Relaxor: what is it good for?

Brahim Dkhil

University Paris-Saclay, CentraleSupélec, CNRS-UMR8580, Labo SPMS
France

université PARIS-SACLAY

CentraleSupélec

cnrs dépasser les frontières

What is a relaxor?

What is a relaxor?

Someone who practices yoga?

What is a relaxor?

Someone who practices yoga?

A sort of veggie diet?

What is a relaxor?

Someone who practices yoga?

A sort of veggie diet?

Me in Cargèse?

Or something else?

Menu

Some basics and ingredients

Electric field effect

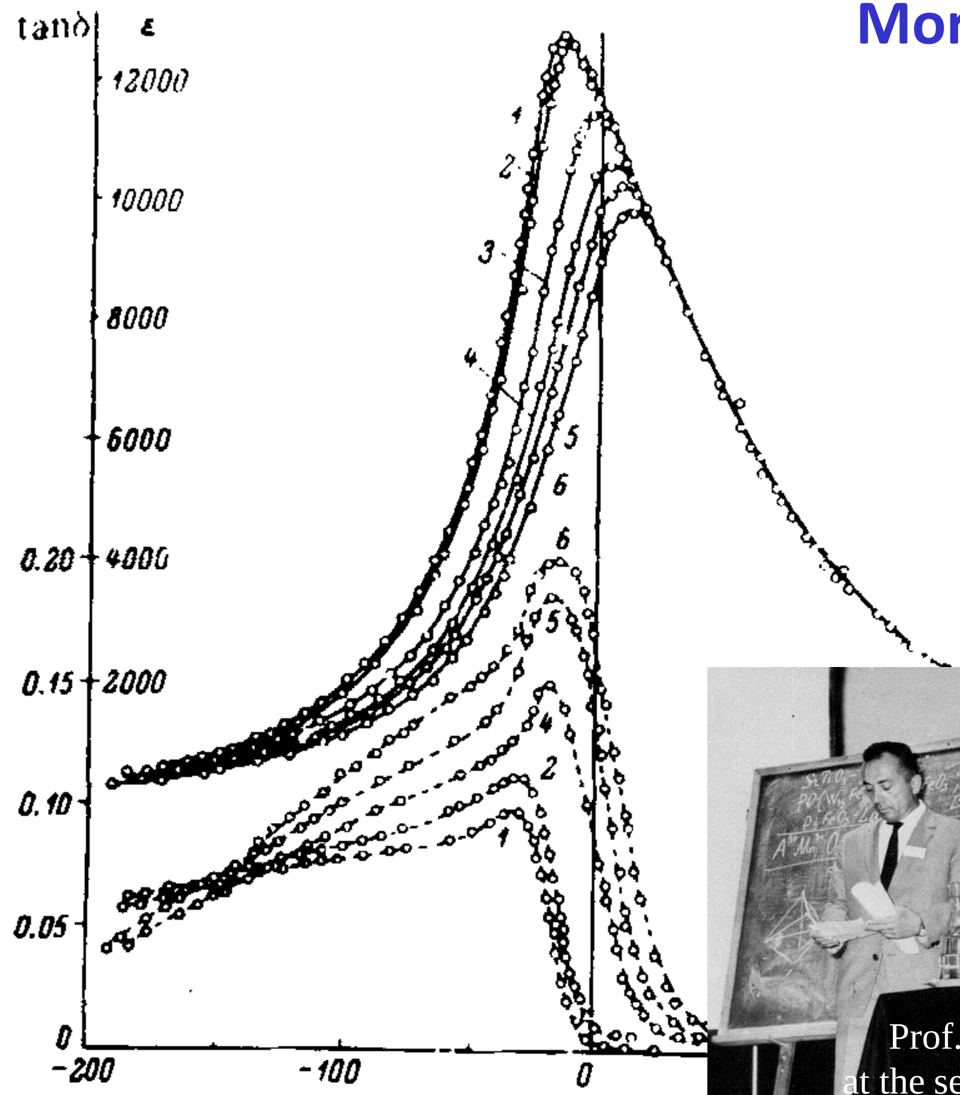
The Physics behind

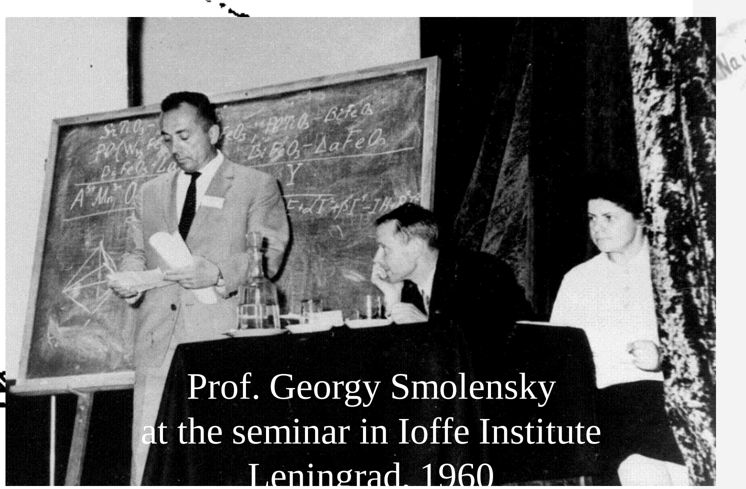
Applications

More than 60 years of relaxors

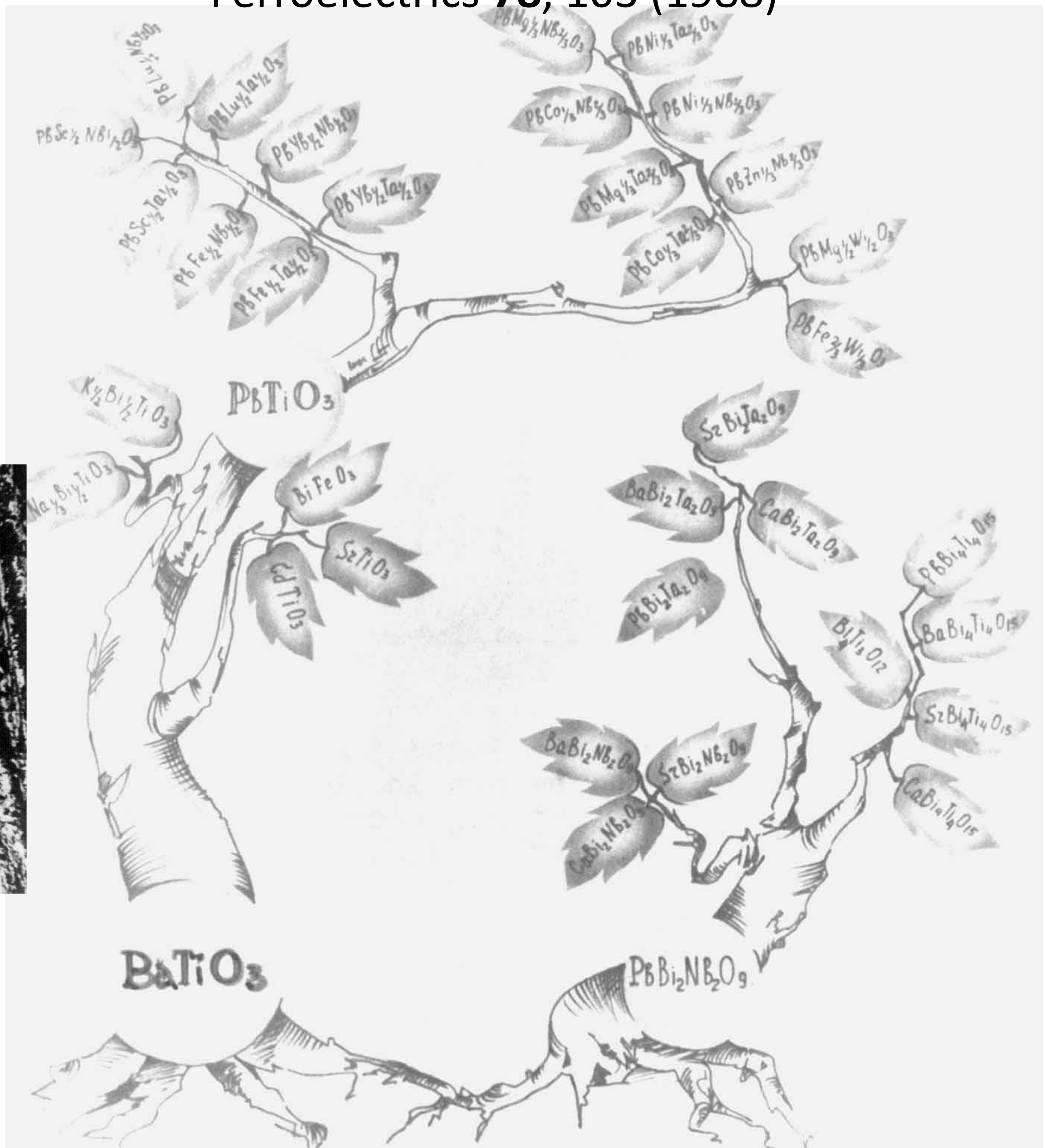
Contribution of Prof G. A. Smolensky to ferroelectricity

Ferroelectrics **78**, 103 (1988)



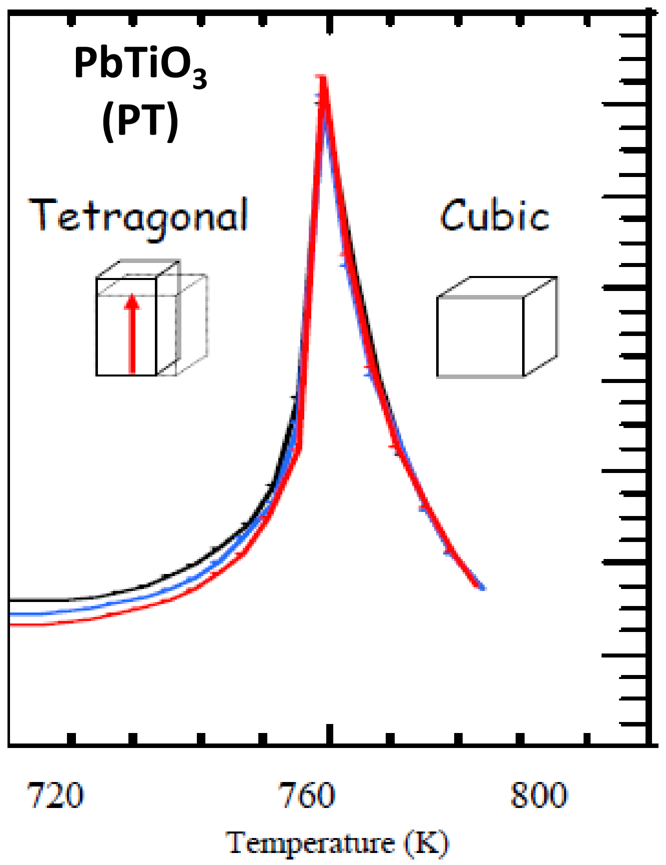


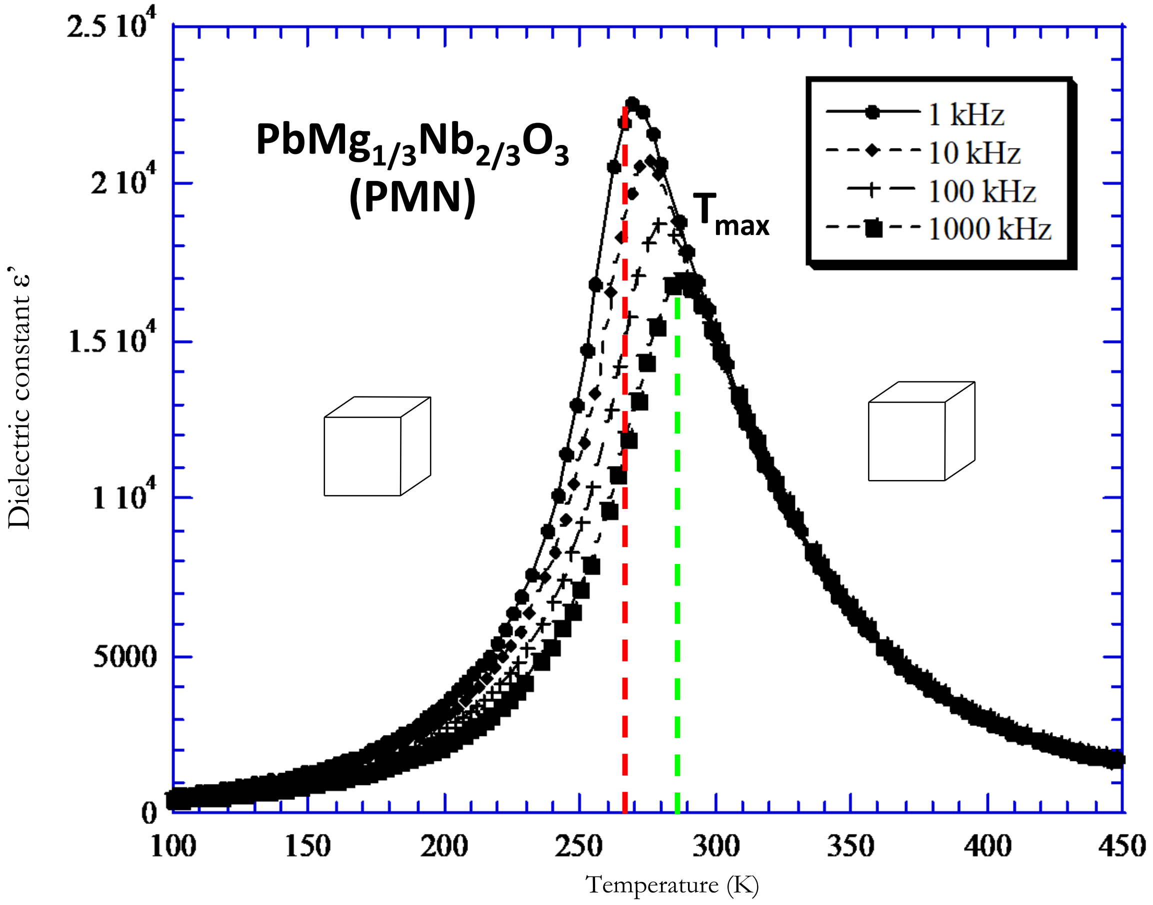
Prof. Georgy Smolensky
at the seminar in Ioffe Institute
Leningrad, 1960



Zh. Tekh. Fiz. **28**, 1491 (1958) [Sov. Phys.-Tech. Phys. **3**, 1380 (1959)]; Zh. Tekh. Fiz. **28**, 2152 (1958) [Sov. Phys.-Tech. Phys. **3**, 1981 (1959)]; Fiz. Tverd. Tela. **2**, 2906 (1960); [Sov. Phys. Solid State **2**, 2584 (1961)]

Normal Ferroelectric to Relaxor Ferroelectric





- No frequency relaxation
- Sharp narrow ε'(T) peak
- Structural phase transition . with macroscopic change at Tc

- Strong frequency dependence
- Very broad ε'(T) anomaly
- No structural phase transition across T_{max}

Relaxor ingredients

- Organic-like :

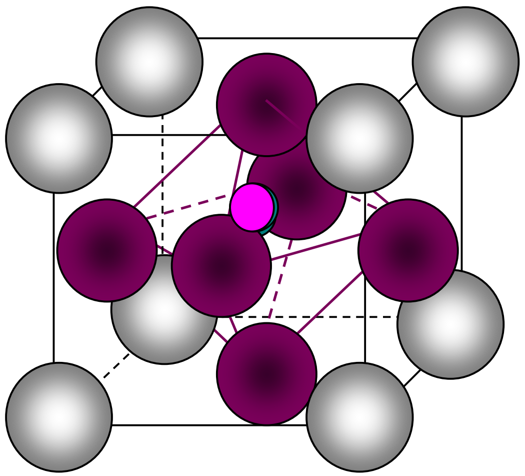
  irradiated vinylidene fluoride-trifluoroethylene copolymers (P(VDF-TrFE))

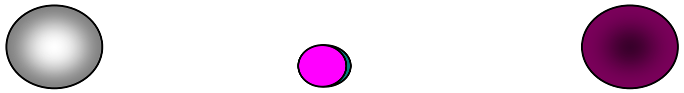
- Inorganic-like : - Tungsten bronze structure-type :

  $Sr_xBa_{1-x}Nb_2O_6$ (SBN), …

  - **Perovskite** structure-type : the most studied

  $PbMg_{1/3}Nb_{2/3}O_3$ (**PMN**), $PbSc_{1/2}Nb_{1/2}O_3$ (PSN), $Na_{1/2}Bi_{1/2}TiO_3$ (NBT), $BaZrTiO_3$ (BZT)…





A	B	O_3	
Pb	$Mg_{1/3}Nb_{2/3}$	O_3	(PMN)
$Na_{1/2}Bi_{1/2}$	Ti	O_3	(NBT)
$Pb_{(1-3x/2)}La_x$	$Zr_{(1-y)}Ti_y$	O_3	(PLZT)
Ba	Zr_xTi_{1-x}	O_3	(BZT)

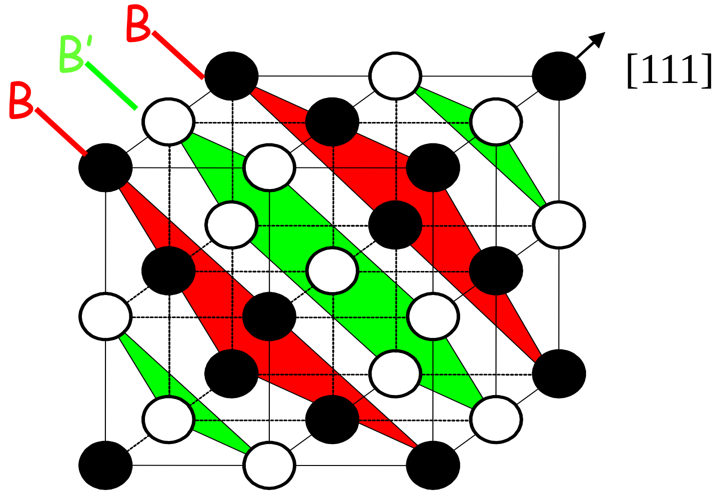
Need of chemical disorder… and some "local" order

Case of $Pb(BB')O_3$

Compound	B-site ordering
$PbCo_{1/2}W_{1/2}O_3$	ordered
$PbMg_{1/2}W_{1/2}O_3$	ordered
$PbYb_{1/2}Nb_{1/2}O_3$	ordered
$PbIn_{1/2}Nb_{1/2}O_3$	ordered or disordered
$PbIn_{1/2}Ta_{1/2}O_3$	ordered or disordered
$PbSc_{1/2}Nb_{1/2}O_3$	ordered or disordered
$PbSc_{1/2}Ta_{1/2}O_3$	ordered or disordered
$PbMg_{1/3}Nb_{2/3}O_3$	disordered
$PbZn_{1/3}Nb_{2/3}O_3$	disordered
$PbMg_{1/3}Ta_{2/3}O_3$	disordered

Normal ferroelectric

Relaxor ferroelectric

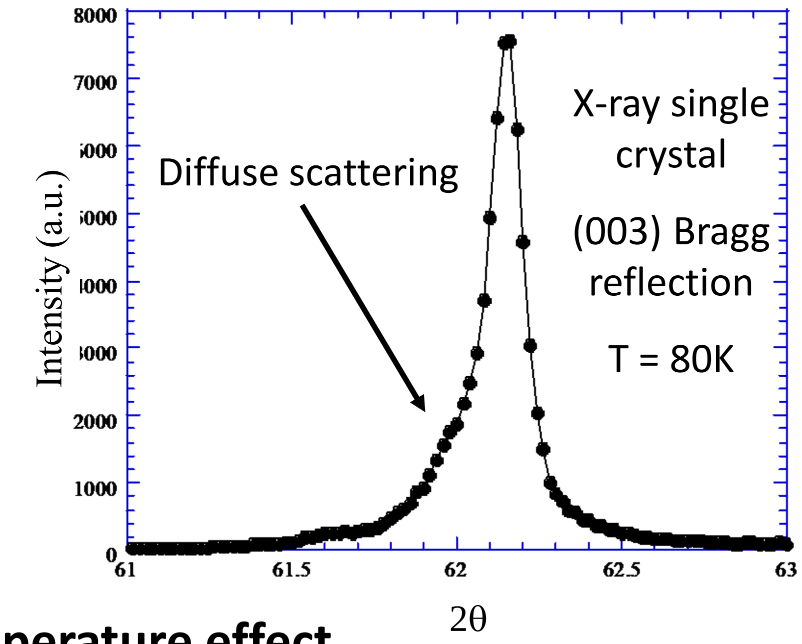


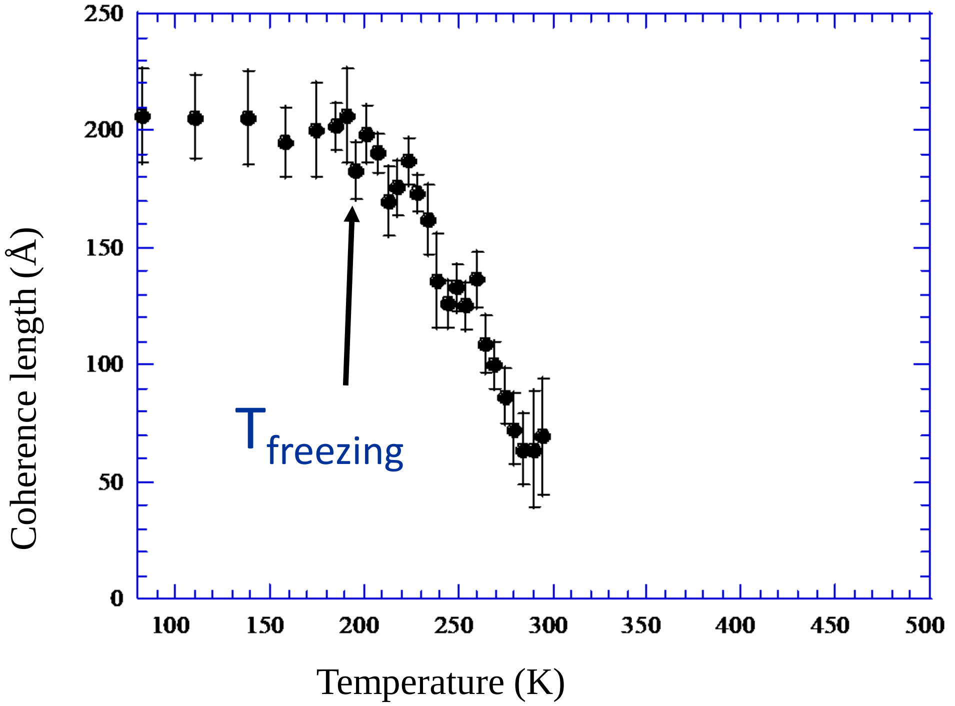
"space charge" : B = Mg^{2+}, B' = Nb^{5+}

⇨ $\{Pb(Mg_{1/2}Nb_{1/2})O_3\}^{-} \equiv$ **random electric field (RF)**

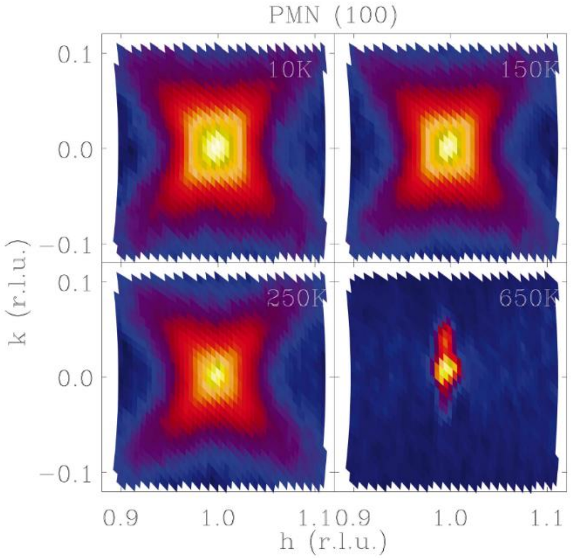
Need also for some polar order/disorder

« Butterfly » Diffuse scattering ⇨ **Polar NanoRegions (PNR)**

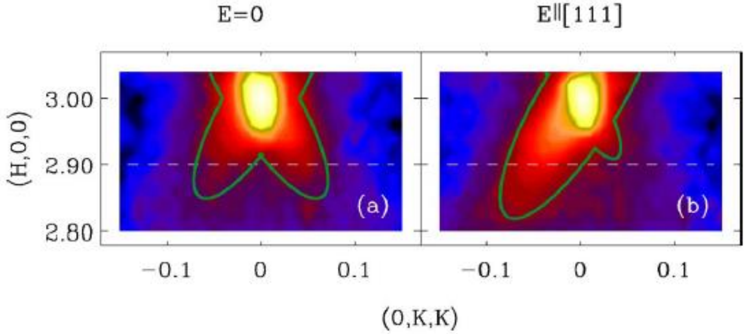




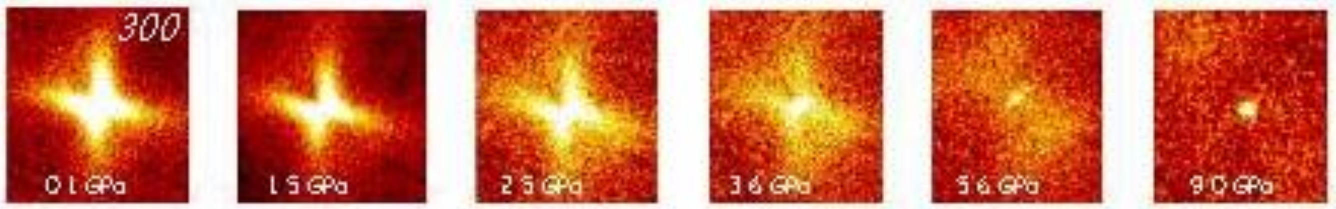
Temperature effect



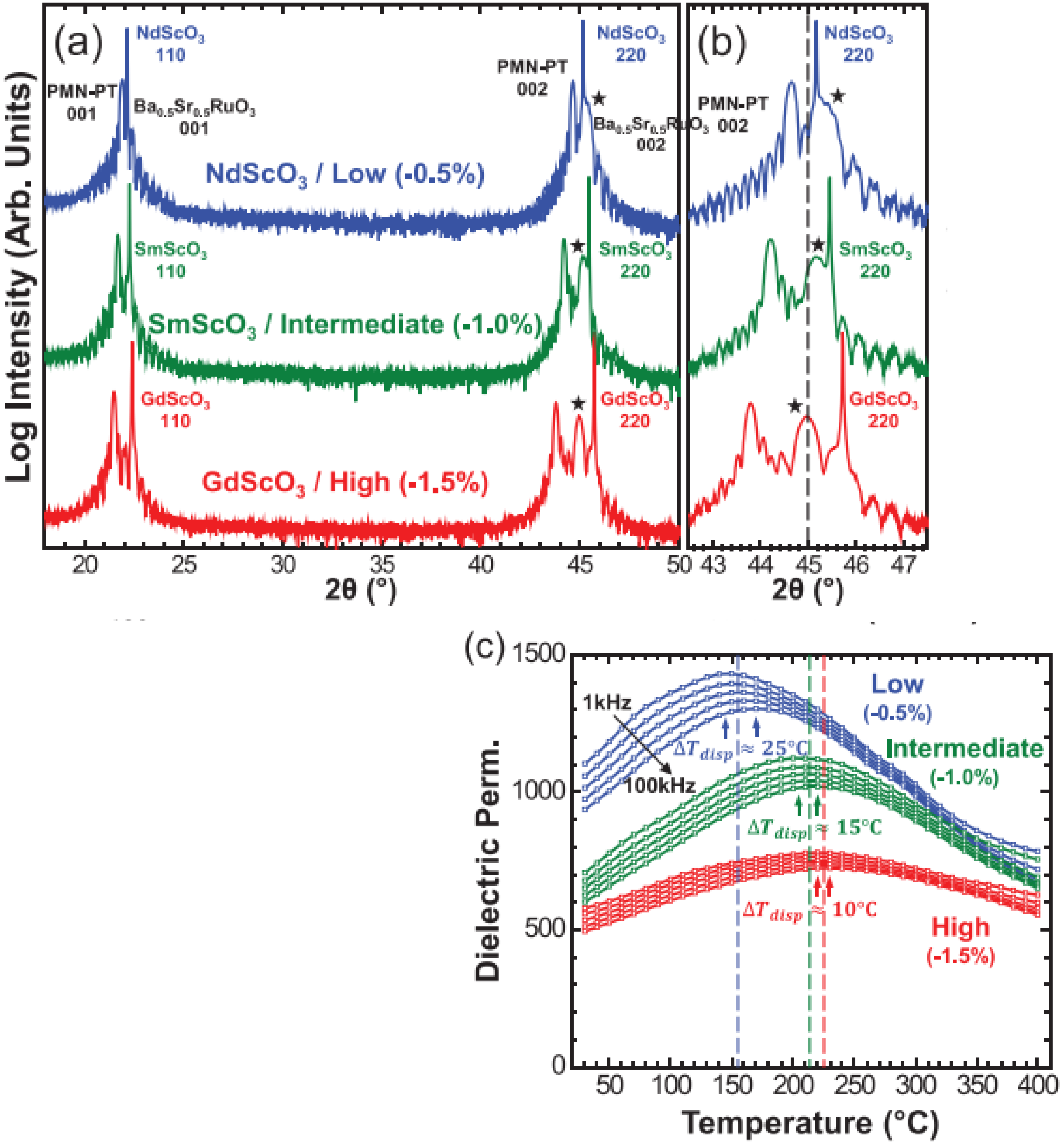
Electric field effect

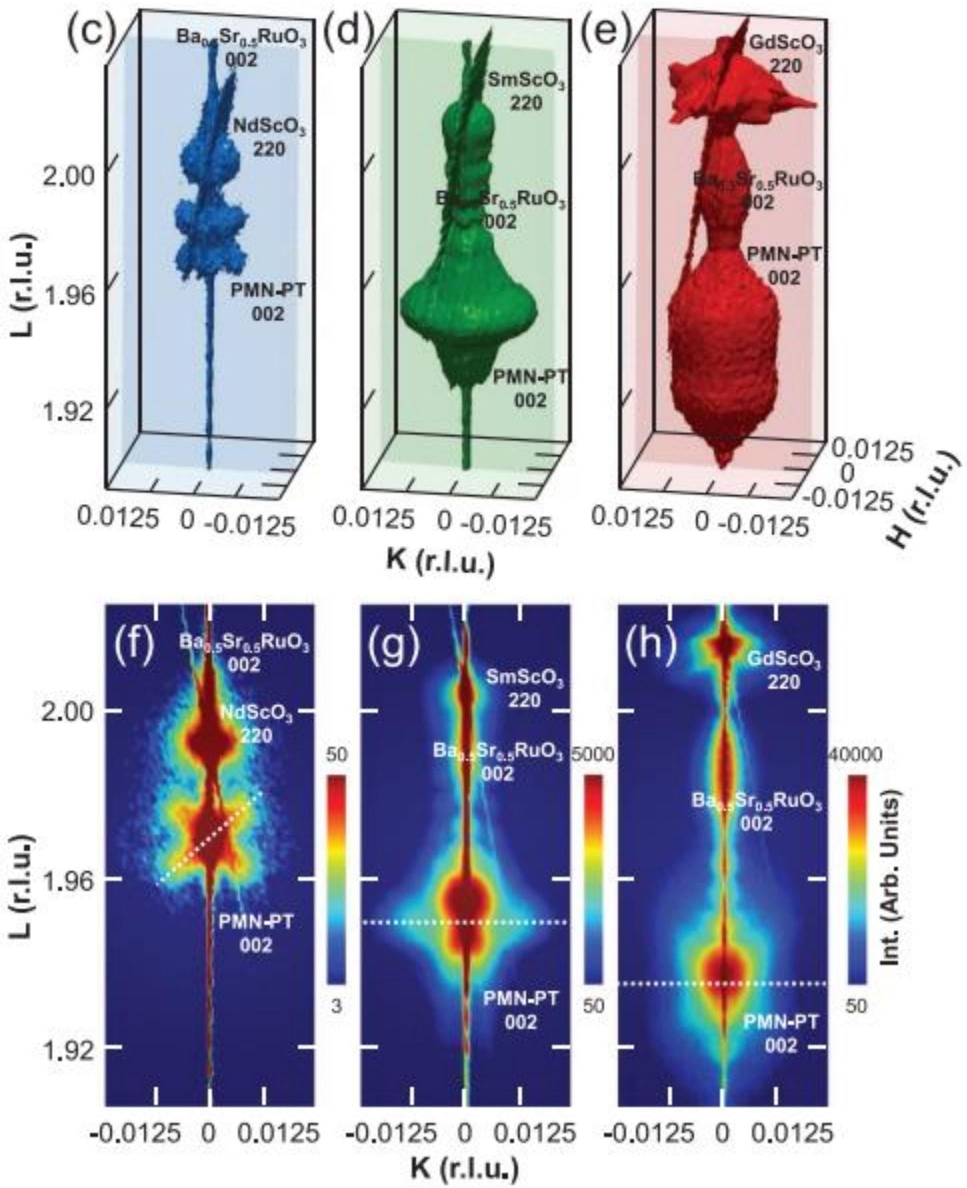


Pressure effect



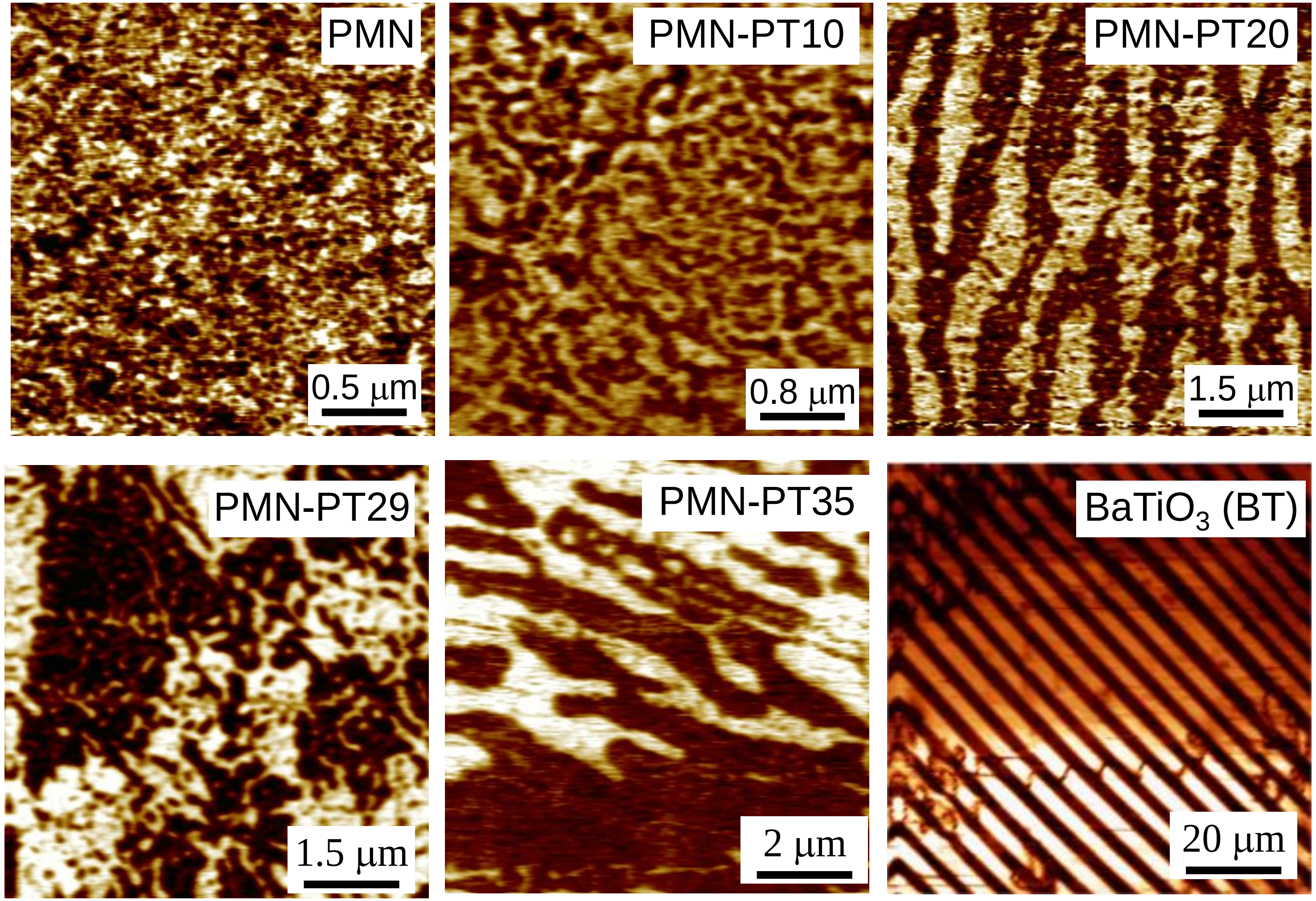
Need also for some polar order/disorder

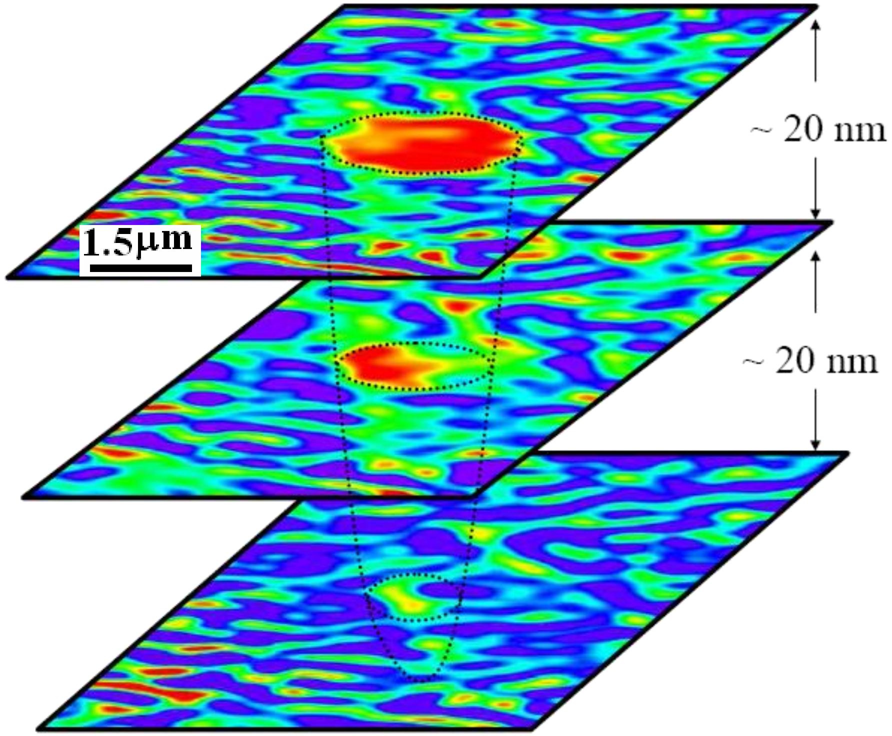




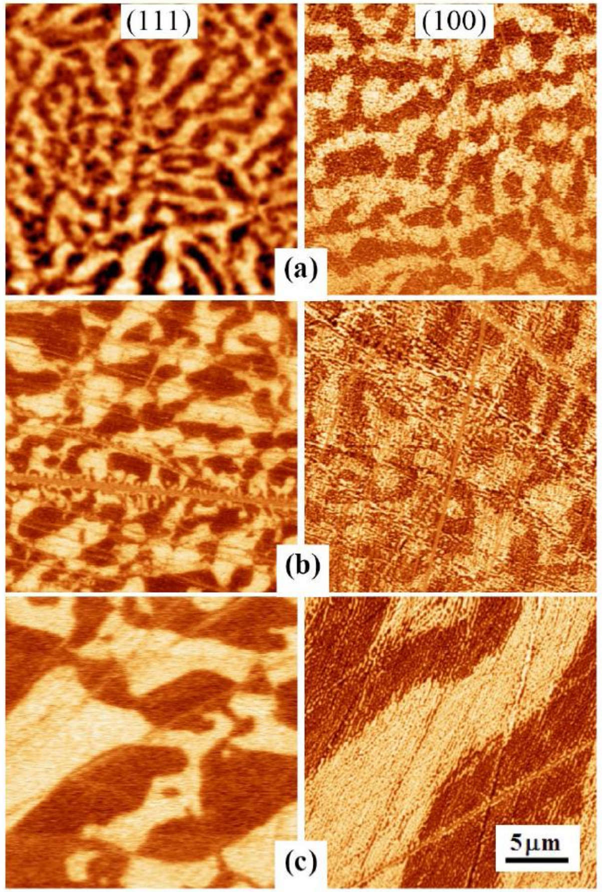
Kim et al., Adv. Mater. 2019, 1901060

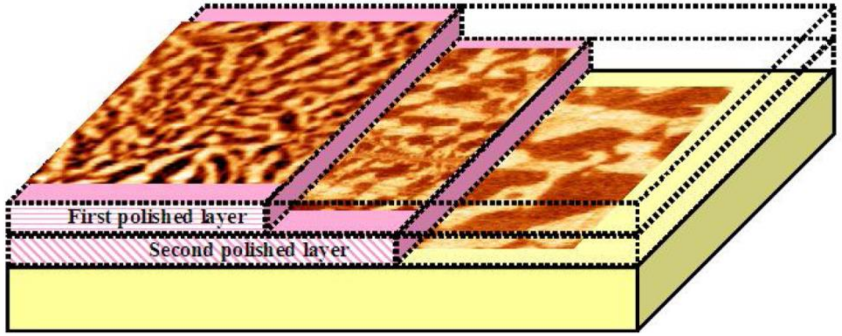
Richness of local polar state: labyrinth domains, no needle-like domains motion

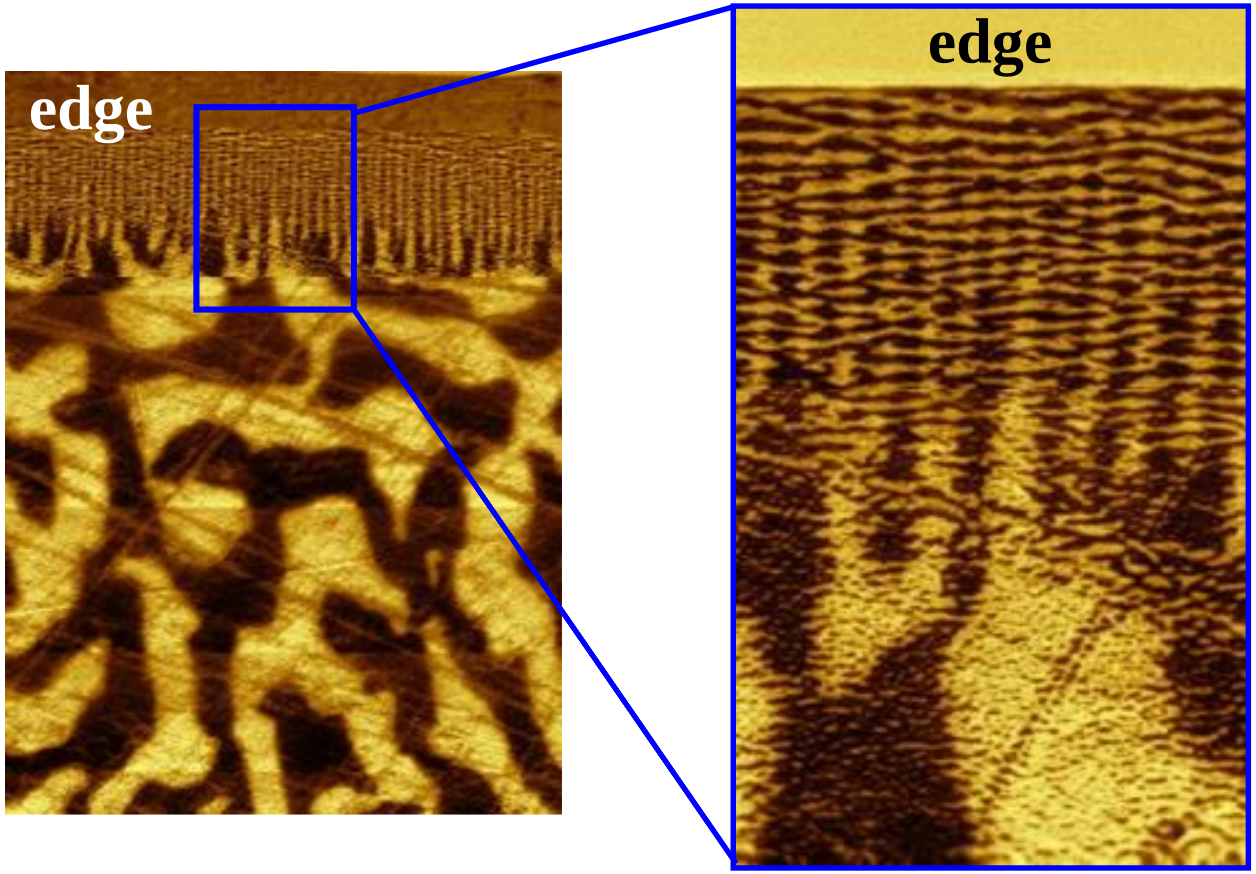




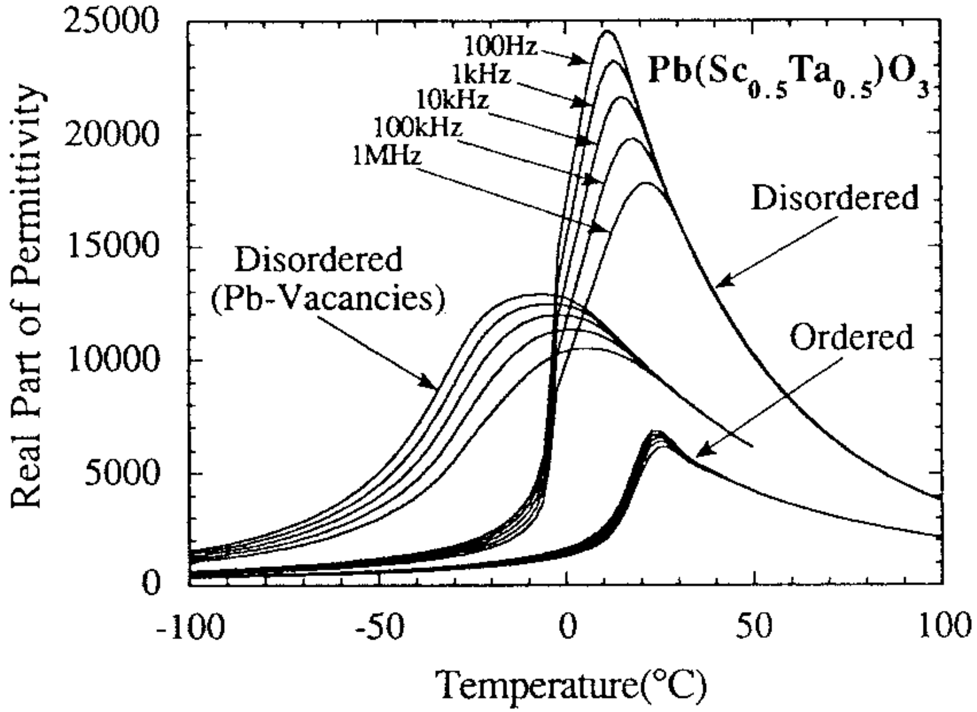
Richness of local polar state: domain branching

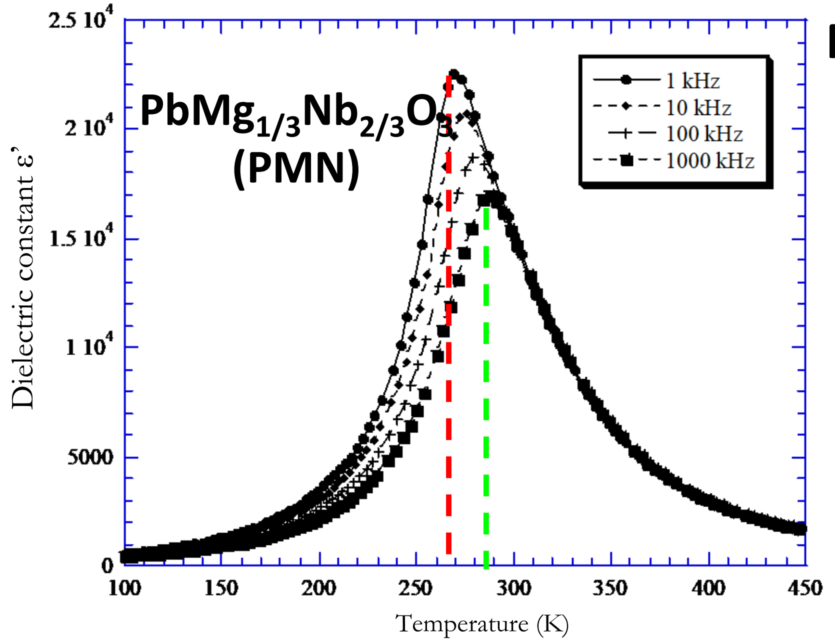






Existence of T_f





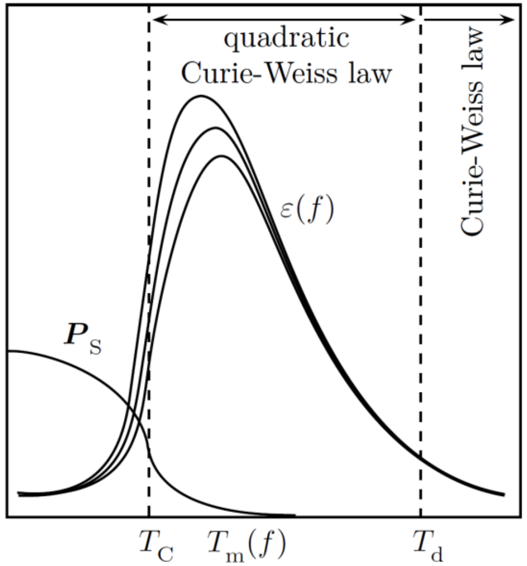
Modified Curie-Weiss law

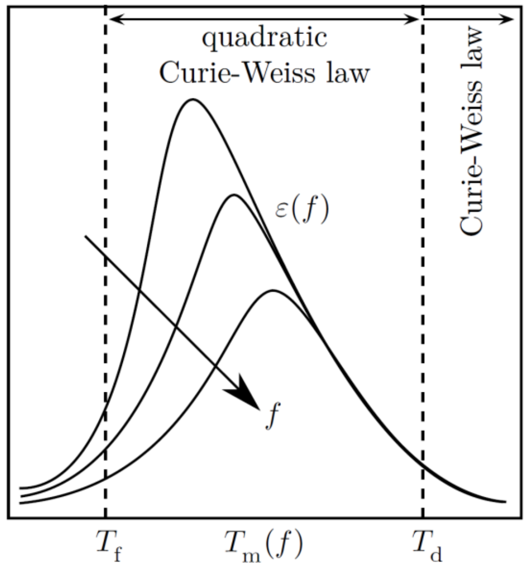
$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \frac{(T - T_m)^{\gamma}}{C_C}$$

Vogel-Fulcher law

$$f = f_0 \exp\left(\frac{T_0}{T_m - T_f}\right)$$

PST, PSN, PMN-PT …

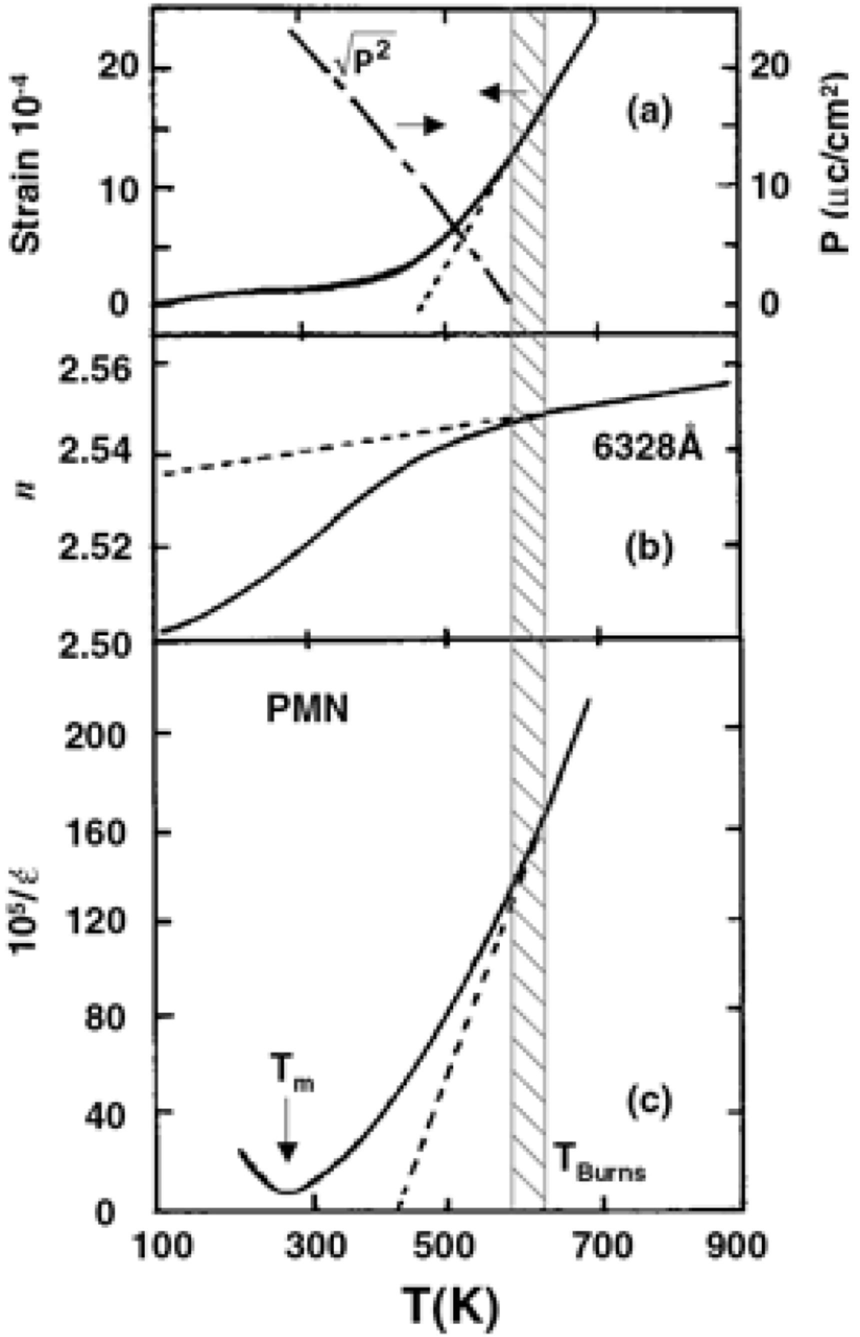




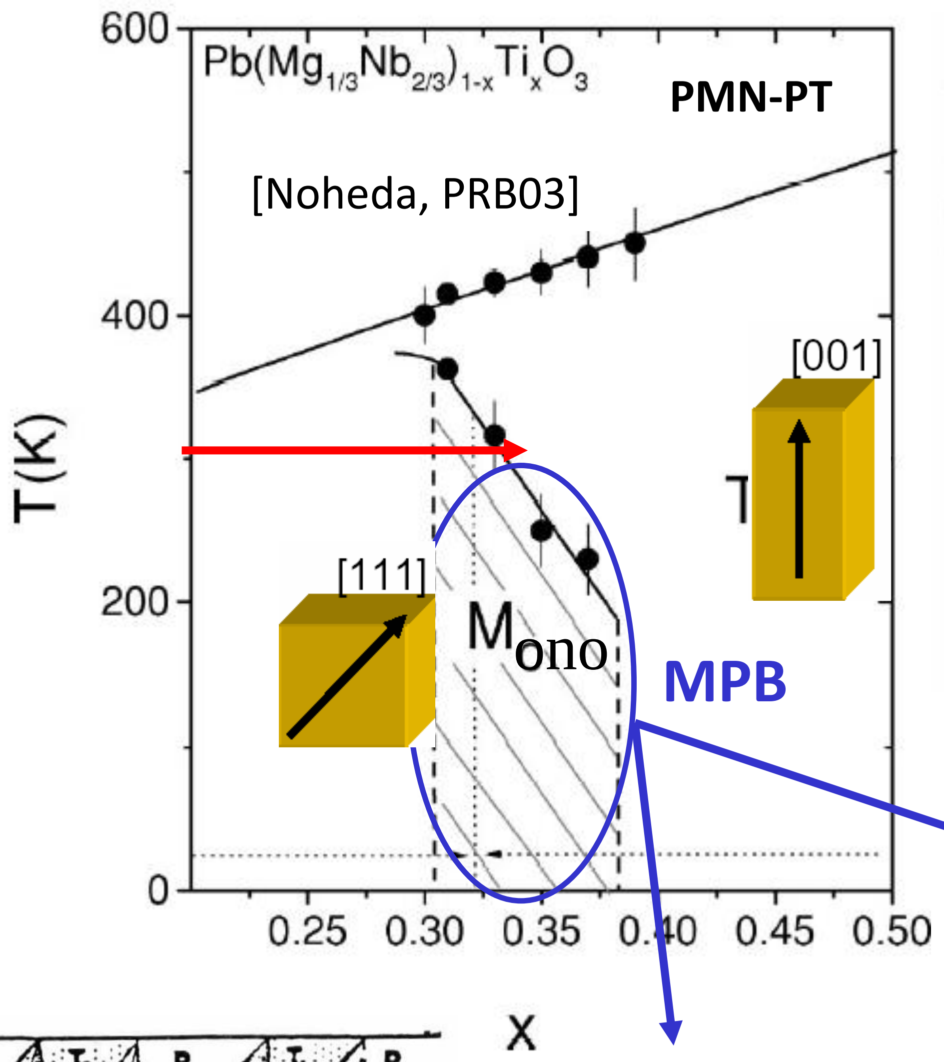
PMN

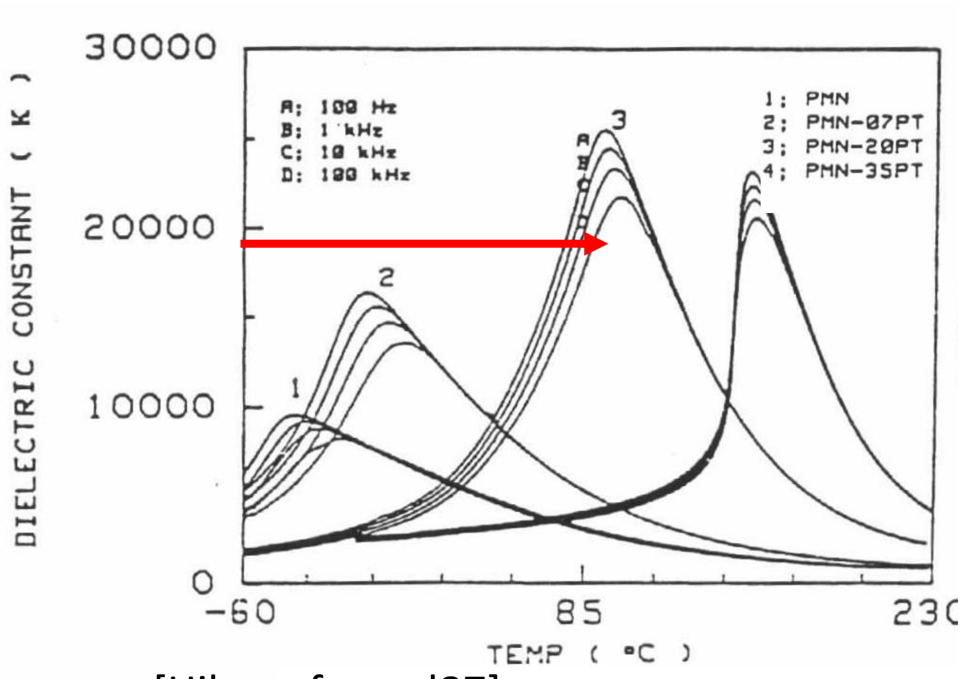
Existence of $T_{freezing}$

Existence of T_d (or T_{Burns})

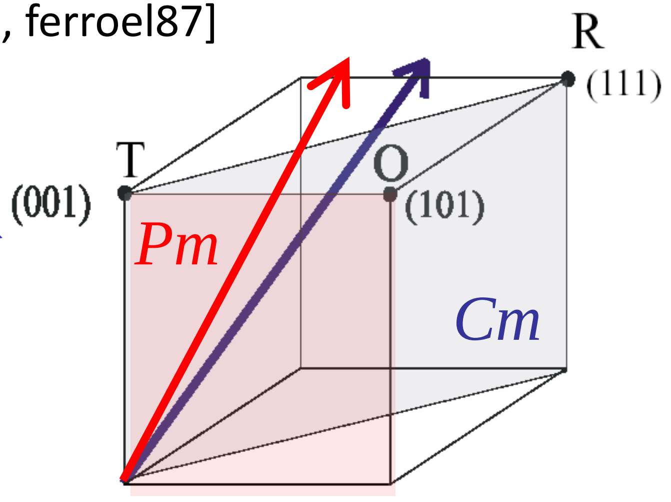


From relaxor to normal ferroelectric through Morphotropic Phase Boundary (MPB)

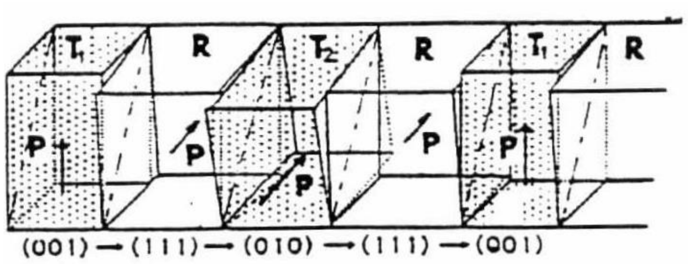




[Hilton, ferroel87]



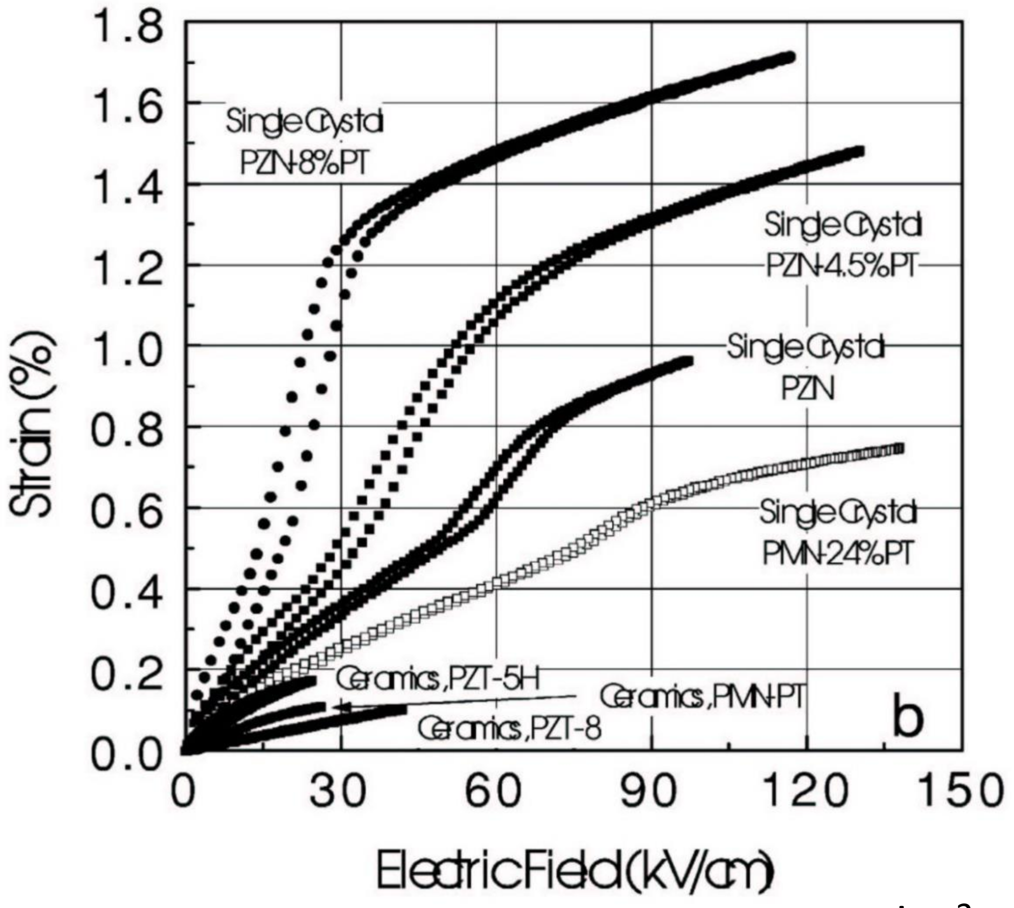
Polarization's rotation



And/Or phase coexistence
at nanoscale

Application interest: Giant piezoelectricity

Morphotropic Phase Boundary



Park&Shrout, JAP82,1804 (1997)

$k_{33}^2 = d_{33}^2 / (s^E_{33}\varepsilon^T_{33})$

PZN-4.5%PT d_{33}~**2200**pC/N ; k_{33}~92%

PMN-33%PT d_{33}~**2200**pC/N ; k_{33}~94%

PYN-46%PT d_{33}~**2500**pC/N ; k_{33}~96%

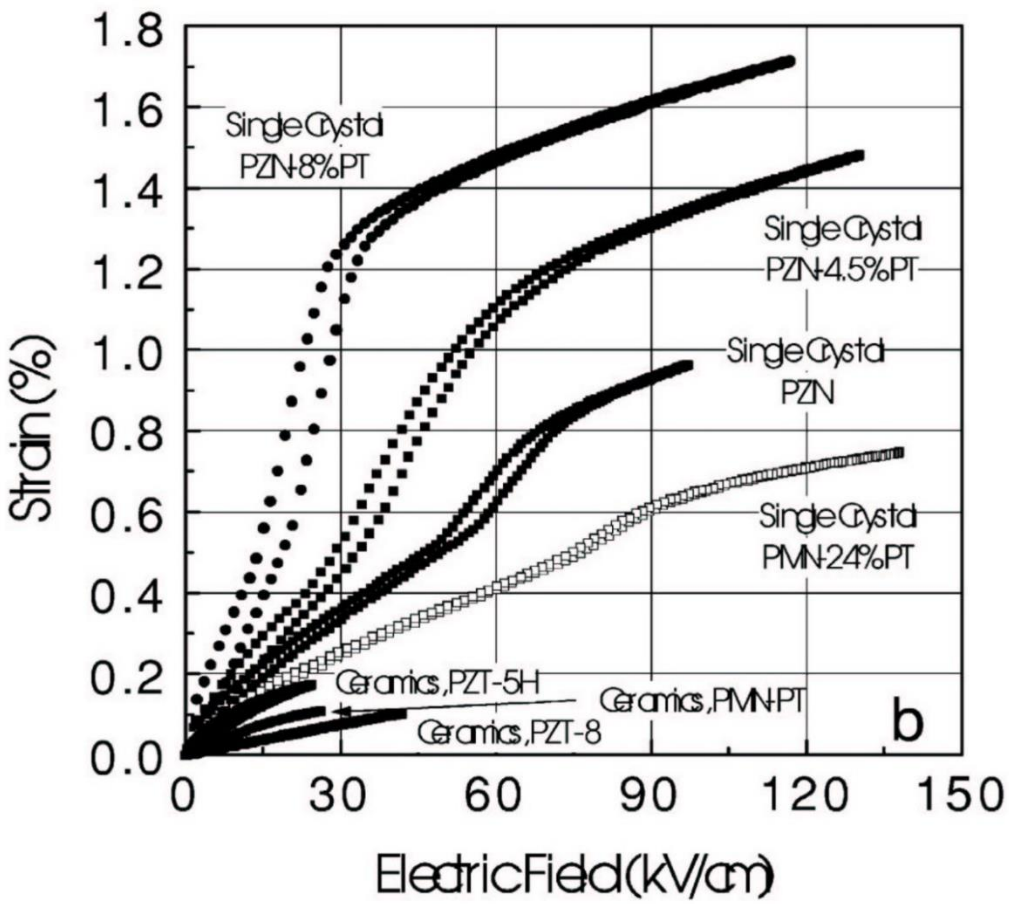
Quartz d_{33}~2.3pC/N ; k_{33}~10%

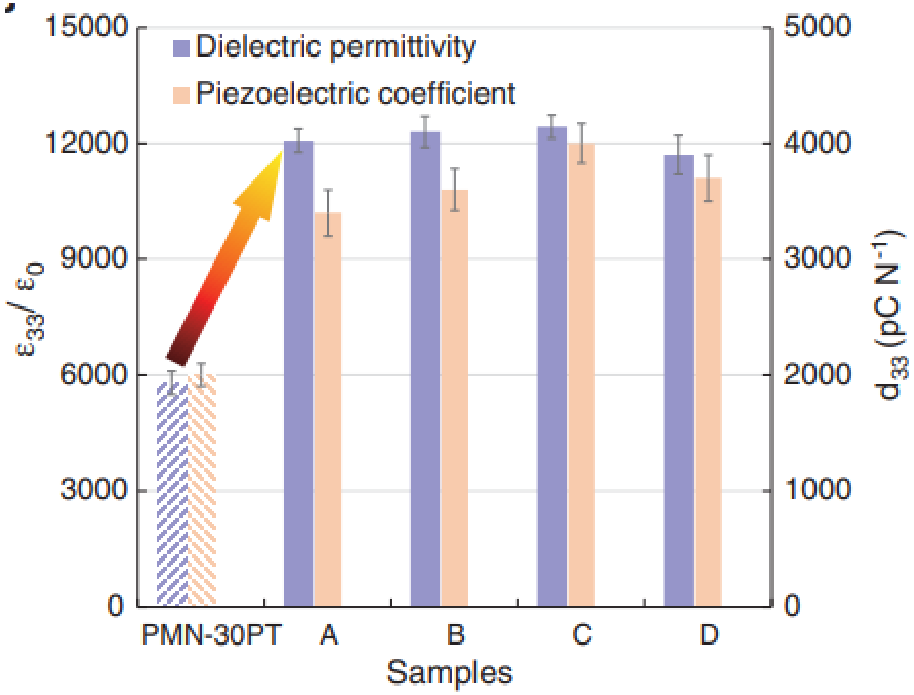
$BaTiO_3$ d_{33}~**190**pC/N ; k_{33}~52%

$Pb(ZrTi)O_3$ (PZT) type VI d_{33}~**690**pC/N ; k_{33}~79%

Application interest: Giant piezoelectricity

Morphotropic Phase Boundary





Li et al., Science 364, 268 (2019)

Park&Shrout, JAP82,1804 (1997)

$k_{33}^2 = d_{33}^2 / (s^E_{33}\varepsilon^T_{33})$

PZN-4.5%PT d_{33}~**2200**pC/N ; k_{33}~92%

PMN-33%PT d_{33}~**2200**pC/N ; k_{33}~94%

PYN-46%PT d_{33}~**2500**pC/N ; k_{33}~96%

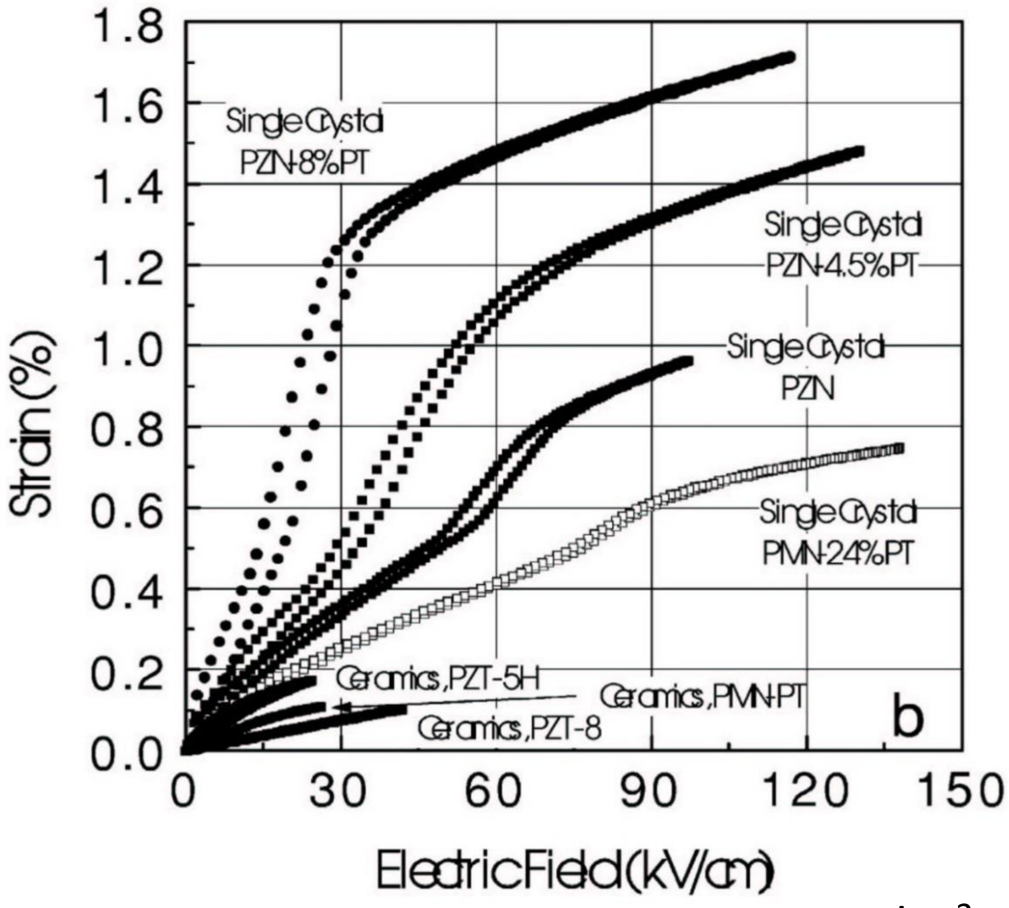
Quartz d_{33}~2.3pC/N ; k_{33}~10%

$BaTiO_3$ d_{33}~**190**pC/N ; k_{33}~52%

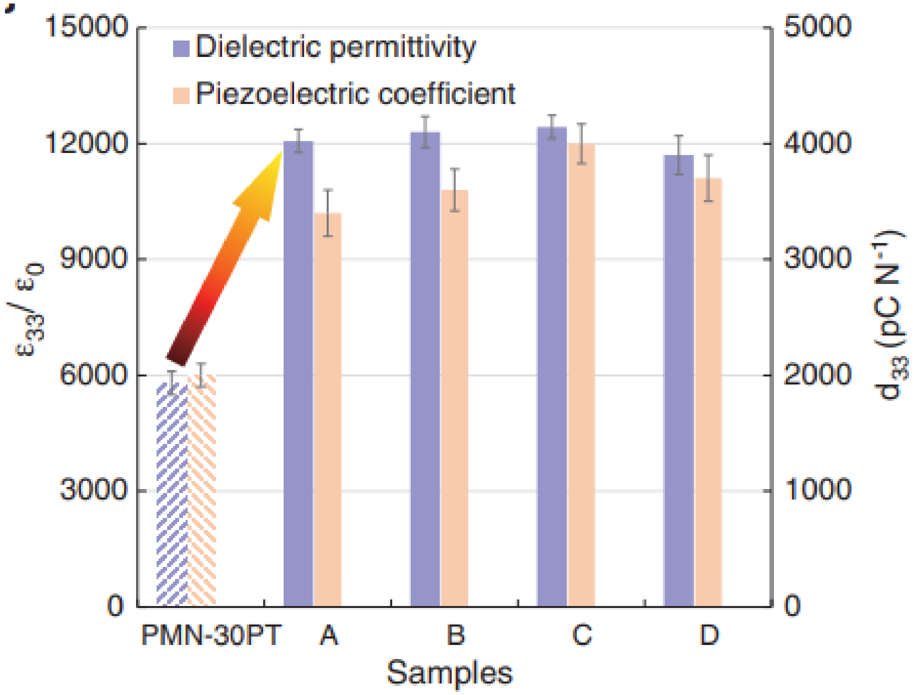
Pb(ZrTi)O_3 (PZT) type VI d_{33}~**690**pC/N ; k_{33}~79%

Application interest: Giant piezoelectricity

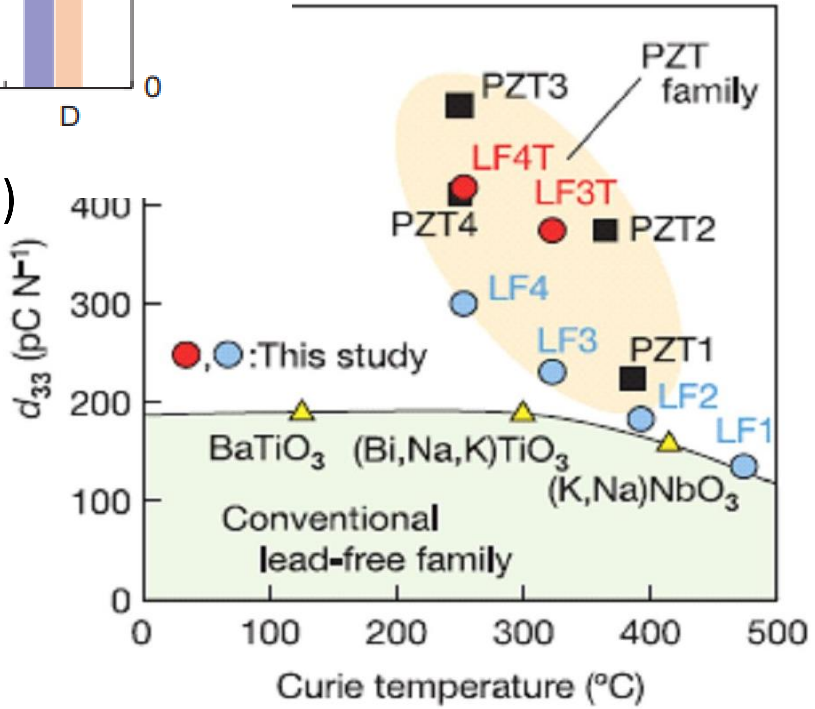
Morphotropic **P**hase **B**oundary



Park&Shrout, JAP82,1804 (1997)



Li et al., Science 364, 268 (2019)



Saito, Nature **432**, 84 (2004)

$k_{33}^2 = d_{33}^2 / (s^E_{33} \varepsilon^T_{33})$

PZN-4.5%PT d_{33}~**2200**pC/N ; k_{33}~92%

PMN-33%PT d_{33}~**2200**pC/N ; k_{33}~94%

PYN-46%PT d_{33}~**2500**pC/N ; k_{33}~96%

Quartz d_{33}~2.3pC/N ; k_{33}~10%

$BaTiO_3$ d_{33}~**190**pC/N ; k_{33}~52%

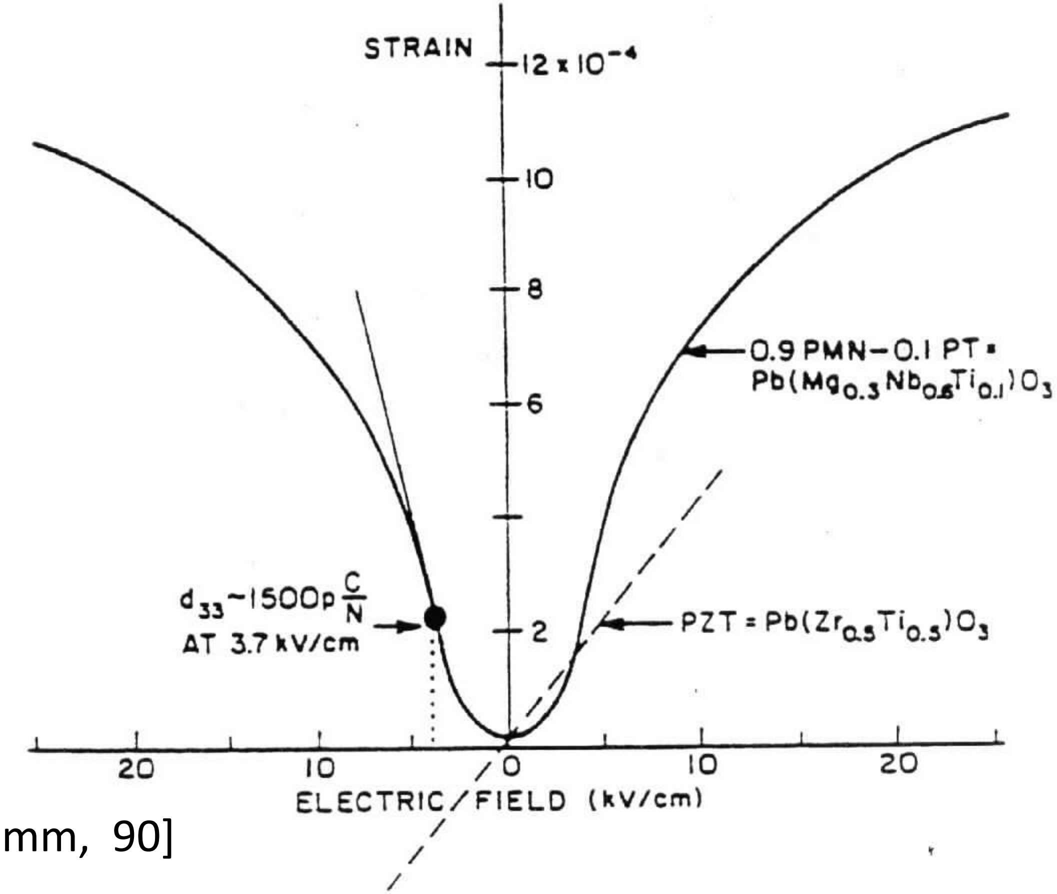
$Pb(ZrTi)O_3$ (PZT) type VI d_{33}~**690**pC/N ; k_{33}~79%

Application interest: Huge electrostriction

$$S_{ij} = d_{kij} E_k + M_{ijkl} E_k E_l + \dots$$

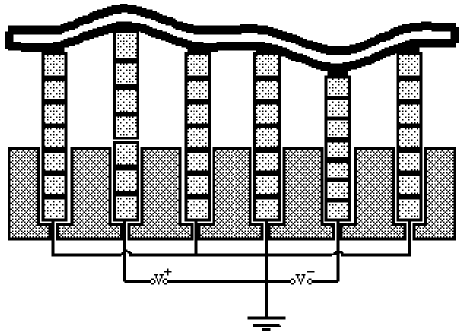
$$S_{ij} = g_{kij} P_k + Q_{ijkl} P_k P_l + \dots$$

Piézoélectricité — Électrostriction



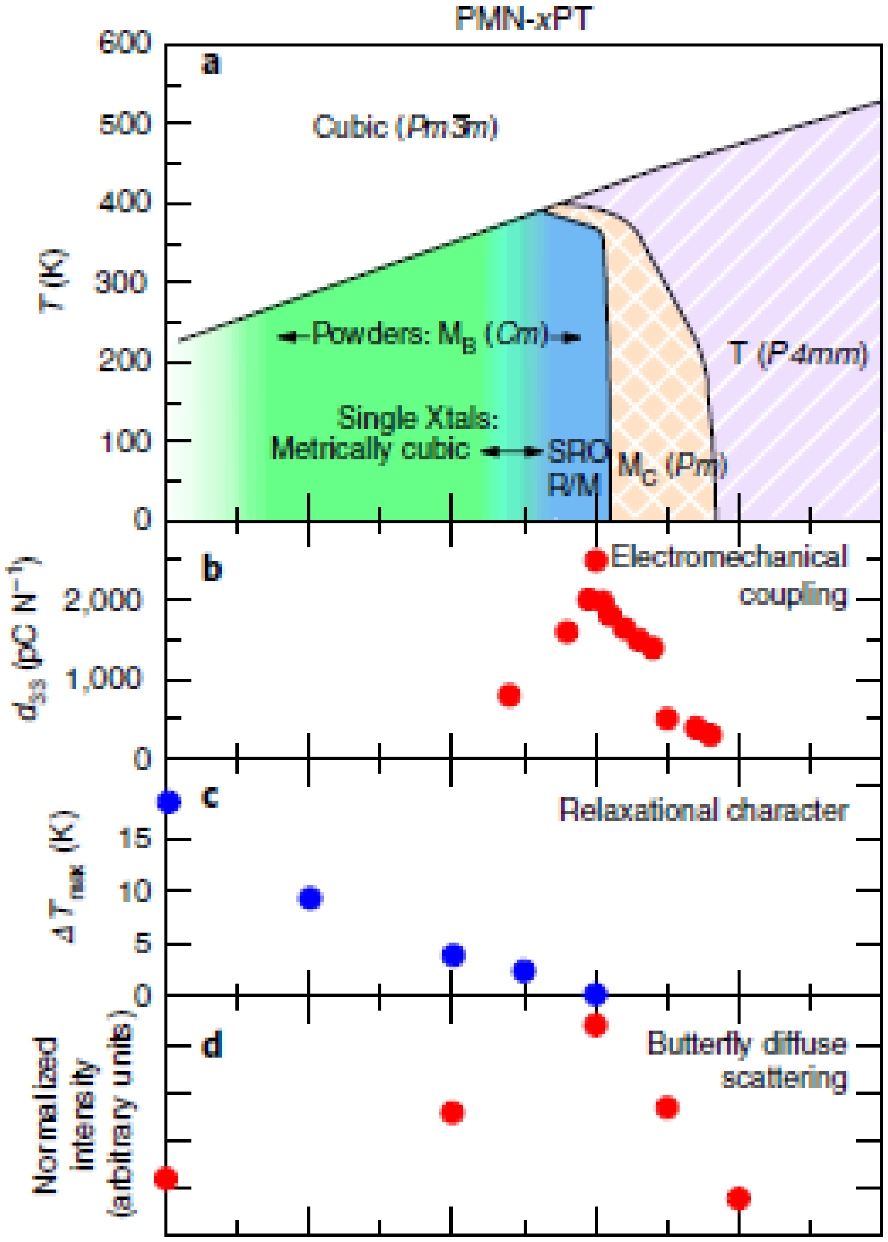
[Newnamm, 90]

Hubble

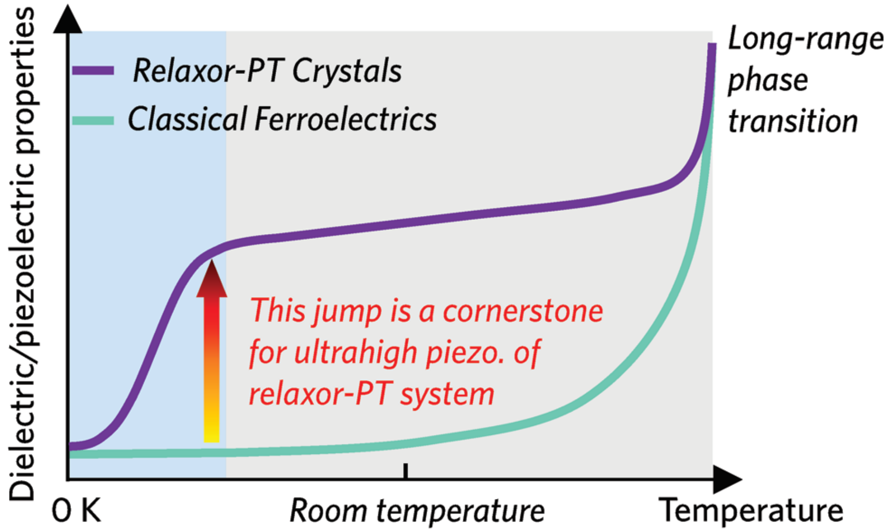


Adaptive optic

Induced-phase in MPB region: role of nanoscale polar clusters



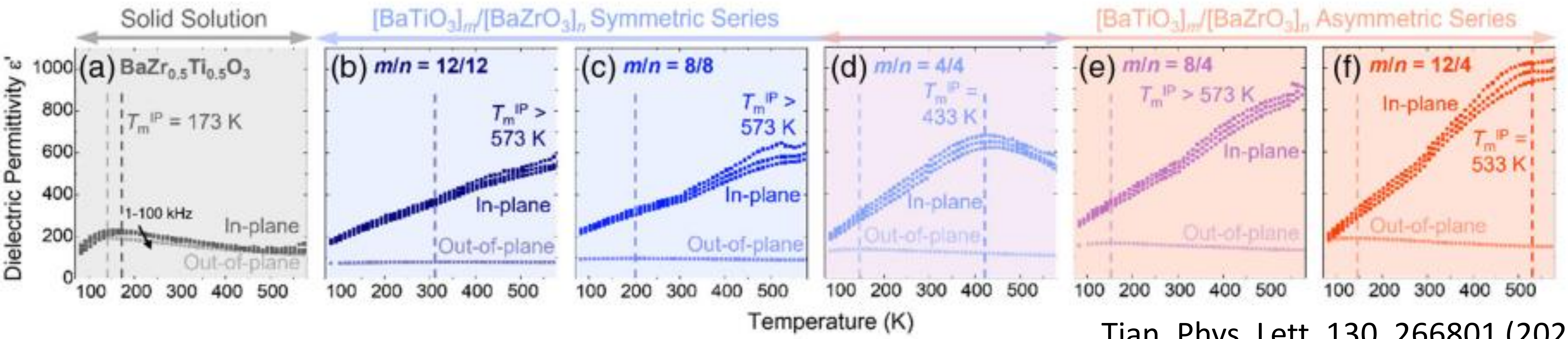
Krogstard et al. Nature Mater. 2018



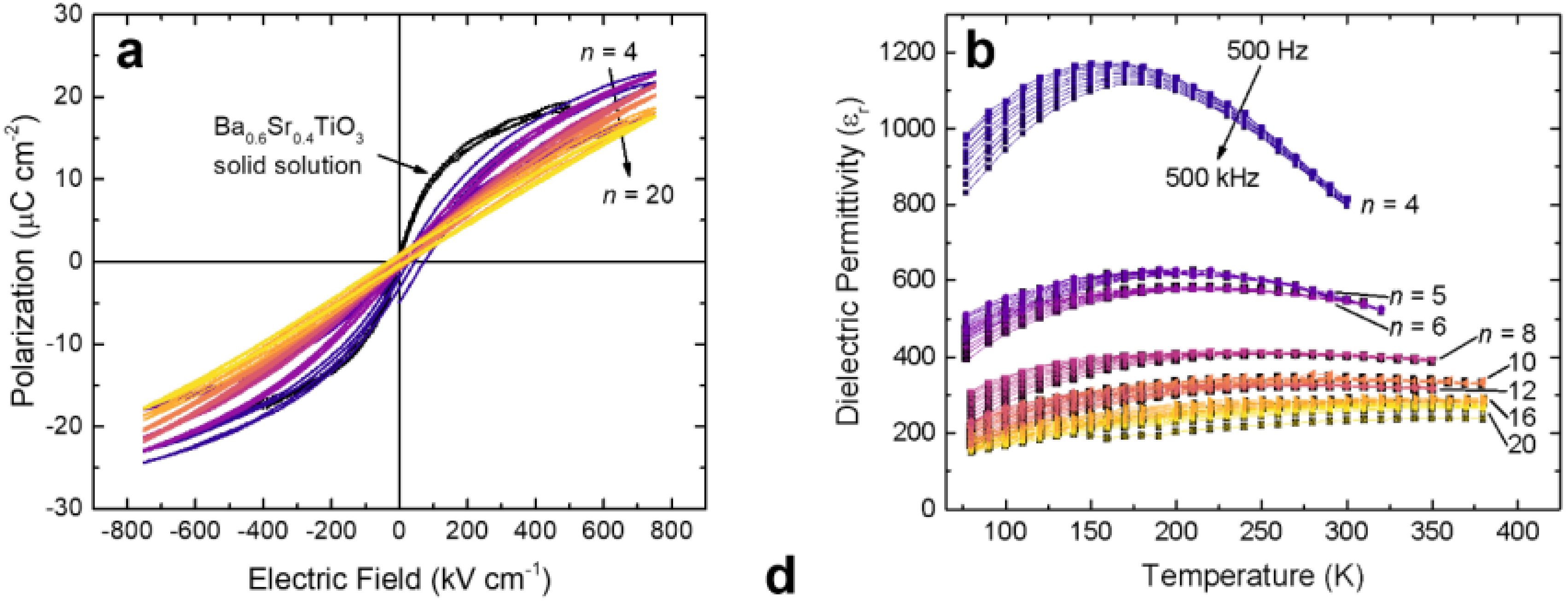
Nanoscale Heterogeneous Polar Regions

Li et al. Adv. Func. Mater 2018

Mimicking « relaxor » bahaviour using multilayers



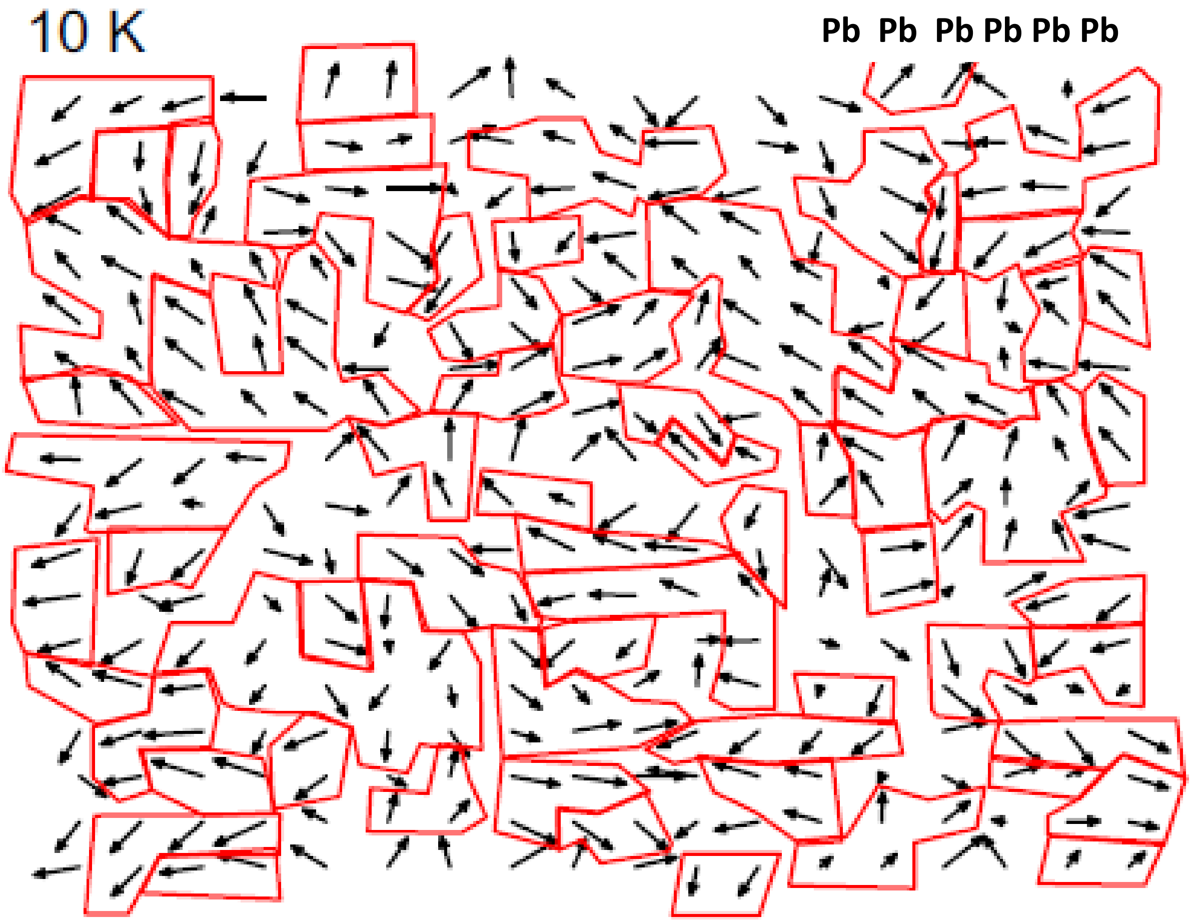
Tian, Phys. Lett. 130, 266801 (2023)



Lupi, Adv. Matter. doi.org/10.1002/adma.202302012 (2023)

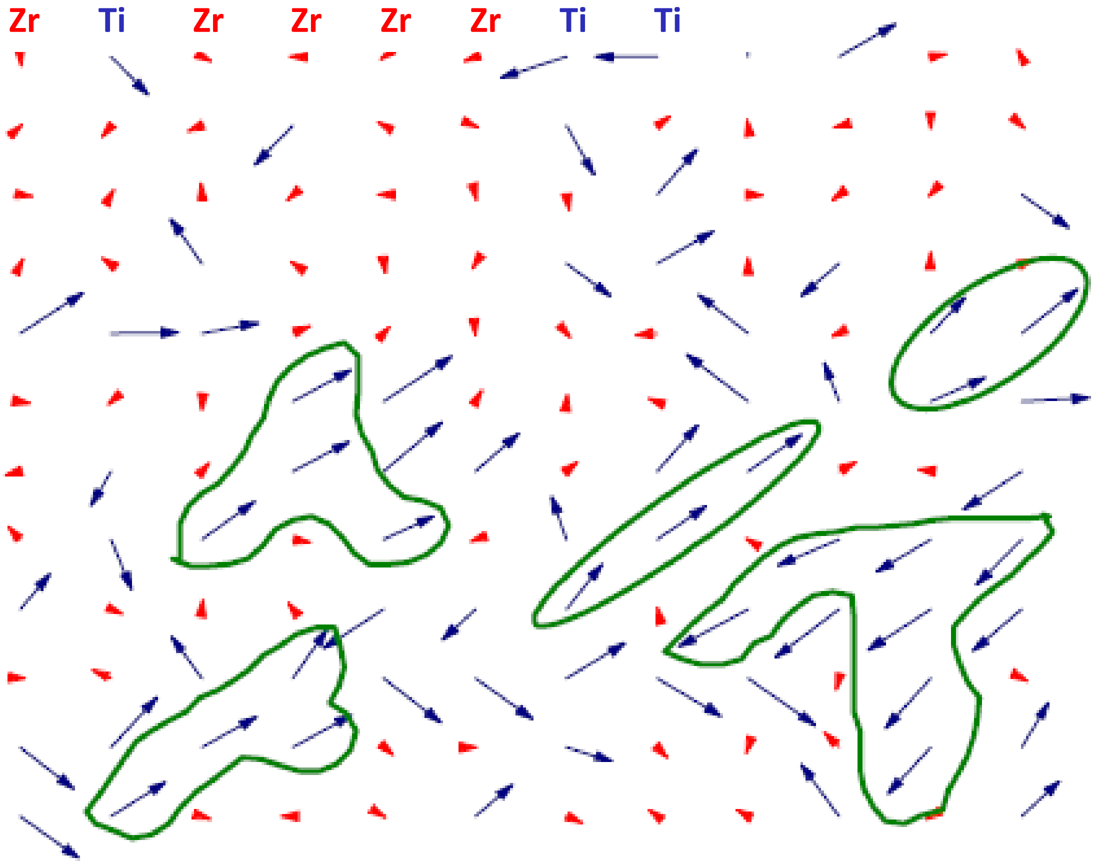
Role/importance of Pb: $Pb(MgNb)O_3$ versus $Ba(TiZr)O_3$

PMN



A. Al Barakaty, Phys. Rev. B **91**, 214117 (2015)

BZT



S. ProsandeevJ. Phys. Cond. Matter. **27**, 223202 (2015)
S. Prosandeev, Phys. Rev. Lett. **110**, 207601 (2015)

Menu

Some basics and ingredients

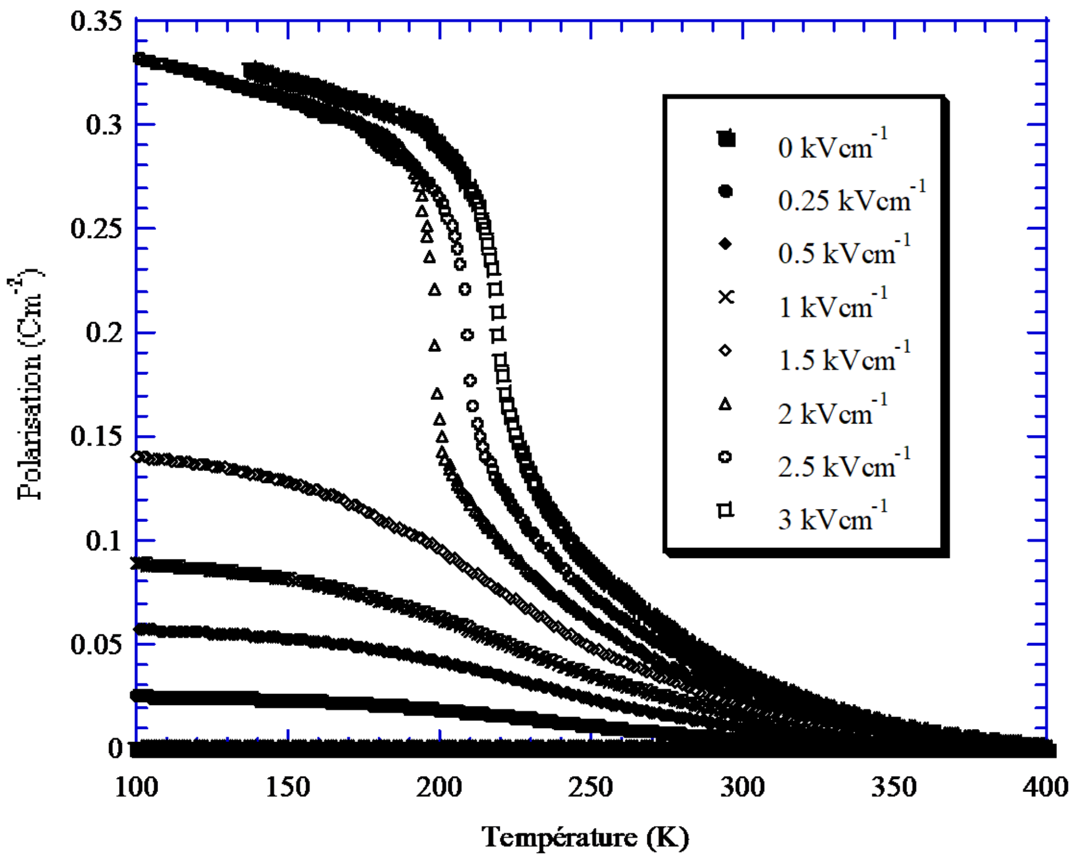
Electric field effect

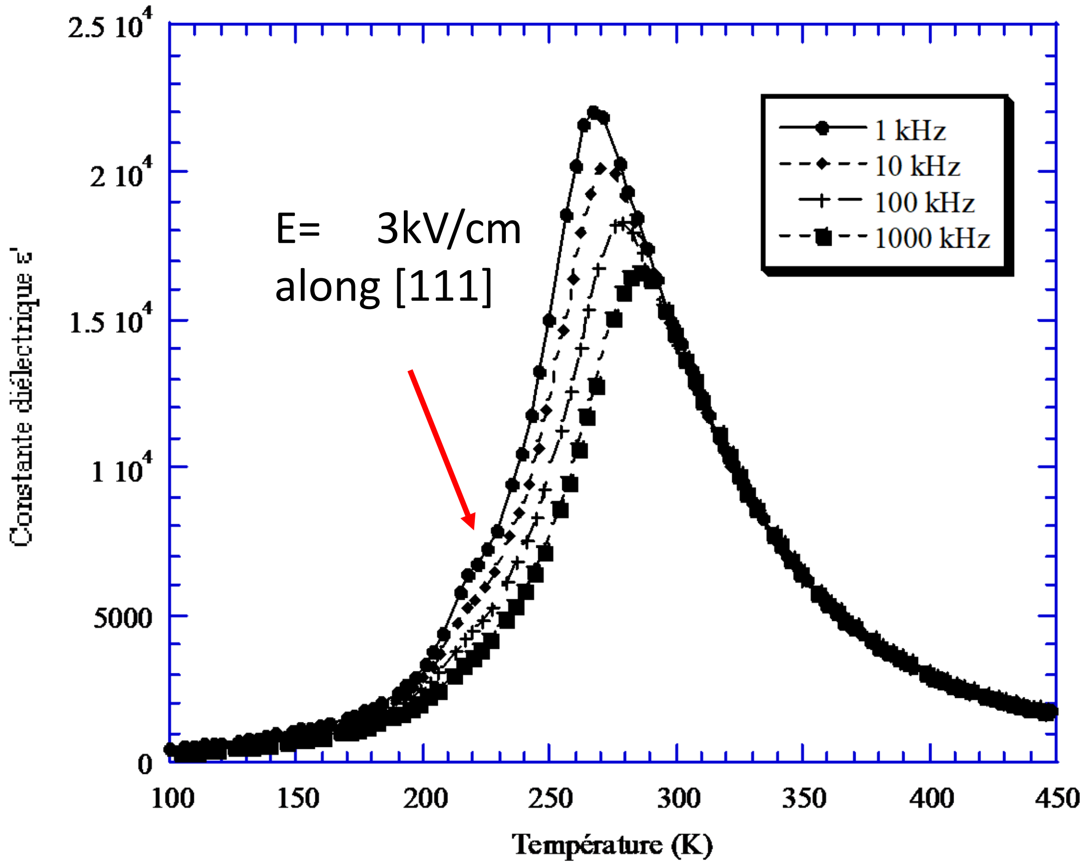
The Physics behind

Applications

Electric-field-induced ferroelectric phase

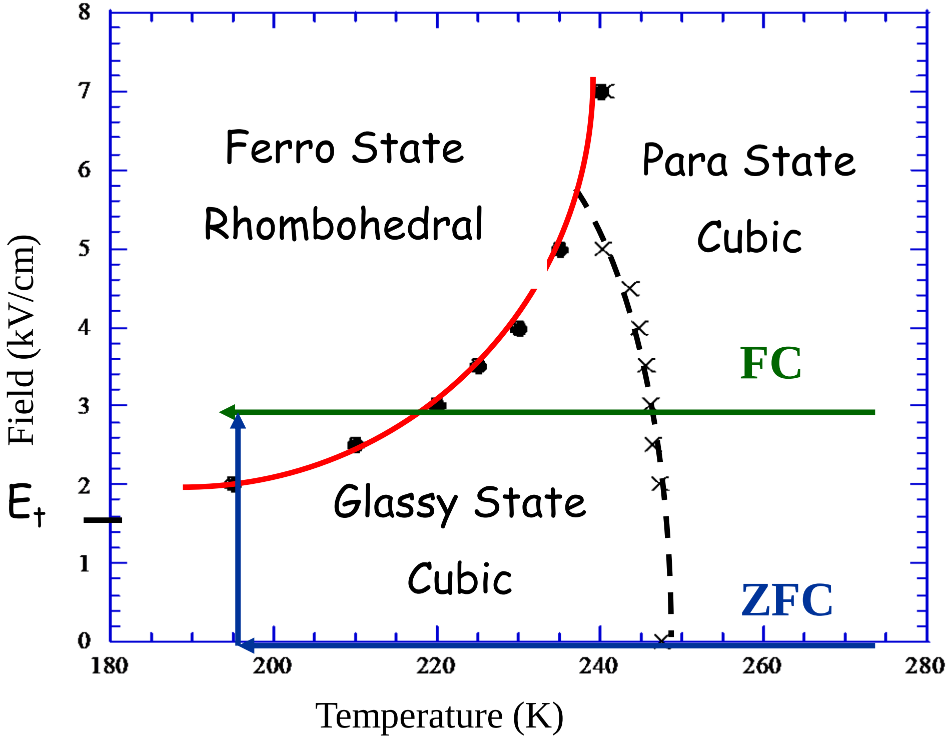
Polarization and dielectric constant obtained under electric field applied along [111]

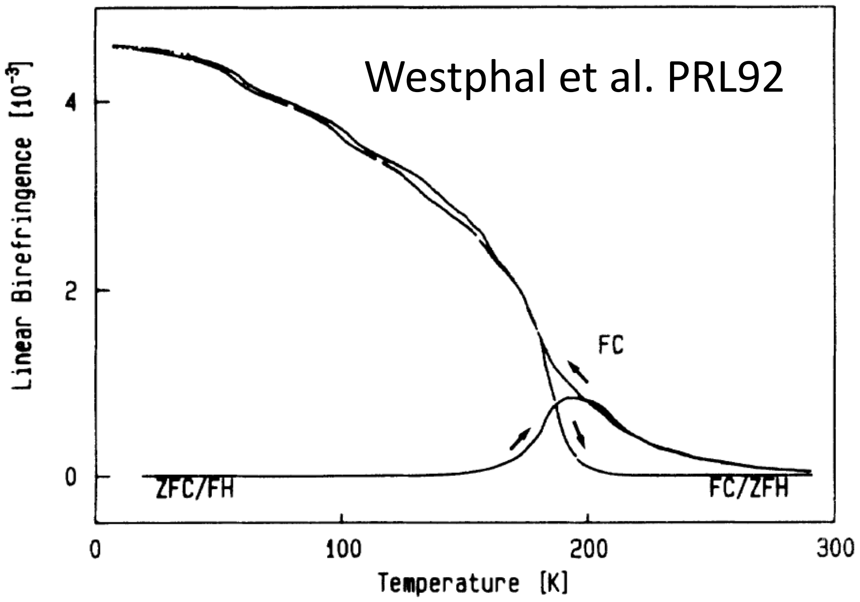




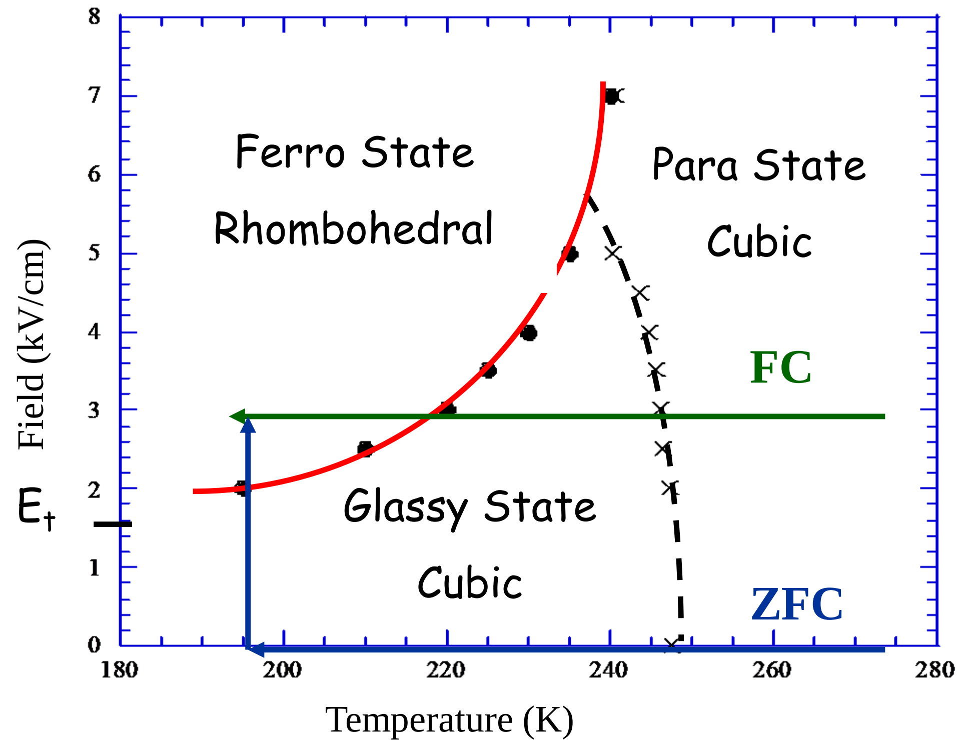
A cooperative long-range ordered ferroelectric state is induced if the electric is higher than a threshold value (E_t~1,7 kV/cm along [111])

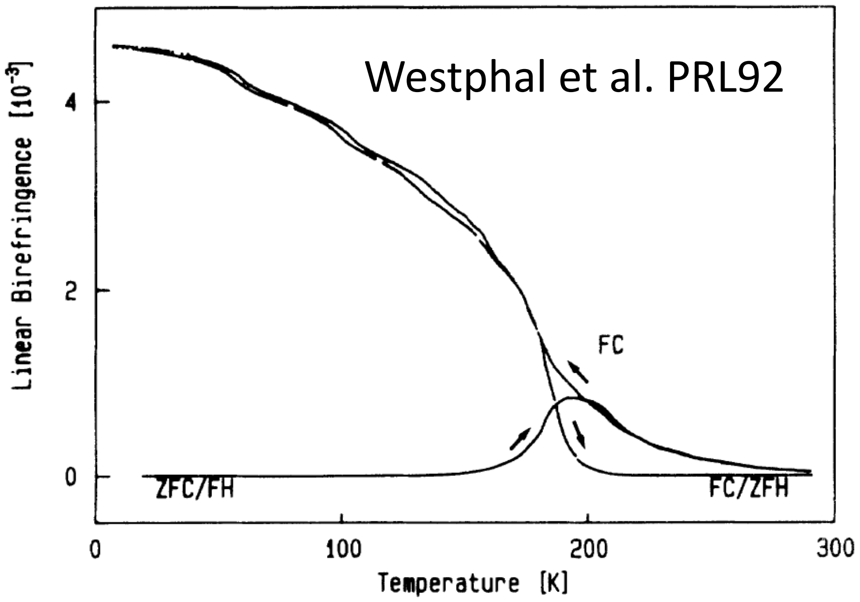
Non-ergodicity and kinetic



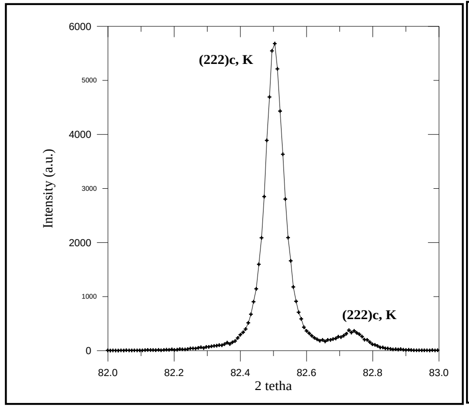


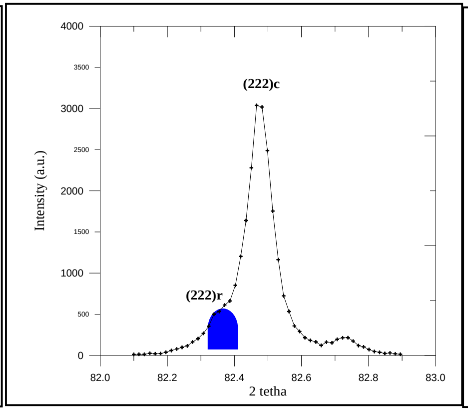
Non-ergodicity and kinetic

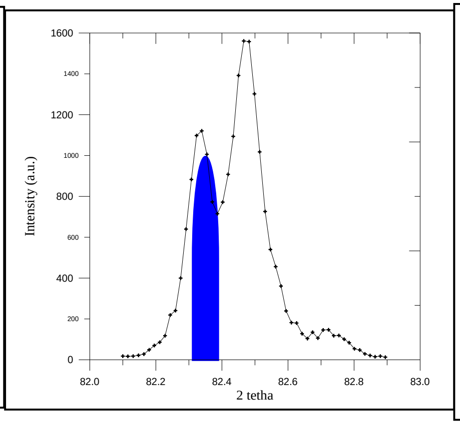


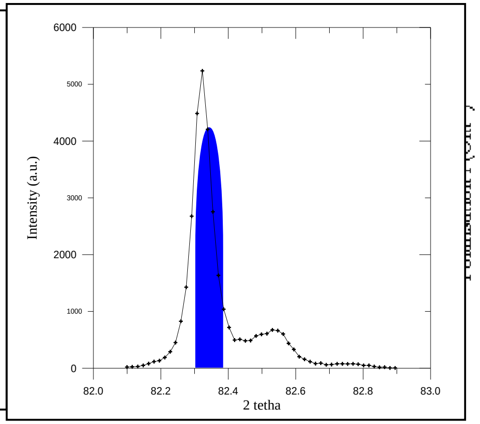


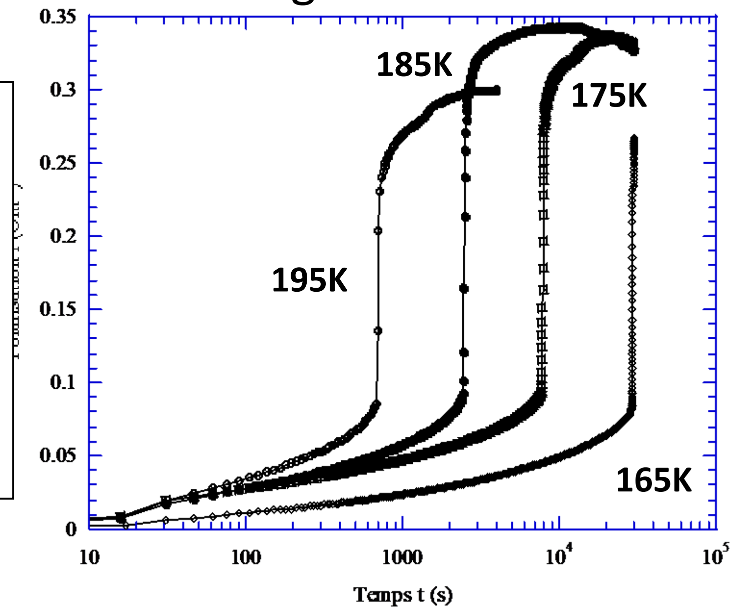
The incubation time τ is strongly dependent on both the temperature and the electric field strength





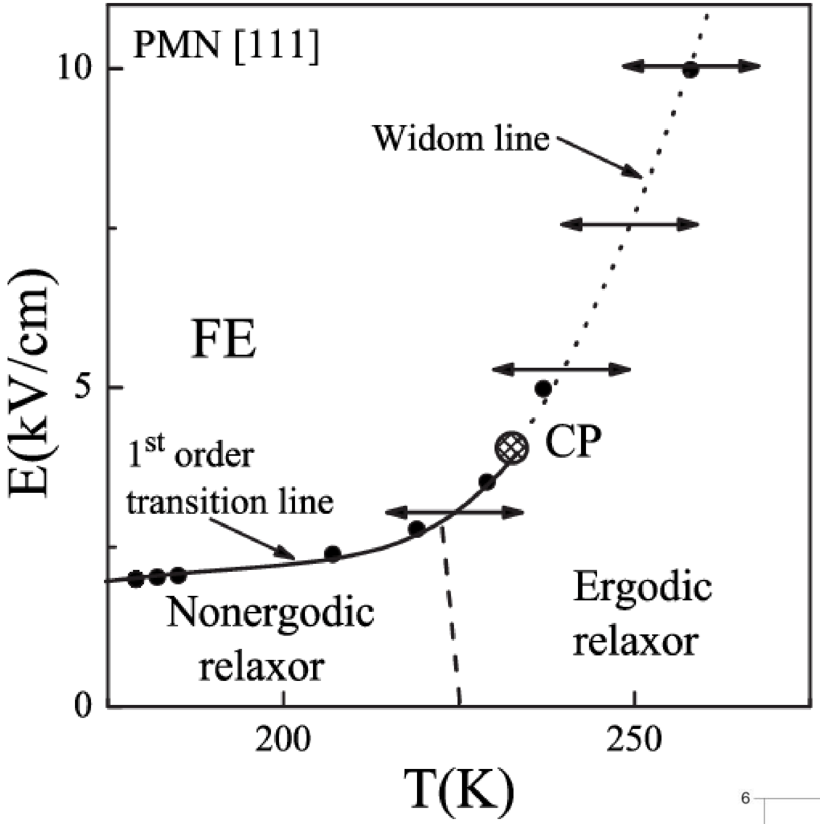


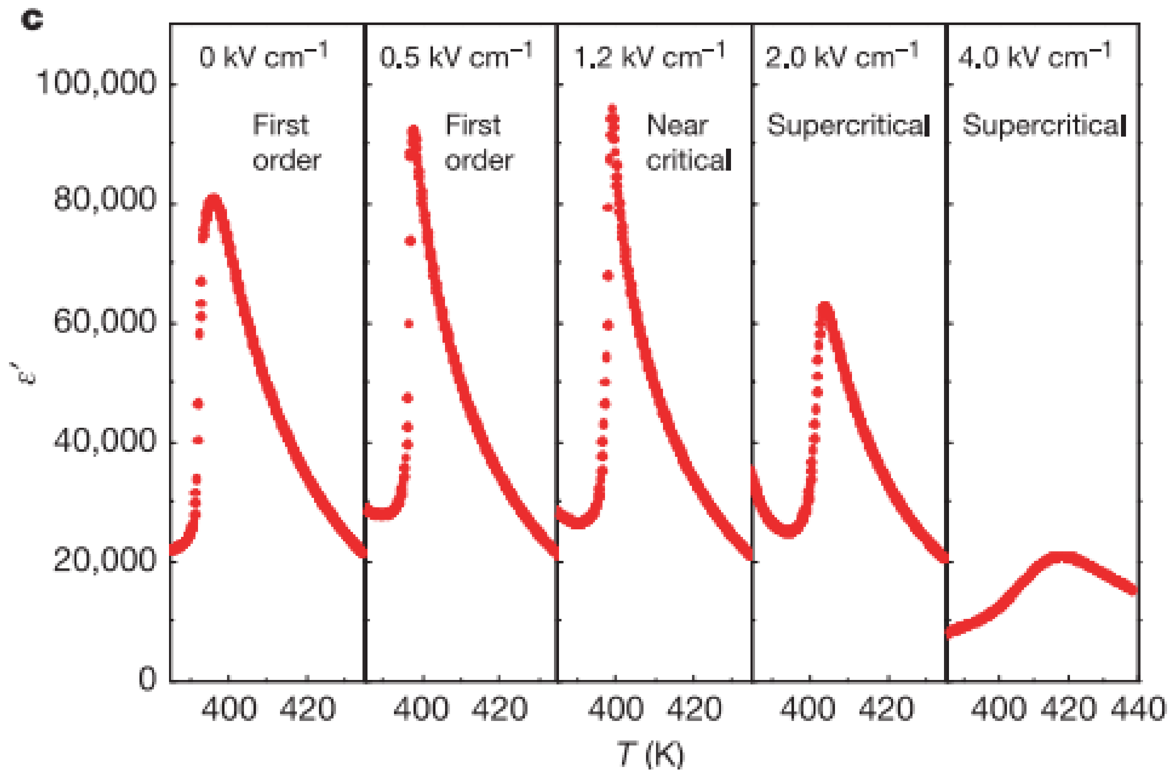




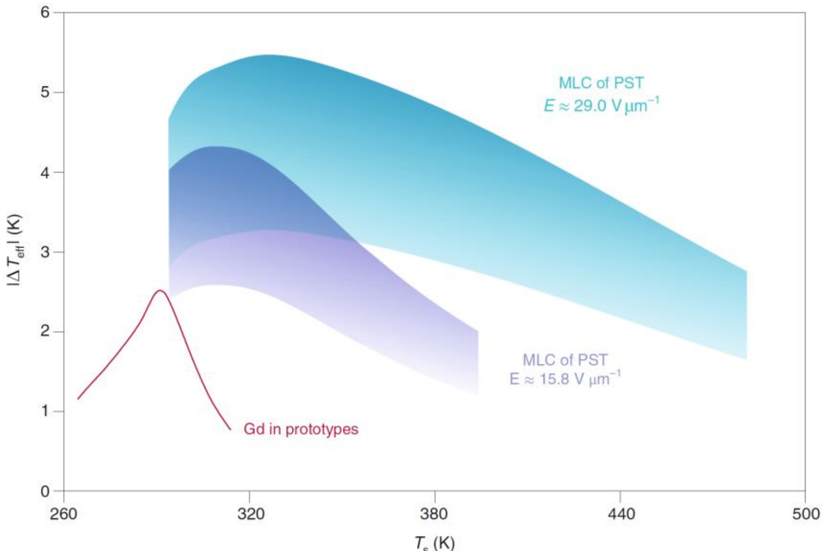
t = 0s **t = 6000s** **t = 7000s** **t = 15000s**

Critical end-point and super-criticality





Kutnjak, Nature, **441**, 956 (2006)



Nair et al., Nature **575**, 468 (2019)

Menu

Some basics and ingredients

Electric field effect

The Physics behind

Applications

Summary of the needed ingredients for relaxors

Perovskite Pb-based-Relaxors (Smolenskii, 1958)

(**PbMgₓ**...)

B-cations distribution
(e.g. **Mg**$^{2+}$/**Nb**$^{5+}$)
= Weak Random Fields (**RFs**)
[Kleemann, IJMP93]
1st ingredient

Polar NanoRegions or Polar NanoDomains or clusters or correlations (**PNRs**)
[Cross, Ferroel87]
2nd ingredient

T_{max}~260K at 1kHz

T_f~220K (~T_c) **T_B~630K** **PMN**

T_c~400K **T_B~740K** **PZN**

"Static/Dynamic????" PNRs appear at **T_{Burns}** [Burns et al., PRB83, Jeong et al., PRL04] and they freeze down (or phase transition) at **$T_{freezing}$** (**T_c**) [Viehland et al., PRB91, Westphal et al., PRL92]

This is not a PFM image and does not correspond to reality!!!!

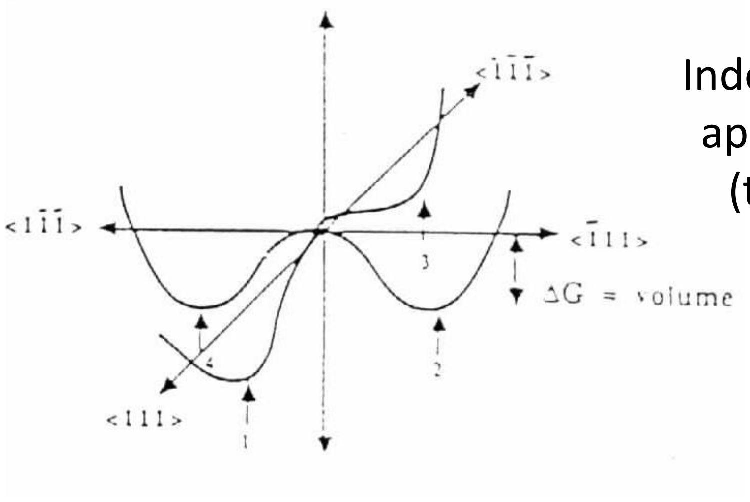
Physical models for relaxors : History and analogies with magnets

- The first one [Smolenskii, JPSCS, 70] : concept of « polar microregions » within chemical inhomogeneity theory (static model)

Physical models for relaxors : History and analogies with magnets

- The first one [Smolenskii, JPSCS, 70] : concept of « polar microregions » within chemical inhomogeneity theory (static model)

- From superparaelectric [Cross, Ferroelectrics, 87] to dipole glass [Viehland, PRB, 91]



Independent polar regions appearing at **T_{Burns}~630K** (thermal fluctuations)

Cluster-glassiness due to dipolar disorder and frustrated interactions

Vogel-Fülcher relationship

$\omega=\omega_0.\exp[-E_a/k(T_{max}-T_f)]$

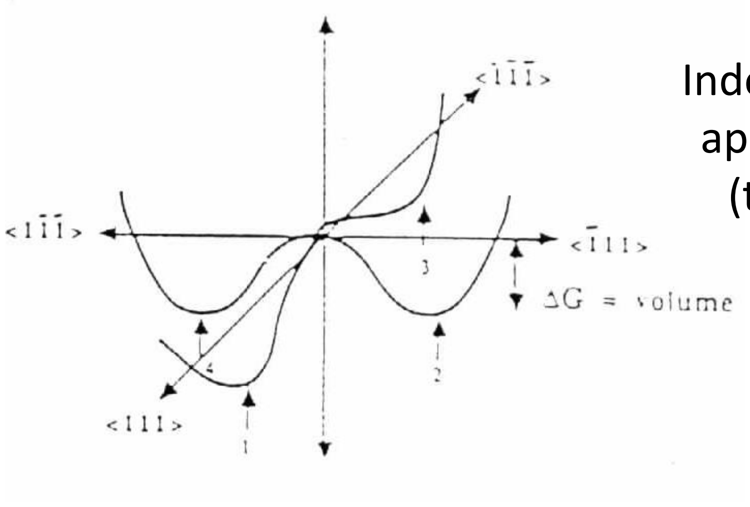
For PMN, E_a=0.0407eV

T_f=217.7K

Physical models for relaxors : History and analogies with magnets

- The first one [Smolenskii, JPSCS, 70] : concept of « polar microregions » within chemical inhomogeneity theory (static model)

- From superparaelectric [Cross, Ferroelectrics, 87] to dipole glass [Viehland, PRB, 91]



Independent polar regions appearing at T_{Burns}~630K (thermal fluctuations)

Cluster-glassiness due to dipolar disorder and frustrated interactions

Vogel-Fülcher relationship
$\omega=\omega_0.\exp[-E_a/k(T_{max}-T_f)]$

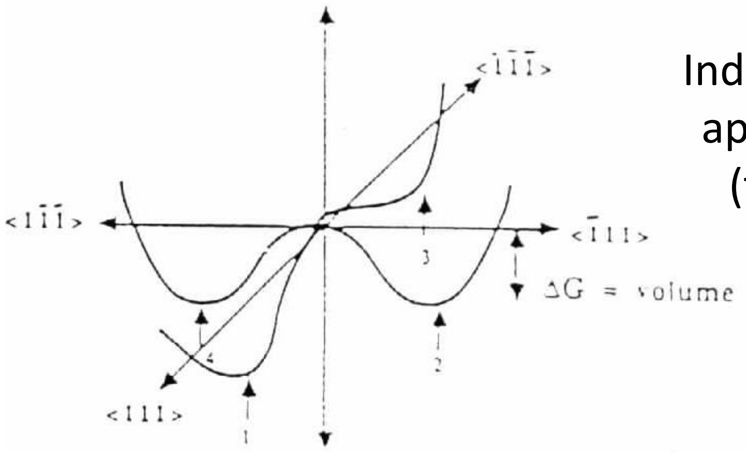
For PMN, E_a=0.0407eV
T_f=217.7K

- Quenched random fields [Westphal, Kleemann et al., PRL, 92] arising from space charges associated to chemical inhomogeneities

Physical models for relaxors : History and analogies with magnets

- The first one [Smolenskii, JPSCS, 70] : concept of « polar microregions » within chemical inhomogeneity theory (static model)

- From superparaelectric [Cross, Ferroelectrics, 87] to dipole glass [Viehland, PRB, 91]



Independent polar regions appearing at T_{Burns}~630K (thermal fluctuations)

Cluster-glassiness due to dipolar disorder and frustrated interactions

Vogel-Fülcher relationship
$\omega=\omega_0.\exp[-E_a/k(T_{max}-T_f)]$

For PMN, E_a=0.0407eV
T_f=217.7K

- Quenched random fields [Westphal, Kleemann et al., PRL, 92] arising from space charges associated to chemical inhomogeneities

- Unifying "hybride" model [Pirc, Blinc, PRB, 99] : Spherical Random Bond Random Field model (SRBRF) ≡ extension of Ising models

Random local electric field

$$H = -\frac{1}{2}\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j - \sum_i \vec{h}_i \cdot \vec{S}_i - g\sum_i \vec{E}_i \cdot \vec{S}_i$$

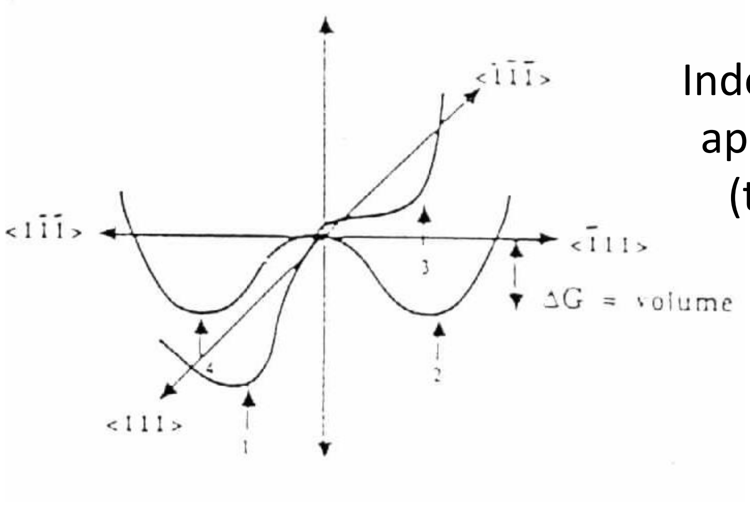
Random bond interaction (length varies)

Effective local field

Physical models for relaxors : History and analogies with magnets

- The first one [Smolenskii, JPSCS, 70] : concept of « polar microregions » within chemical inhomogeneity theory (static model)

- From superparaelectric [Cross, Ferroelectrics, 87] to dipole glass [Viehland, PRB, 91]



Independent polar regions appearing at T_{Burns}~630K (thermal fluctuations) → Cluster-glassiness due to dipolar disorder and frustrated interactions

Vogel-Fülcher relationship
$\omega=\omega_0.\exp[-E_a/k(T_{max}-T_f)]$

For PMN, E_a=0.0407eV
T_f=217.7K

- Quenched random fields [Westphal, Kleemann et al., PRL, 92] arising from space charges associated to chemical inhomogeneities

- Unifying "hybride" model [Pirc, Blinc, PRB, 99] : Spherical Random Bond Random Field model (SRBRF) ≡ extension of Ising models

Random local electric field

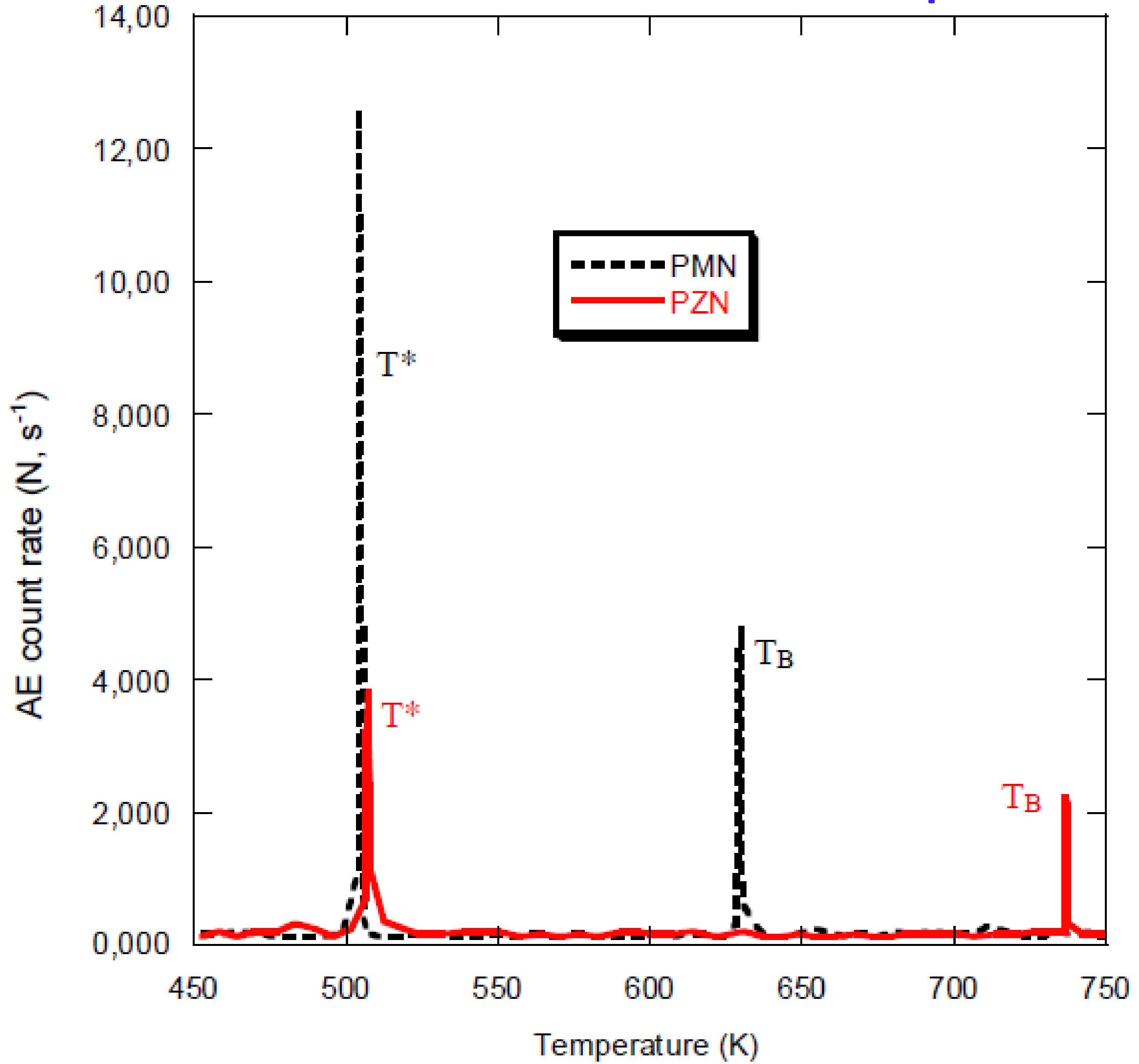
$$H = -\frac{1}{2}\sum_{ij} J_{ij}\vec{S}_i\cdot\vec{S}_j - \sum_i \vec{h}_i\cdot\vec{S}_i - g\sum_i \vec{E}_i\cdot\vec{S}_i$$

Random bond interaction (length varies)

Effective local field

What else….

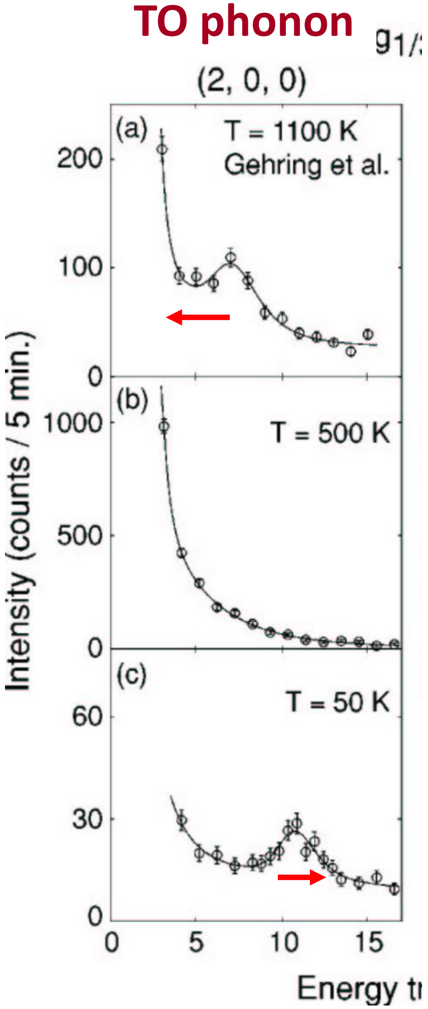
An additional "critical" temperature T*



Phys. Rev. B **80**, 064103 (2009)

T* was overlooked in previous data…

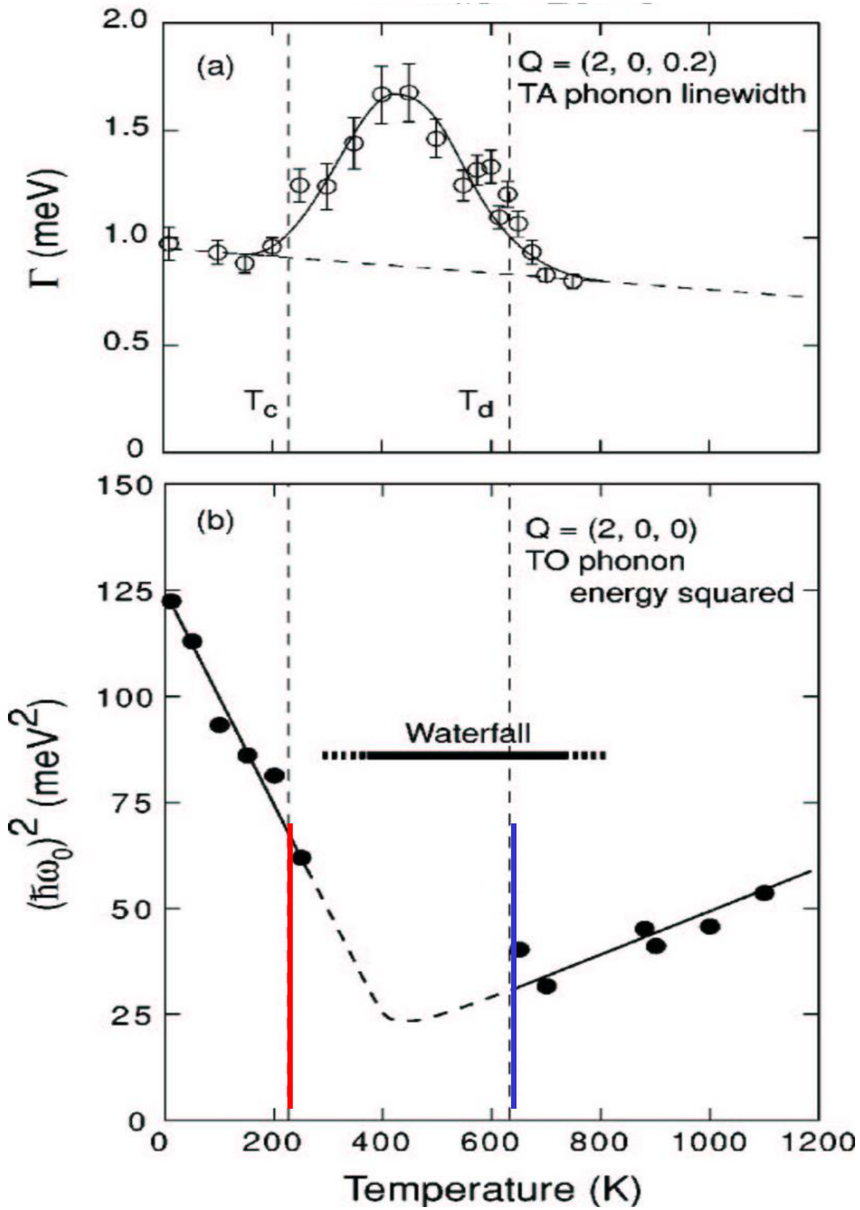
TO phonon



TA mode linewidth

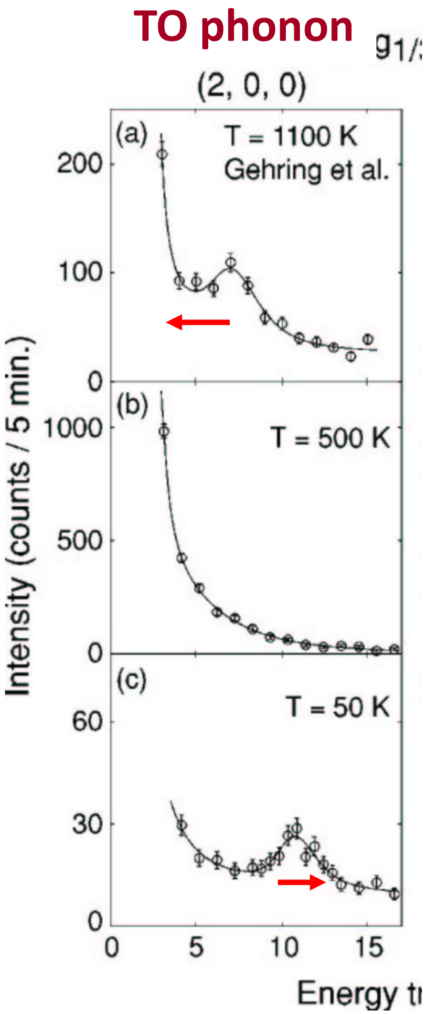
(200) Brillouin zone, inelastic neutron scattering

TO mode energy squared



A. Naberezhnov et al., EPJB1999, P.M. Gehring et al., PRL2001, S. Wakimoto et al., PRB2003, J. Hlinka, PRL2006, ….

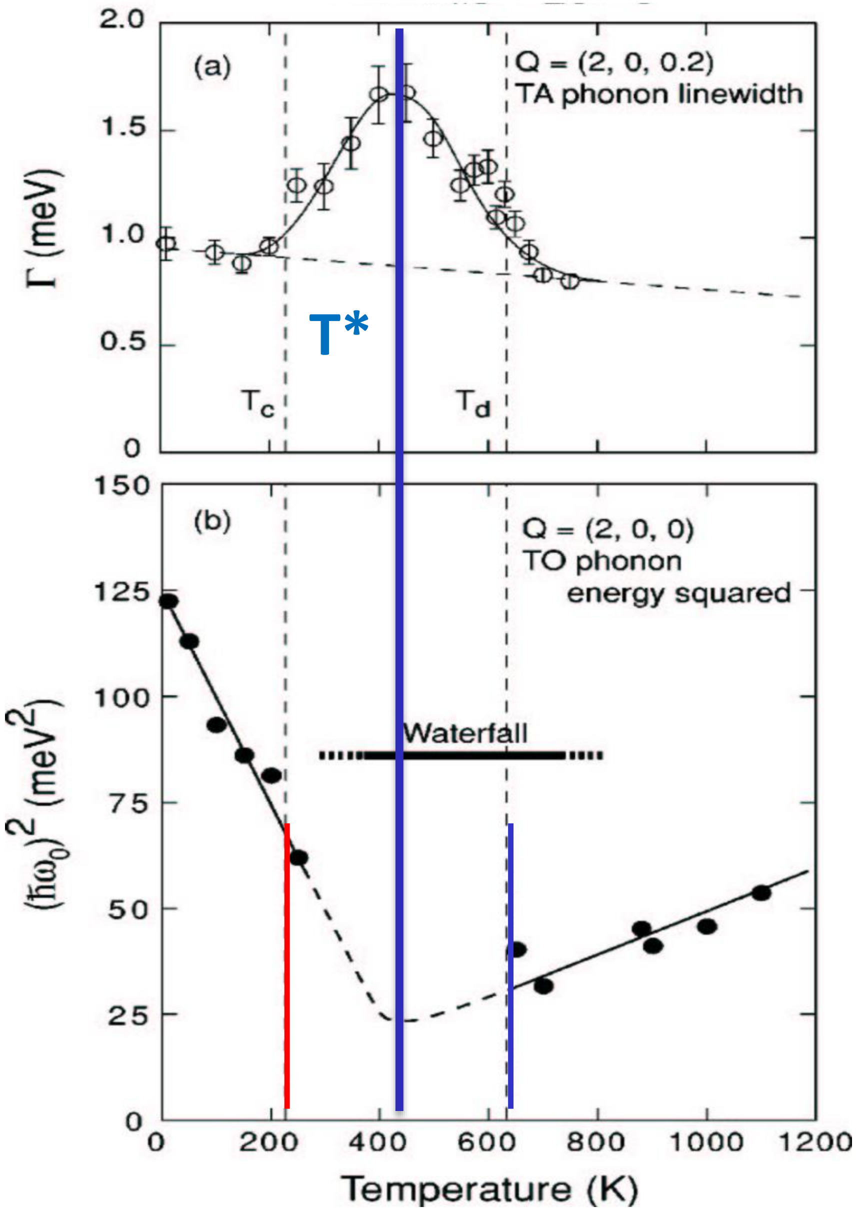
T* was overlooked in previous data…



TA mode linewidth

(200) Brillouin zone, inelastic neutron scattering

TO mode energy squared

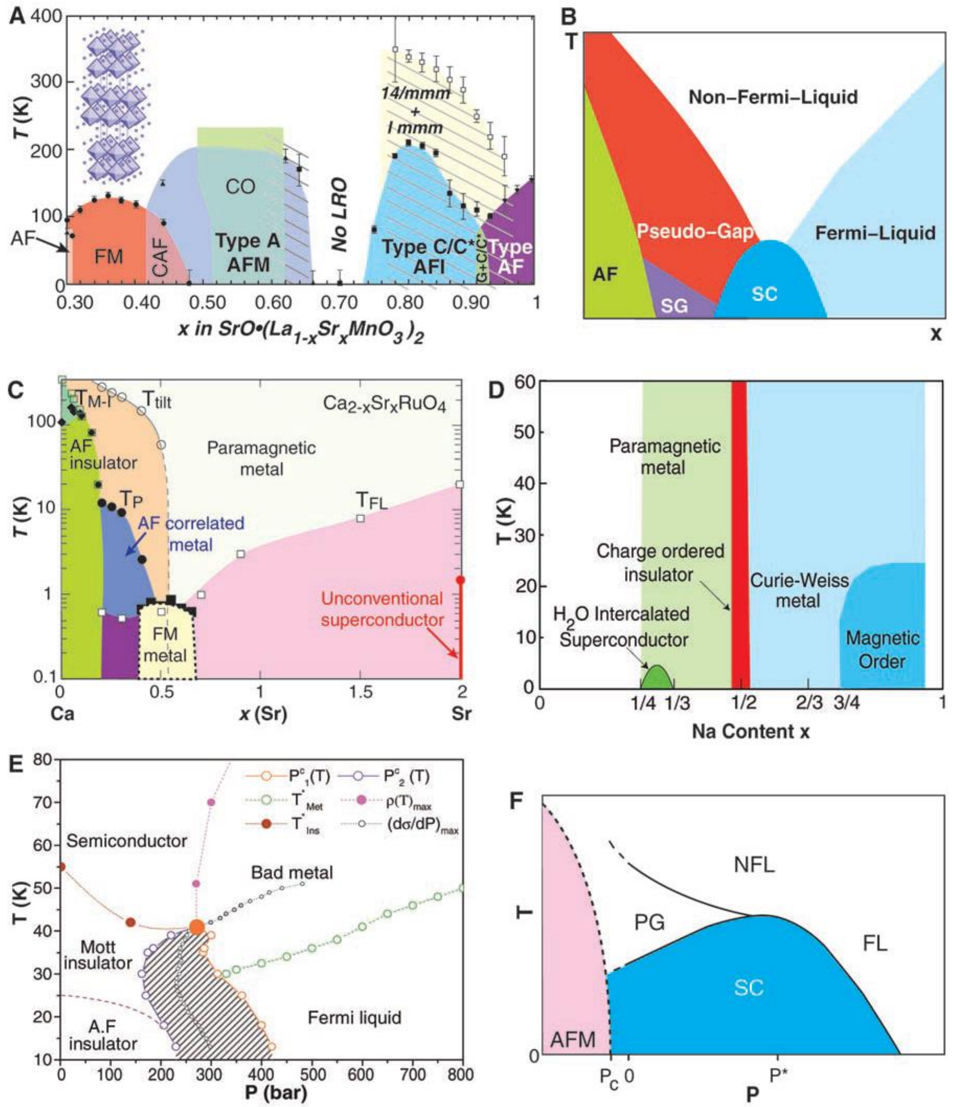


A. Naberezhnov et al., EPJB1999, P.M. Gehring et al., PRL2001, S. Wakimoto et al., PRB2003, J. Hlinka, PRL2006, ….

Comparison with other "super" condensed matter systems

Interestingly (in Colossal MagnetoResistance, High-Temperature SuperConductor, Diluted Magnetic Semiconductors)

[E. Dagotto, NJP05, Science05]



Comparison with other “super” condensed matter systems

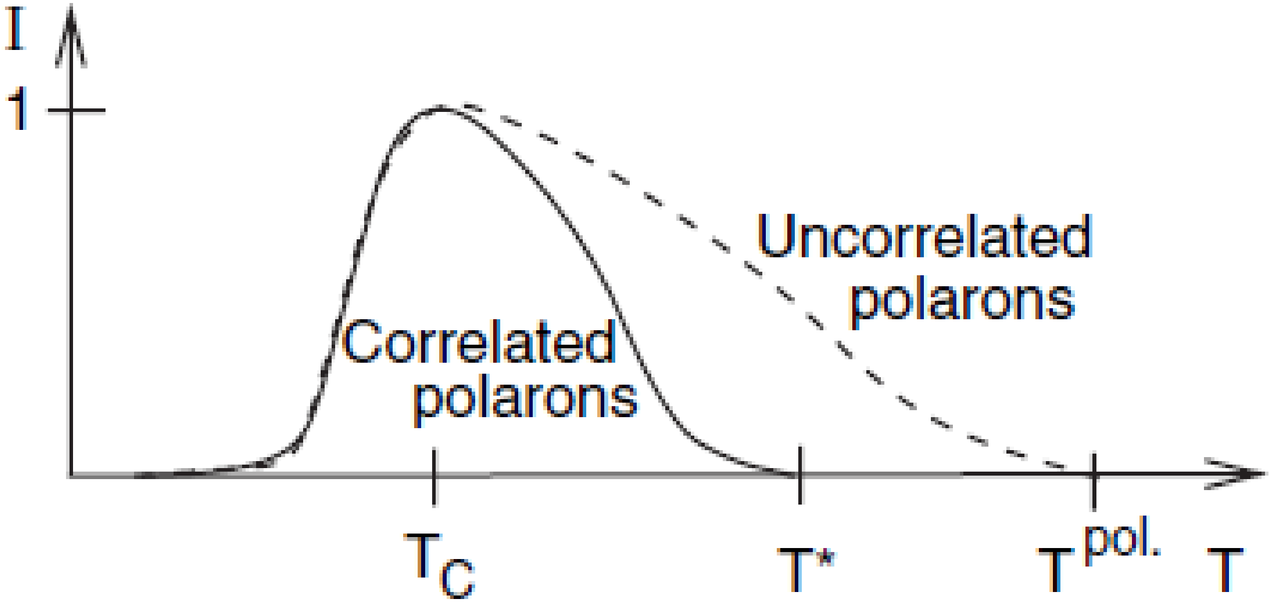
Interestingly (in Colossal MagnetoResistance, High-Temperature SuperConductor, Diluted Magnetic Semiconductors)

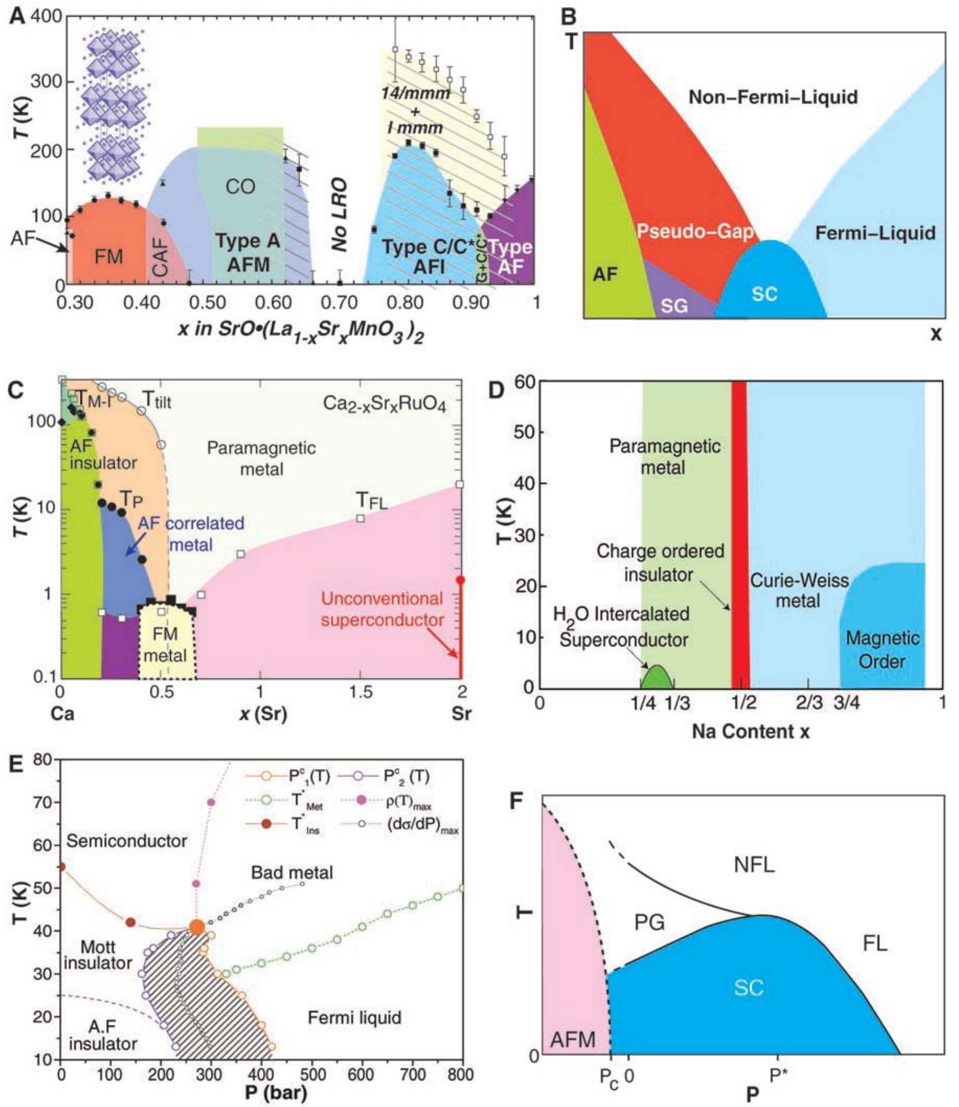
[E. Dagotto, NJP05, Science05]

1) “Colossal/Giant effect” was reported,
also for relaxors, huge electostriction/giant piezoelectricity

2) Nanoclusters appear at T*, also in relaxors

3) Temperature evolution, also in relaxors ($T^{pol.} = T_{Burns}$)





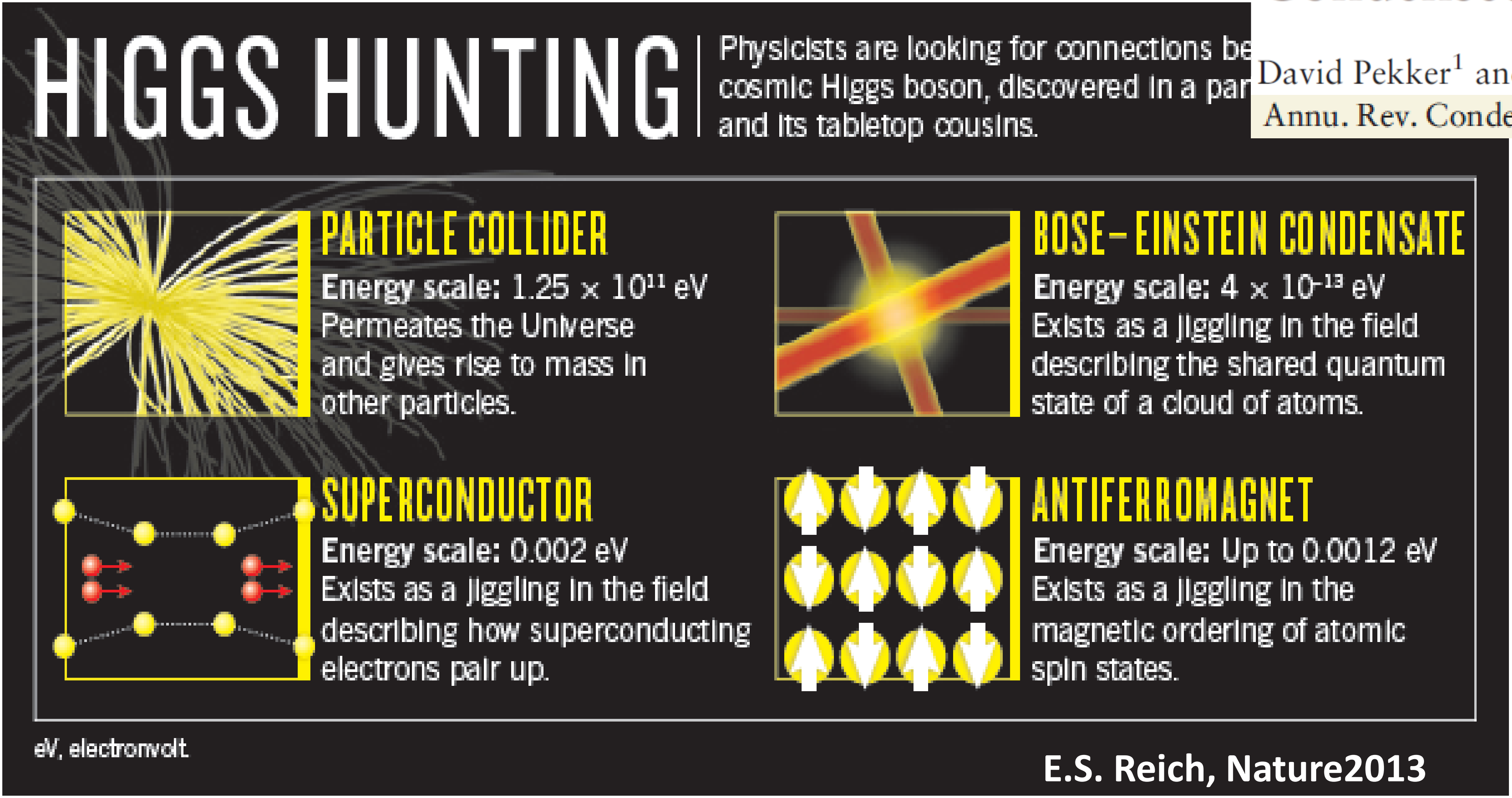
Spontaneously breaking of continuous symmetry

Important in many branches of physics: superconductors, superfluids, … and even Higgs boson.

Amplitude/Higgs Modes in Condensed Matter Physics

David Pekker[1] and C.M. Varma[2]

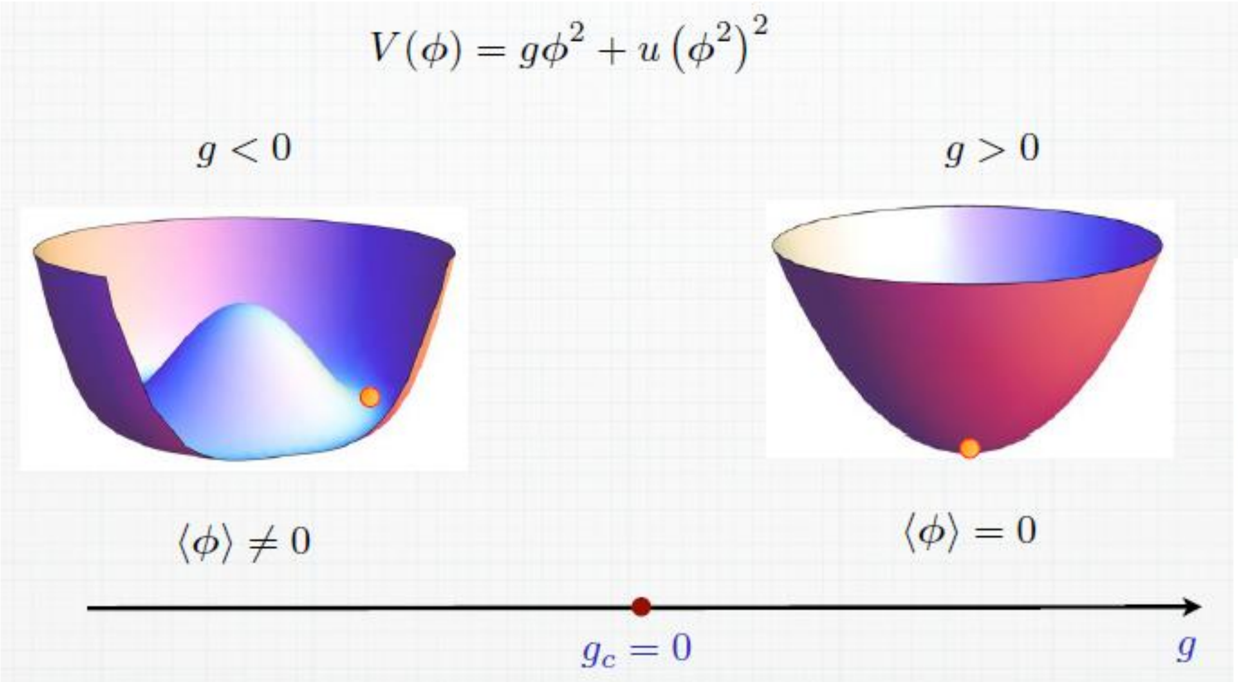
Annu. Rev. Condens. Matter Phys. 2015. 6:269–97

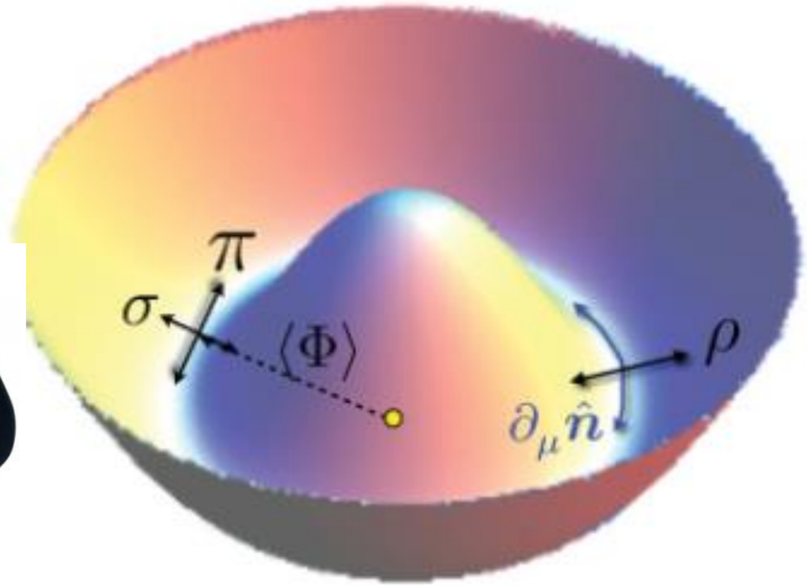


E.S. Reich, Nature2013

Can relaxor be invited at this table?

Are relaxors relatives to Higgs via a spontaneous breakdown of continuous symmetry?





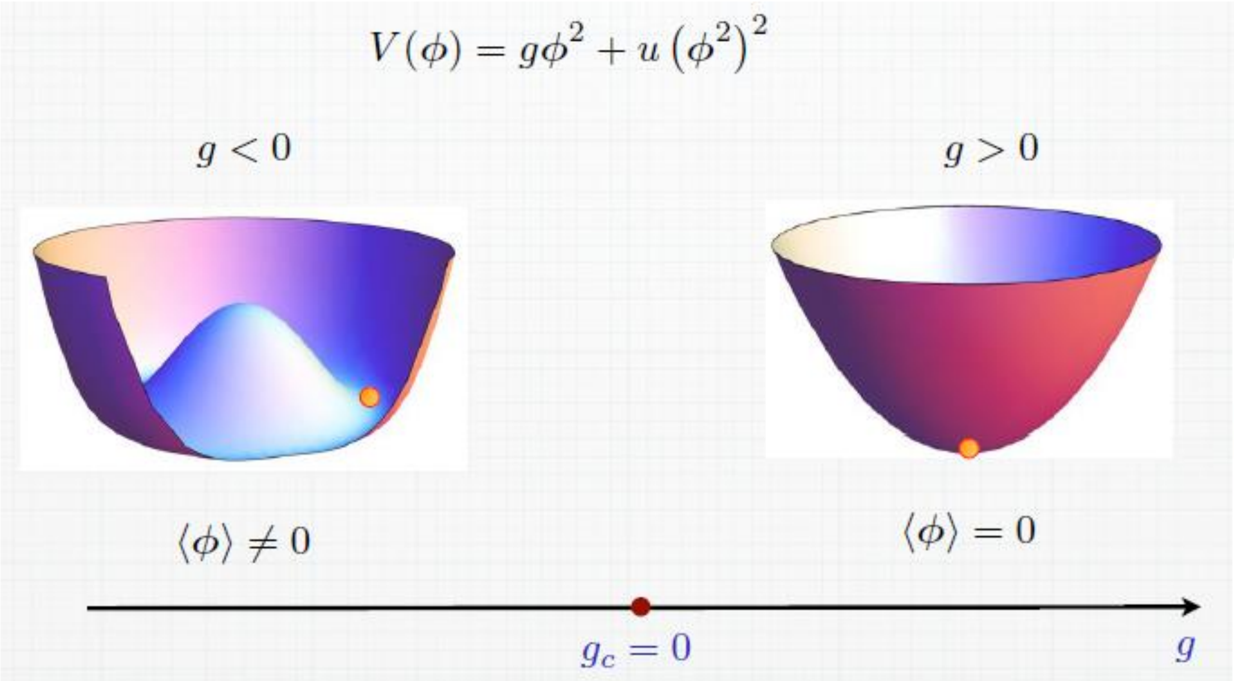
Gazit et al., PRL2013

Collective oscillations
Goldstone and Higgs modes

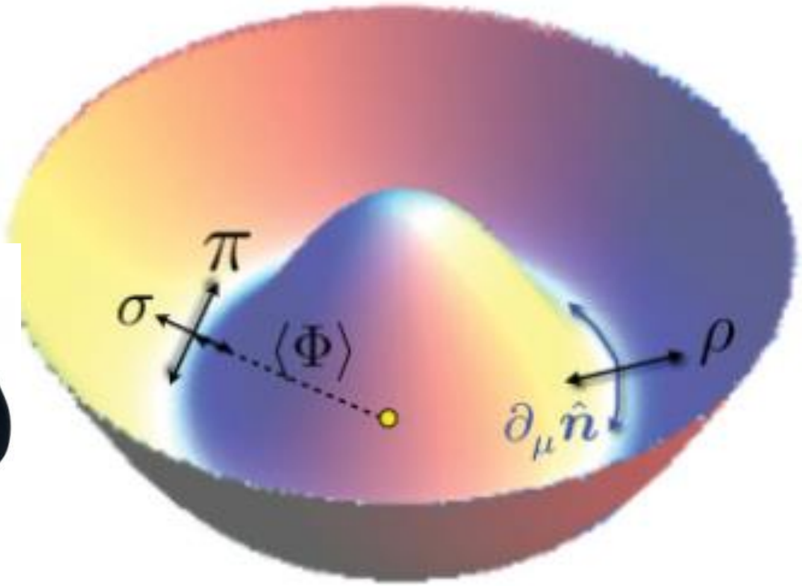
Collective modes or ‘giant matter wave’ with spectacular frictionless flow properties appear (Bose–Einstein condensation) emerge

Dynamic order parameter **Φ=IΦIe$^{i\varphi}$** near a quantum phase transition between an ordered (IΦI $\neq$ 0) and a disordered phase (IΦI = 0).

Are relaxors relatives to Higgs via a spontaneous breakdown of continuous symmetry?



Gazit et al., PRL2013

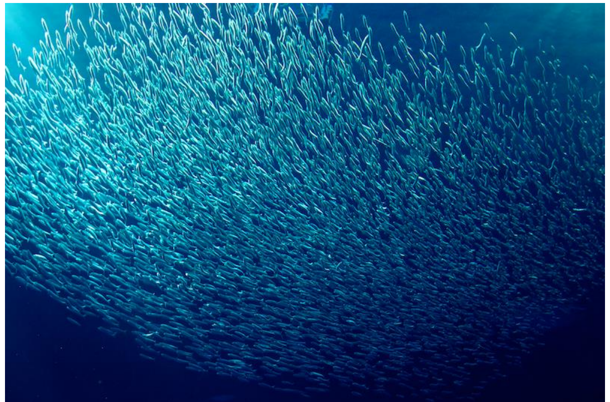


Collective oscillations
Goldstone and Higgs modes

Collective modes or ‘giant matter wave’ with spectacular frictionless flow properties appear (Bose–Einstein condensation) emerge

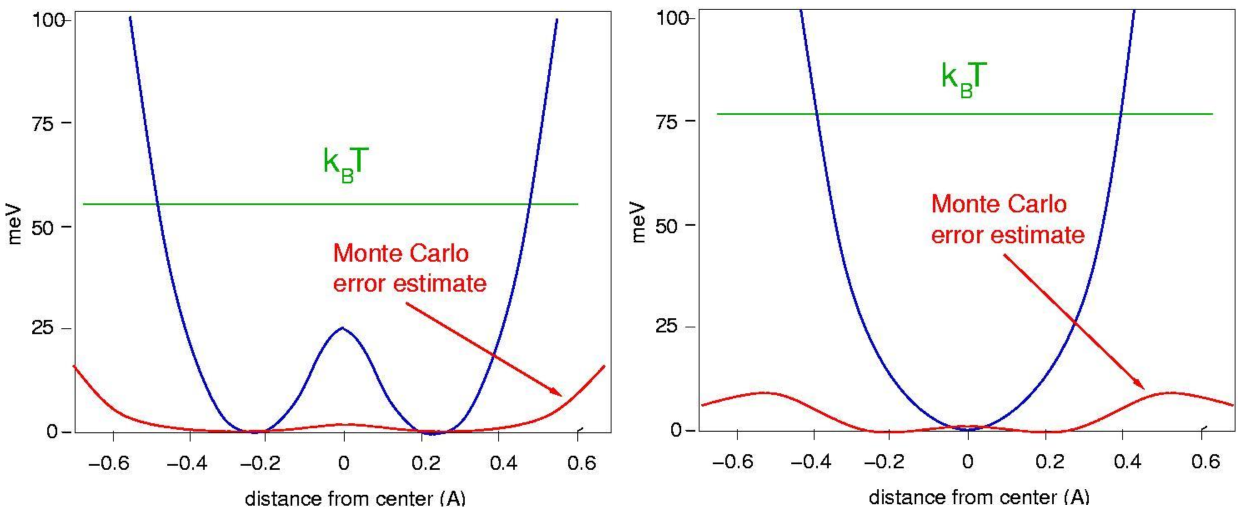
Dynamic order parameter **Φ=IΦIe$^{i\varphi}$**
near a quantum phase transition between an ordered (IΦI ≠ 0) and a disordered phase (IΦI = 0).

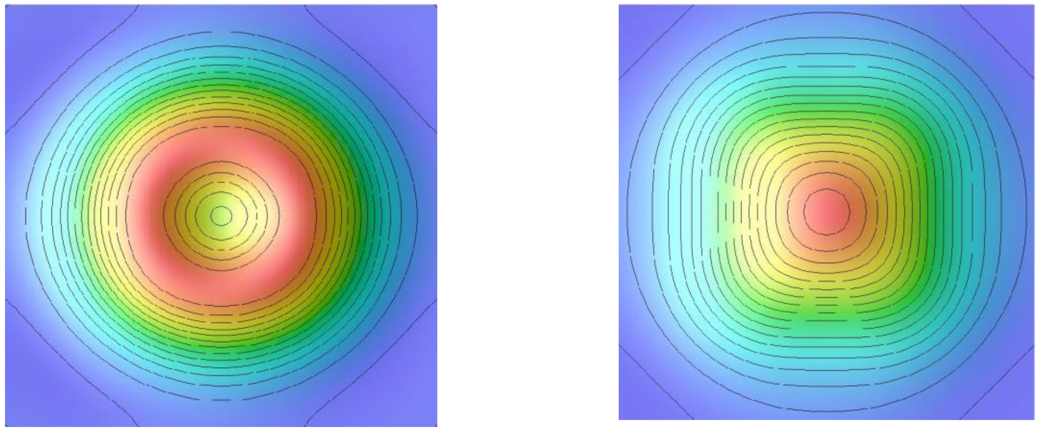
Munoz, Rev. Mod. Phys. 90, 031001 (2018)



A spontaneous broken continuous symmetry at T_B?

Gram-Charlier treatment [Kiat et al. JPCM99]
Probability Distribution Function for Pb



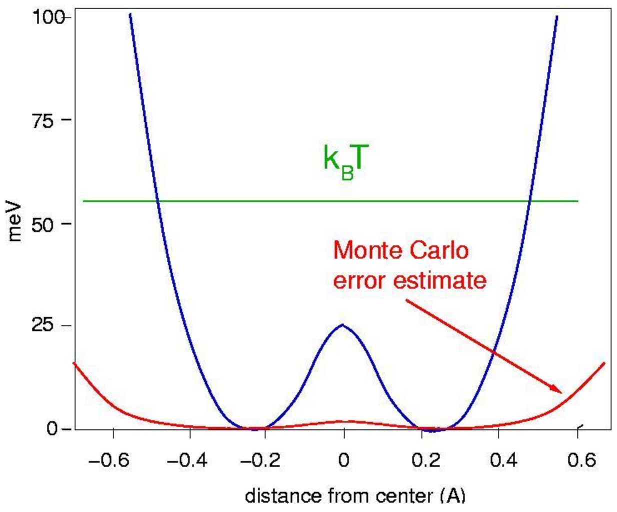


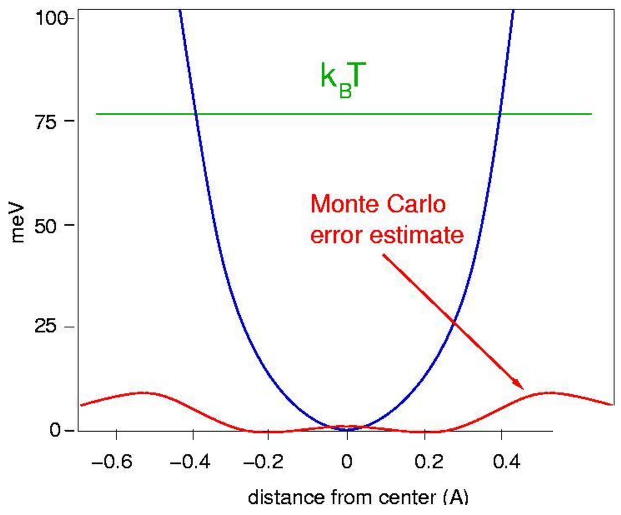
Below T_B, ALL Pb ions are displaced (Mexican hat potential)

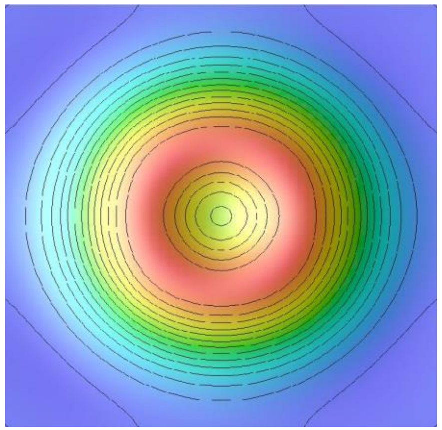
Prosandeev, Phys. Rev. B 102, 104110 (2020)

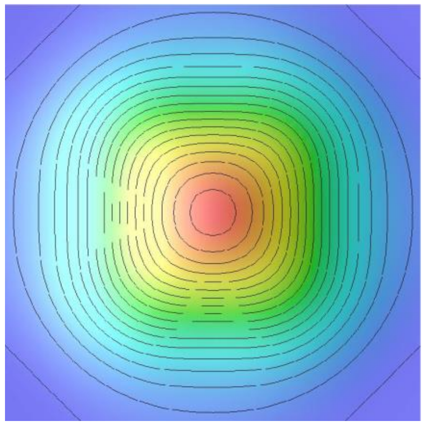
A spontaneous broken continuous symmetry at T_B?

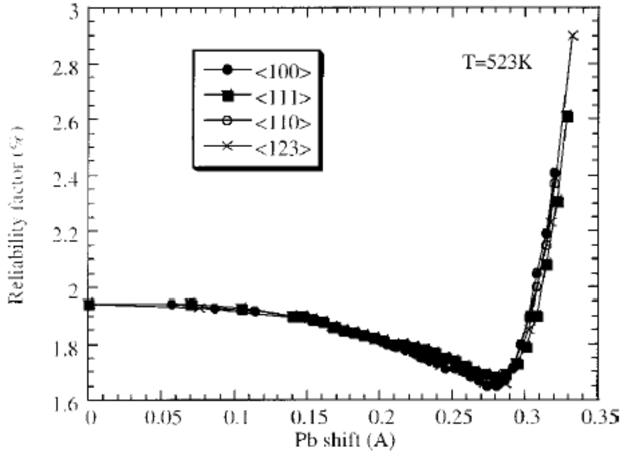
Gram-Charlier treatment [Kiat et al. JPCM99]
Probability Distribution Function for Pb

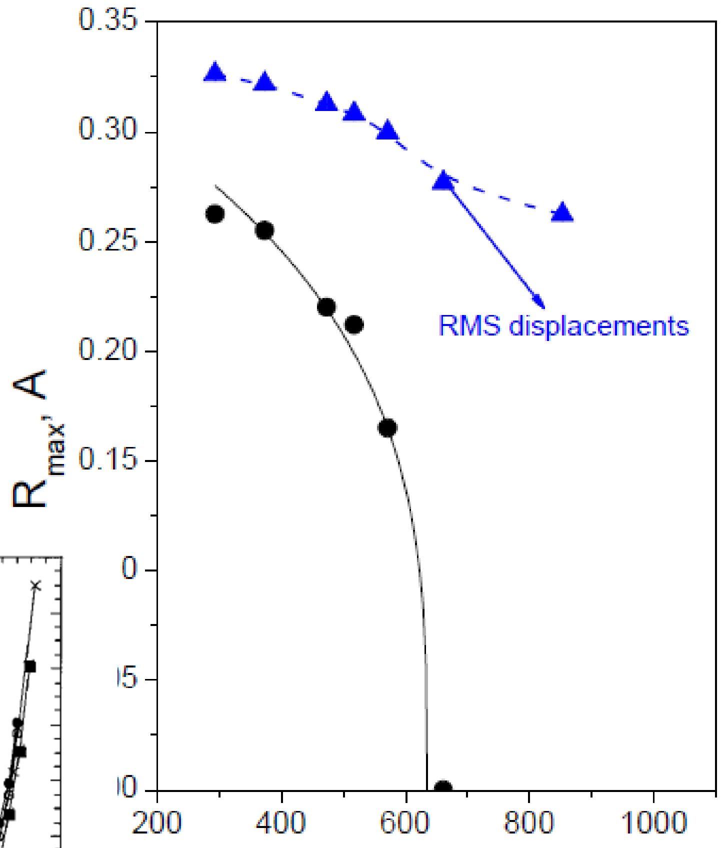












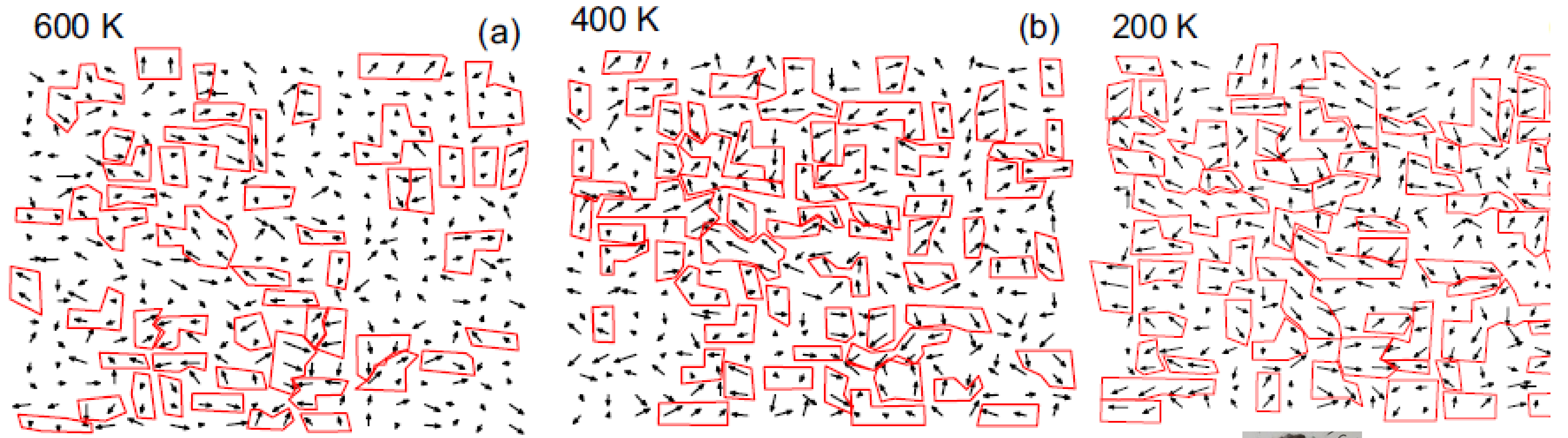
New order parameter : $\phi = |\phi| e^{i\varphi}$

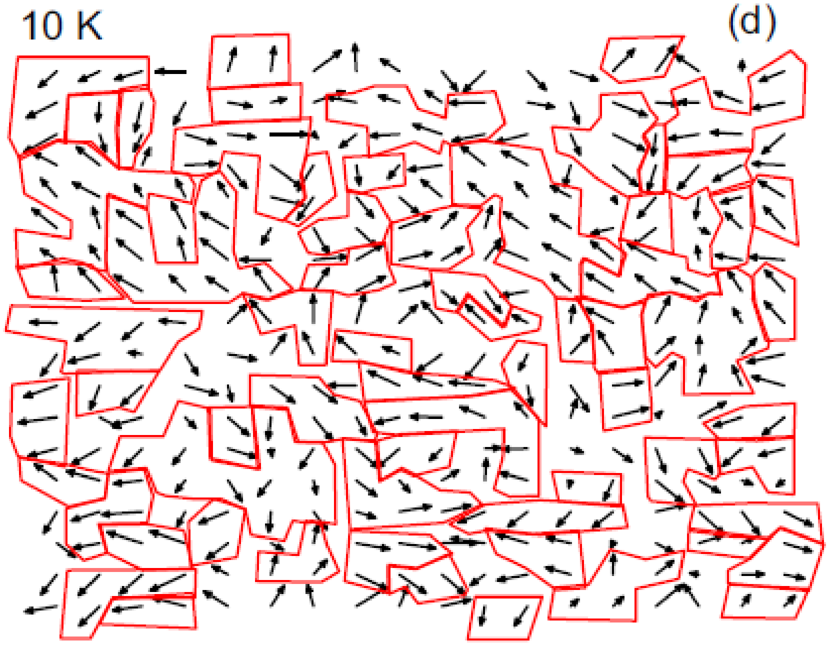
Amplitude Pb shift : scalar $|\phi| = A(T_B - T)^{\gamma}$

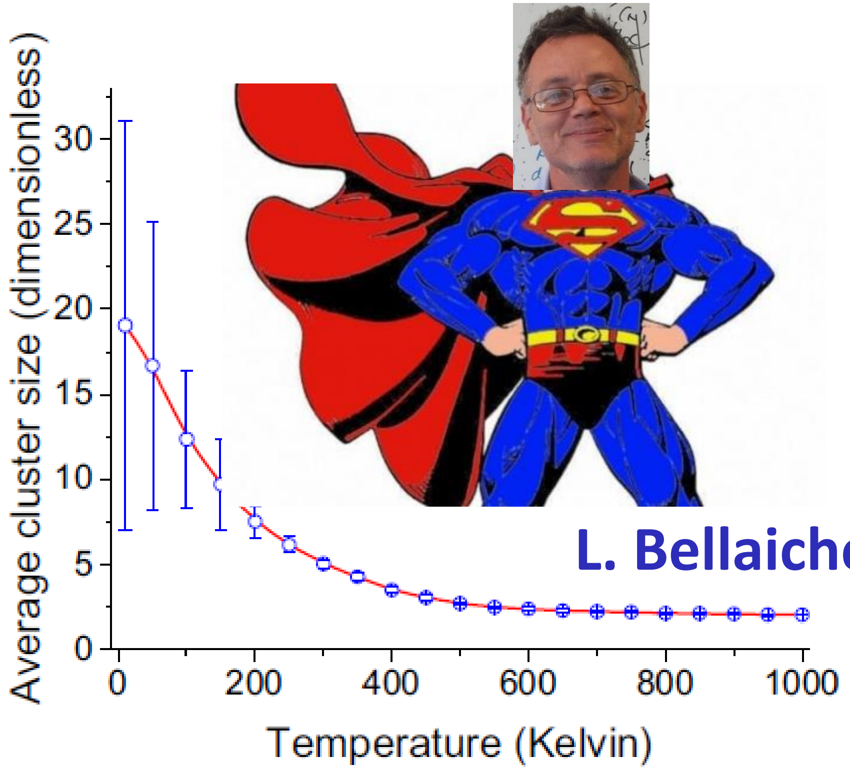
Below T_B, ALL Pb ions are displaced (Mexican hat potential)

Prosandeev, Phys. Rev. B 102, 104110 (2020)

Help from modelling: SuperHamiltonian



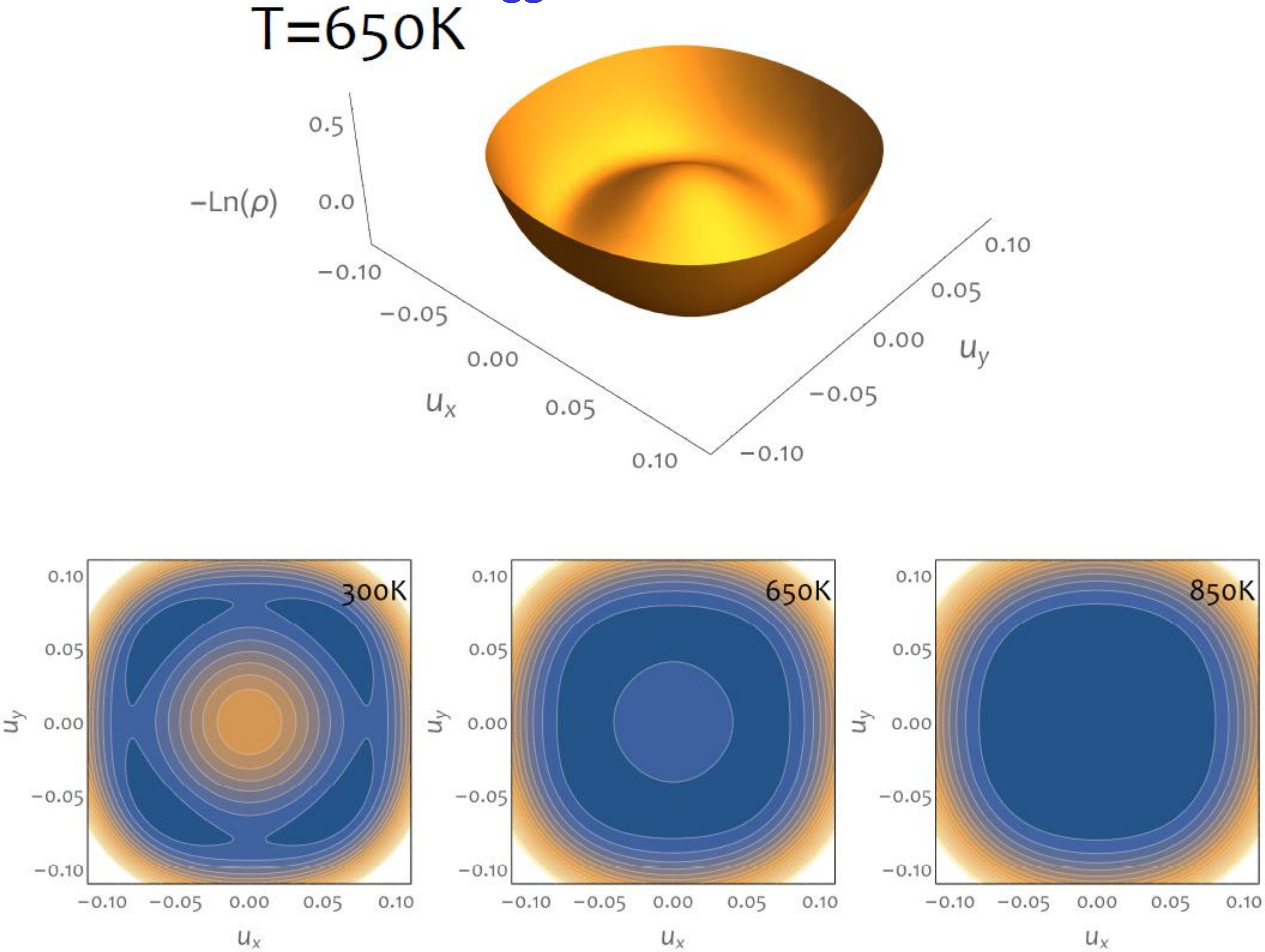




L. Bellaiche and his group

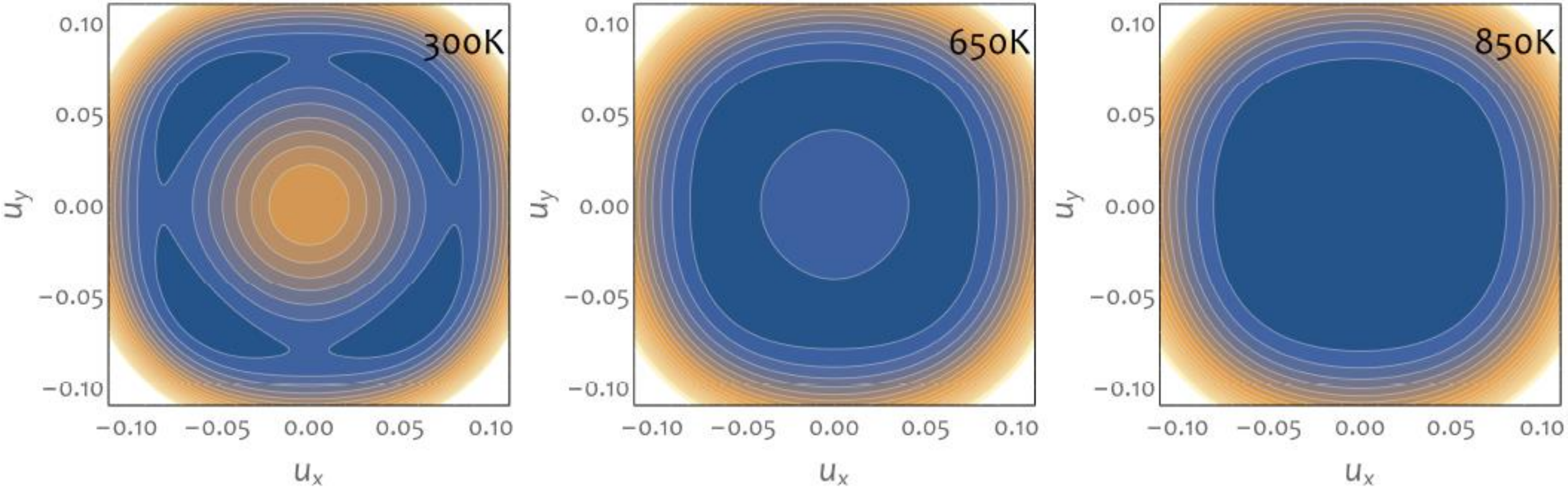
A. Al Barakaty, Phys. Rev. B **91**, 214117 (2015)

Back to Higgs and its Mexican hat…

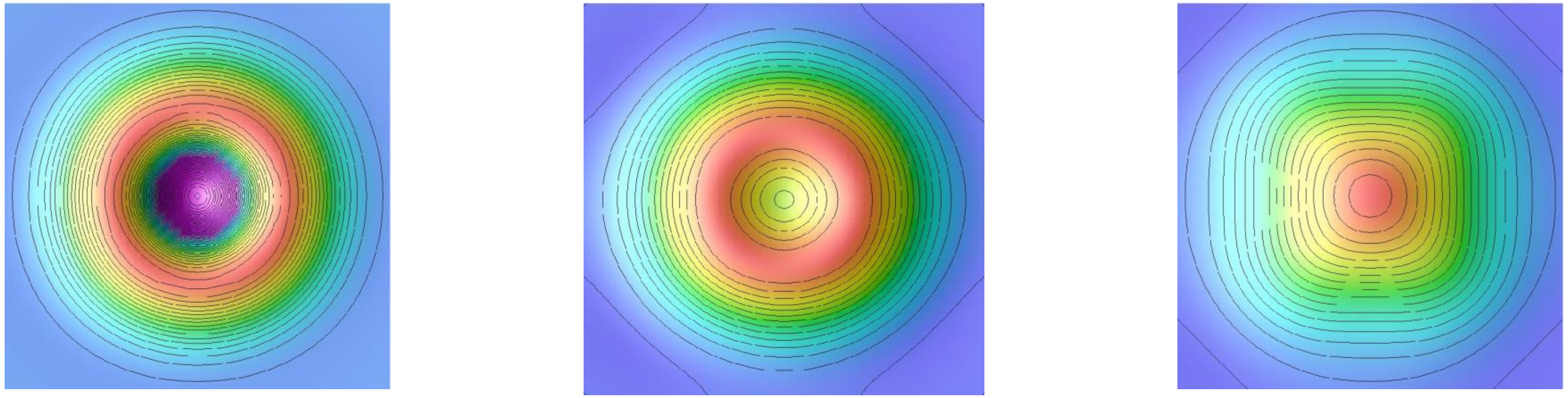


Back to Higgs and its Mexican hat…

Modeling



Experiment



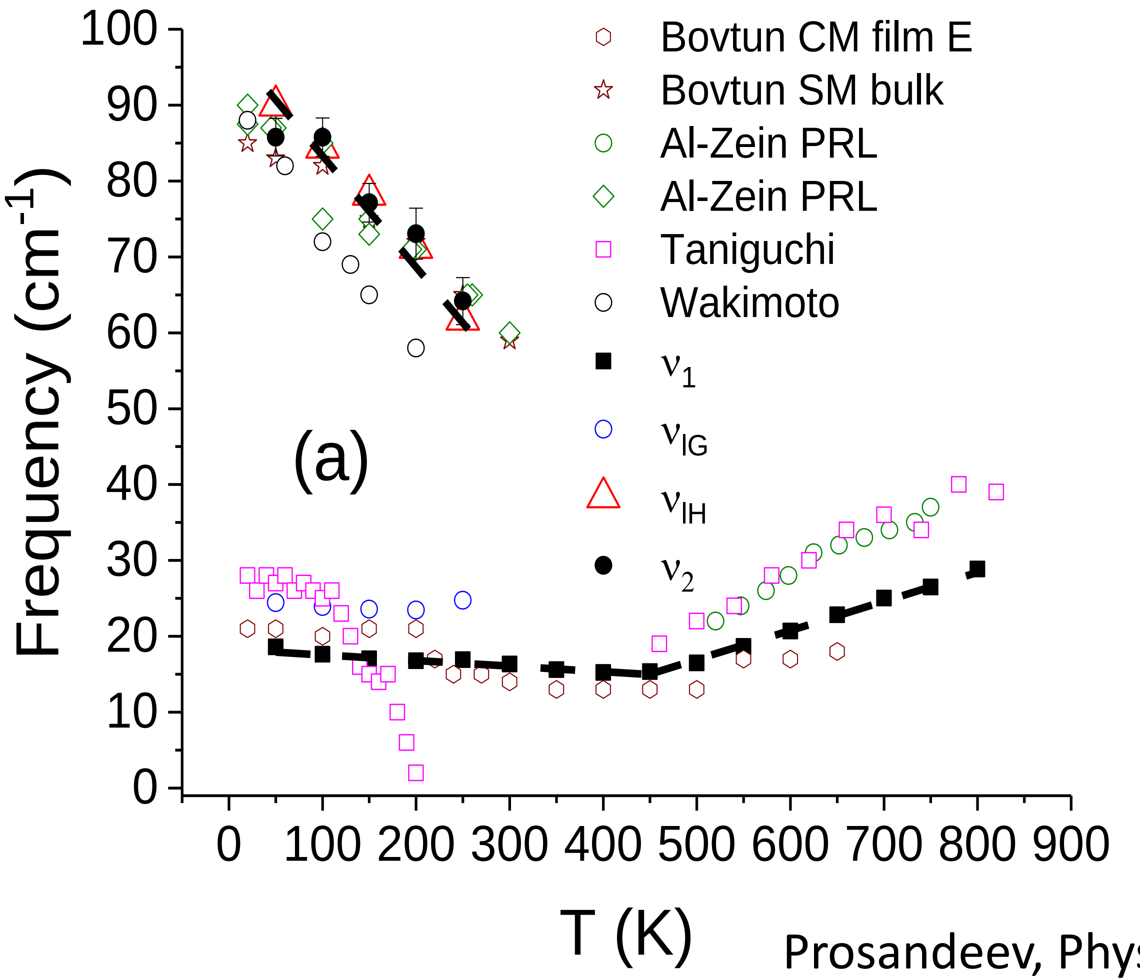
Prosandeev, Phys. Rev. B 102, 104110 (2020)

We have the Mexican hat, where are the collective excitations?

Molecular Dynamics simulation

A: Higgs-like (amplitudon) mode

E_1: Goldstone-like (phason) mode



Prosandeev, Phys. Rev. B 102, 104110 (2020)

Menu

Some basics and ingredients

Electric field effect

The Physics behind

Applications

Relaxor applications

Giant piezoelectric

Huge dielectric

Strong electrostrictive

Large tunability

Significant electrooptics

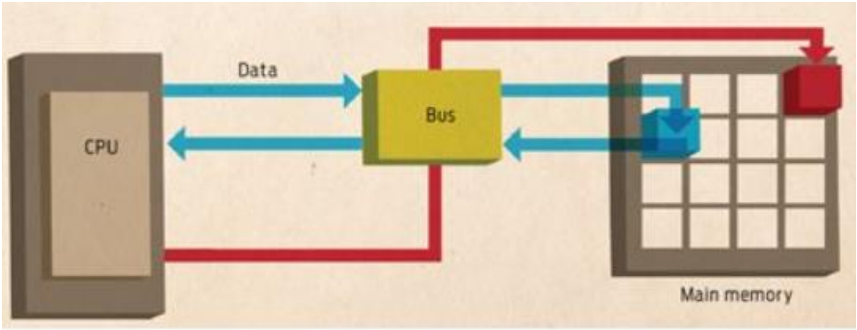
Big pyroelectric

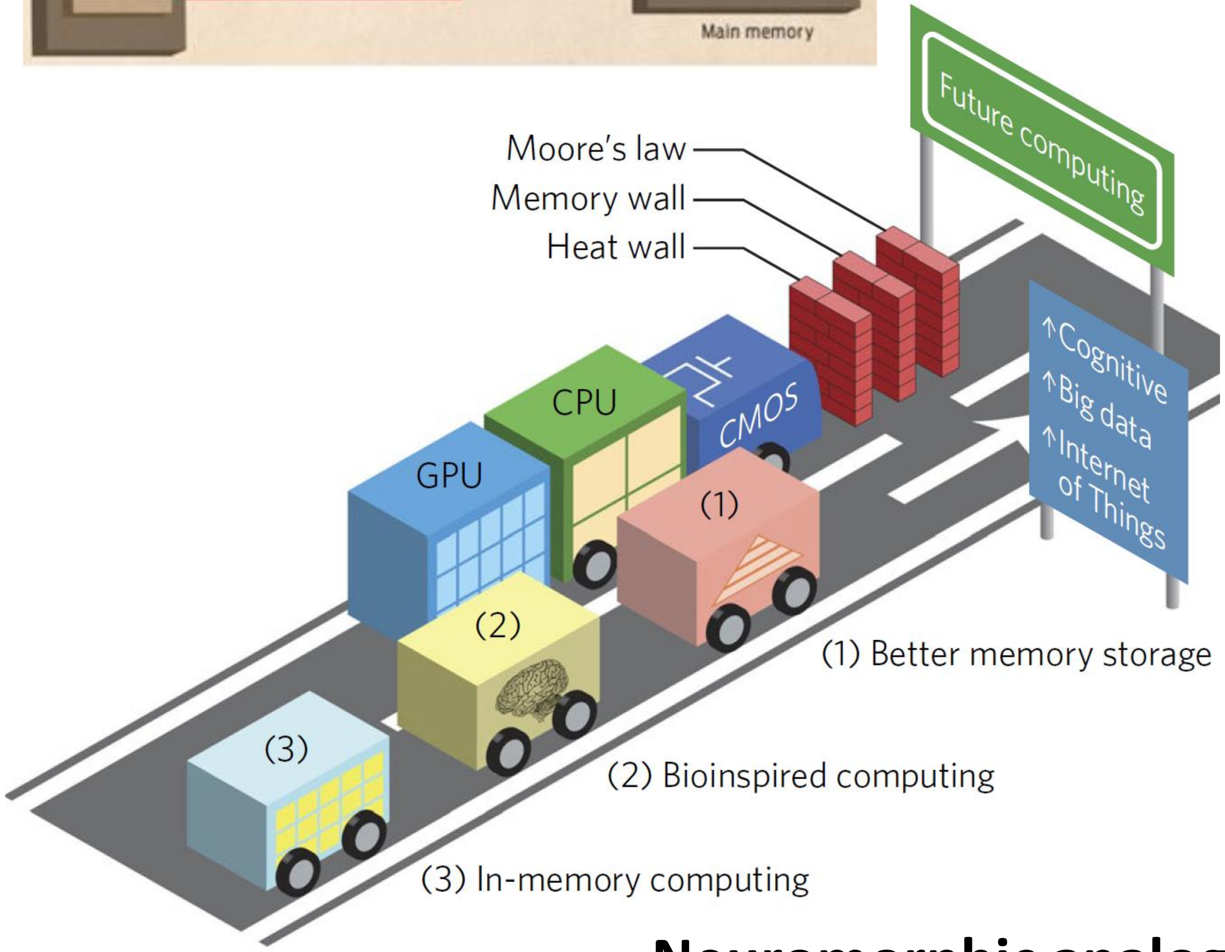
High energy storage

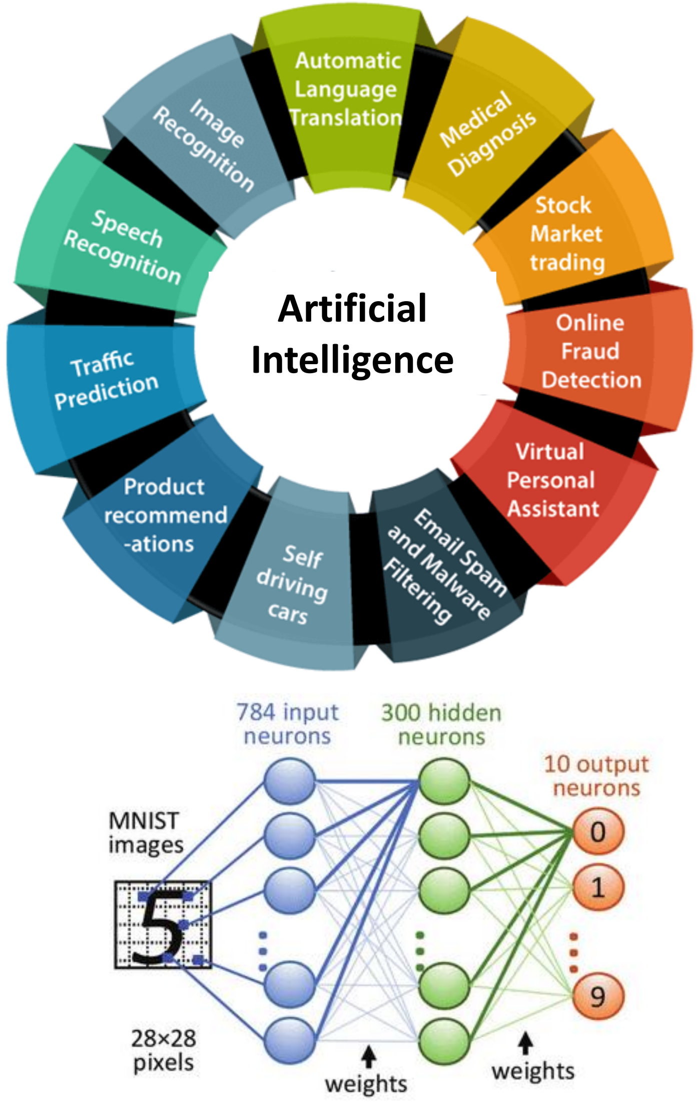
Strong electrocaloric

Context

Von Neumann digital and sequential architecture

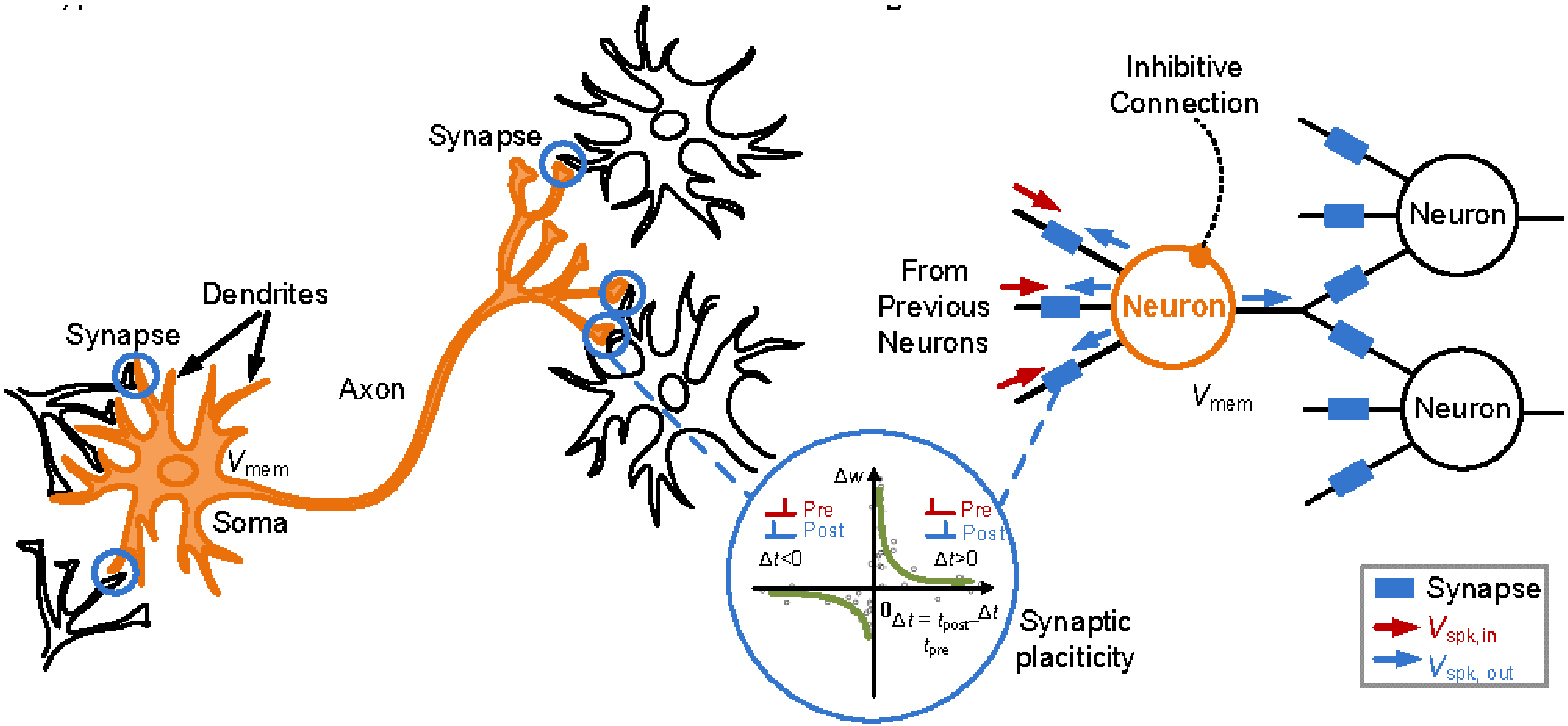






Neuromorphic analog and parallel architecture

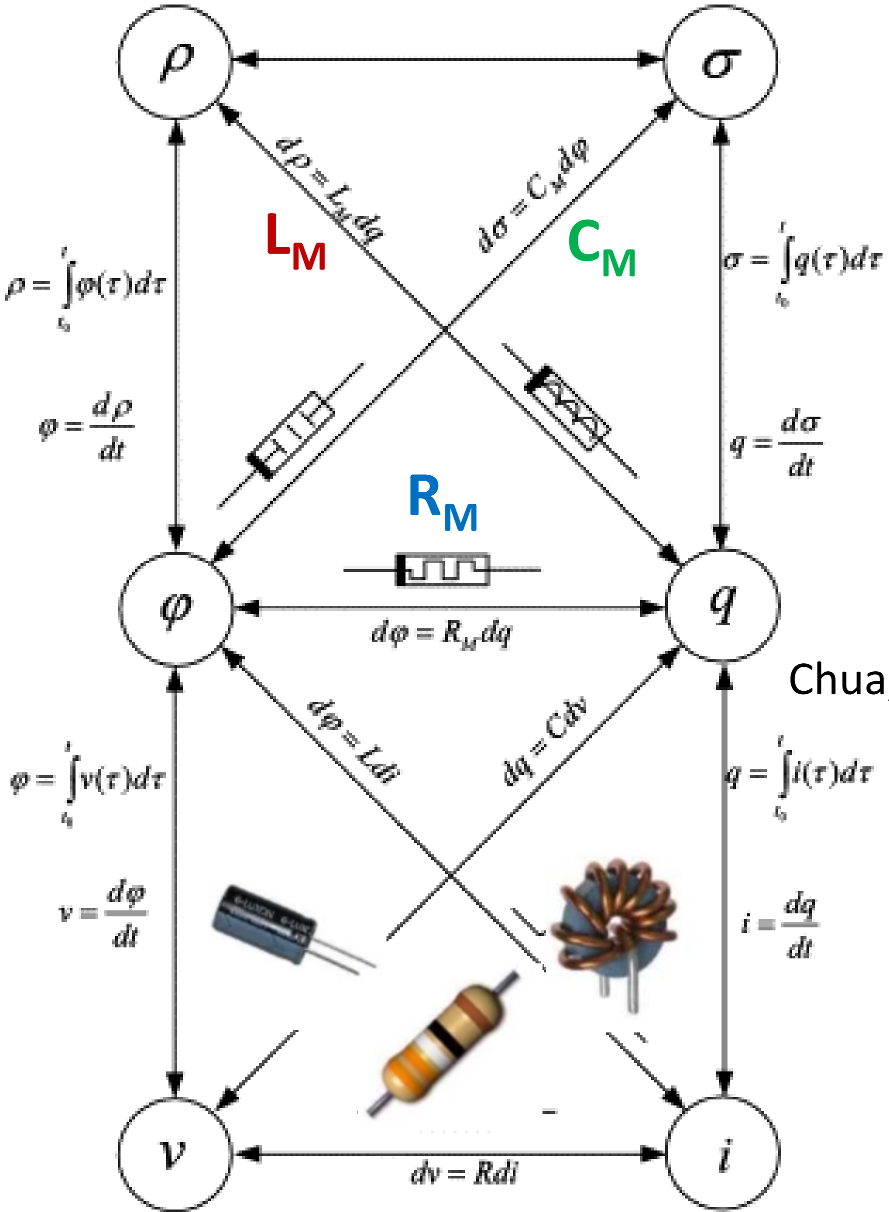
Bio-inspired neuromorphic computing



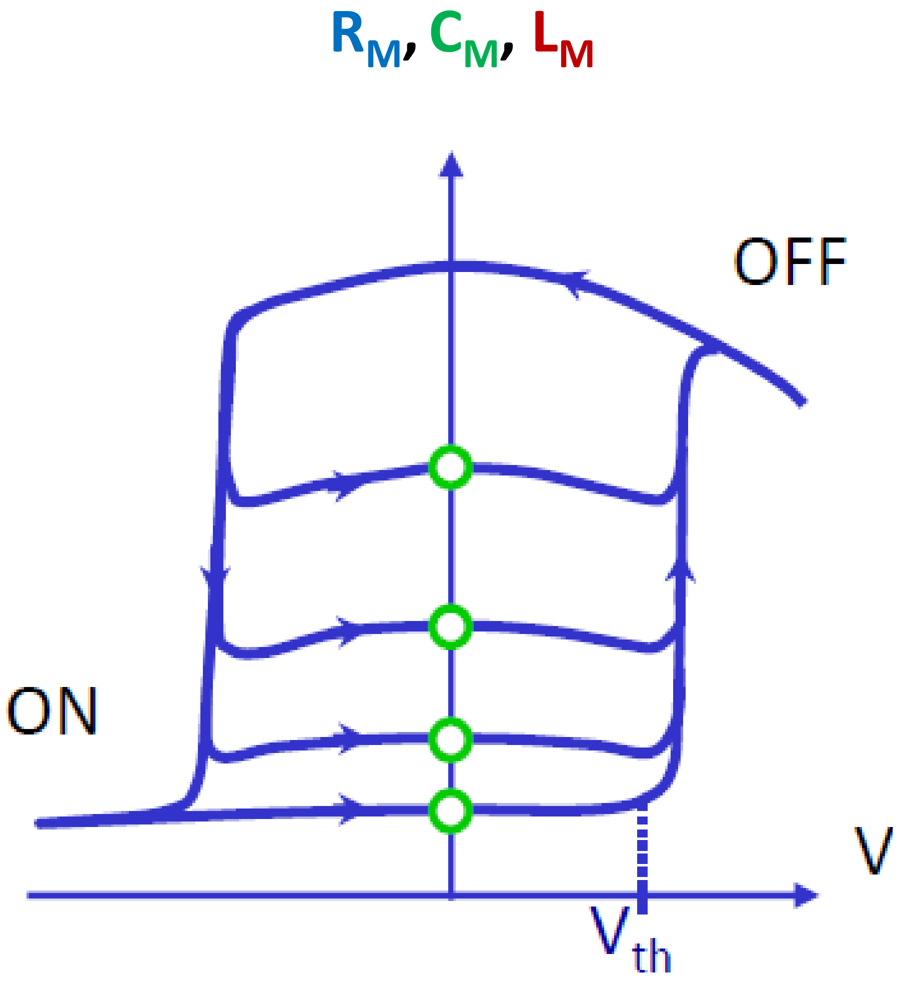
Long Term Potentiation (strengthening = learning)

Long Term Depression (weakening = forgetting)

MemRistor, memCapacitor, memInductor to mimick synapses

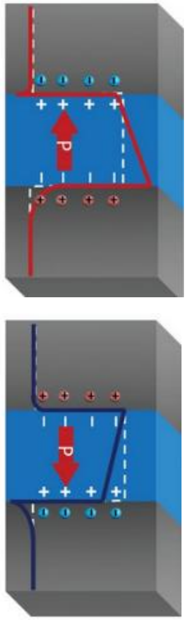


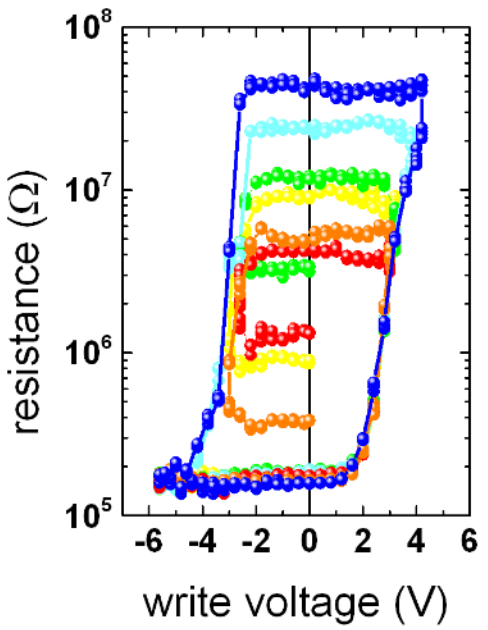
Chua, IEEE 1971

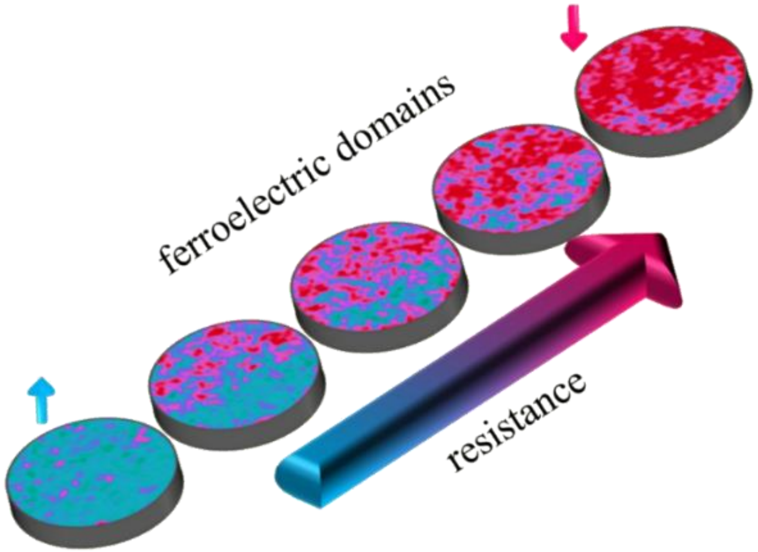


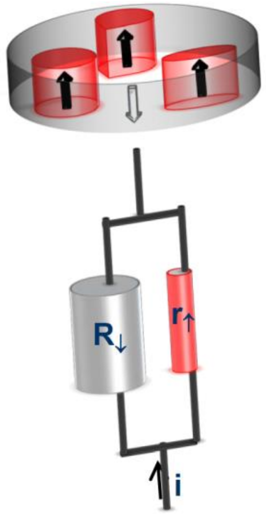
Ferroelectric-based Memristor/Synapse

Through Ferroelectric Tunnel Junction (FTJ)







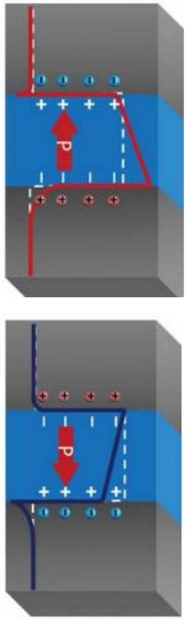


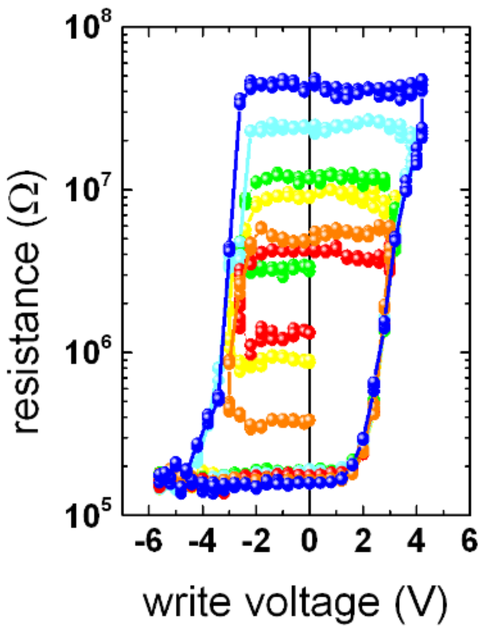
$$\frac{1}{R} = \frac{1-s}{R_\uparrow} + \frac{s}{R_\downarrow}$$

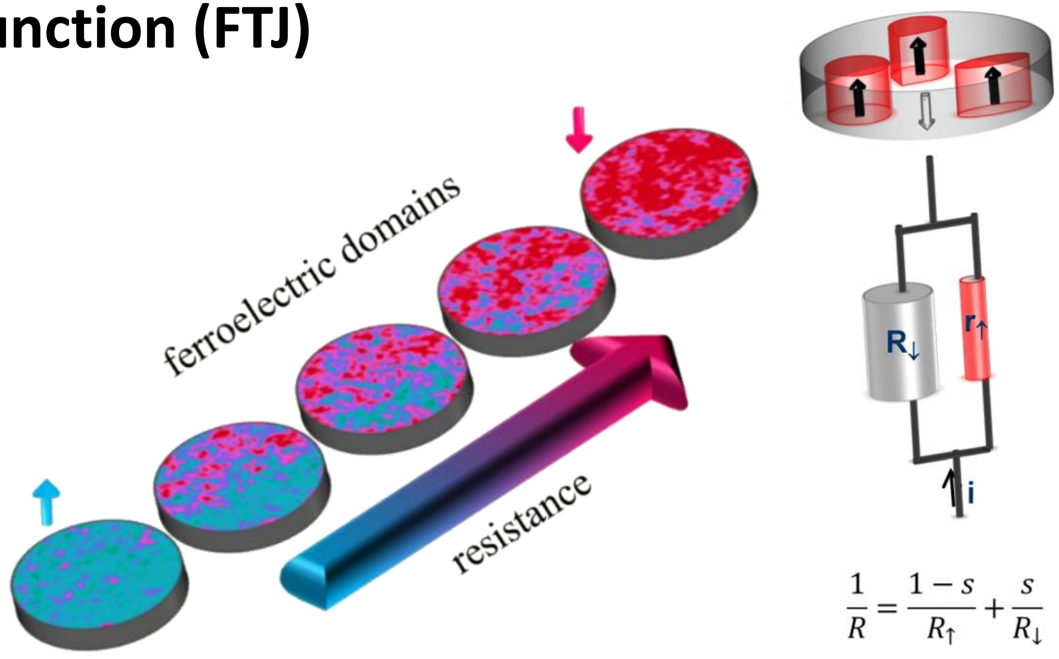
Chanthbouala et al. Nature Mater. **11**, 860 (2012)

Ferroelectric-based Memristor/Synapse

Through Ferroelectric Tunnel Junction (FTJ)



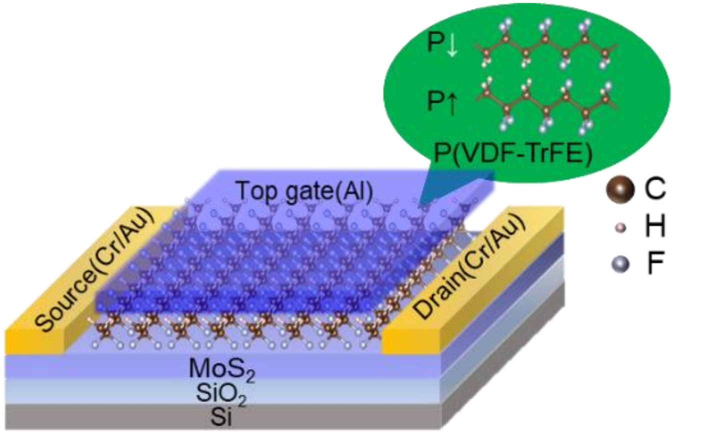


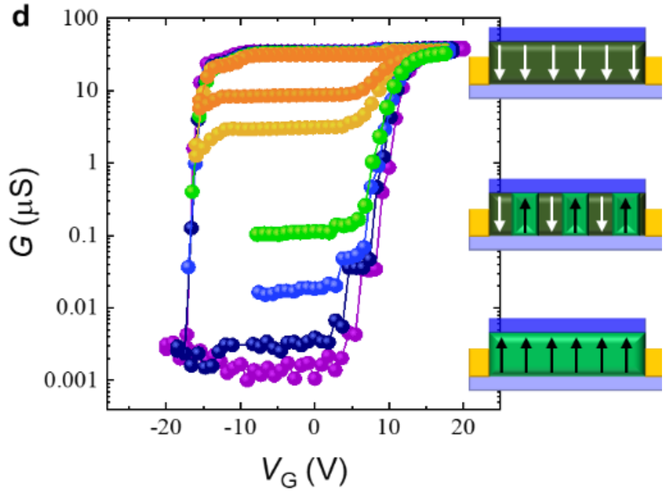


$$\frac{1}{R} = \frac{1-s}{R_\uparrow} + \frac{s}{R_\downarrow}$$

Chanthbouala et al. Nature Mater. **11**, 860 (2012)

Through Ferroelectric Field Effect Transistor (FeFET)

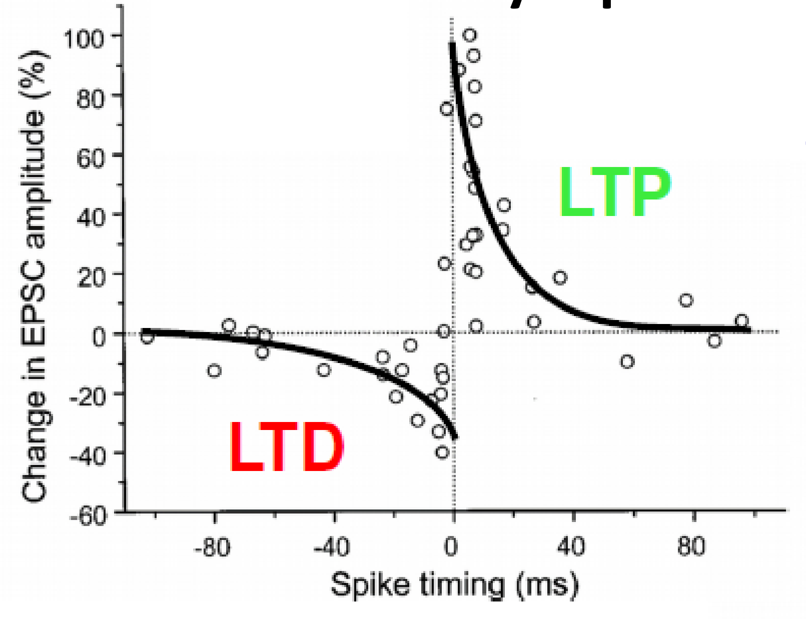




Tian, et al., Nature Comm. **7**, 11502(2016), Adv. Electron. Mater. **5**, 1800600 (2019)

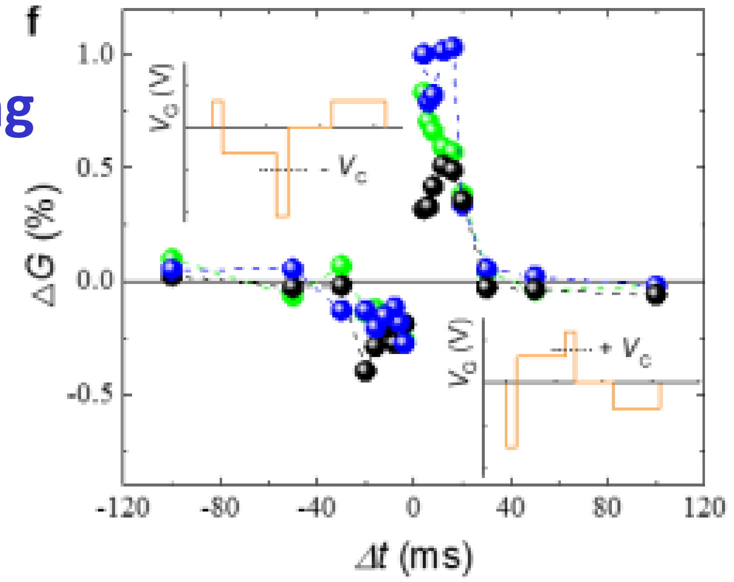
Ferroelectric memristor using a FeFET

Bio-synapse



Artificial-synapse using a FeFET

STDP learning

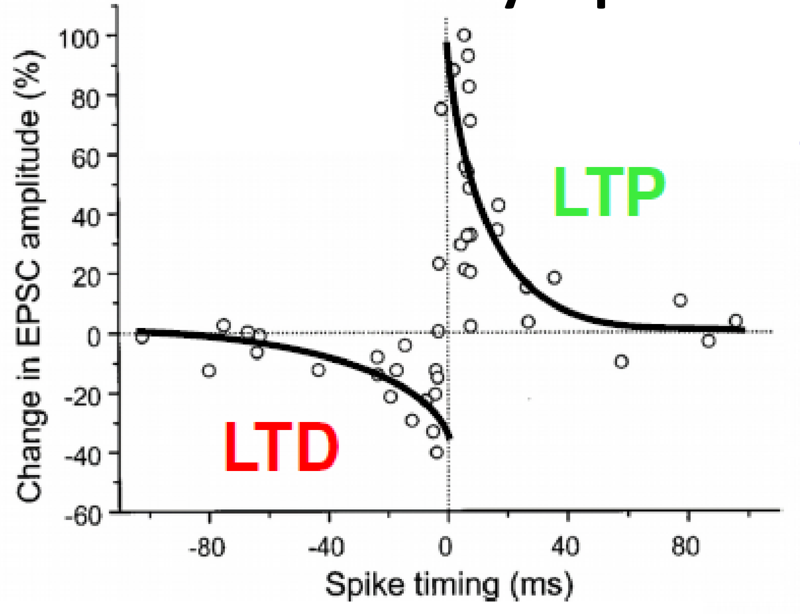


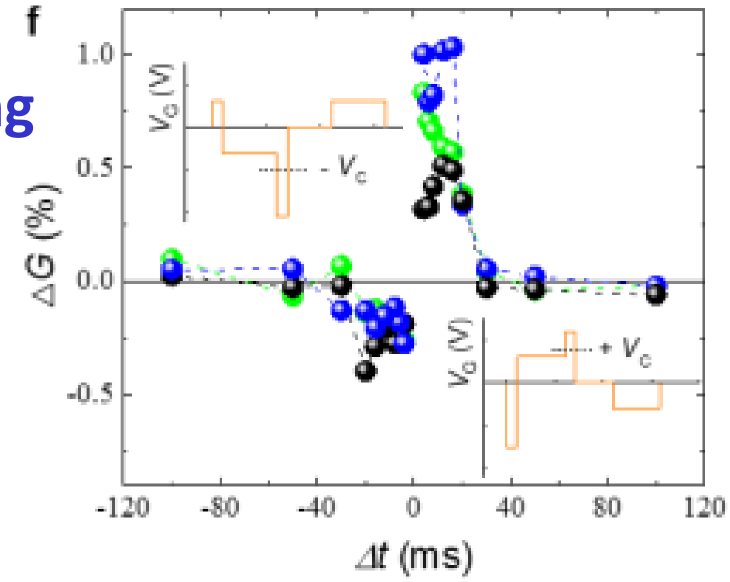
Yan et al., Adv. Electron. Mater**7**, 2001276 (2021), Appl. Phys. Rev. **9**, 021309 (2022)

Ferroelectric memristor using a FeFET

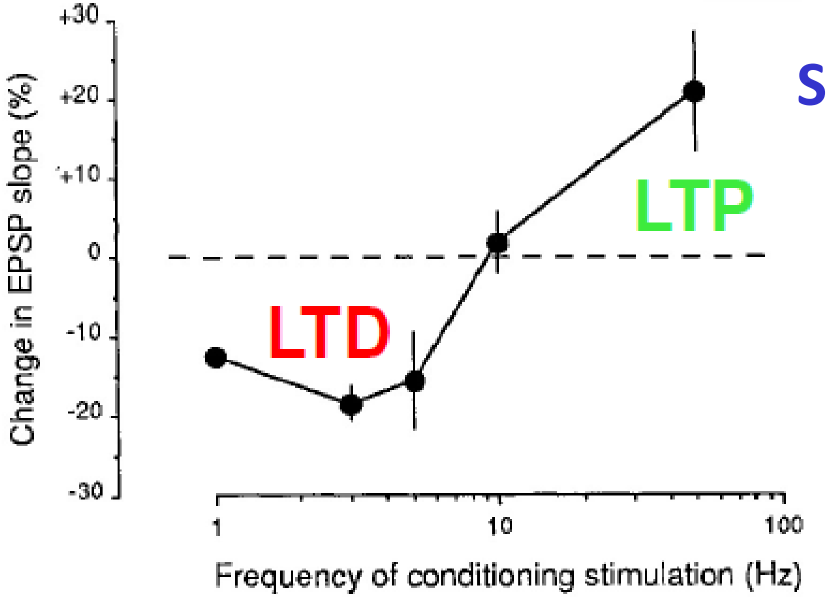
Bio-synapse | **Artificial-synapse using a FeFET**

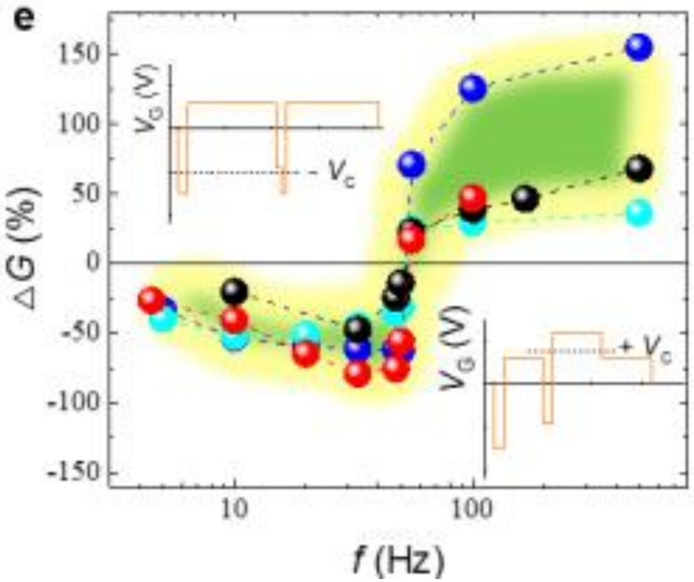
STDP learning





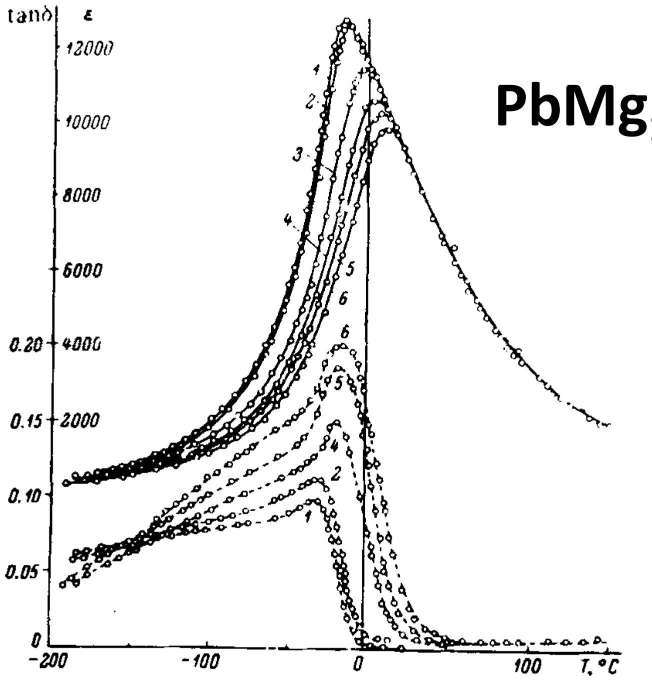
SRDP learning





Yan et al., Adv. Electron. Mater**7**, 2001276 (2021), Appl. Phys. Rev. **9**, 021309 (2022)

Relaxor-based Synapse: Reminder



Smolenskii&Agranovskaya, Zh. Tekh. Fiz. **28**, 1491 (1958)

$PbMg_{1/3}Nb_{2/3}O_3$ (PMN)

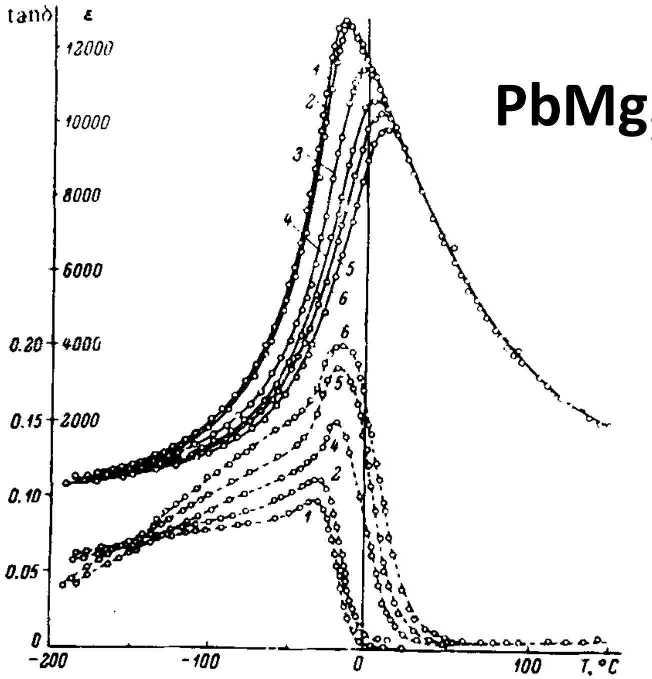
Dynamic

Polar nanoregions

Non-ergodicity

10 K

Relaxor-based Synapse: Reminder



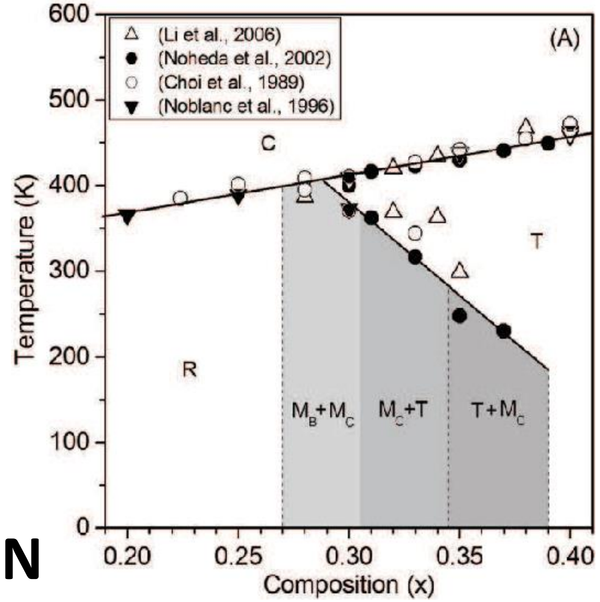
Smolenskii&Agranovskaya, Zh. Tekh. Fiz. **28**, 1491 (1958)

$PbMg_{1/3}Nb_{2/3}O_3$ (PMN)

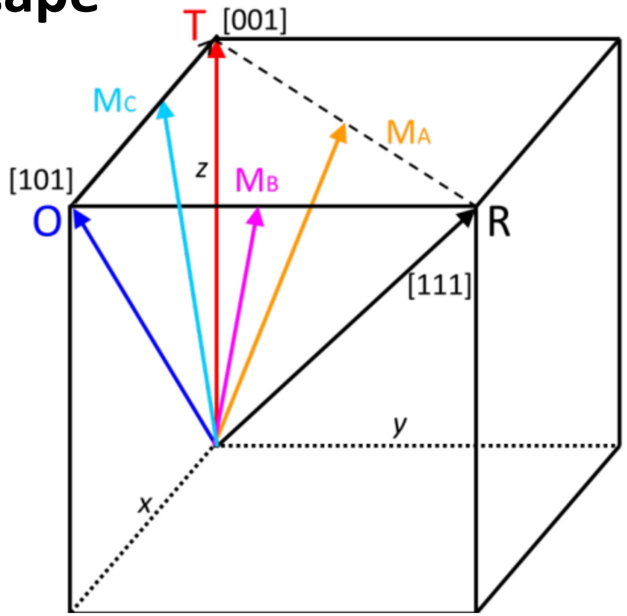
10 K

Dynamic
Polar nanoregions
Non-ergodicity

Flat energy landscape



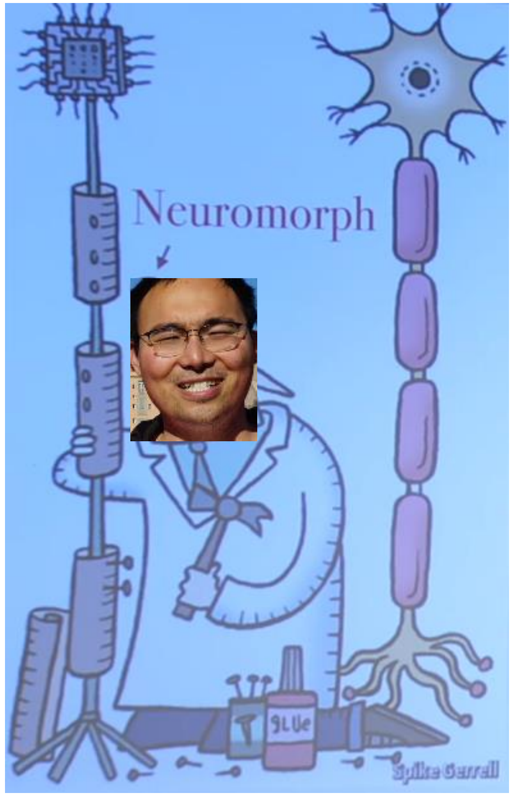
← PMN **PT →**



Relaxor-based MemCAPACITOR/Synapse

Exploit the flat energy landscape of relaxor-based systems

The main element

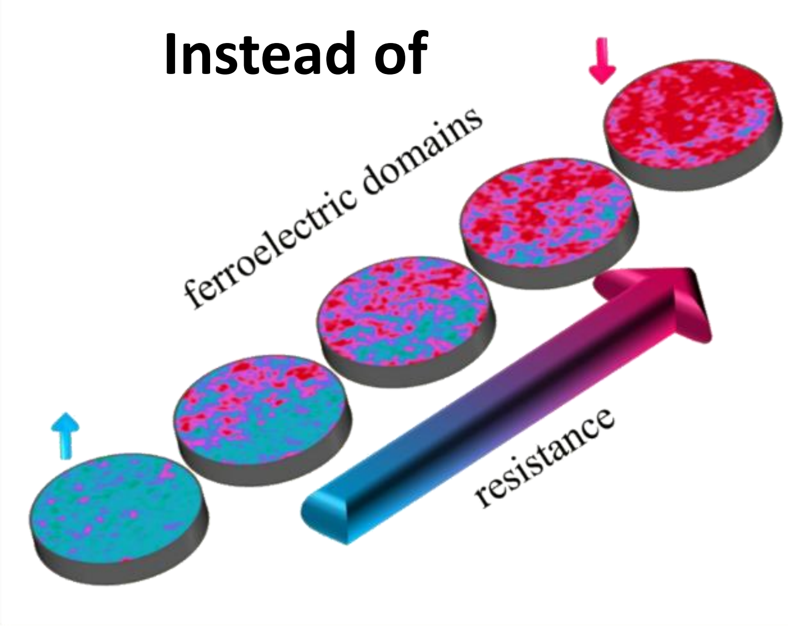


Long Cheng et al, unpublished

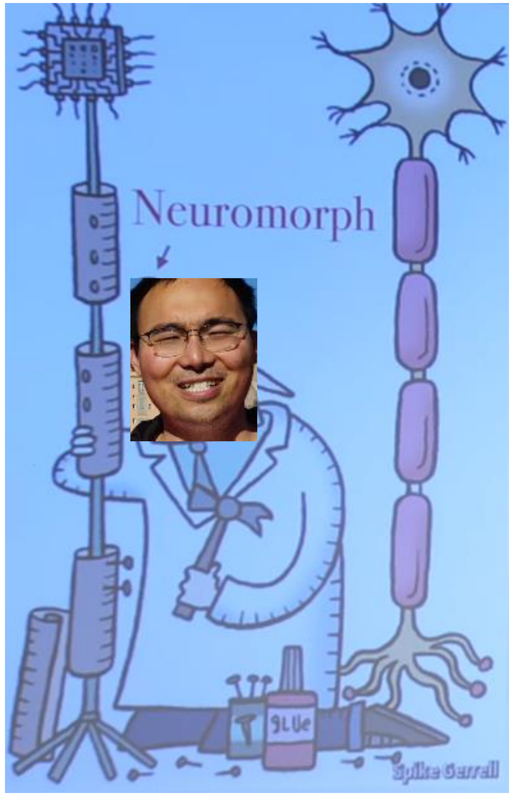
Relaxor-based MemCAPACITOR/Synapse

Exploit the flat energy landscape of relaxor-based systems

Instead of



The main element

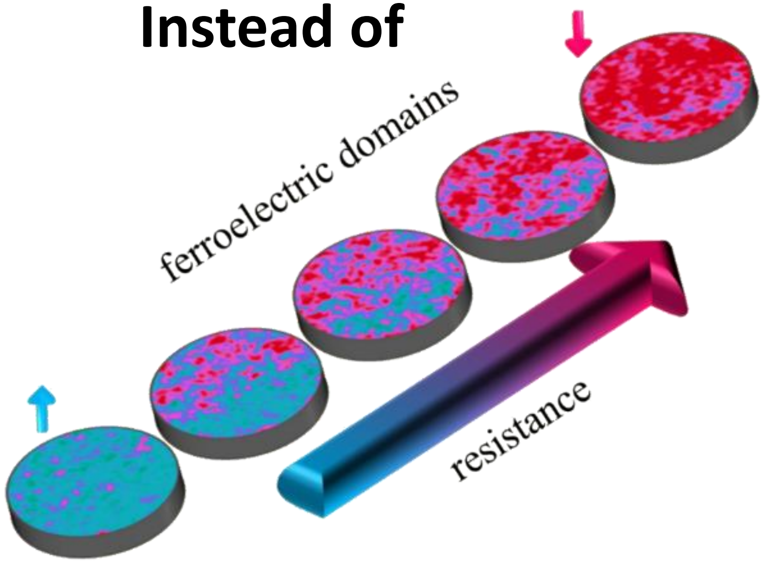


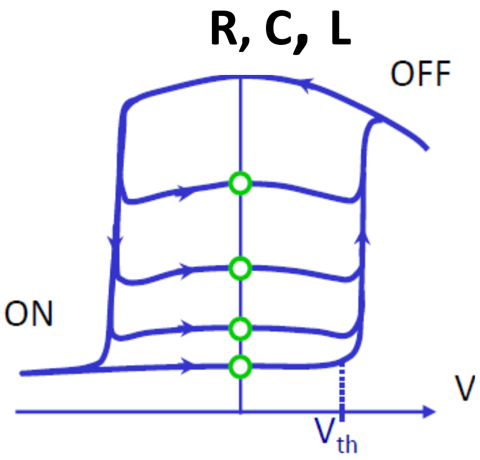
Long Cheng et al, unpublished

Relaxor-based MemCAPACITOR/Synapse

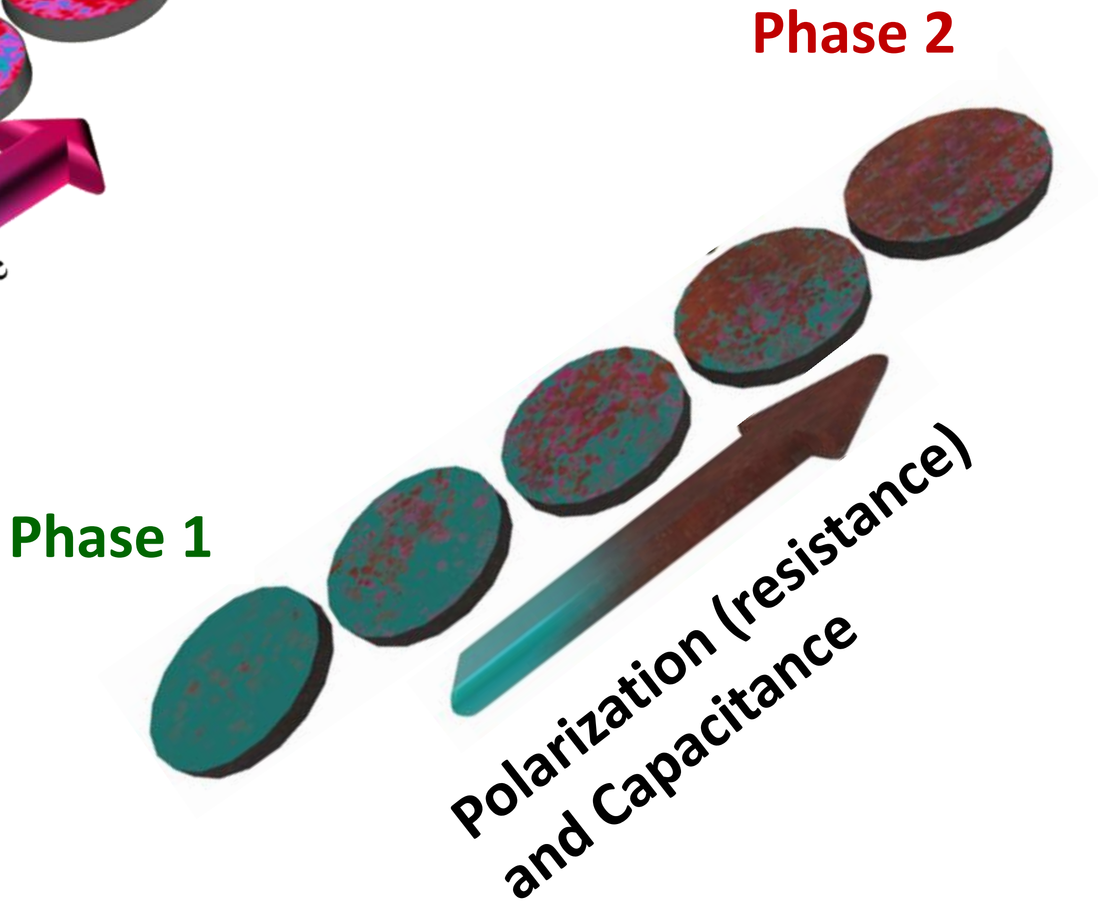
Exploit the flat energy landscape of relaxor-based systems

Instead of



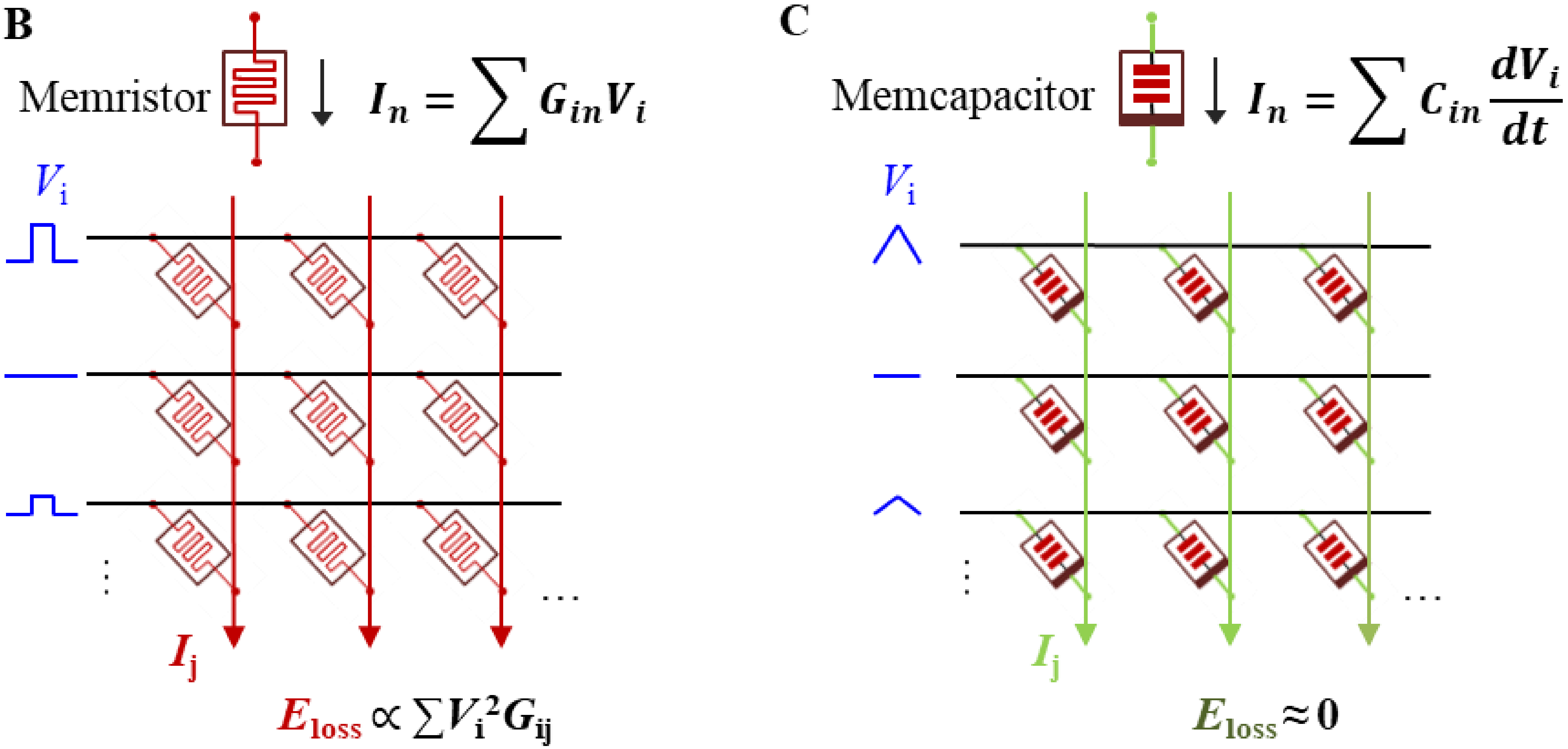


Basic concept



Long Cheng et al, unpublished

MemRistor, memCapacitor, memInductor to mimick synapses

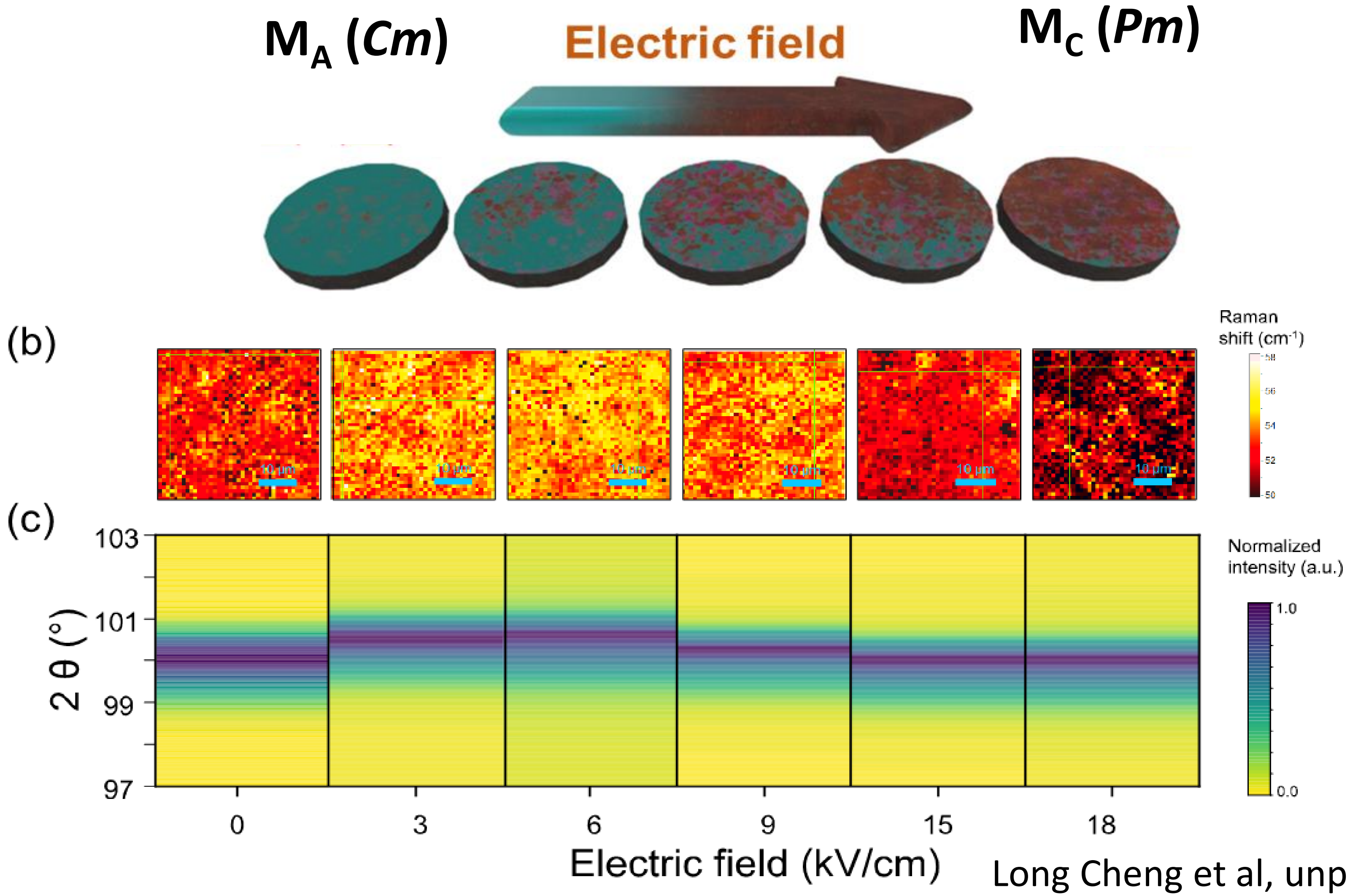


Tian et al., Exploration, 20220126 (2023)

Relaxor-based MemCAPACITOR/Synapse

Exploit the flat energy landscape of relaxor-based systems

Proof of concept on a (001) PMNPT single crystal

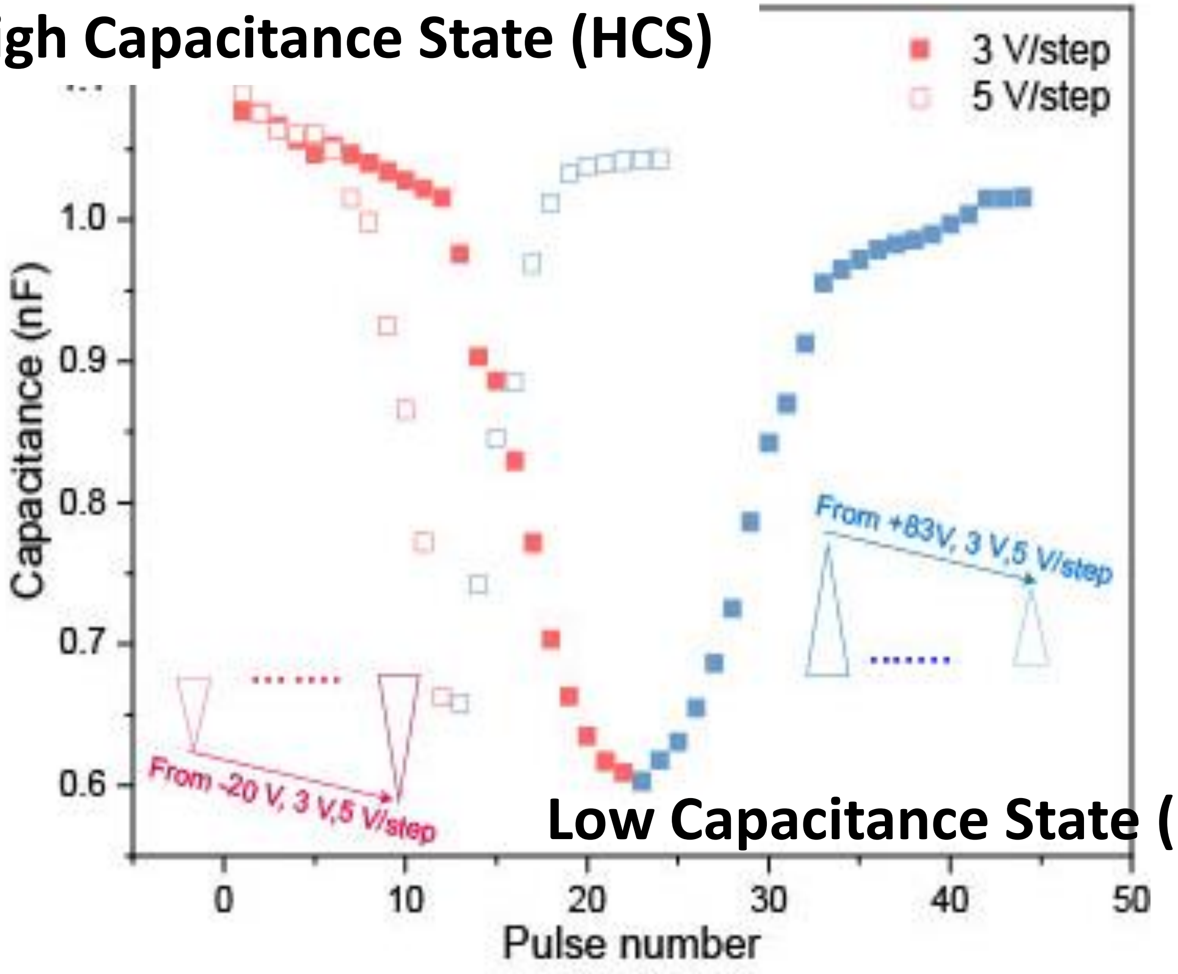


Long Cheng et al, unpublished

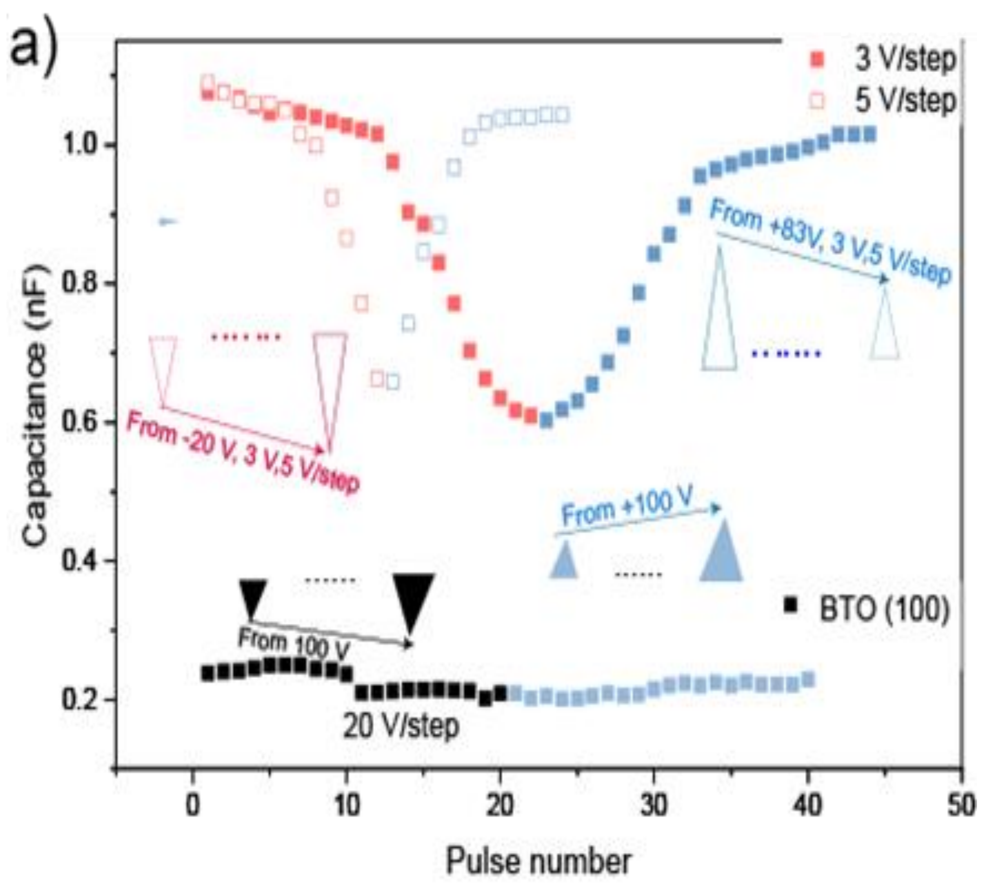
Relaxor-based MemCAPACITOR/Synapse

Exploit the flat energy landscape of relaxor-based systems

High Capacitance State (HCS)

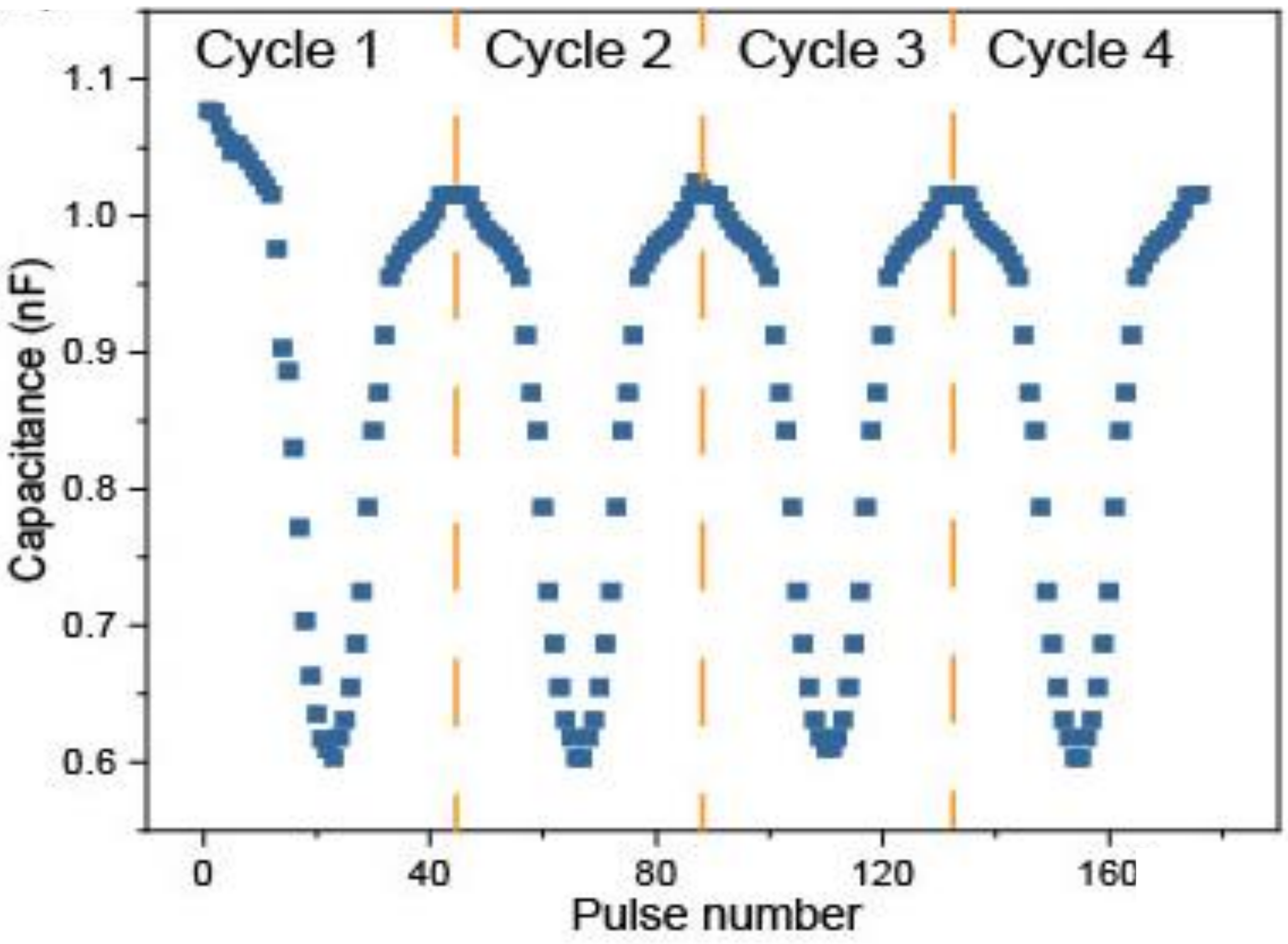


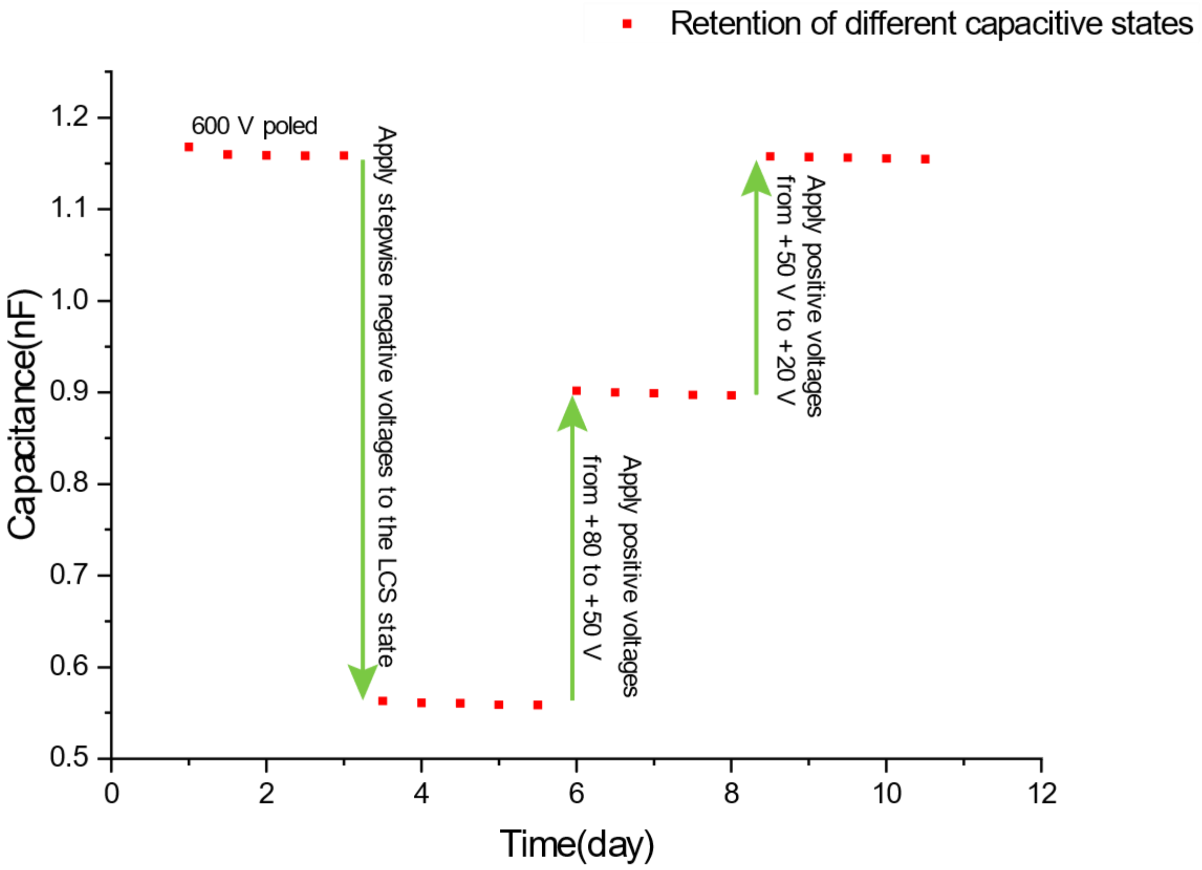
Low Capacitance State (LCS)



Long Cheng et al, unpublished

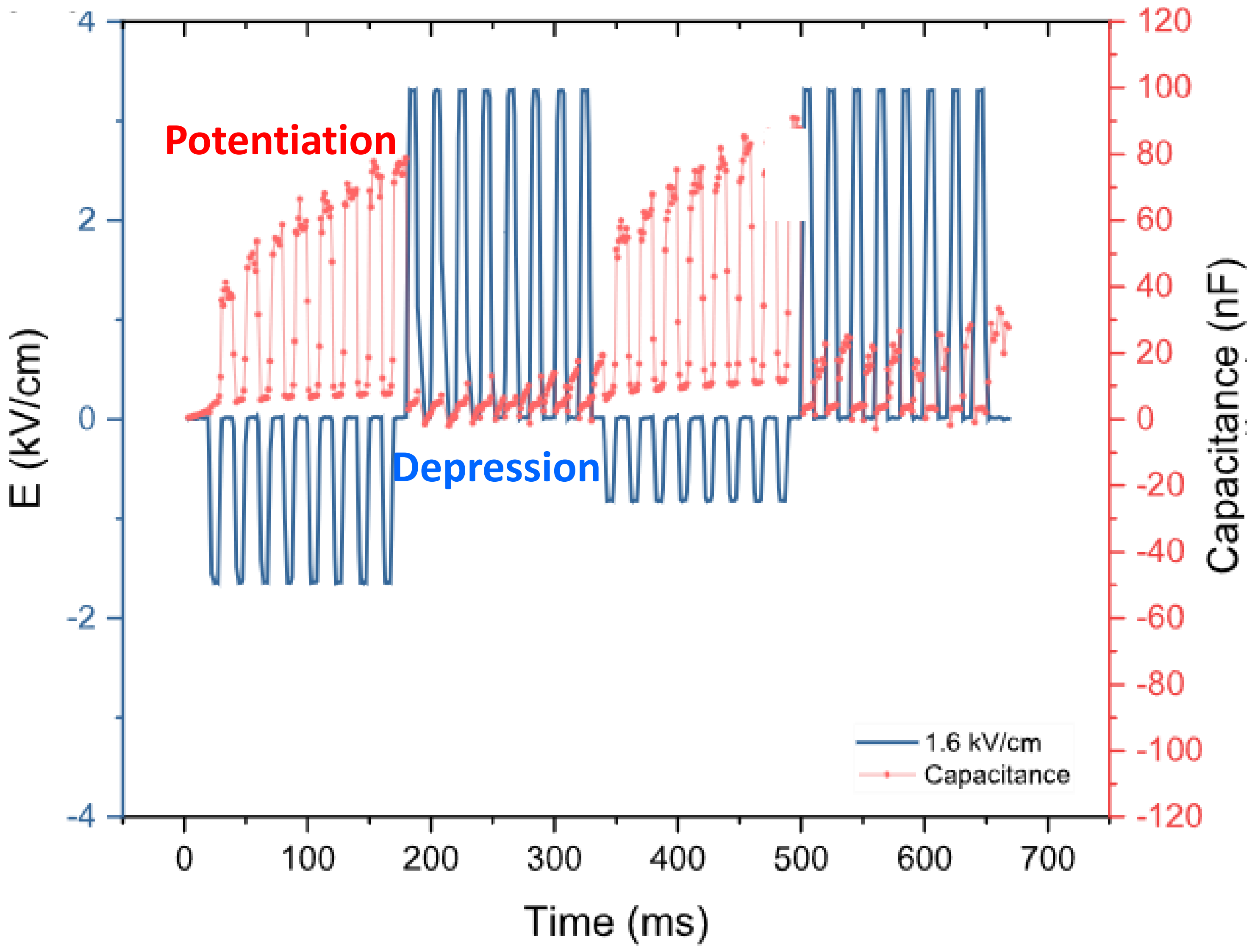
Relaxor-based MemCAPACITOR/Synapse





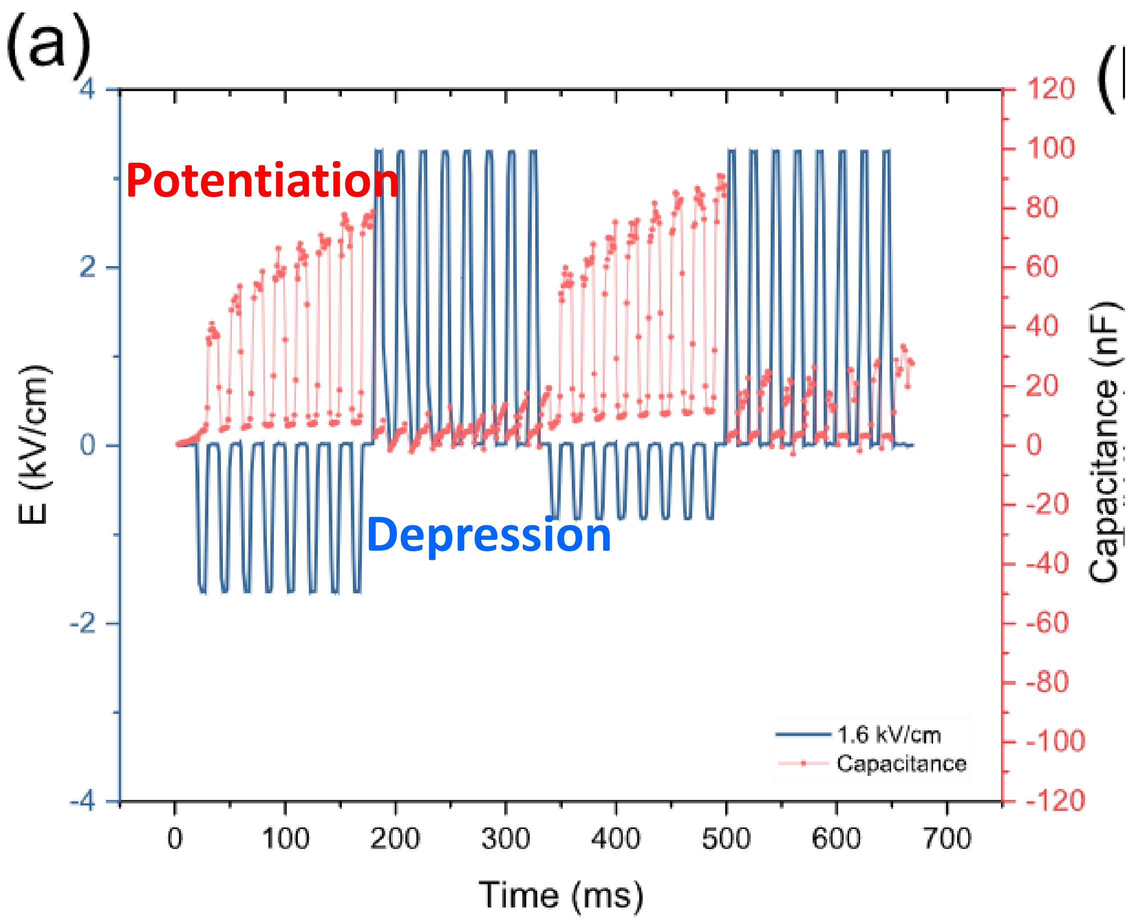
Long Cheng et al, unpublished

Relaxor-based MemCAPACITOR/Synapse

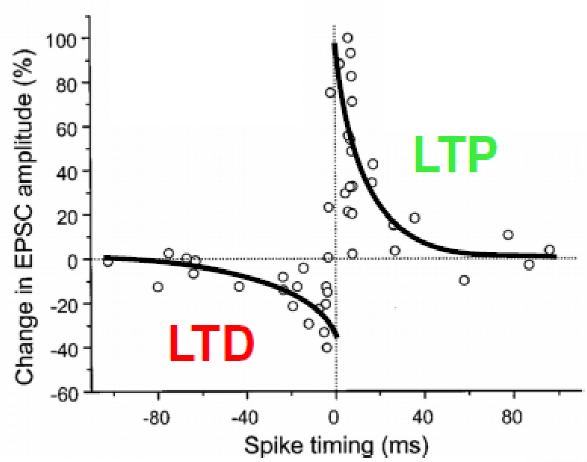


Long Cheng et al, unpublished

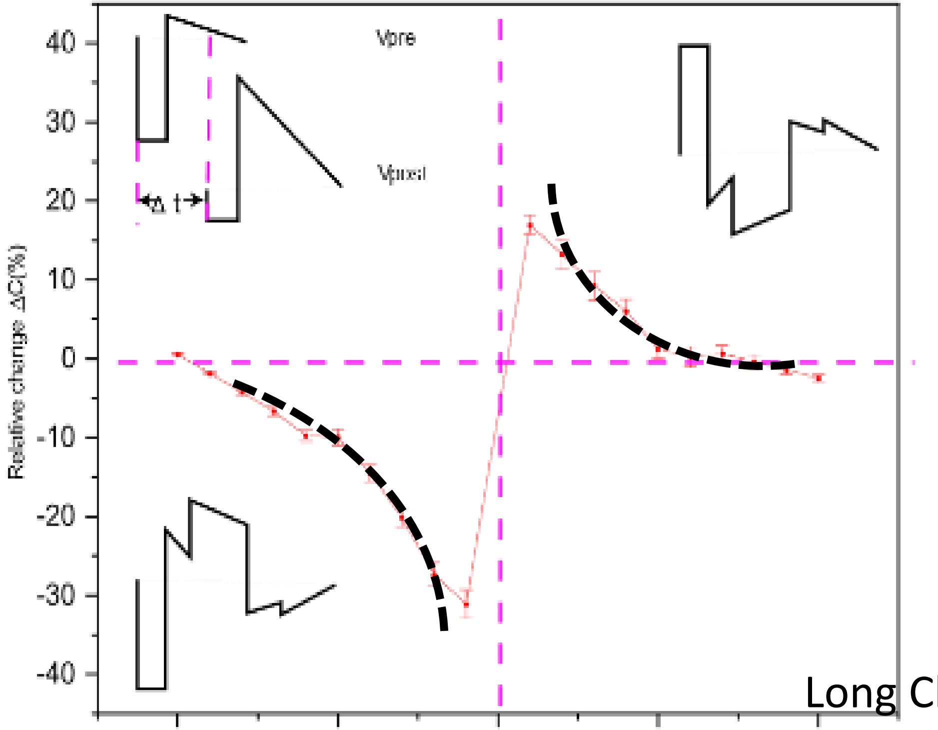
Relaxor-based MemCAPACITOR/Synapse



Bio-synapse (STDP rule)



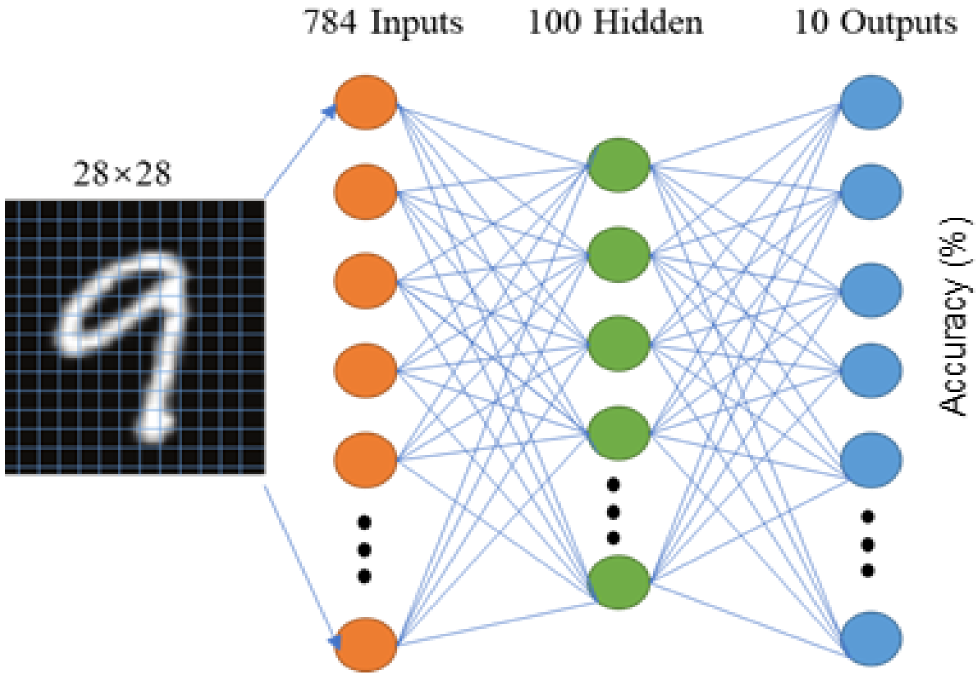
Artificial-memcapacitor synapse

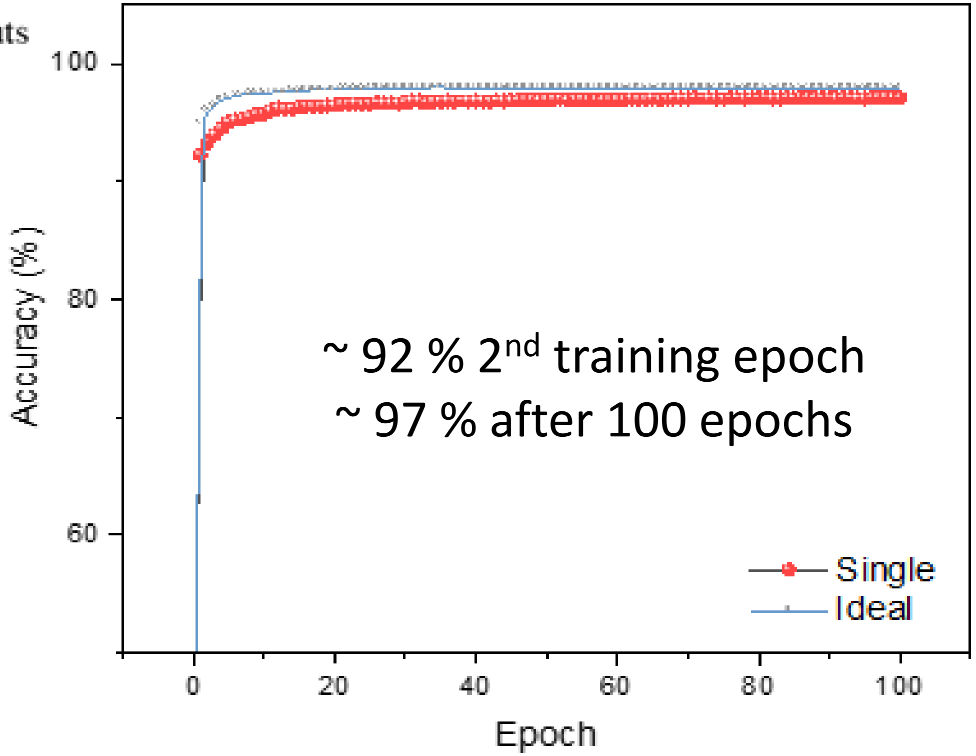


Long Cheng et al, unpublished

Relaxor-based MemCAPACITOR/Synapse

Network for classification of MNIST hand-written digit images



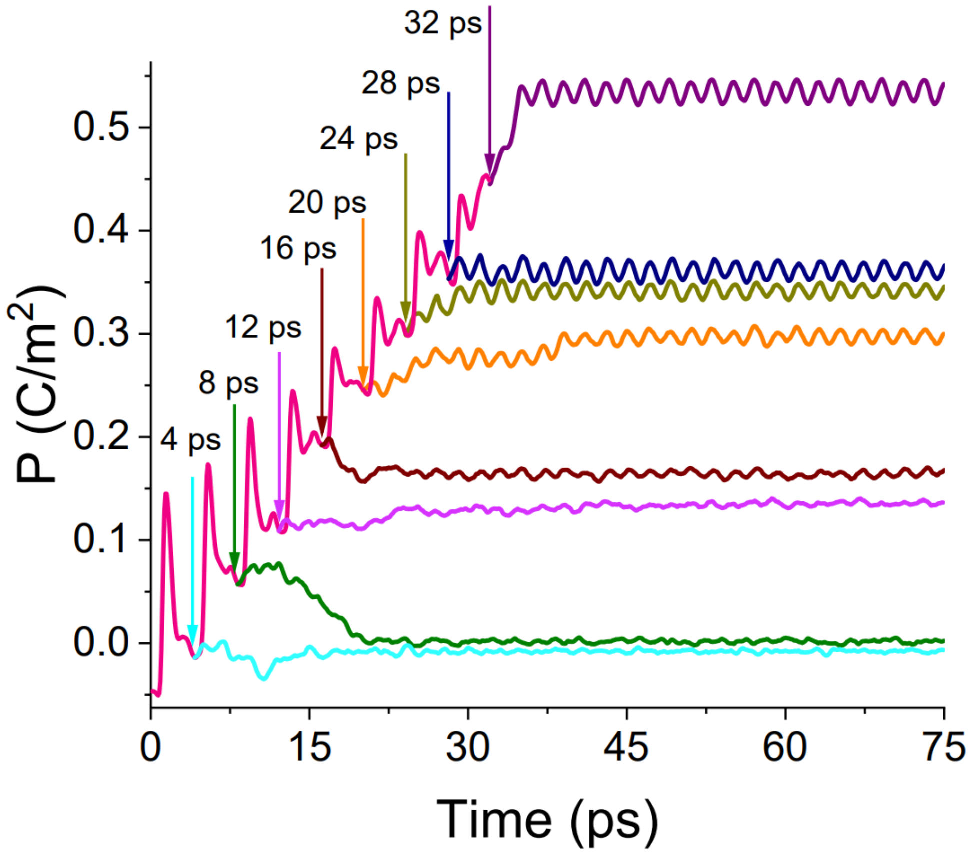


Long Cheng et al, unpublished

Conclusion

Relaxors are good for

1- various and unexplored applications



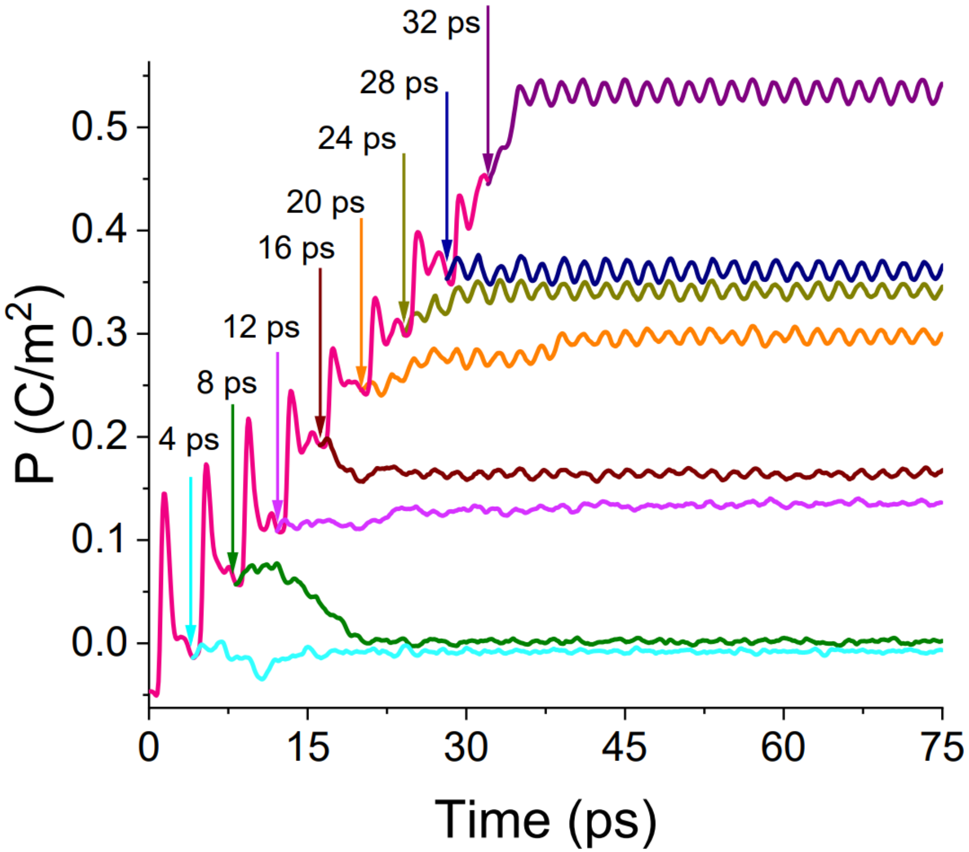
Prosandeev et al., PRL126, 027602 (2021)

Conclusion

Relaxors are good for

1- various and unexplored applications

2- new physics or exploring other fields



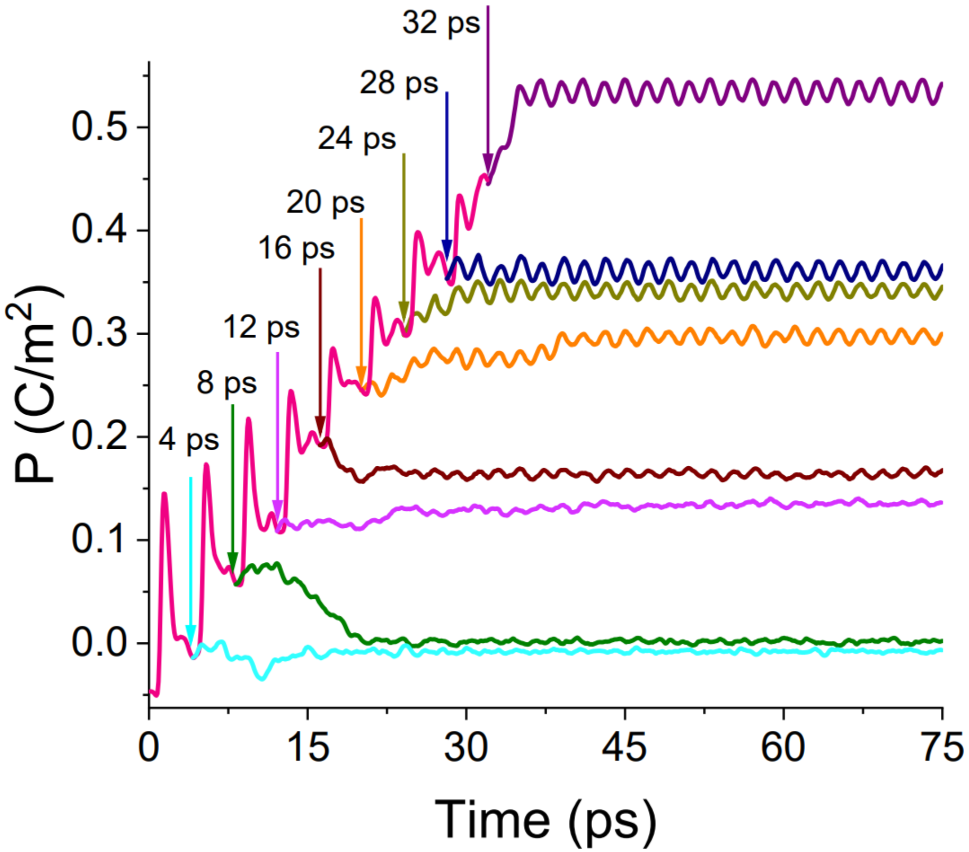
Prosandeev et al., PRL126, 027602 (2021)

Conclusion

Relaxors are good for

1- various and unexplored applications

2- new physics or exploring other fields



Prosandeev et al., PRL126, 027602 (2021)

Thanks