# Design of memcapacitors for neuromorphic computation using magnetoelectric coupling from first principles”


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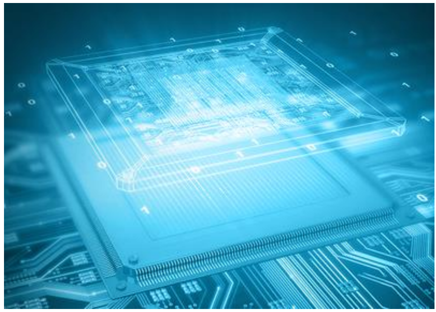
**School of Energy & Chemical Engineering**

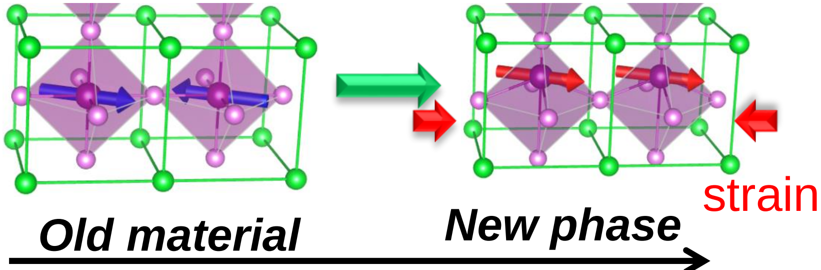
**UNIST**

*미래소재 디스커버리 사업*

KOMAG
2018

## *Theoretical prediction → Experimental realization → Additional prediction*




# I. Neuromorphic computer

Multi dielectric constants

*Multiple-order*-transition

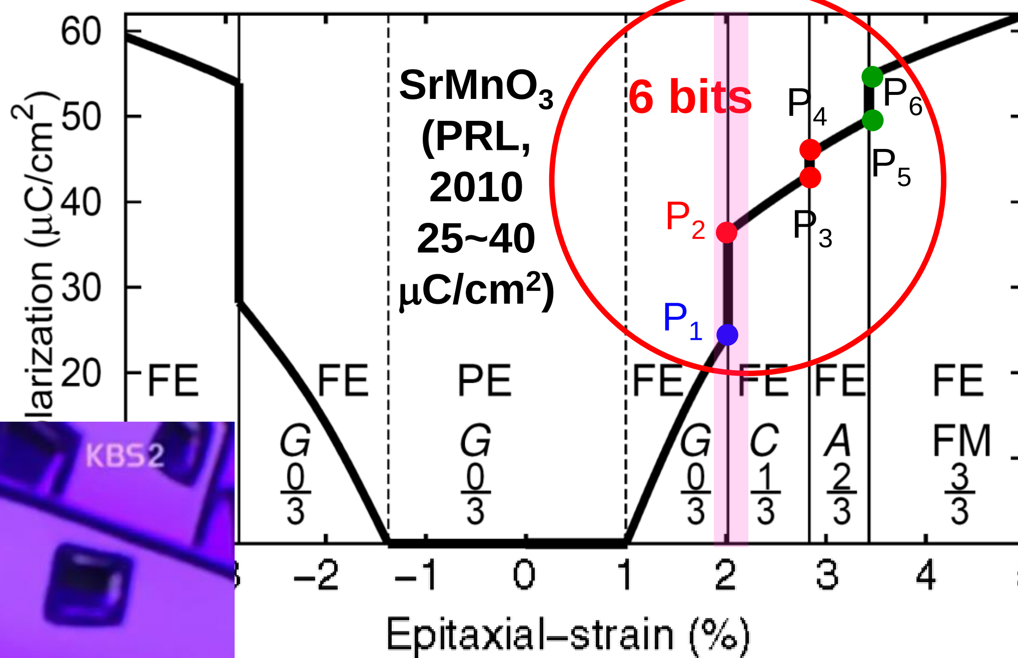
(*Spin-dipole-lattice*)

- **SrMnO3 (PRL, 2010~)**,

SrCoO3 (PRL, 2011~),

LaMnO3 (PRB, 2013~)

**CrPS4 (JPCM, 2017~)**




# Theoretical prediction (2010, PRL) → Experimental realization

## Strong spin-phonon coupling in infrared and Raman spectra of $SrMnO_3$

ba,[1,*] V. Goian,[1] V. Skoromets,[1] J. Hejtmánek,[1] V. Bovtun,[1] M. Kempa,[1] F. Borodavka,[1] P. Vaněk,[1] A
J. H. Lee,[3] O. Pacherová,[1] and K. M. Rabe[3]
[1]Institute of Physics ASCR, Na Slovance 2, 182 21 Prague 8, Czech Republic
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[3]Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA
(Received 24 October 2013; revised manuscript received 10 February 2014; published 25 February 2014)

Infrared reflectivity spectra of cubic $SrMnO_3$ ceramics reveal 18% stiffening of the lowest-frequency phonc below the antiferromagnetic phase transition occurring at $T_N = 233$ K. Such a large temperature chang of the polar phonon frequency is extraordinary and we attribute it to an exceptionally strong spin-phonc coupling in this material. This is consistent with our prediction from first-principles calculations. Moreove polar phonons become Raman active below $T_N$, although their activation is forbidden by symmetry in th $Pm\bar{3}m$ space group. This gives evidence that the cubic $Pm\bar{3}m$ symmetry is locally broken below $T_N$ due to strong magnetoelectric coupling. Multiphonon and multimagnon scattering is also observed in Raman spectr Microwave and THz permittivity is strongly influenced by hopping electronic conductivity, which is caused b small nonstoichiometry of the sample. Thermoelectric measurements show room-temperature concentration free carriers $n_e = 3.6 \times 10^{20}$ cm$^{-3}$ and the sample composition S… very unusual temperature behavior: THz conductivity increases o… decreases on cooling. We attribute this to different conductivity …

IR, *PRB* (2014)

## Strain-induced coupling of electrical polarization and structural defects in $SrMnO_3$ films

Carsten Becher[1], Laura Maurel[2], Ulrich Aschauer[1], Martin Lilienblum[1], César Magén[3,4], Dennis Meier[1], Eric Langenberg[2], Morgan Trassin[1], Javier Blasco[4,5], Ingo P. Krug[6†], Pedro A. Algarabel[4,5], Nicola A. Spaldin[1], José A. Pardo[2,7] and Manfred Fiebig[1*]

**Local perturbations in complex oxides, such as domain walls[1,2], strain[3,4] and defects[5,6], are of interest because they can modify the conduction or the dielectric and magnetic response, and can even promote phase transitions. Here, we show that the interaction between different types of local perturbations in oxide thin films is an additional source of functionality. Taking $SrMnO_3$ as a model system, we use nonlinear optics to verify the theoretical prediction that strain induces a polar phase, and apply density functional theory to show that strain simultaneously increases the concentration of oxygen vacancies. These vacancies couple to the polar domain walls, where they establish an electrostatic barrier to electron migration. The result is a state with locally structured room-temperature conductivity consisting of conducting nanosized polar domains encased by insulating domain boundaries, which we resolve using scanning probe microscopy. Our 'nanocapacitor' domains can be individually charged, suggesting stable capacitance nanobits with a potential for information storage technology.**

Polar order in the strained $SrMnO_3$ films was verified by second harmonic generation (SHG), that is, frequency doubling of the probing light wave (see Methods). SHG is particularly powerful in detecting polar phases, because, in the leading order, it occurs only in non-centrosymmetric media. It thus emerges free of background when the inversion symmetry is broken by the formation of a polar state. Temperature-dependent SHG measurements of … decrease in the SHG signal in strained $SrMnO_3$ films below 250 K

SHG, *Nature Nanotechnology* (2015)

## Nature of antiferromagnetic order in epitaxially strained multiferroic $SrMnO_3$ thin films

L. Maurel,[1,2,3] N. Marcano,[2,4] T. Prokscha,[5] E. Langenberg,[1,6] J. Blasco,[2,3] R. Guzmán,[7] A. Suter,[5] C. Magén,[3,7,8] L. Morellón,[1,3] M. R. Ibarra,[1,3] J. A. Pardo,[1,7,9] and P. A. Algarabel[2,3,*]
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[2]Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain
[3]Departamento de Física de la Materia Condensada, Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain
[4]Centro Universitario de la Defensa, Academia General Militar, Crta. Huesca s/n, 50090 Zaragoza, Spain
[5]Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute-CH-5232 Villingen PSI, Switzerland
[6]Centro de Investigación en Química Biológica y Materiales Moleculares, Universidad de Santiago de Compostela, C/ Jenaro de la Fuente s/n, 15782 Santiago de Compostela, Spain
aboratorio de Microscopías Avanzadas, Instituto de Nanociencia de Aragón, Universidad de Zaragoza, C/ Mariano Esquillor s/ 50018 Zaragoza, Spain
[8]Fundación ARAID, C/ María de Luna 11, planta 1ª, Edificio CEEI Aragón, 50018 Zaragoza, Spain
partamento de Ciencia y Tecnología de Materiales y Fluidos, Universidad de Zaragoza, C/ María de Luna 3, 50018 Zaragoza, S
(Received 8 May 2015; revised manuscript received 24 June 2015; published 17 July 2015)

Epitaxial films of $SrMnO_3$ and bilayers of $SrMnO_3/La_{0.67}Sr_{0.33}MnO_3$ have been deposited by pulsed laser deposition on different substrates, namely, $LaAlO_3$ (001), $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$ (001), and $SrTiO_3$ (001), allowing us to perform an exhaustive study of the dependence of antiferromagnetic order and exchange bias field on epitaxial strain. The Néel temperatures ($T_N$) of the $SrMnO_3$ films have been determined by low-energy muon spin spectroscopy. In agreement with theoretical predictions, $T_N$ is reduced as the epitaxial strain increases. From the comparison with first-principles calculations, a crossover from G-type to C-type antiferromagnetic orders is proposed at a critical tensile strain of around $1.6 \pm 0.1$%. The exchange bias (coercive) field, obtained for the bilayers, increases (decreases) by increasing the epitaxial strain in the $SrMnO_3$ layer, following an exponential dependence with temperature. Our experimental results can be explained by the existence of a spin-glass (SG) state at the interface between the $SrMnO_3$ and $La_{0.6…}$ … the different exchange interactions present in t…

Neutron, *PRB* (2015)

## Polar-Graded Multiferroic $SrMnO_3$ Thin Films

Roger Guzmán,[*,†,○] Laura Maurel,[‡,§] Eric Langenberg,[§,⊥] Andrew R. Lupini,[∥] Pedro A. Algarabel,[§,⊥] José A. Pardo,[†,‡,#] and César Magén[*,†,§,∇]
[†]Laboratorio de Microscopías Avanzadas (LMA), Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain
[‡]Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain
[§]Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50009 Zaragoza, Spain
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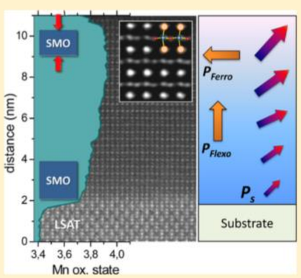
[∇]Fundación ARAID, 50004 Zaragoza, Spain

Supporting Information

ABSTRACT: Engineering defects and strains in oxides provides a promising route for the quest of thin film materials with coexisting ferroic orders, multiferroics, with efficient magnetoelectric coupling at room temperature. Precise control of the strain gradient would enable custom tailoring of the multiferroic properties but presently remains challenging. Here we explore the existence of a polar-graded state in epitaxially strained antiferromagnetic $SrMnO_3$ thin films, whose polar nature was predicted theoretically and recently demonstrated experimentally. By means of aberration-corrected scanning transmission electron microscopy we map the polar rotation of the ferroelectric polarization with atomic resolution, both far from and near the domain walls, and find flexoelectricity resulting from vertical strain gradients. The origin of this particular strain state is a gradual distribution of oxygen vacancies across the film thickness, according to electron energy loss spectroscopy. Herein we present a chemistry-mediated route to induce polar rotations in oxygen-deficient multiferroic films, resulting in flexoelectric polar rotations an… piezoelectricity.




KEYWORDS: Multiferroics, ferroelectricity, flexoelectricit…

TEM, *Nano Lett.* (2016)

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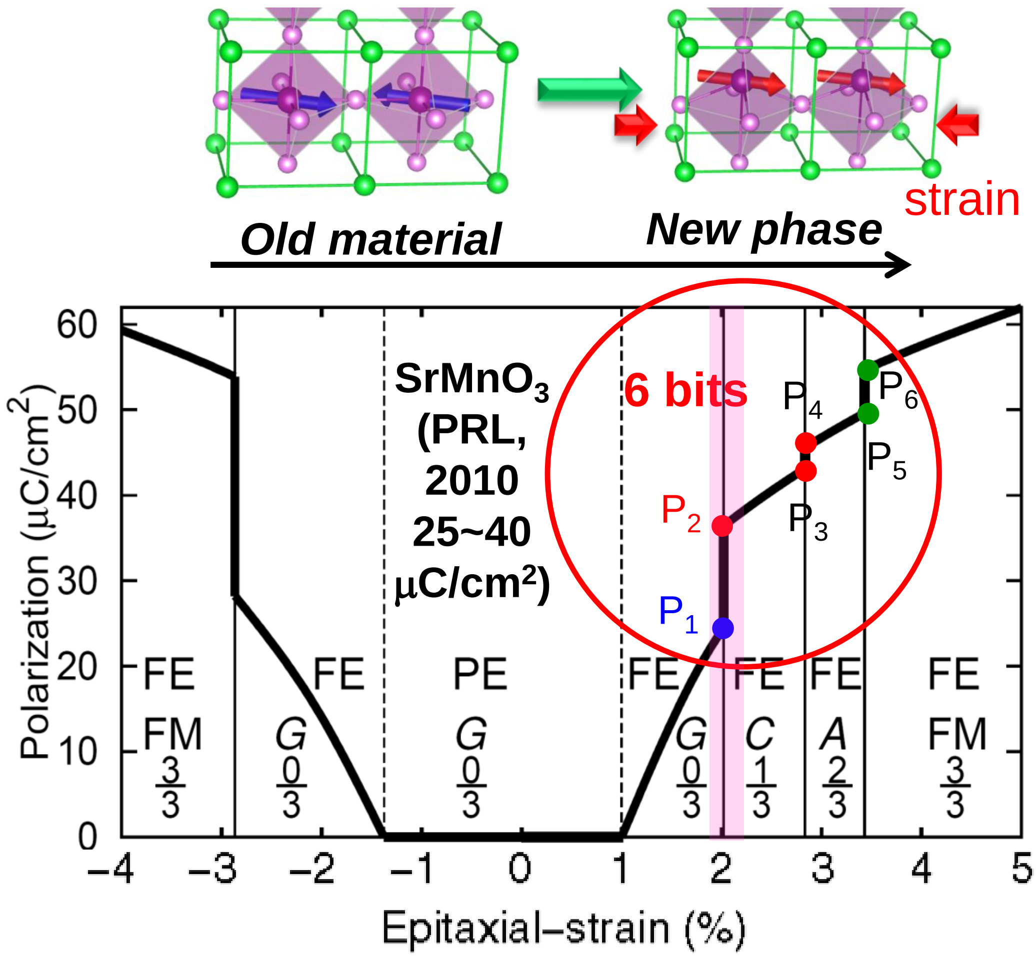
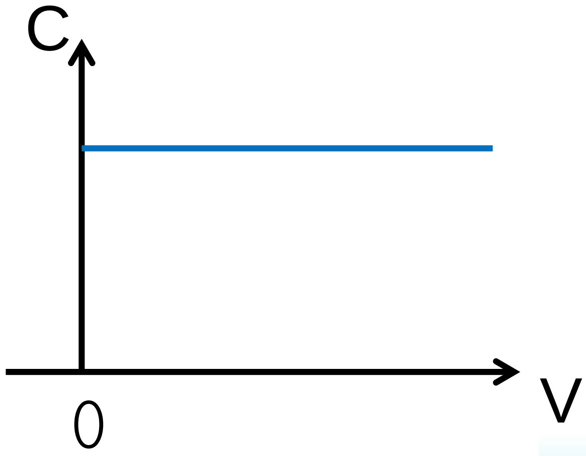
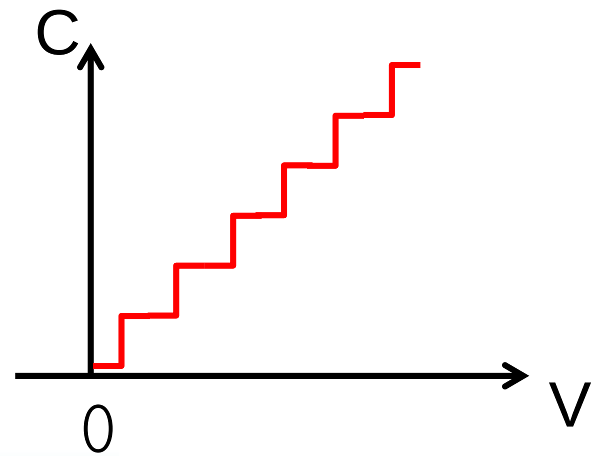


# Von Neumann --> Neuromorphic architecture

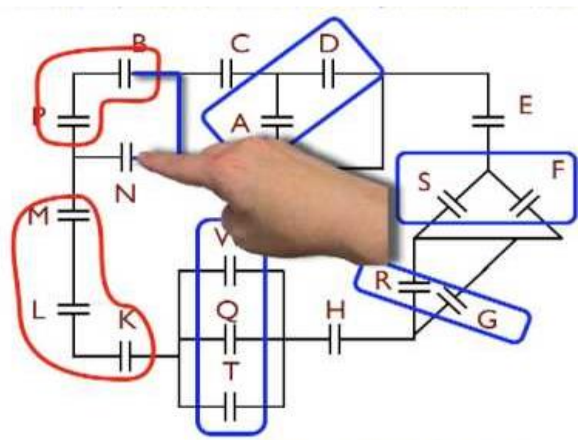
## Capacitor

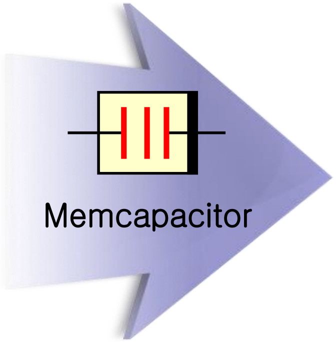



## Memcapacitor



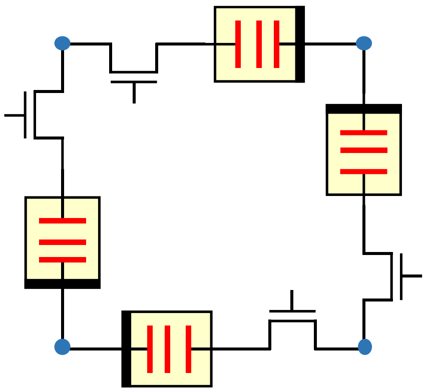

Complex device




- Flexible nano
- Ultralow power
- Fast computation

Simplified device



No materials found yet with multi dielectric constants

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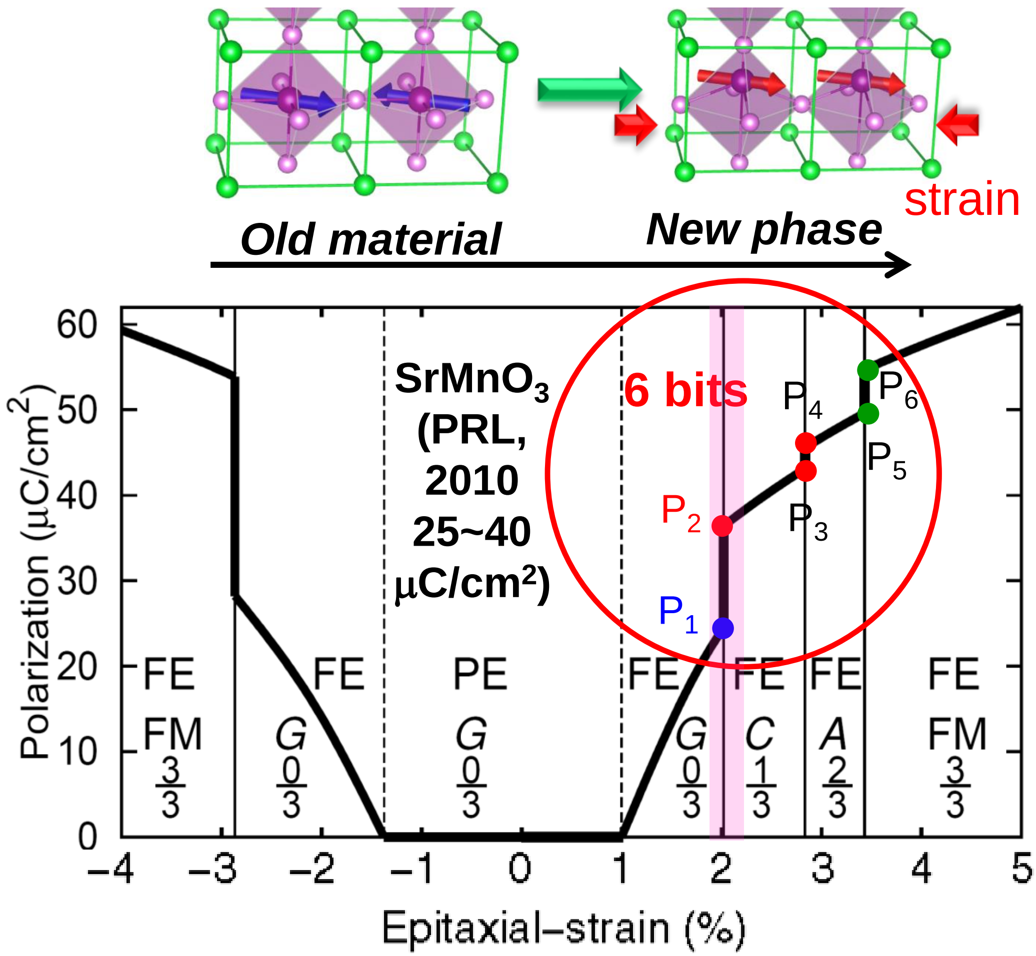
  **CrPS4 (JPCM, 2017~)**



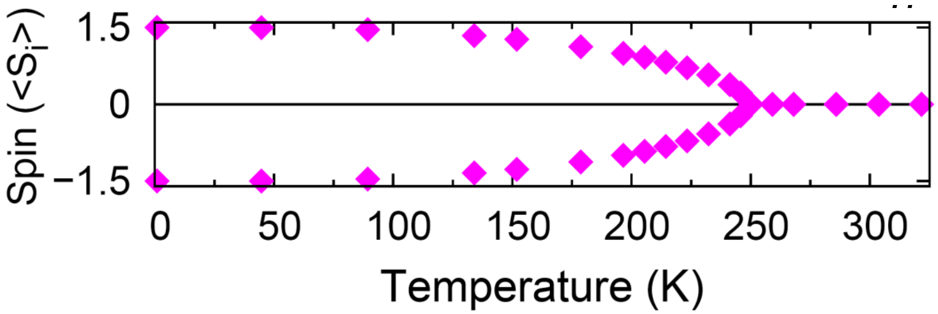
# Measurement of the coupling in cubic $SrMnO_3$

$$\tilde{K}_{\tau\alpha\tau'\alpha'} = \boxed{K^{PM}_{\tau\alpha\tau'\alpha'}} - \sum_{i\neq j} \boxed{J''_{ij,\tau\alpha\tau'\alpha'}} \langle \vec{S}_i \cdot \vec{S}_j \rangle$$

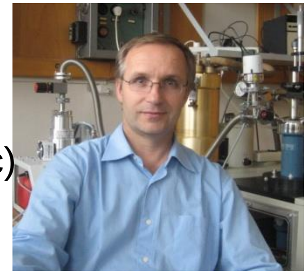
: atomic displacement, $J_{i,j}$ : magnetic interaction

Lee & Rabe, PRB 84, 104440 (11)

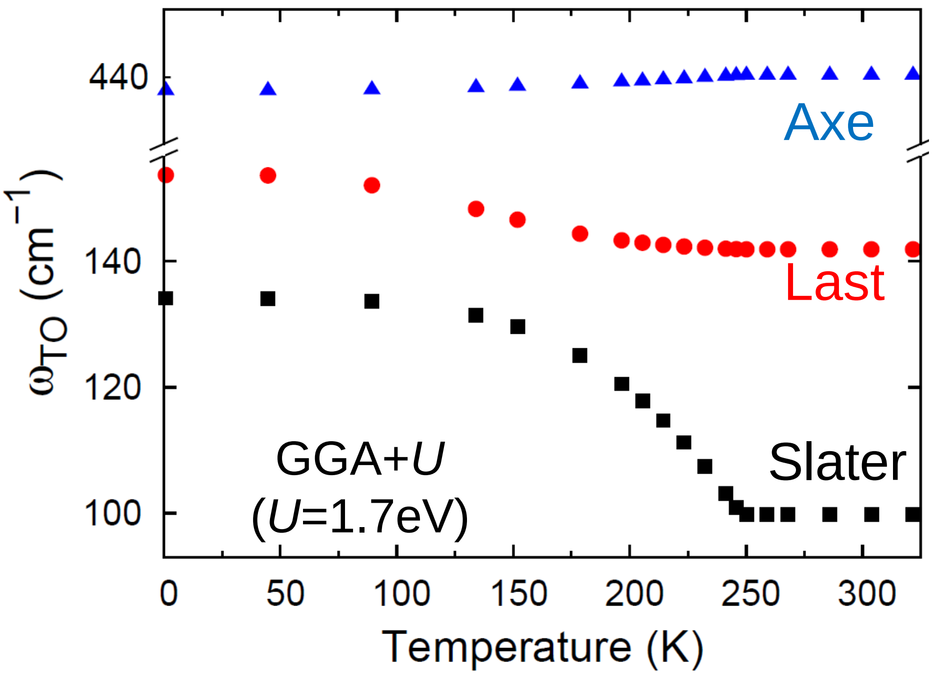
Mean-field

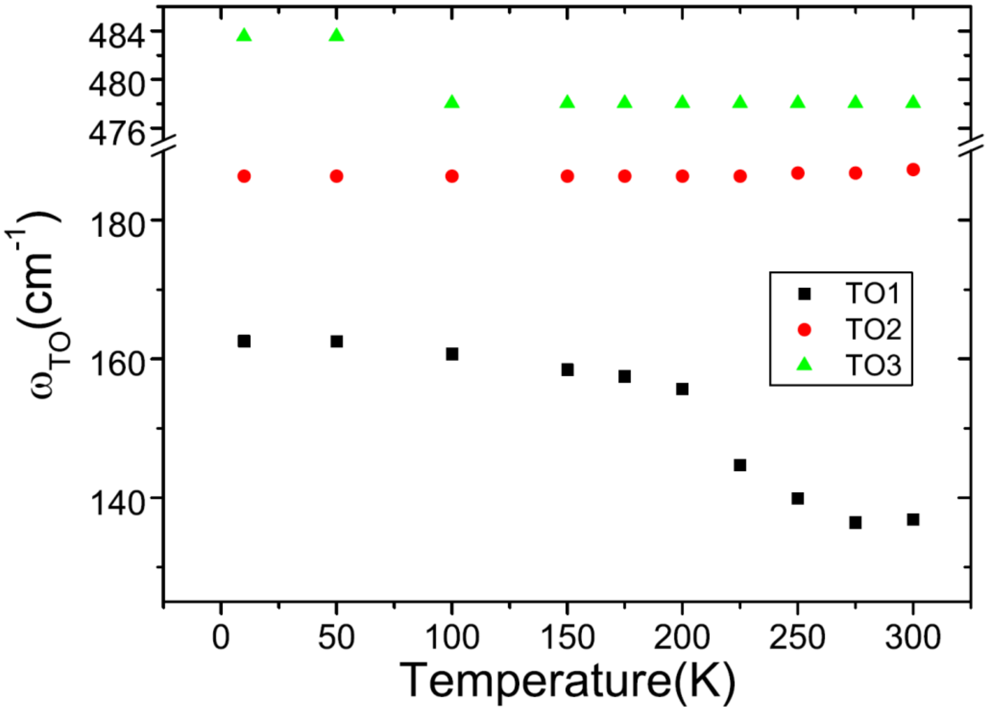


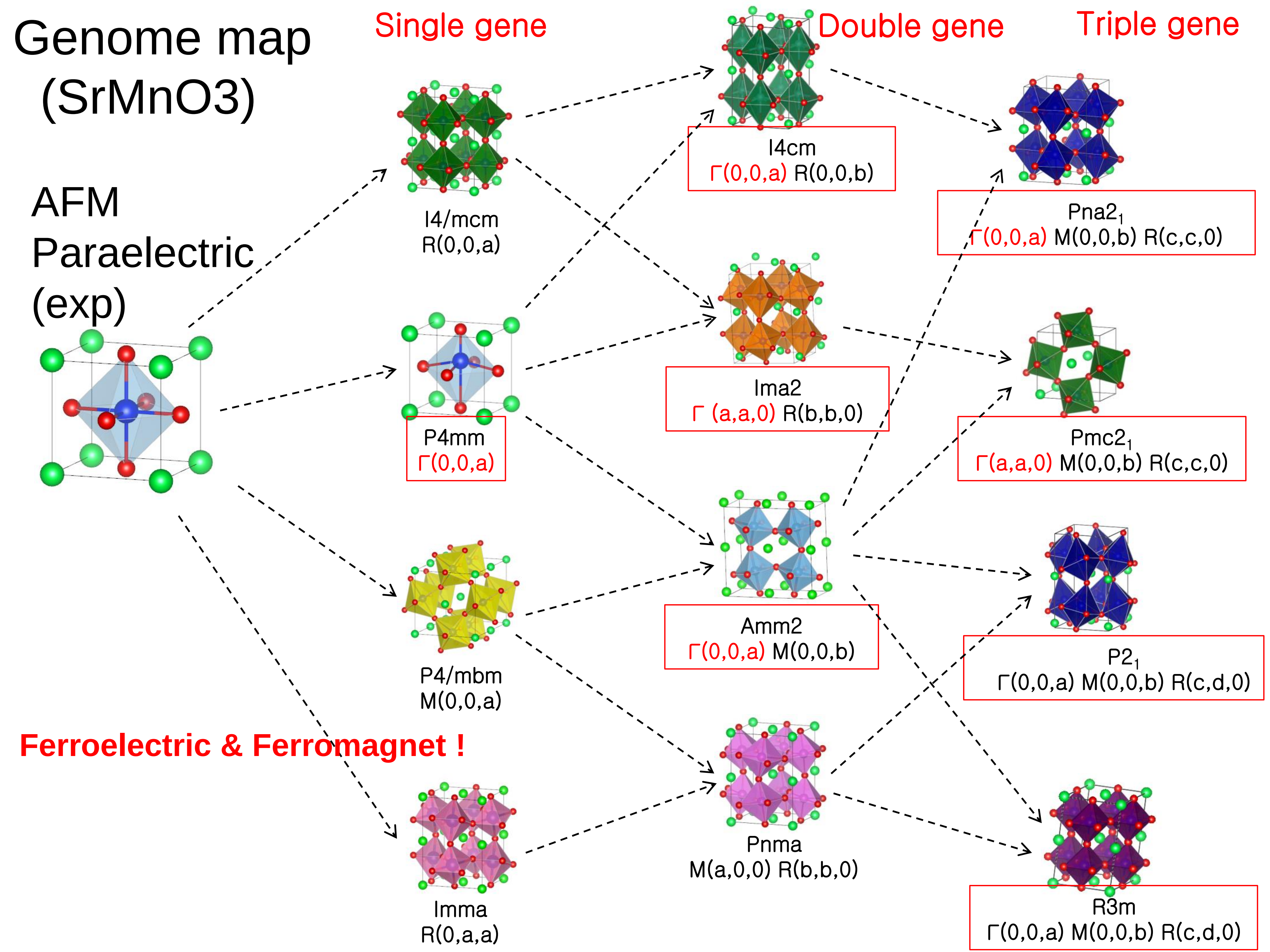

S. Kamba (Academic of Sciences of the Czech Republic)

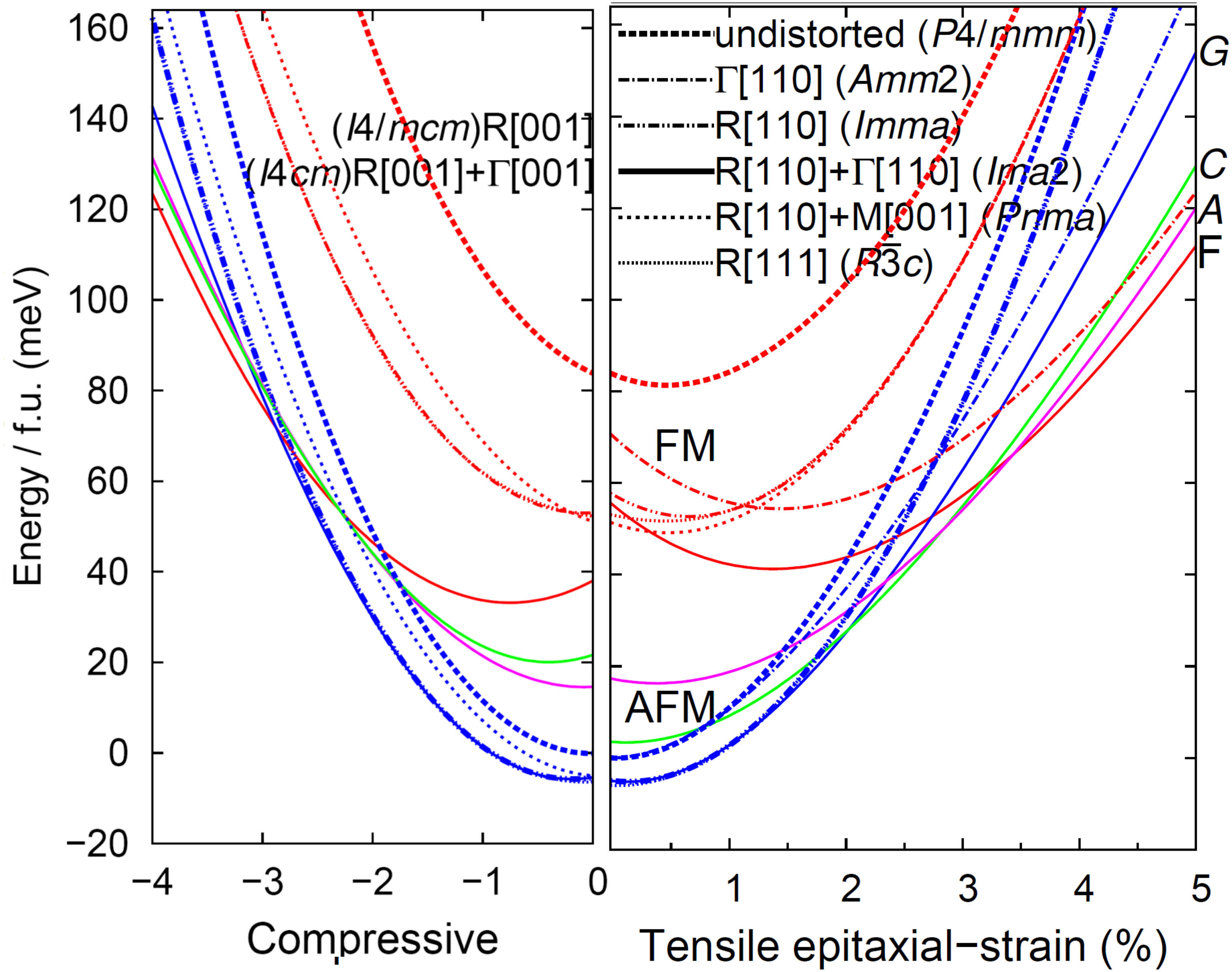


IR exp. (ceramic)

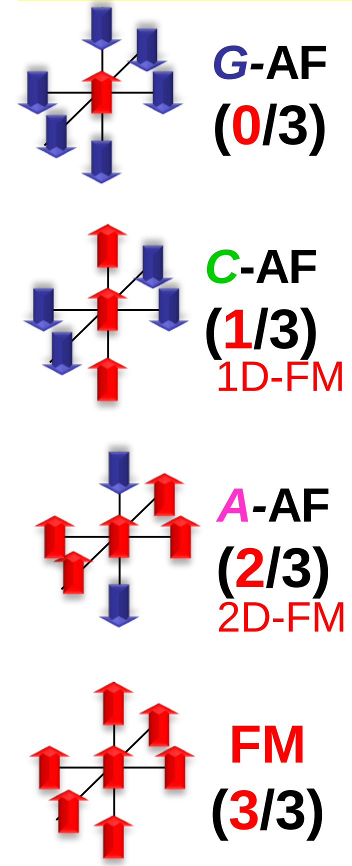



Genome map
(SrMnO3)
Single gene
Double gene
Triple gene
AFM
Paraelectric
(exp)
I4/mcm
R(0,0,a)
P4mm
Γ(0,0,a)
P4/mbm
M(0,0,a)
Imma
R(0,a,a)
I4cm
Γ(0,0,a) R(0,0,b)
Ima2
Γ (a,a,0) R(b,b,0)
Amm2
Γ(0,0,a) M(0,0,b)
Pnma
M(a,0,0) R(b,b,0)
Pna2$_1$
Γ(0,0,a) M(0,0,b) R(c,c,0)
Pmc2$_1$
Γ(a,a,0) M(0,0,b) R(c,c,0)
P2$_1$
Γ(0,0,a) M(0,0,b) R(c,d,0)
R3m
Γ(0,0,a) M(0,0,b) R(c,d,0)
Ferroelectric & Ferromagnet !




# $SrMnO_3$ with epitaxial strain




- **How does the electric *P* evolve?**

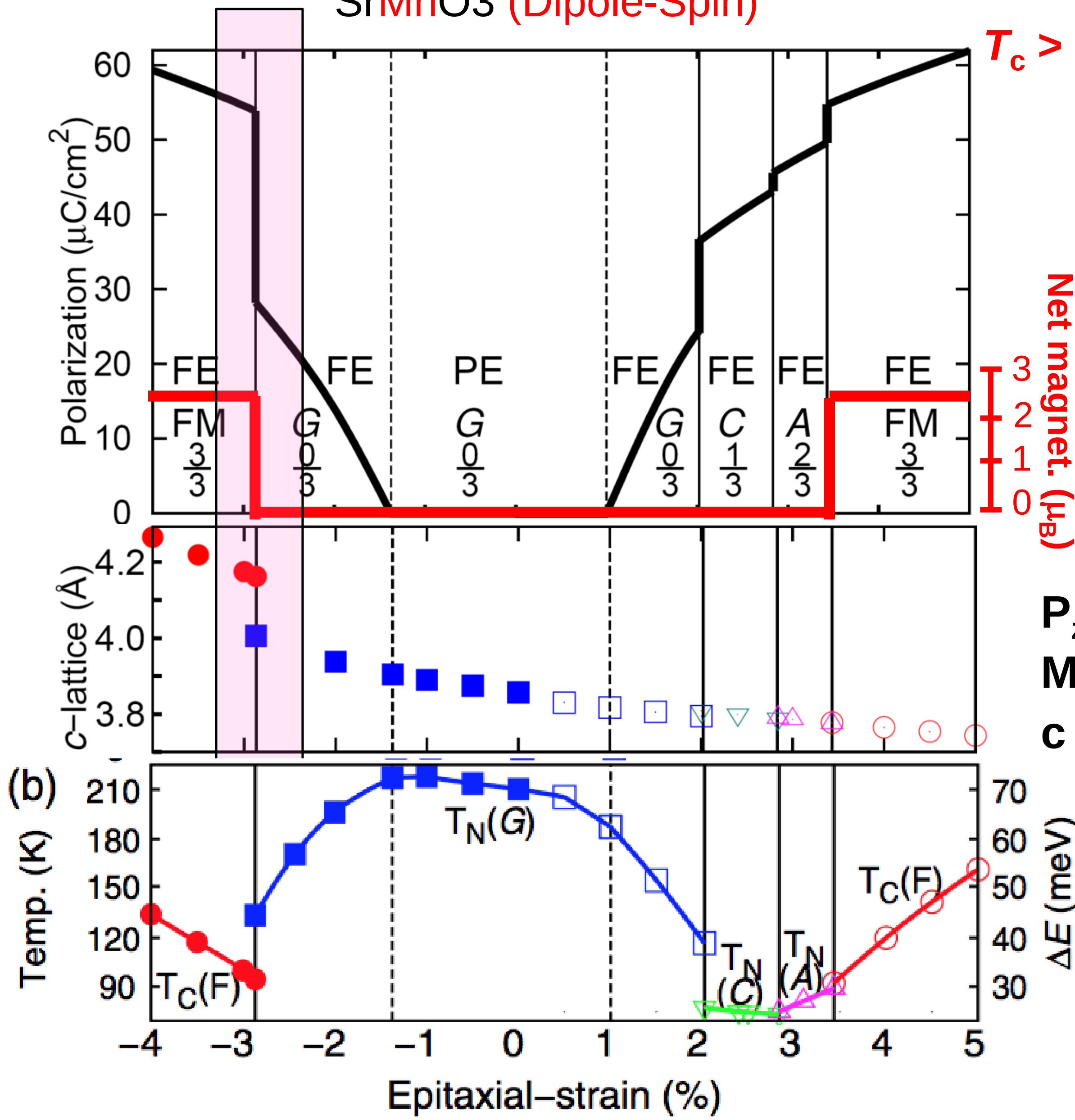
# Multiple- vs. single- order parameter transition

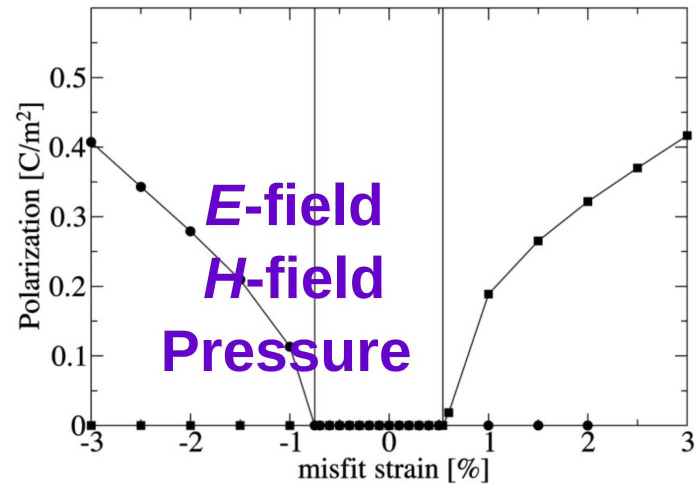
SrMnO3 (Dipole-Spin)

cf) SrTiO3 (Dipole)

$T_c$ > 100 K

Exp: Nature (04), Theo.:PRB (05)

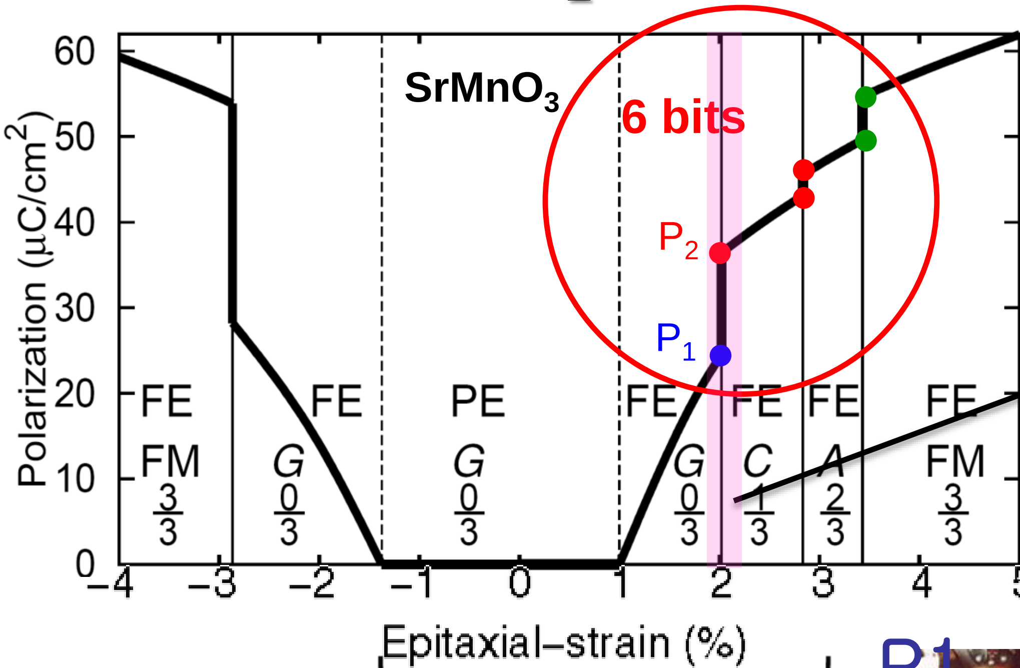


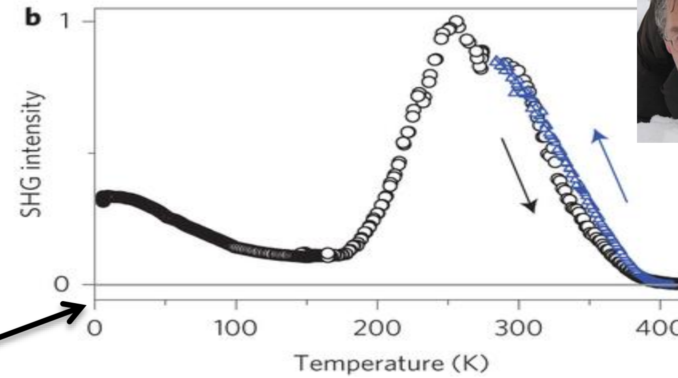




| | |
|---|---|
| $P_z$=50μC/cm² | $P_z$=30μC/cm² |
| M = 3 $\mu_B$ | M = 0 $\mu_B$ |
| c = 4.2 Å | c = 4.0 Å |
| = 0.5 eV | $E_g$ = 1.0 eV |

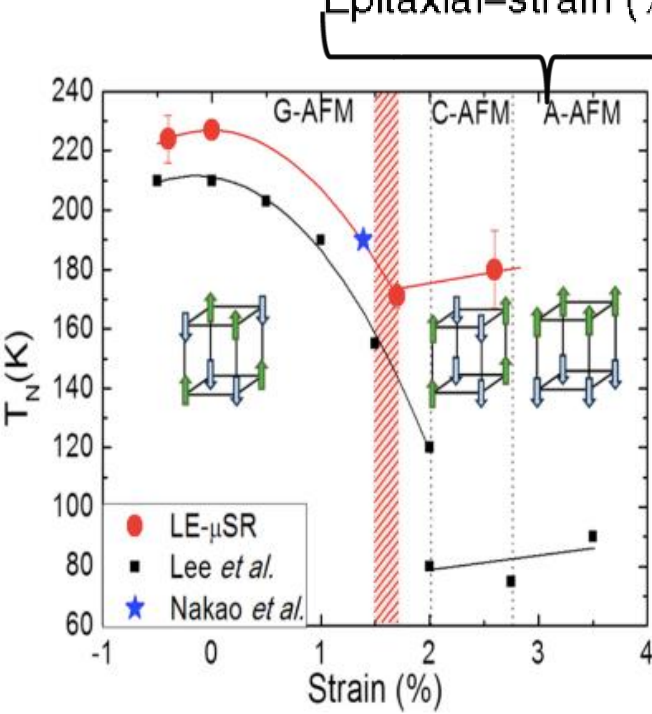
strain

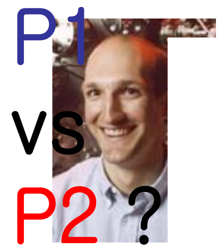
# Experimental Conformation



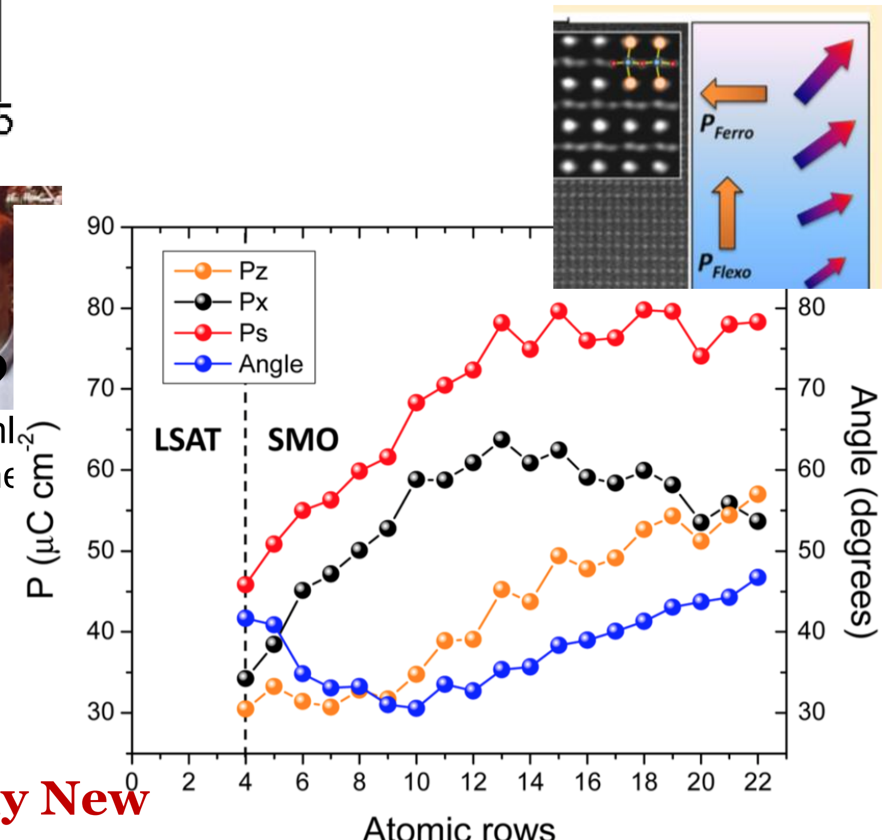

SHG, M. Fiebig et al, Nat. Nanotech (2015)




D. Schl
(Corne

Algarabel et al.,
PRB (2015)
(Neutron)

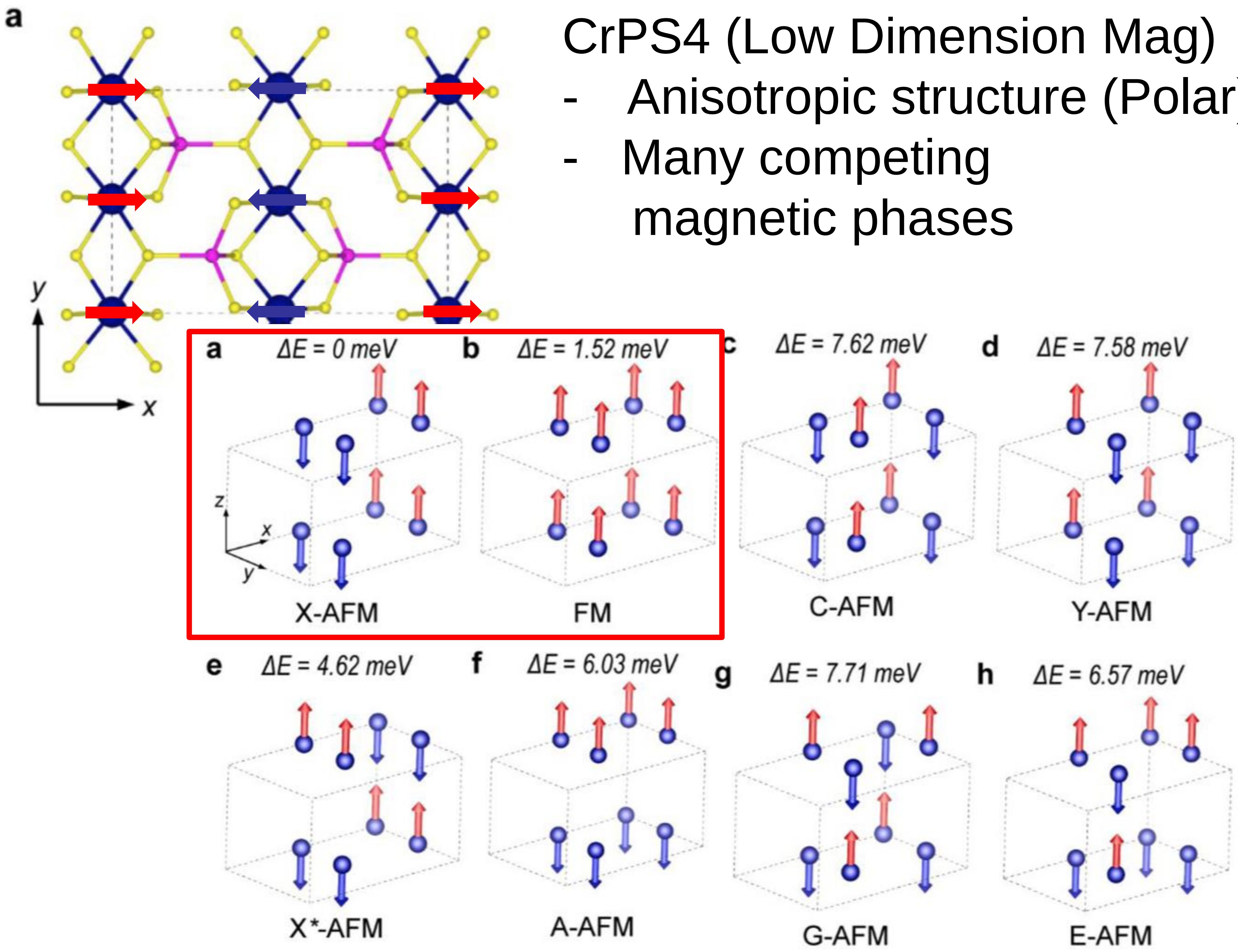



**Completely New Multiferroic Phases !**

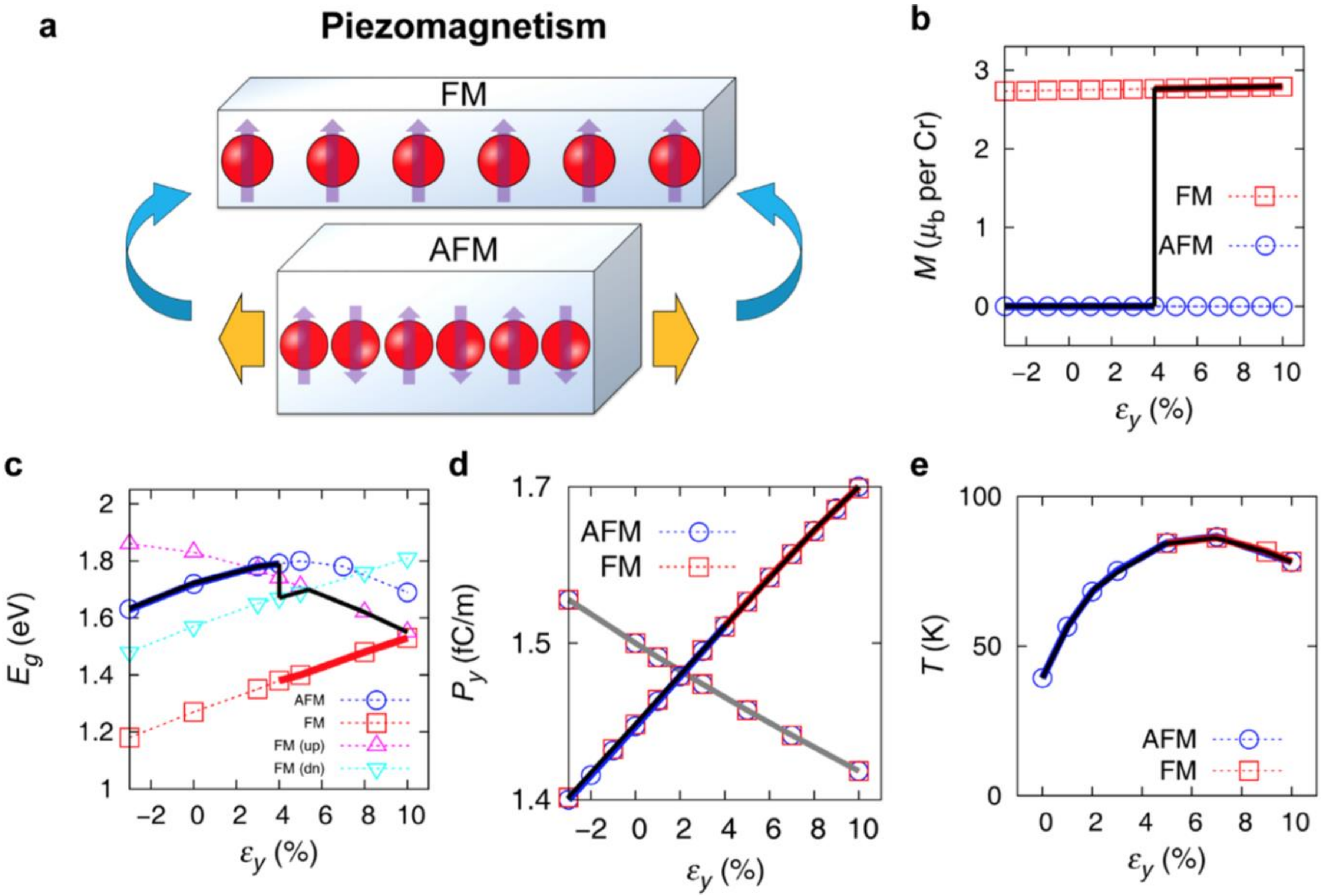
TEM, Guzman et al, Nano Letters (2016)

# CrPS4 (Low Dimension Mag)

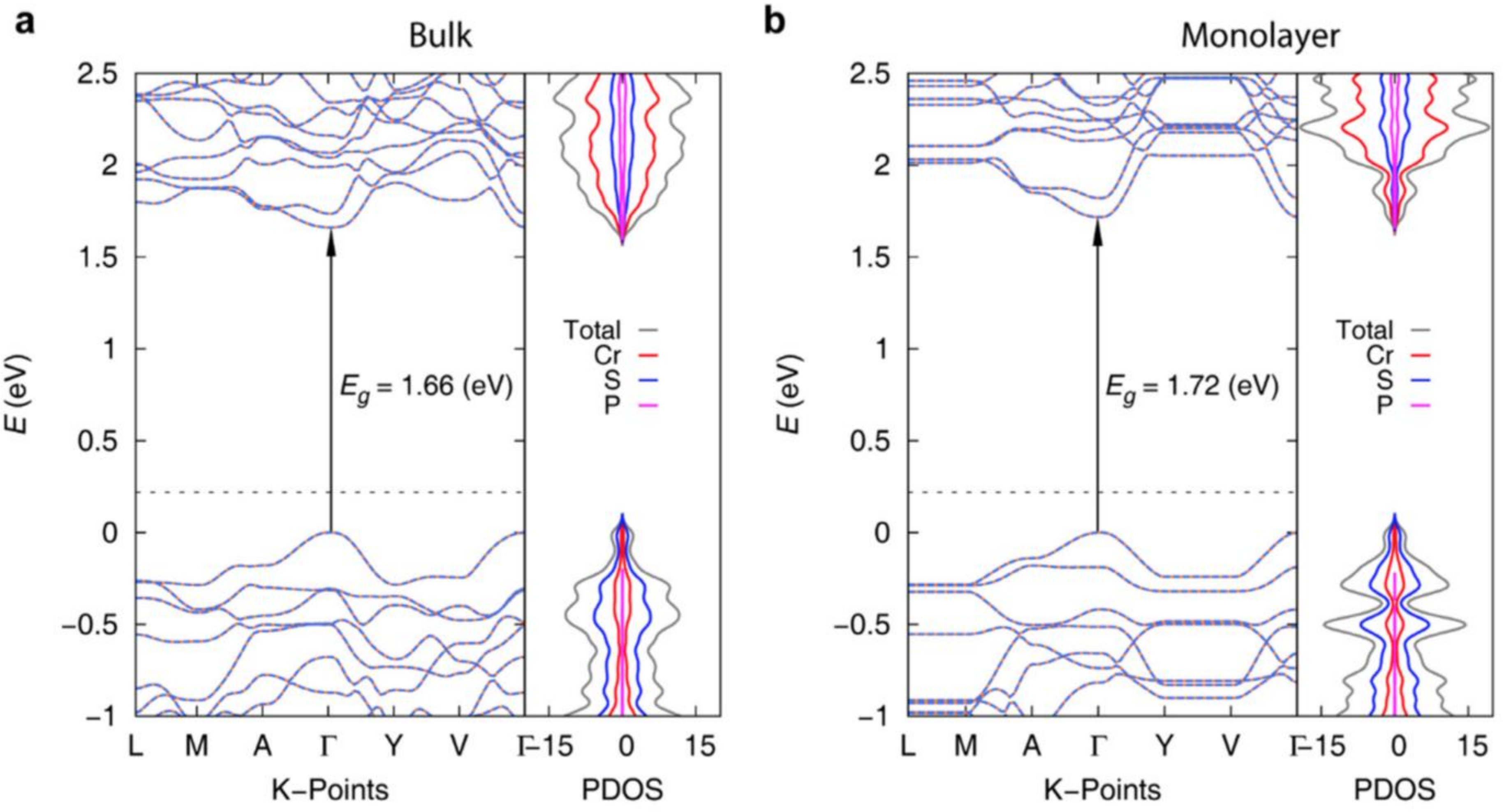
- Anisotropic structure (Polar)
- Many competing magnetic phases



# CrPS4 (FM semiconductor)
# - Competing AFM vs FM at 4 % uniaxial strain

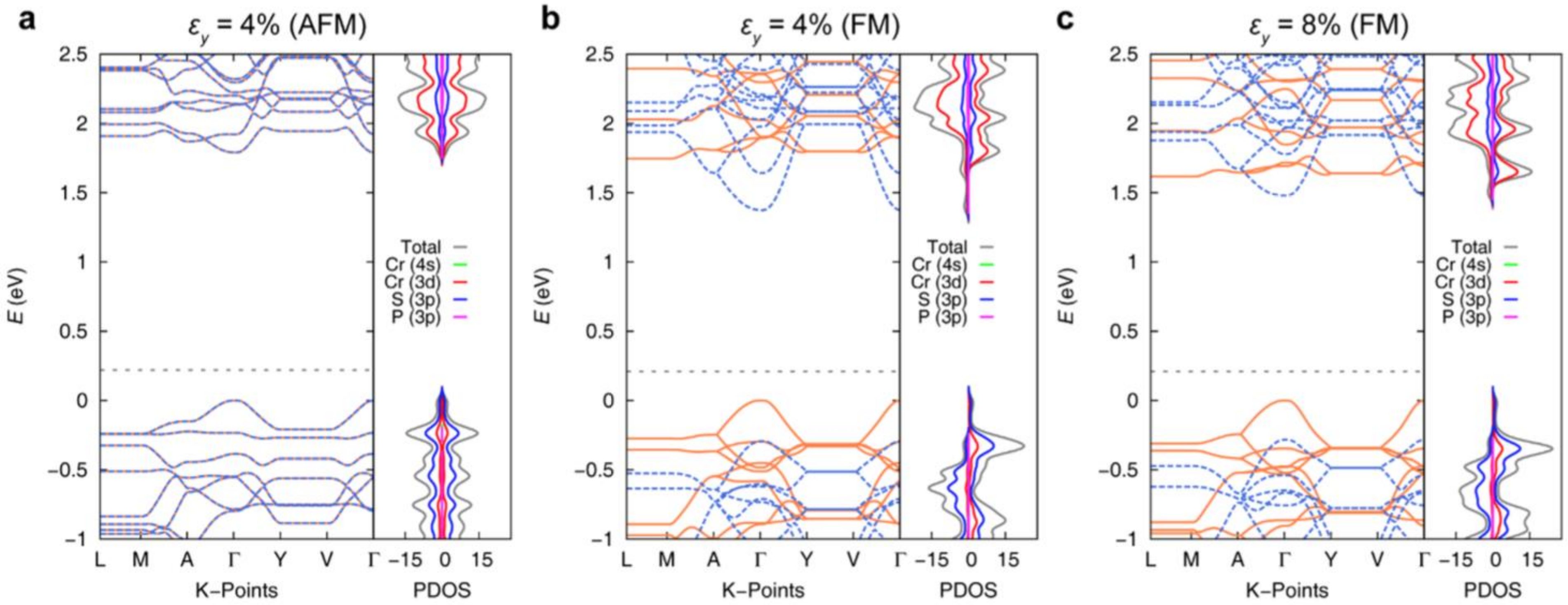


# Bulk – monolayer band gap – direct gap




Slight increase in band gap of monolayer
Charge transfer gap

# Ferroelectric Ferromagnetic Semiconductor

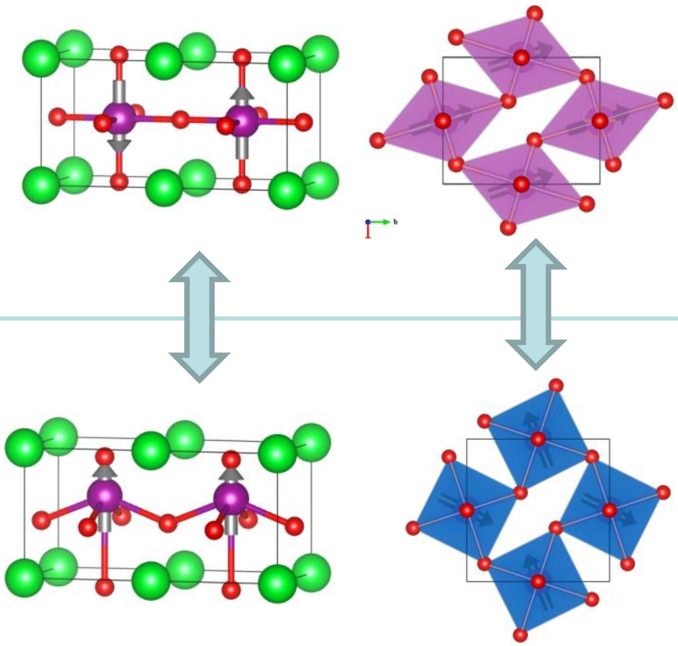



Robust Ferromagnetic Semiconductor

$E_g$ increases with uniaxial strain

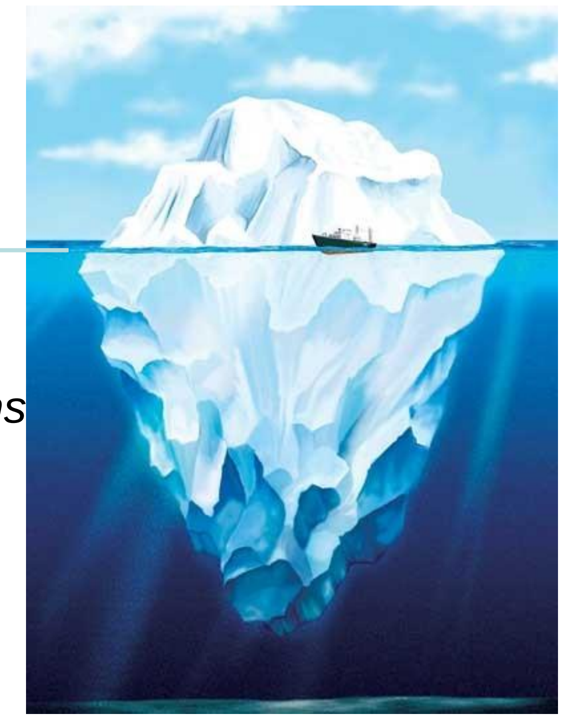
# Direction – Completely *New* states from Materials genome

***"Order parameters changed more easily in multiples than single."***



**Ground state**
*One combination*

**Meta states**
*Different combinations of order parameters*



**Smart dielectric constants from metastates**

**Multi-bits memory, memcapacitors at room-*T***

**Candidates of graduates/postdocs are welcomed!**

**(Quantum Materials for Energy Conversion (QMEC),**
**junhee@unist.ac.kr)**