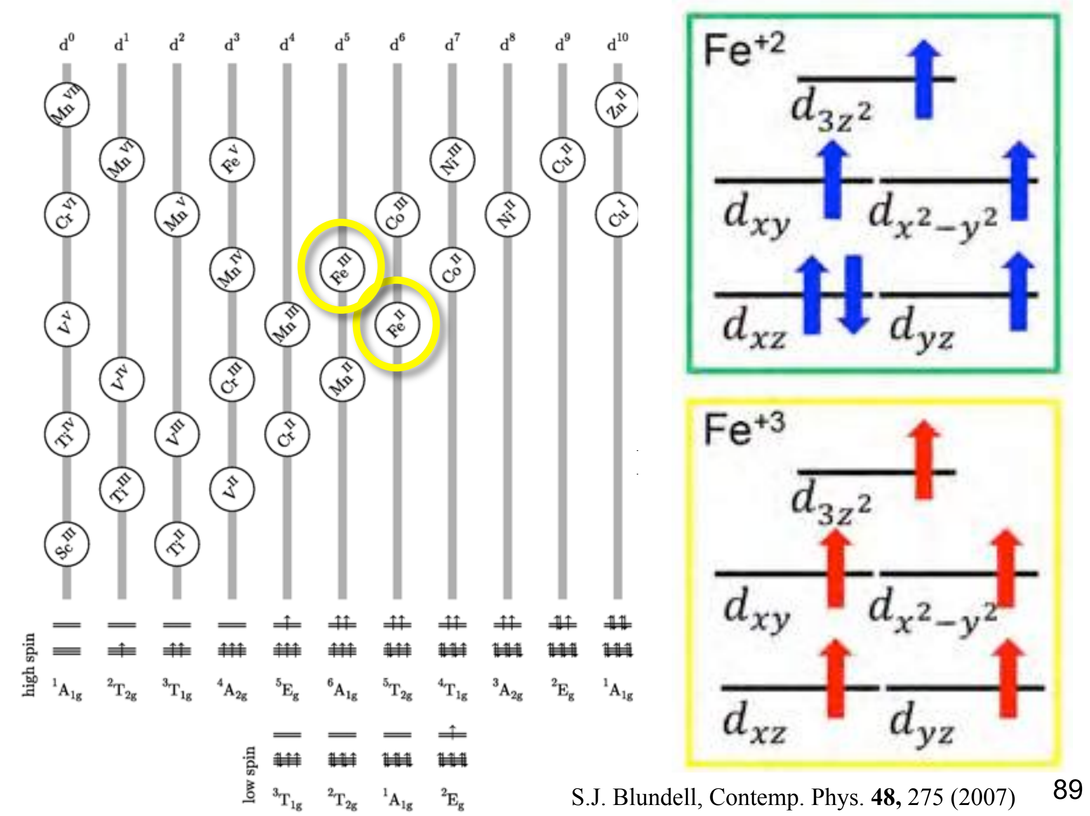
Non-Polar

De Groot, J. *et al. Phys. Rev. Lett.*
108, 187601 (2012).

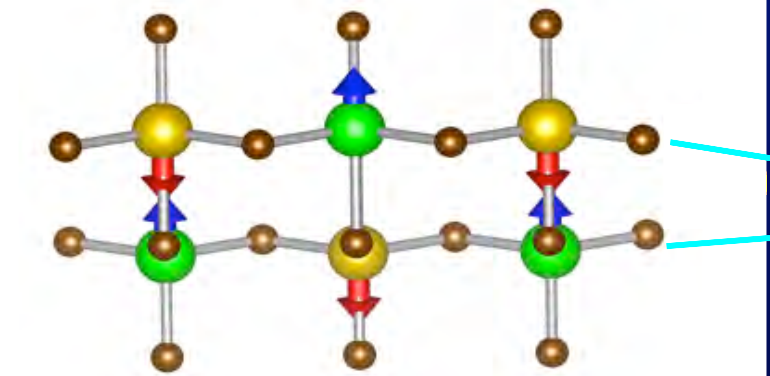
The Idea: $(LuFeO_3)_m$ / $(LuFe_2O_4)_n$ Superlattices

$LuFe_2O_4$





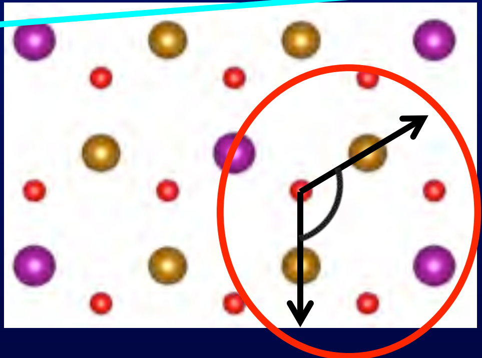
S.J. Blundell, Contemp. Phys. **48,** 275 (2007)



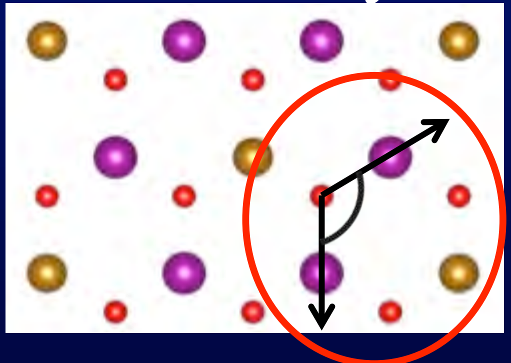
$$M = g\mu_B(3\underset{5/2}{S_{Fe^{3+}}} - 3\underset{4/2}{S_{Fe^{2+}}})/6 = 0.5\ \mu_B/Fe$$

In-plane interactions

top layer

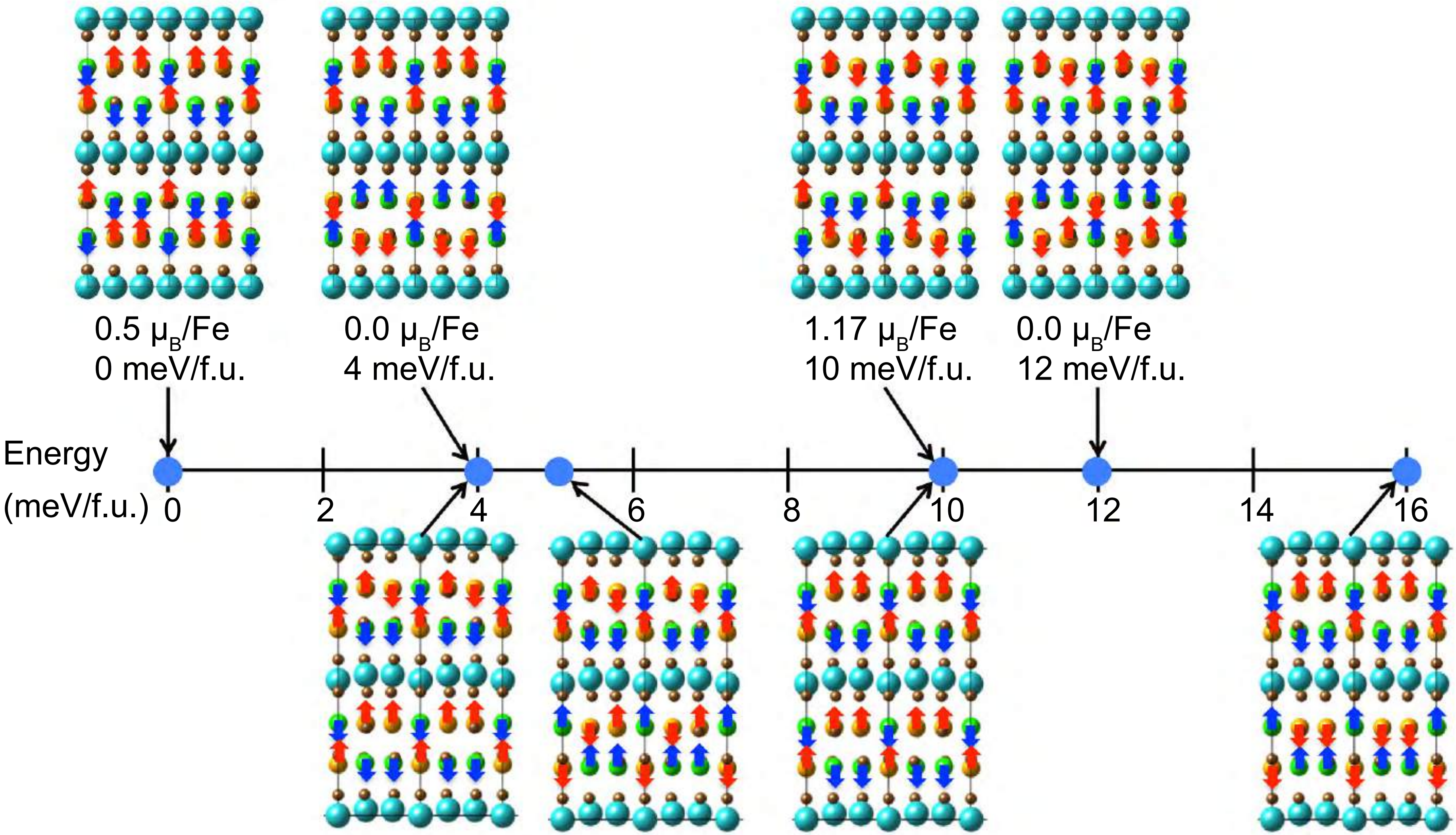


bottom layer



First-Principles DFT: $LuFe_2O_4$

Spin Configurations



Energy (meV/f.u.) 0 2 4 6 8 10 12 14 16

COI

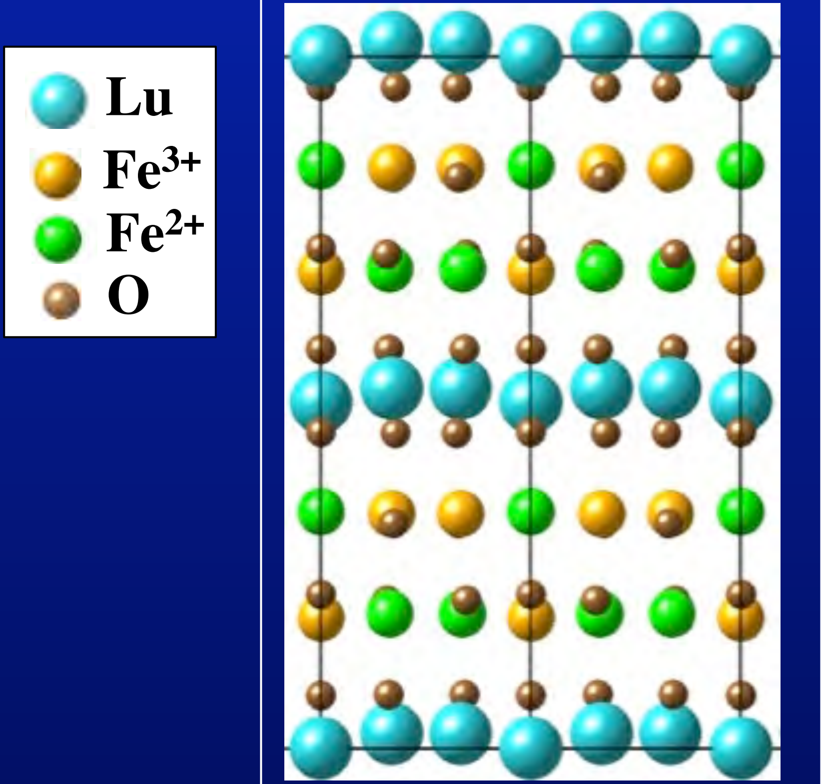
Magn.:	0.5 μ_B/Fe	0.0 μ_B/Fe	1.17 μ_B/Fe	0.0 μ_B/Fe
Energy:	0 meV/f.u.	4 meV/f.u.	10 meV/f.u.	12 meV/f.u.

COII

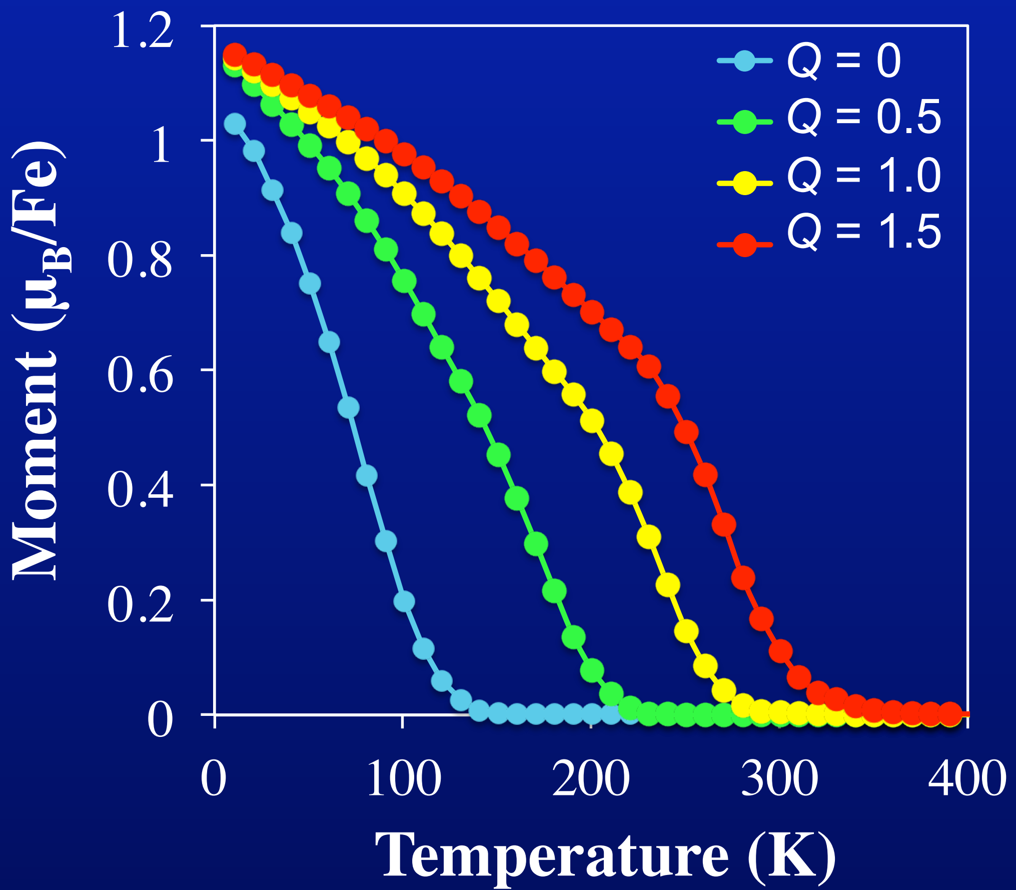
Magn.:	1.17 μ_B/Fe	0.0 μ_B/Fe	0.5 μ_B/Fe	0.0 μ_B/Fe
Energy:	4 meV/f.u.	5 meV/f.u.	10 meV/f.u.	16 meV/f.u.

First-Principles DFT: $LuFe_2O_4$

COII



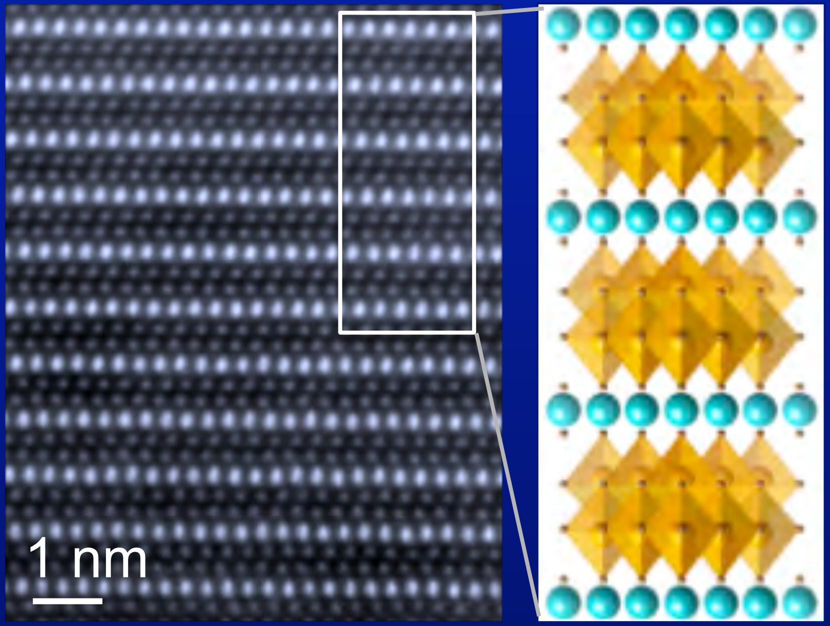
Energy: ~ 4 meV/Fe
Group: *Cm*
Moment: ~1.16 μ_B/Fe
Ferroelectric

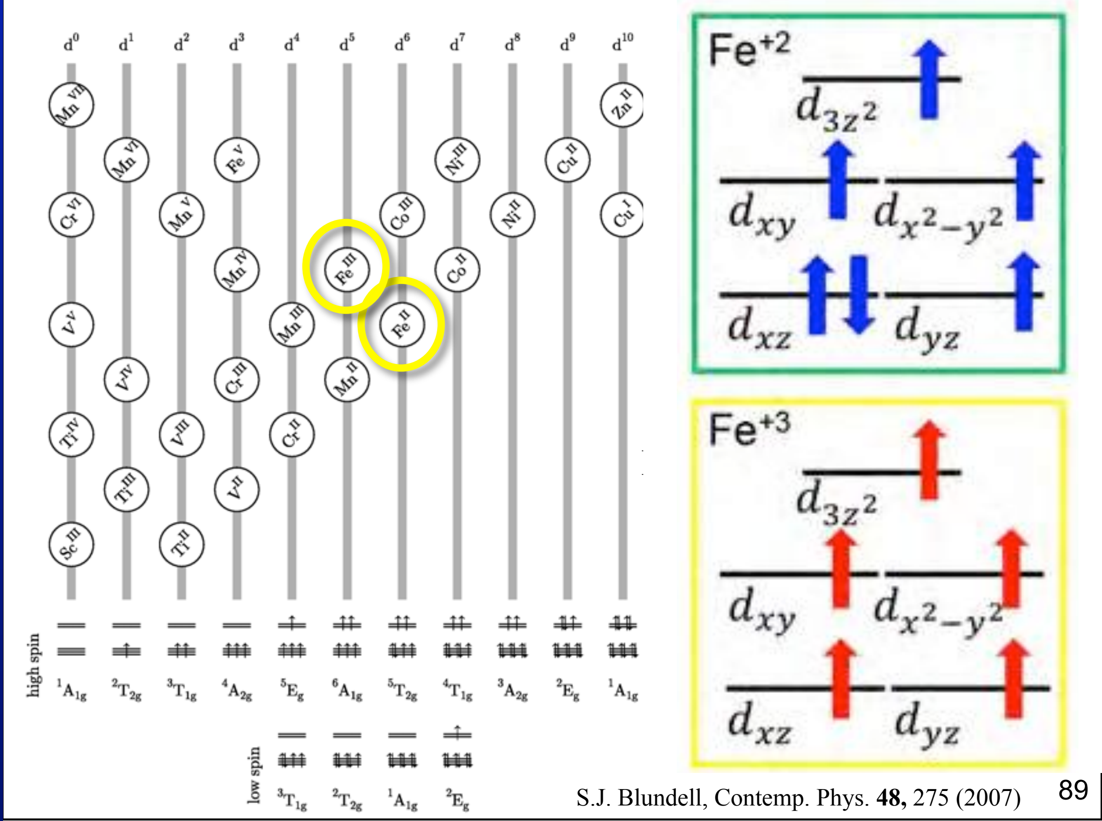


Lu Distortions (“*Q*”) increase magnetic transition in $LuFe_2O_4$ to above room-temperature.

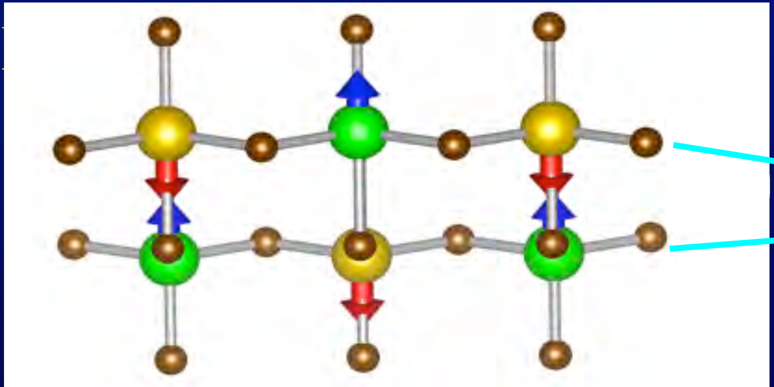
The Idea: $(LuFeO_3)_m$ / $(LuFe_2O_4)_n$ Superlattices

$LuFe_2O_4$





S.J. Blundell, Contemp. Phys. **48,** 275 (2007)



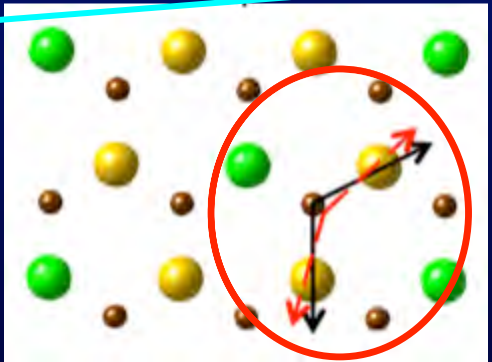
$$M = g\mu_B(3S_{Fe^{3+}} - 3S_{Fe^{2+}})/6 = 0.5\ \mu_B/Fe$$

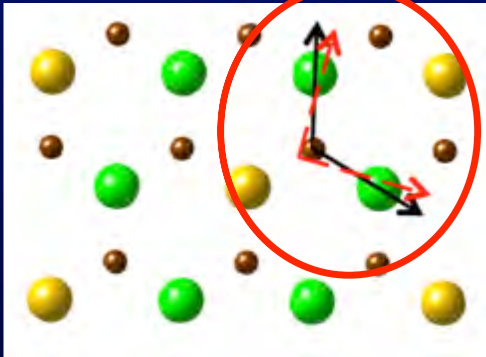
$\quad\quad 5/2 \quad\quad 4/2$

In-plane interactions

top layer

bottom layer





$Lu_2Fe_3O_7$: A Natural $(LuFeO_3)_1$ / $(LuFe_2O_4)_1$ Superlattice

$Lu_2Fe_3O_7$
$T_{C, FM}$ ~ 270 K

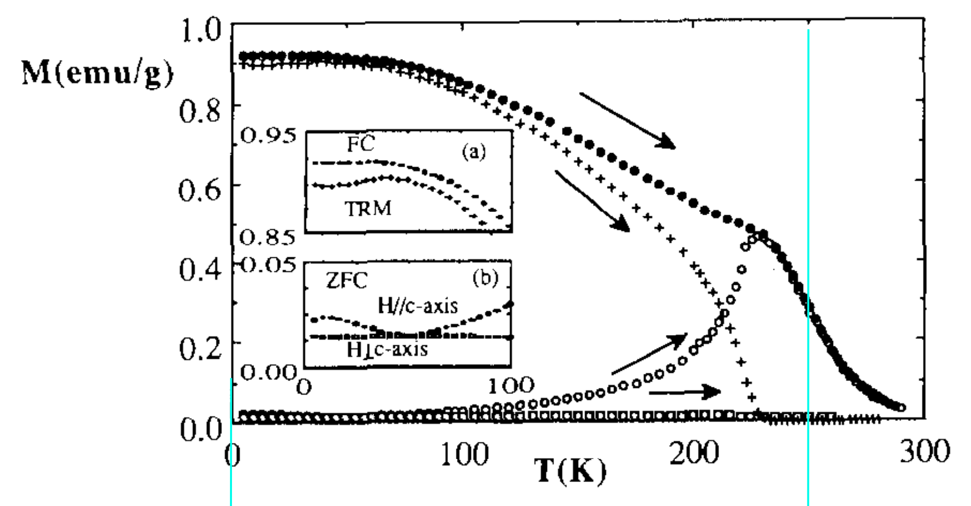
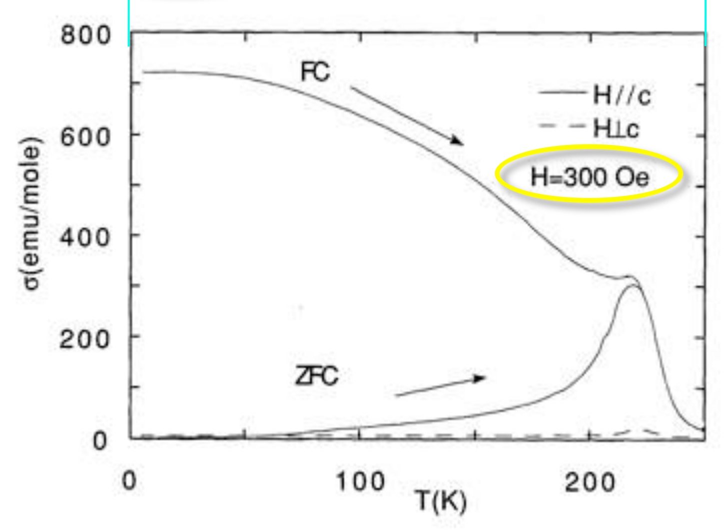


Fig. 1. Thermomagnetization curves of single crystal $Lu_2Fe_3O_7$ in 300 Oe. Circles and squares show those of the

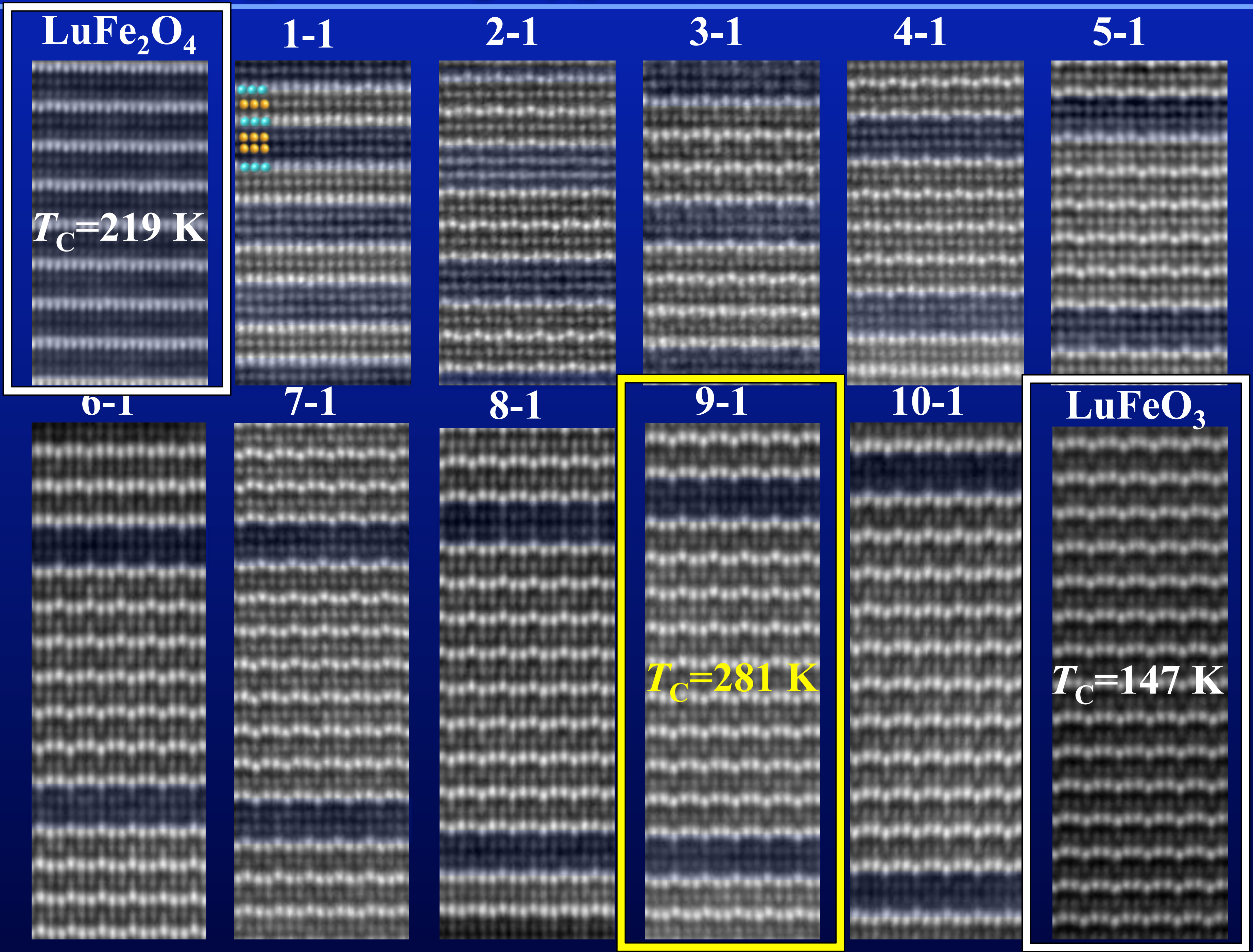
J. Iida, M. Tanaka, and S. Funahashi,
"Magnetic Property of Single Crystal $Lu_2Fe_3O_7$,"
J. Magn. Magn. Mater. **104-107** (1992) 827-828.

$LuFe_2O_4$
$T_{C, FM}$ ~ 240 K



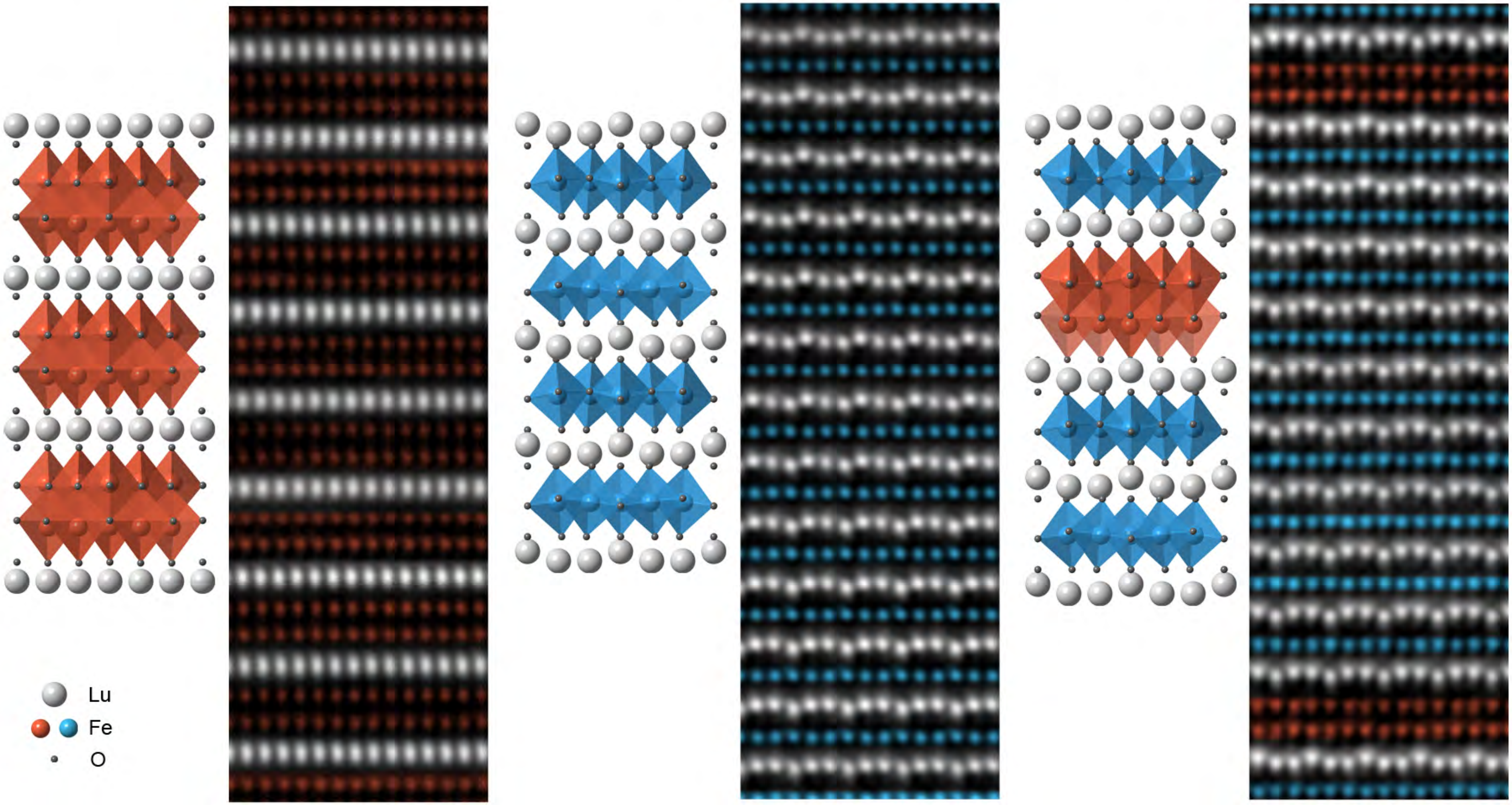
J. Iida, M. Tanaka, Y. Nakagawa,
S. Funahashi, N. Kimizuka,
and S. Takekawa,
Journal of the Physical Society of Japan **62** (1993) 1723-1735.

$(LuFeO_3)_m$ / $(LuFe_2O_4)_n$ Superlattices on (111) YSZ



Ferroelectric Puckering *enhances* Ferrimagnetism

Ferrimagnetic + Ferroelectric = Multiferroic

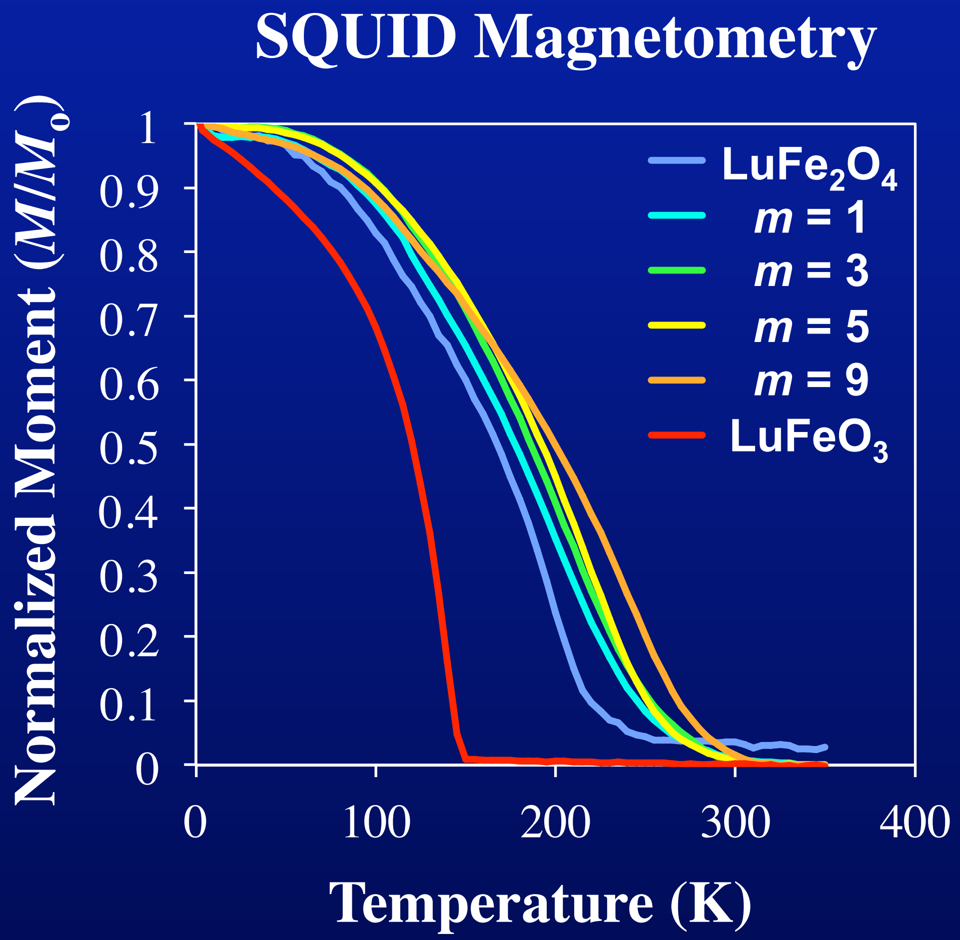


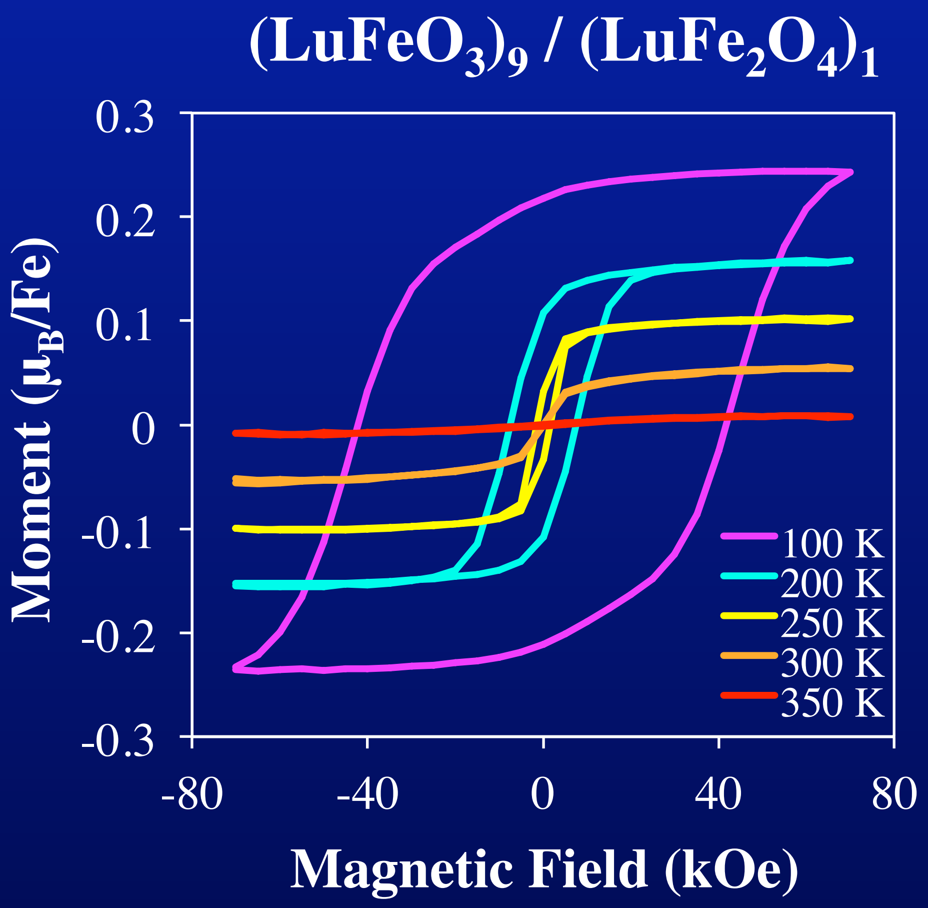
$LuFe_2O_4$

$LuFeO_3$

$(LuFeO_3)_9$ /
$(LuFe_2O_4)_1$ SL

Quantifying Magnetic Moment: $(LuFeO_3)_m$ / $(LuFe_2O_4)_n$

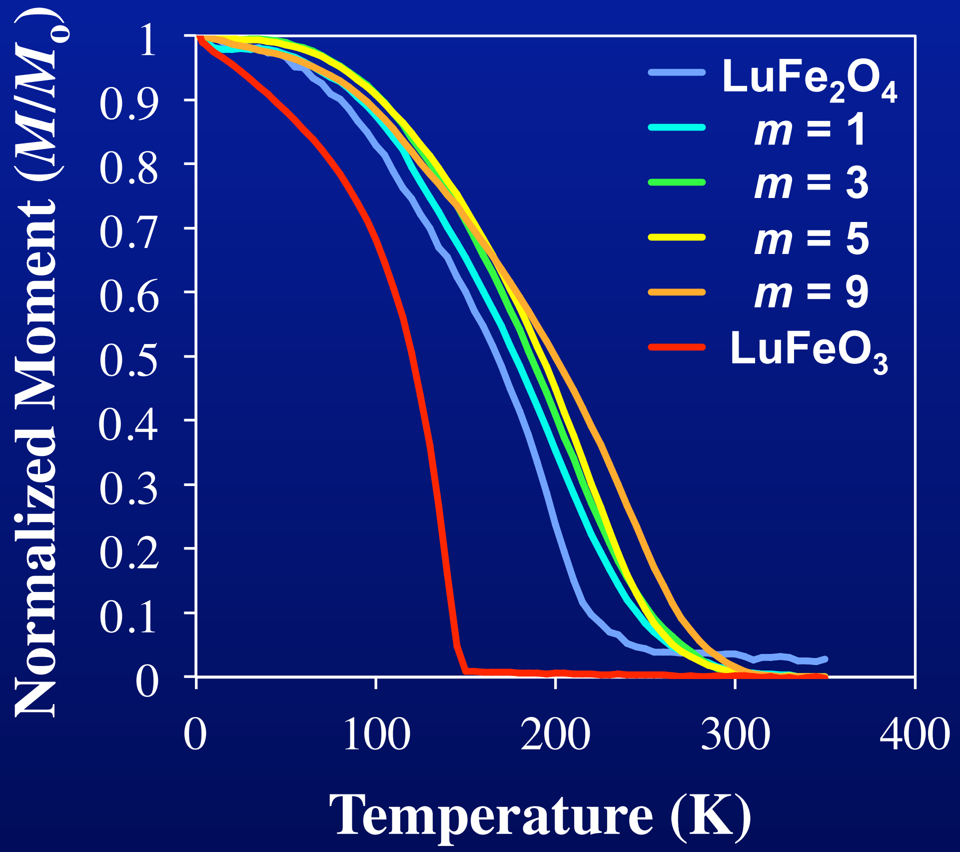




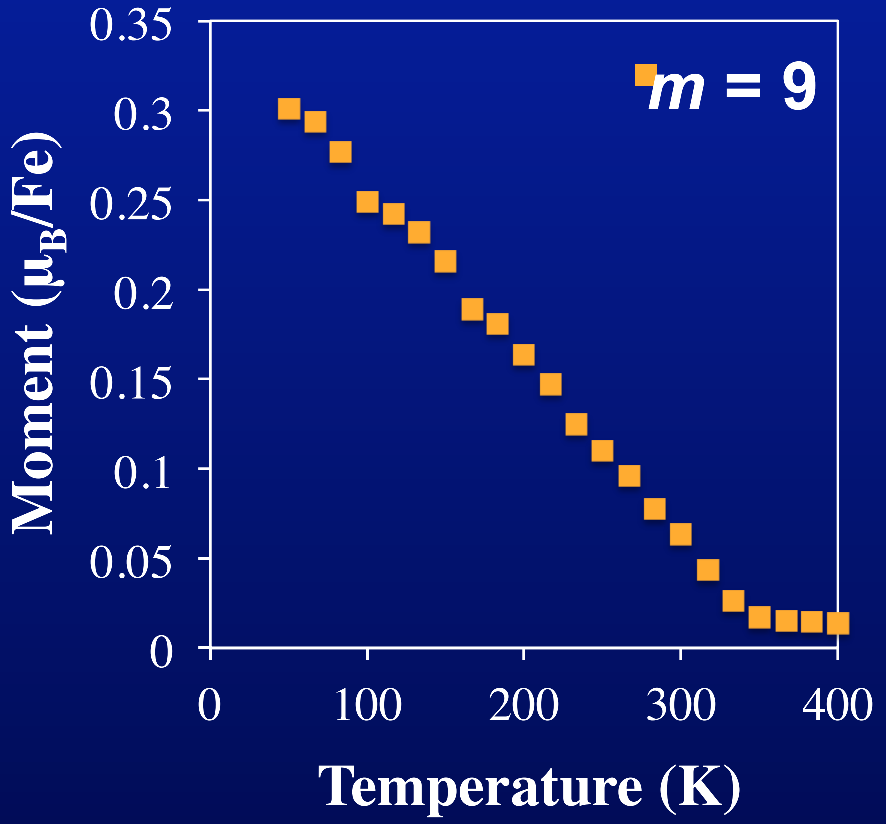
All $(LuFeO_3)_m$ / $(LuFe_2O_4)_1$ superlattices have a higher T_C than both $LuFeO_3$ and $LuFe_2O_4$

Quantifying Magnetic Moment: $(LuFeO_3)_m$ / $(LuFe_2O_4)_n$

SQUID Magnetometry

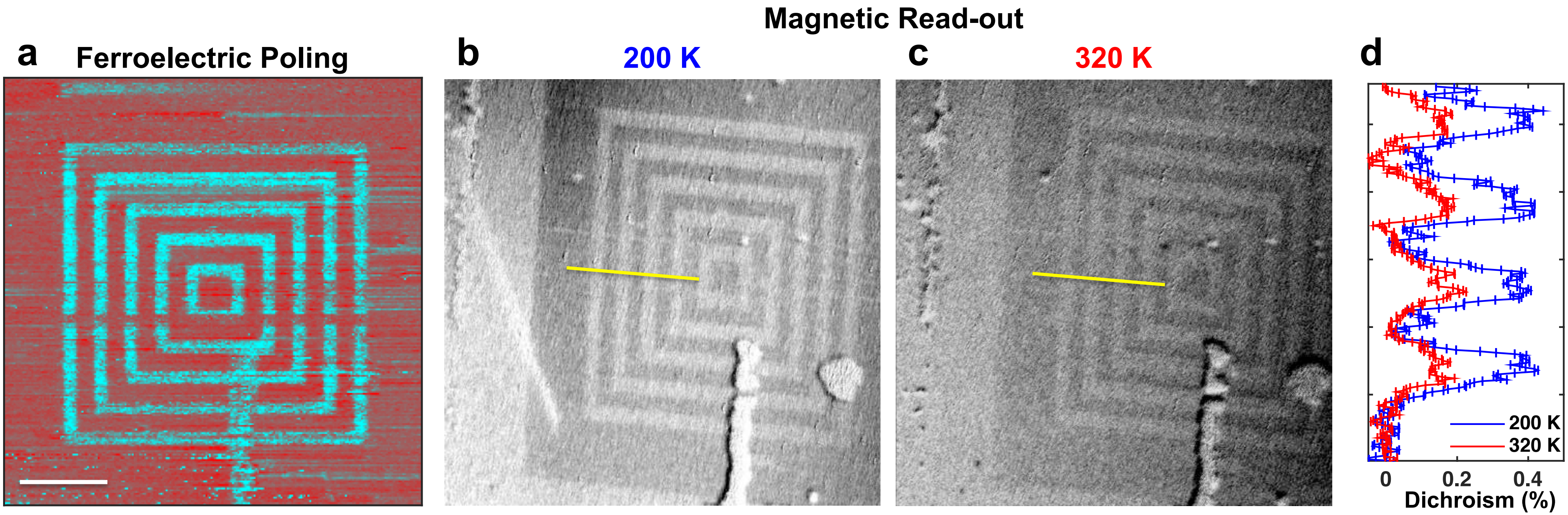


$(LuFeO_3)_9$ / $(LuFe_2O_4)_1$



Ferromagnetic fluctuations in $(LuFeO_3)_9$ / $(LuFe_2O_4)_1$ superlattice persist above room-temperature

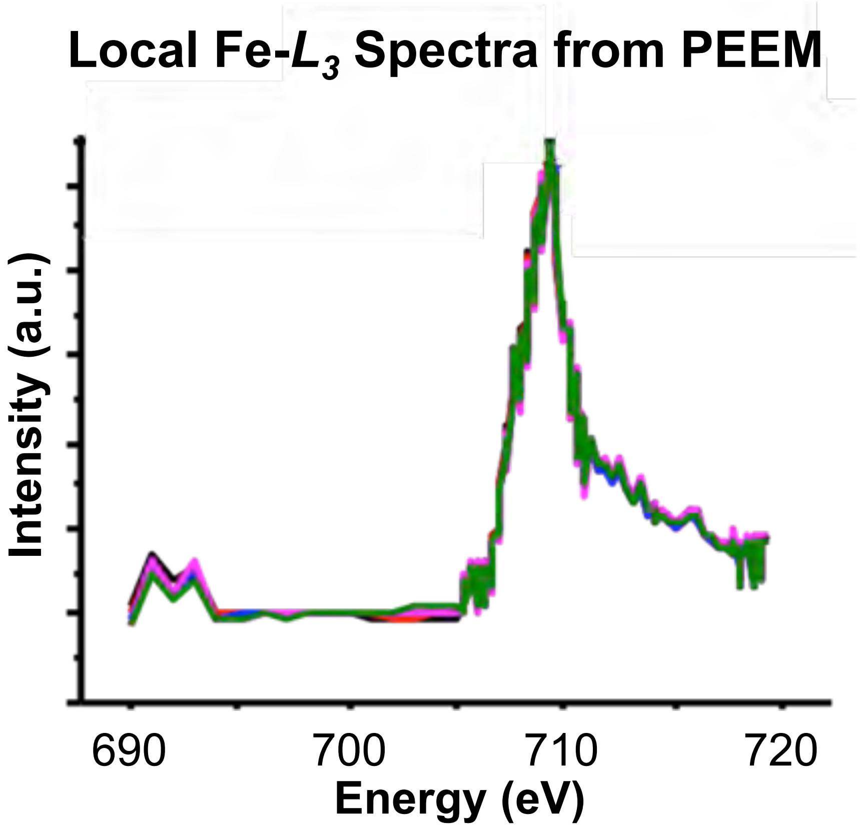
Polarization coupled to Magnetism!

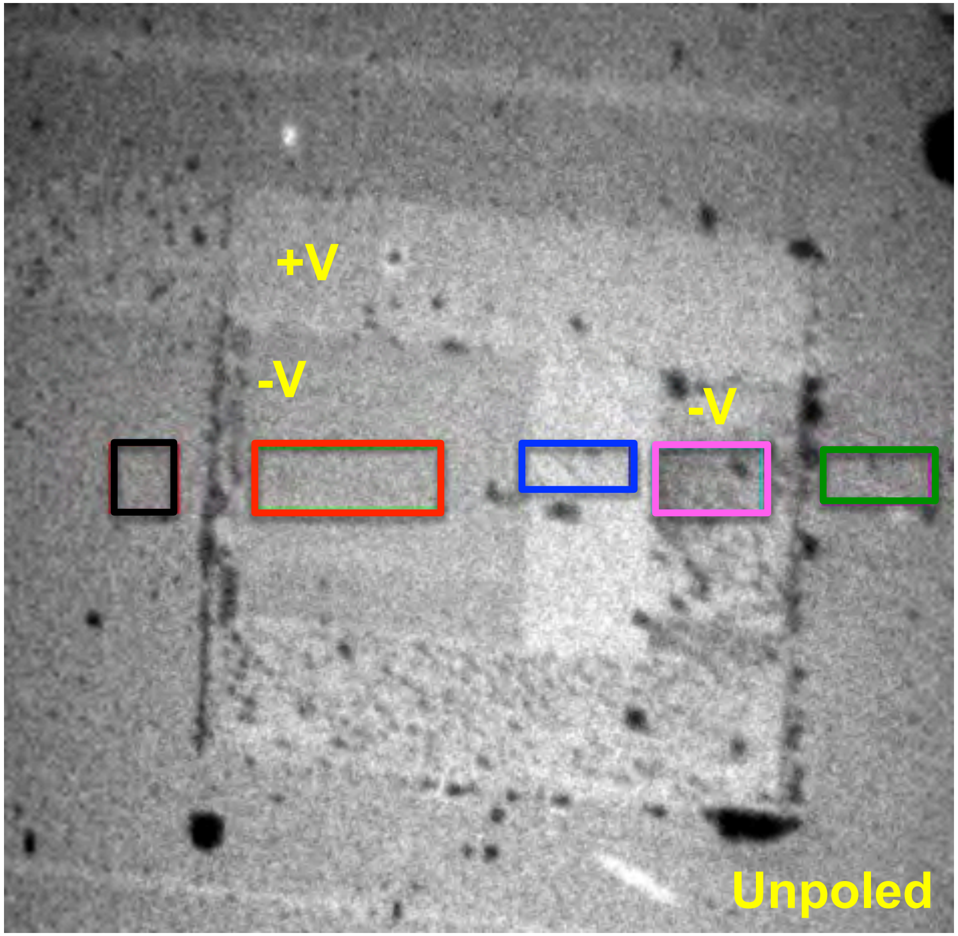


$(LuFeO_3)_9$ / $(LuFe_2O_4)_1$ superlattice

J.A. Mundy, C.M. Brooks, M.E. Holtz, J.A. Moyer, H. Das, A.F. Rébola, J.T. Heron, J.D. Clarkson, S.M. Disseler, Z. Liu, A. Farhan, R. Held, R. Hovden, E. Padgett, Q. Mao, H. Paik, R. Misra, L.F. Kourkoutis, E. Arenholz, A. Scholl, J.A. Borchers, W.D. Ratcliff, R. Ramesh, C.J. Fennie, P. Schiffer, D.A. Muller, and D.G. Schlom, *Nature* **537** (2016) 523–527.

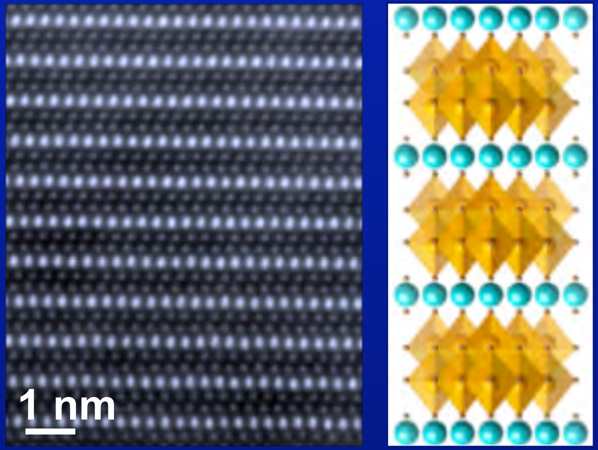
Electrical Poling Does Not Induce Local Modulation in Fe Valence





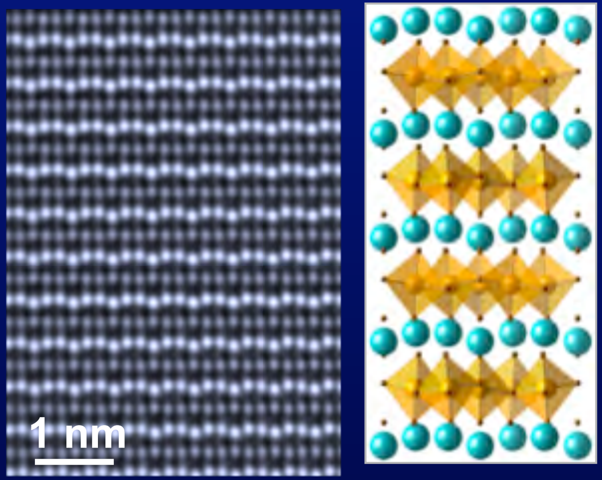
- PEEM is used to locally record Fe valence spectra demonstrating no detectable shift in the spectra (e.g. valence modulation) post-poling.
- XMCD-PEEM from the same region showed distinct magnetic order between the poled regions in this sample.

Highest T_C Ferrimagnetic Ferroelectric



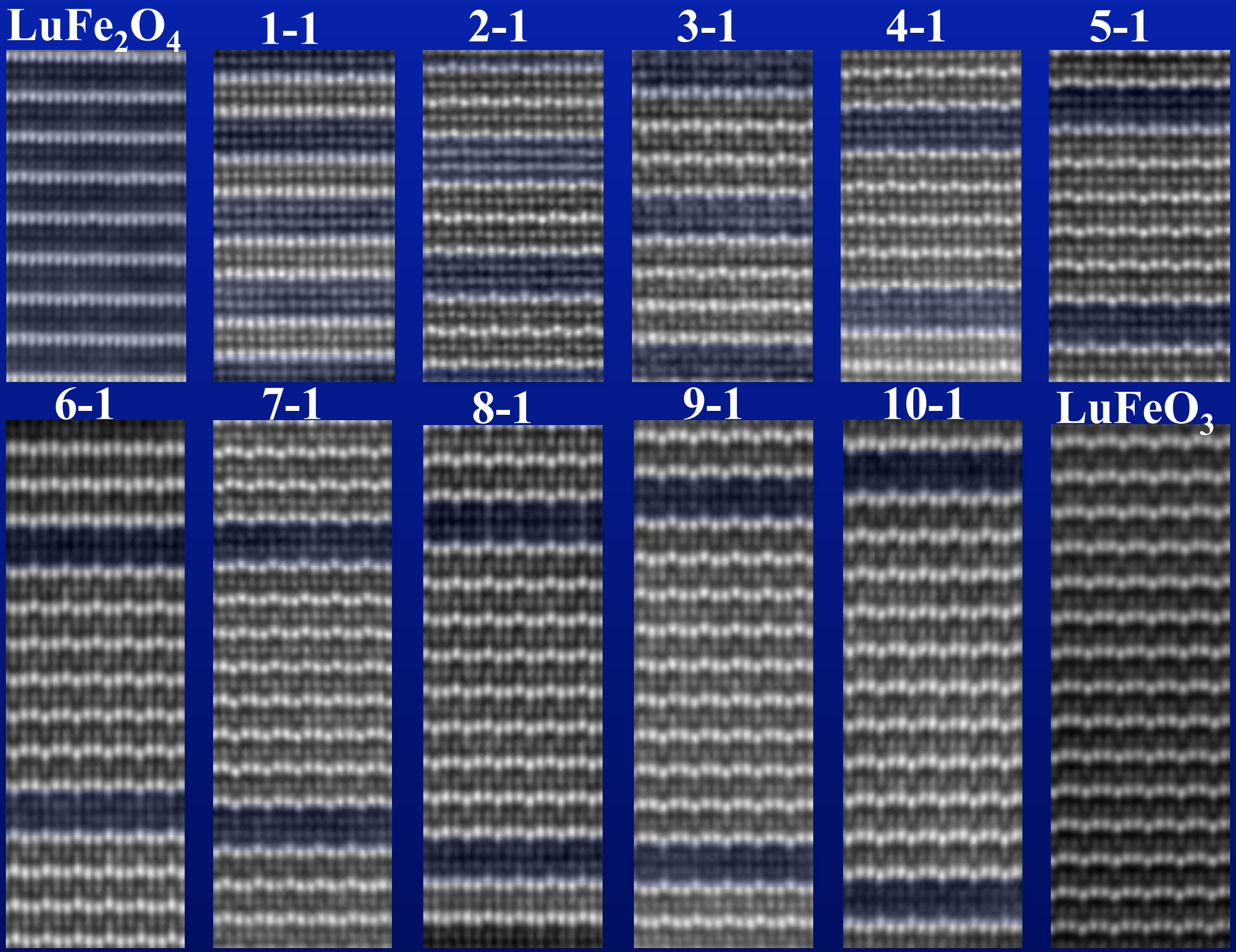
$LuFe_2O_4$
(a ferrimagnet)

+



$LuFeO_3$
(a geometric ferroelectric)

=

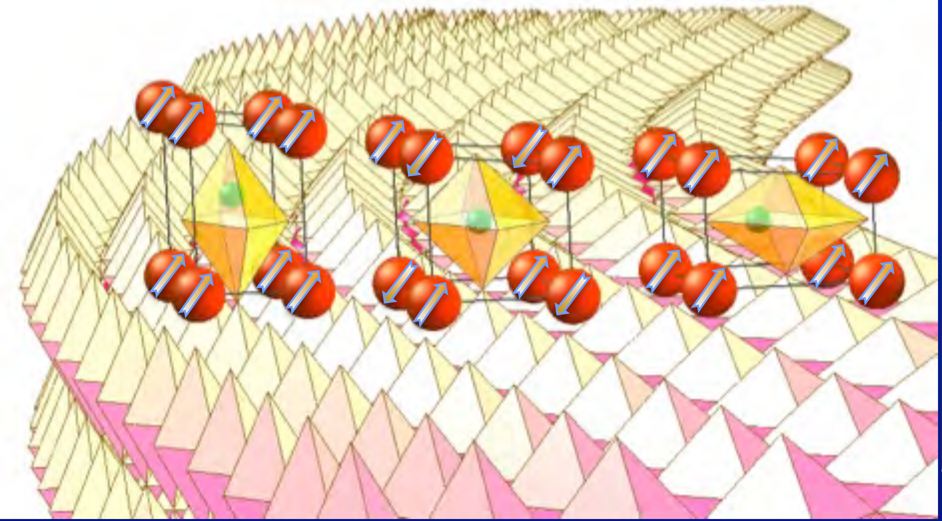


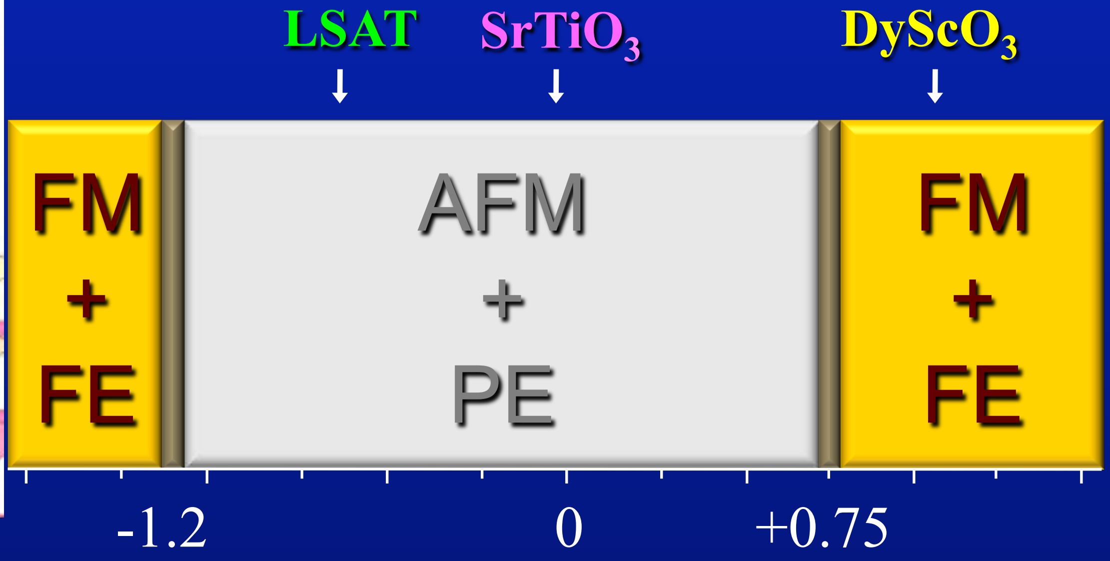
$(LuFeO_3)_m$ / $(LuFe_2O_4)_n$ superlattices

Ferrimagnetic Ferroelectric

(puckering and polarization-doping from ferroelectric *enhance* ferrimagnetism)

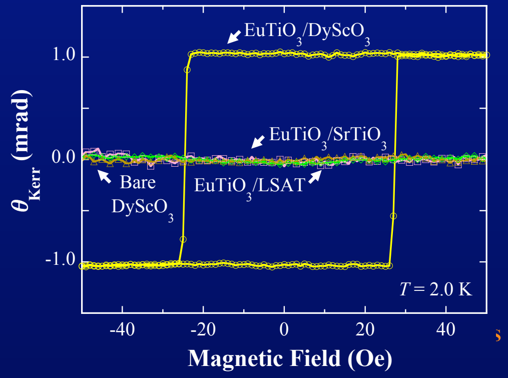
Strongest Ferromagnetic Ferroelectric

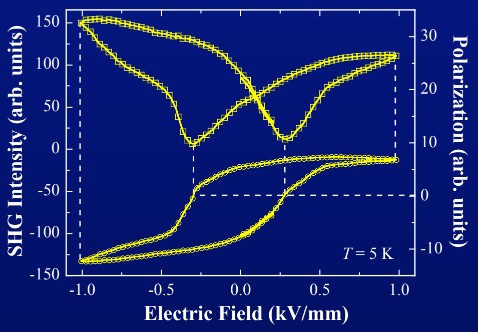




Biaxial Strain (%), ε_s

C.J. Fennie and K.M. Rabe
Physical Review Letters **97** (2006) 267602.





22 nm thick $EuTiO_3$ (a boring dielectric) **+ 1.1% Strain** (by growing it commensurately) **= Multiferroic** (1000× stronger than prior ferromagnetic ferroelectrics)

J.H. Lee, L. Fang, E. Vlahos, X. Ke, Y.W. Jung, L.F. 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.

Conclusions

Using Thin-Film Alchemy:

- Hidden Ground States can be Accessed
- Superior Properties shown to Exist
- Theory + Synthesis is a Powerful Combination (Materials by Design)
- Imagine what Properties Await!