Screening of Charge and Structural Motifs in Oxides

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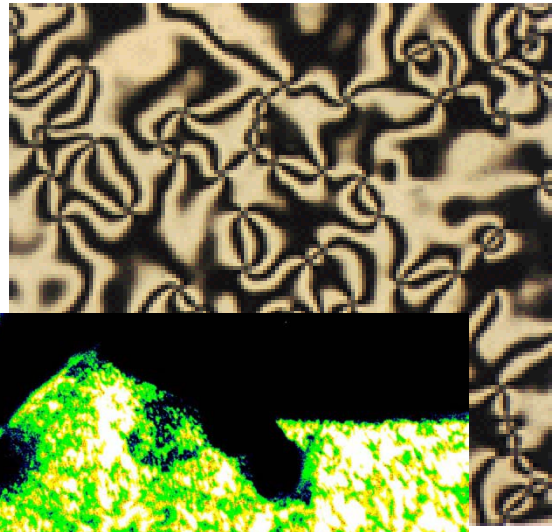
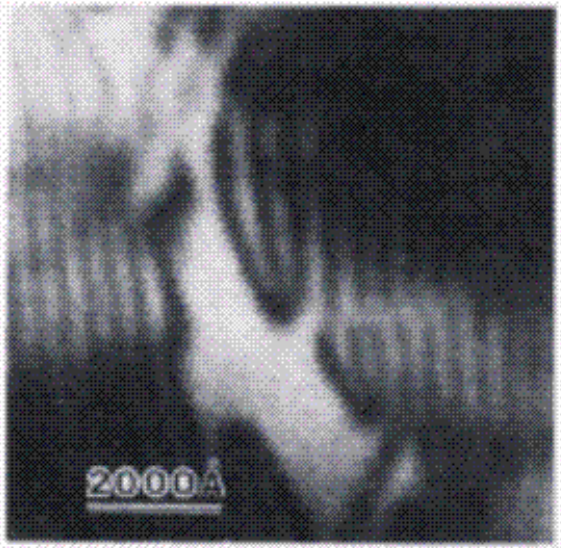
“Soft” matter is not confined to soft materials

Soft condensed matter physics is the study of materials with mesoscale structures often entropically dominated; e.g. liquid crystals, complex fluids, membranes.
“Softness” implies pliable rearrangement to external forces

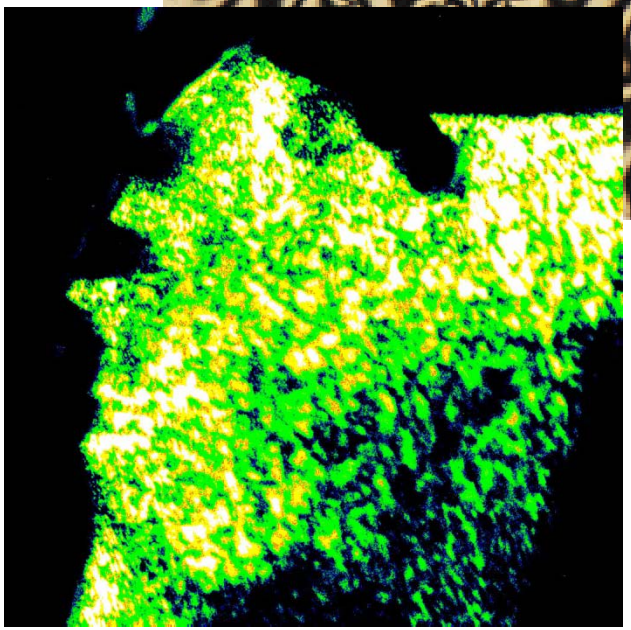
Defects in nematic liquid crystal



“Stripes” of charge-density wave in $TaSe_2$



C.H.Chen



30 nm patches of charge-order in $LaCaMnO_3$
Loudon & Midgley

Outline

Use of “functional” transition metal oxides requires both control of doping, and control of phase transitions

- Coulomb charges, and elastic strains produce long-range forces that are resolved by “screening” – which leads to metallicity (Coulomb) and softness (elasticity)

1. Screening of built-in charges and dipoles
   - Origin of 2D electron gas in oxide heterostructures
   - Switching of thin ferroelectric films under ambient conditions
   - Li-ion battery electrodes
2. Screening of structural motifs
   - Rigidity and dynamics of domain walls – structural “plasmons”
   - “Jamming” of Jahn-Teller distortions in manganites
   - Optimising the electrocaloric effect

Why are heterostructure oxides interesting?

- Transition metal oxides are responsible for some interesting and useful physics and materials science: magnetism, superconductivity, ferroelectricity, ...
- We use oxides to make batteries, capacitors, photovoltaics, ...
- Physically, these are systems where the carriers are “small” (strongly correlated). Strong correlations means high energy density and therefore “useful”
- Control of doping by chemistry is the usual route, and it’s challenging
- In semiconductors, we have learned to modulation dope, and this has been responsible for much modern semiconductor technology and essentially ALL of modern semiconductor physics

Doping in oxides: physics or electrochemistry?

- $LaAlO_3/SrTiO_3$ (polar-insulator)
  - Introduction: interface 2DEG, “polar catastrophe” argument
  - Net interface charges – formal argument
  - Model test – n-p superlattices
  - Origin of 2DEG in reality – surface redox?

- $BaTiO_3/La_{0.7}Sr_{0.3}MnO_3$ (ferroelectric-half metal)
  - Introduction: ferroelectric screening
  - Redox calculations
  - Magnetoelectric and tunneling electroresistance

An example: LaAlO3 / SrTiO3

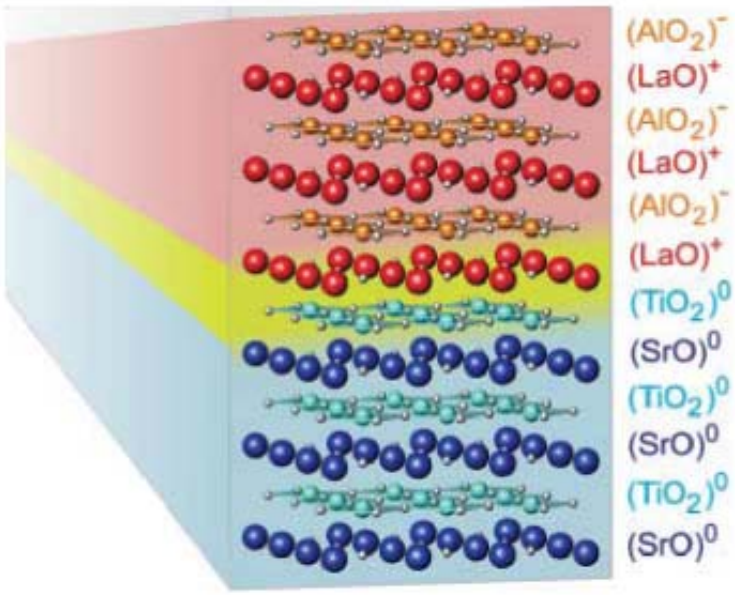
Interface between two band insulators is (sometimes) conducting

A Ohtomo & H Hwang, Nature **427, 423 (2004)**

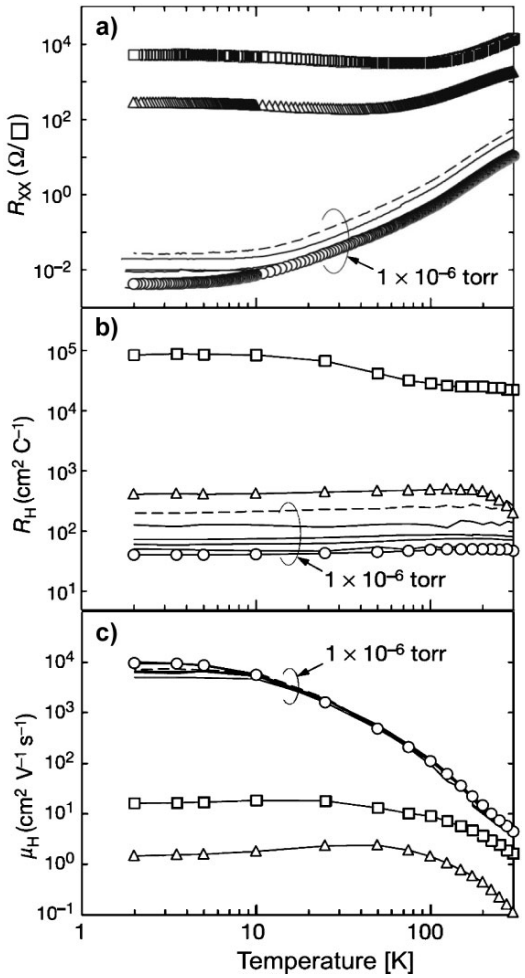
Whence the carriers?
Two (at least) points of view

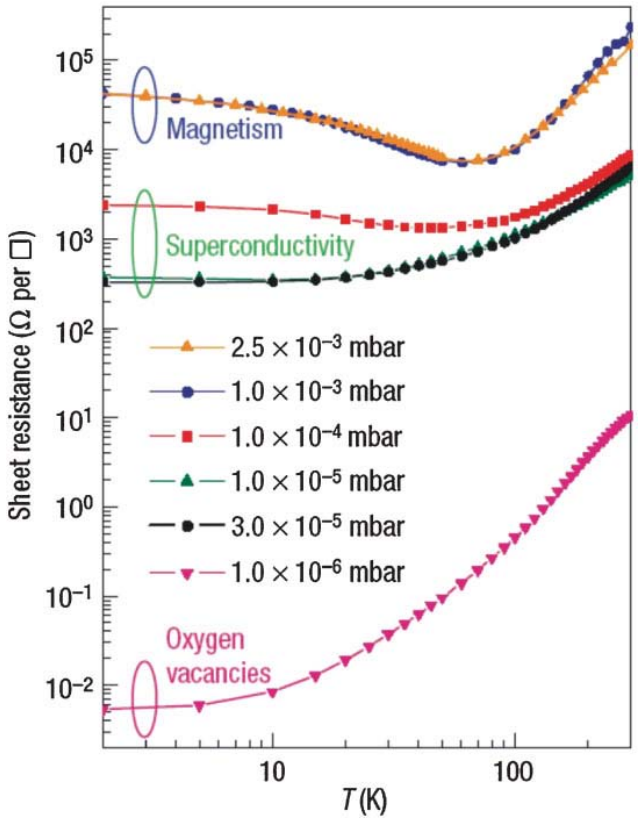
Ideal interface is charged (polar catastrophe)
- produces electrical potential
- attracts (mobile?) carriers

Charged interfaces may destabilise growth
- produces (neutralising) charged defects
- also generates carriers



$LaAlO_3/SrTiO_3$ conductivity depends on growth conditions





Sheet resistance of n-type SrTiO3/LaAlO3 interfaces. Temperature dependence of the sheet resistance for SrTiO3/LaAlO3 conducting interfaces, grown at various partial oxygen pressures A. Brinkman et al Nat.Mater. 2007, 6, 493

Ohtomo and Hwang Nature 427, 423 2004

Surface polar adsorbates

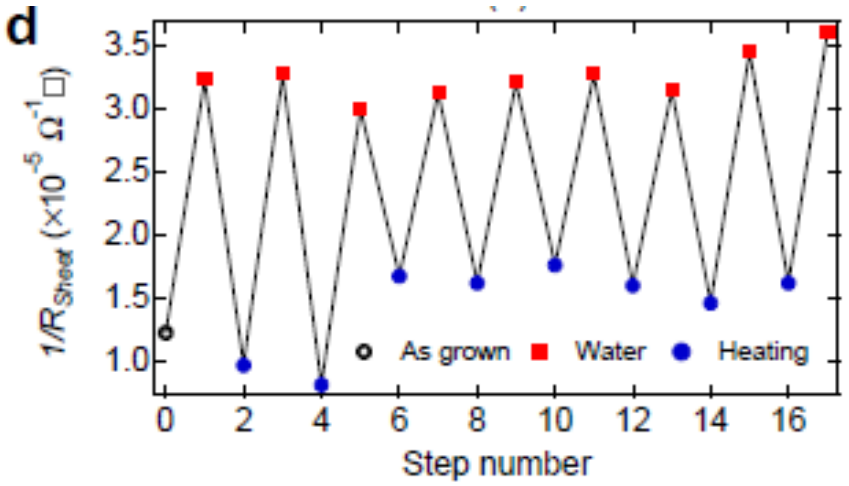
Carrier density and conductivity depends on details of growth and also (reversibly) on surface adsorbates

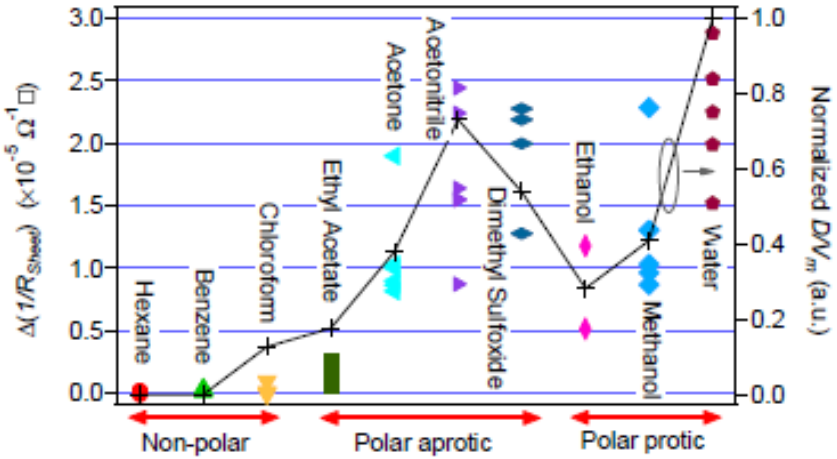
- AFM used to modulate buried interface layer conduction

  e.g. Cen *et al. Nature Mater.* ***7, 298-302 (2008).***

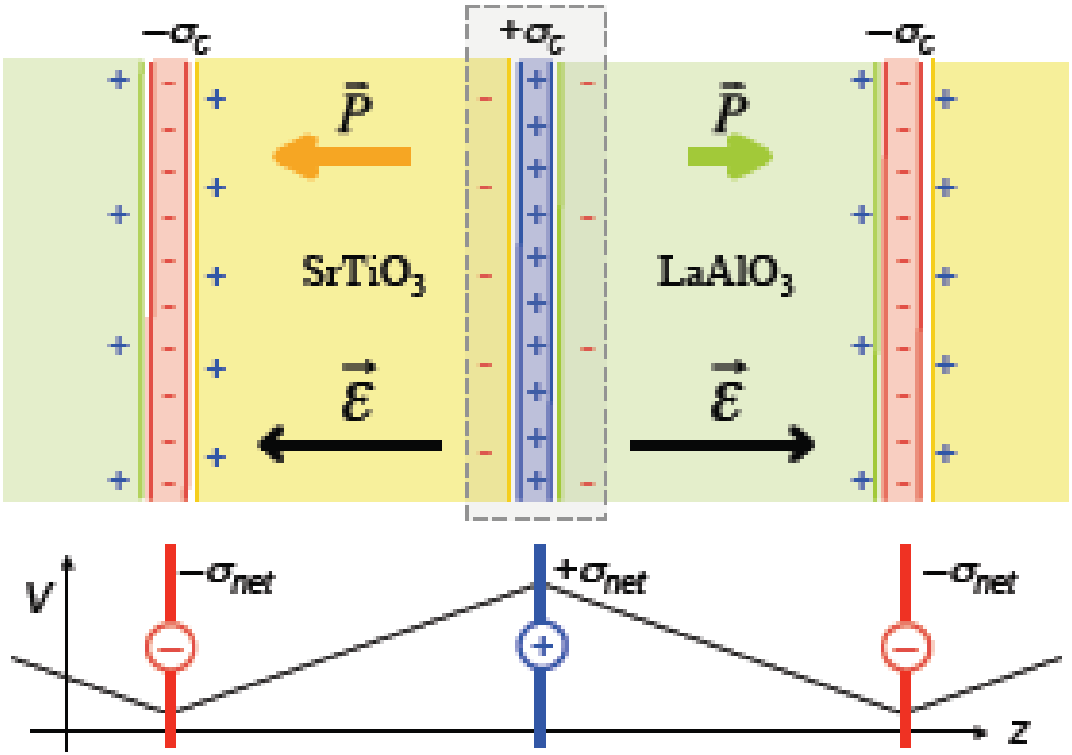
- Carrier density at buried interface in LAO/STO is modulated by surface adsorption of polar molecules

  Xie *et al* Arxiv1105:3891





Capacitor Plate Model for STO/LAO

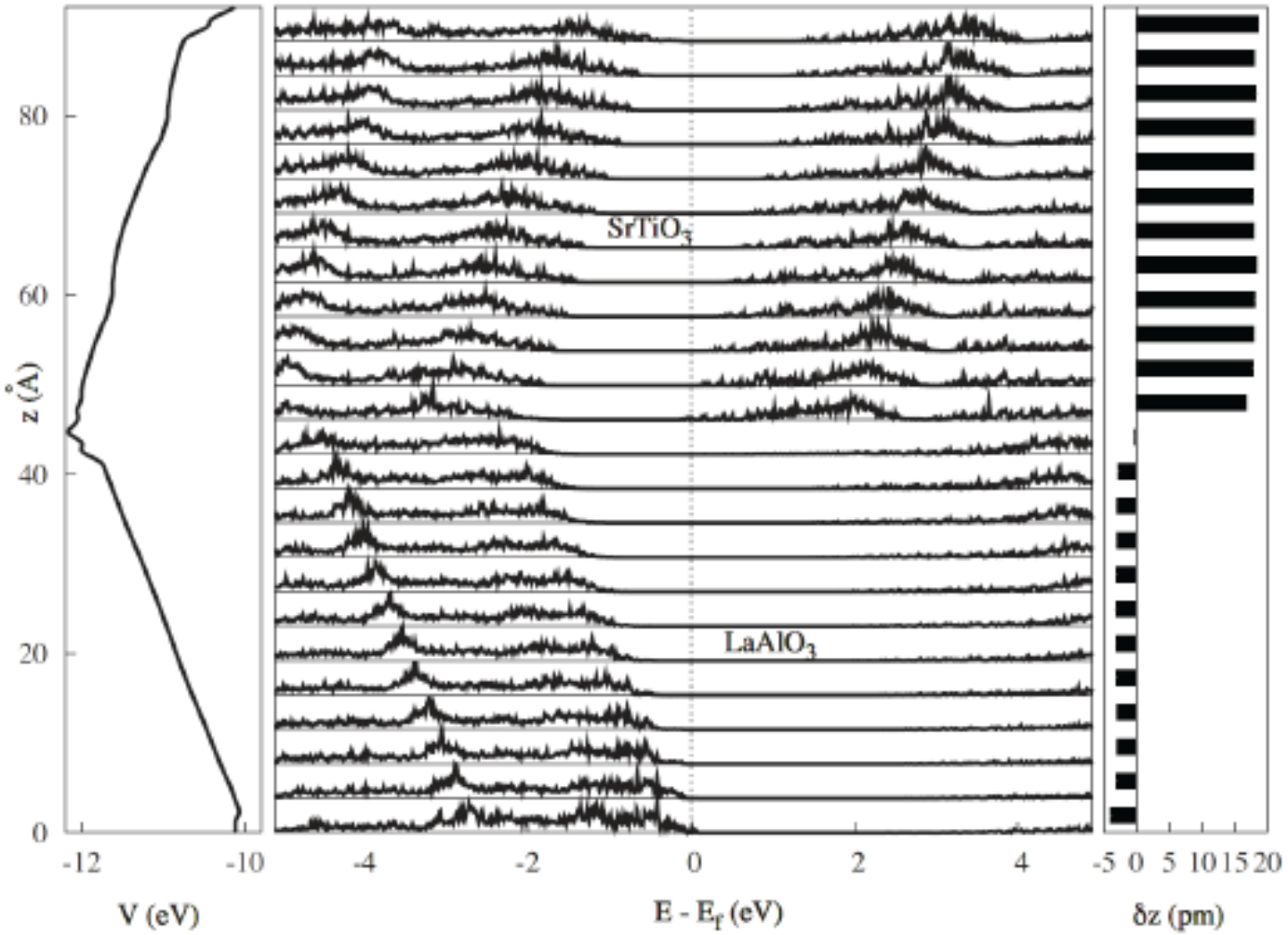


$$\sigma_c - P_{\mathrm{LAO}} - P_{\mathrm{STO}} = 2\epsilon_0 \mathcal{E}^0;$$

σ_c is the chemical charge density – formal ionic charges

12x 12 superlattice of LaAlO3 / SrTiO3

Bristowe et al PRB 80, 045425 (2009)

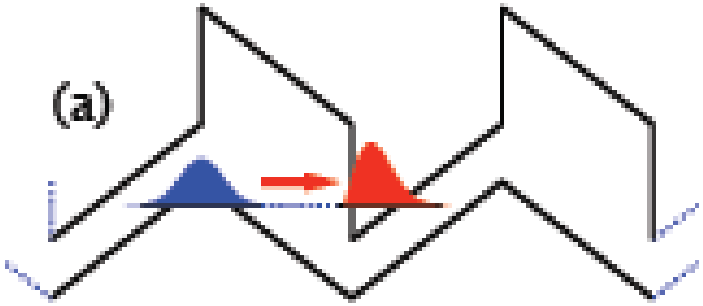


.... science fiction interlude ....

Self- modulation doping: Mobile charges in coupled valence and conduction bands

- Once $\mathcal{E} > E_{gap}/d$, mobile (?) carriers appear at the two interfaces.
- Beyond a critical spacing d_c ~ few unit cells the charge transferred compensates the formal ionic charge
- The potential difference between the interfaces is pinned approximately at the gap (owing to large DoS).
- Carrier density grows with d but is generally quite small, for example

  $n_{12/12}$ = 0.073 e/unit cell
- In LAO/STO strong screening -> large effective Bohr radius
- Potentially interesting Coulomb correlations – Mott transition for excitons; superfluids and solids etc.



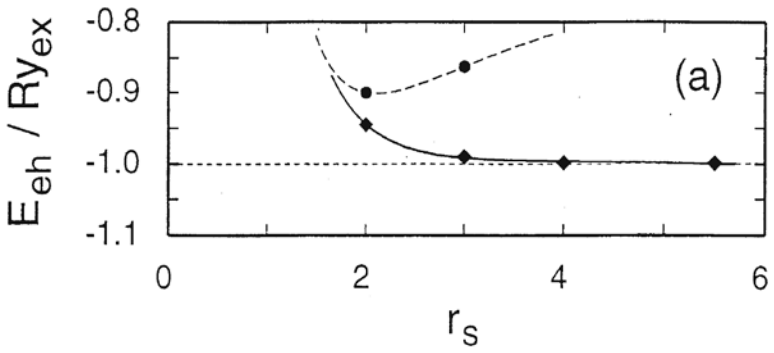
$$a_0^2 \approx (a_B \epsilon / m^*)^2 + d^2$$

$$\frac{1}{\pi a_0^2} \simeq 0.002 \text{ e/cell}$$

Ultracapacitor / Photovoltaic

- Excitons: add electrons and holes in pairs
- Energy cost = Energy gap – binding energy + interaction energy
  - Tuned by external bias ~ 0
- Capacitance is theoretically very large
  - Store one exciton/Bohr radius (Mott density)
- Intrinsic photovoltaic
  - Enormous internal field ~ V/nm

Energy per pair (in exciton Rydberg) as a function of density



$$1/n = \frac{4\pi}{3}(a_{Bohr} r_s)^3$$

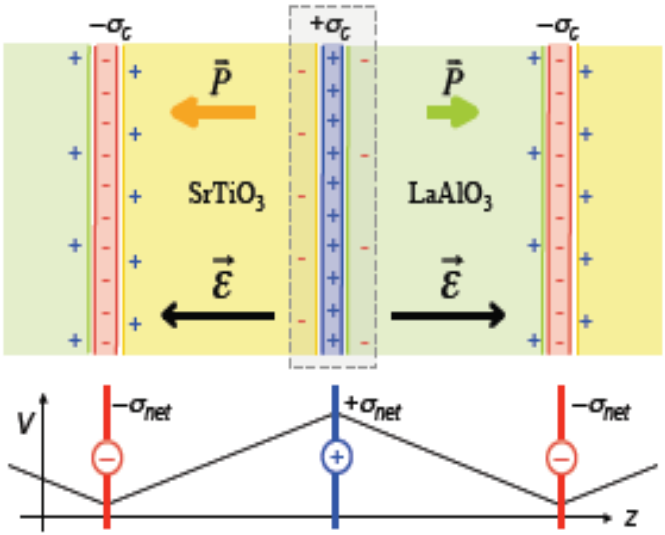
Zhu et al, PRB 54, 13575 (1996)

Model solar battery ?

If mass and dielectric constant ~ 1, plane separation ~ few lattice constants

This becomes a model system for a combined photovoltaic and storage device with charge density ~ 1 e-h pair per unit cell

Storage capacity comparable to gasoline



... back to reality ....

Not particularly consistent with experiments

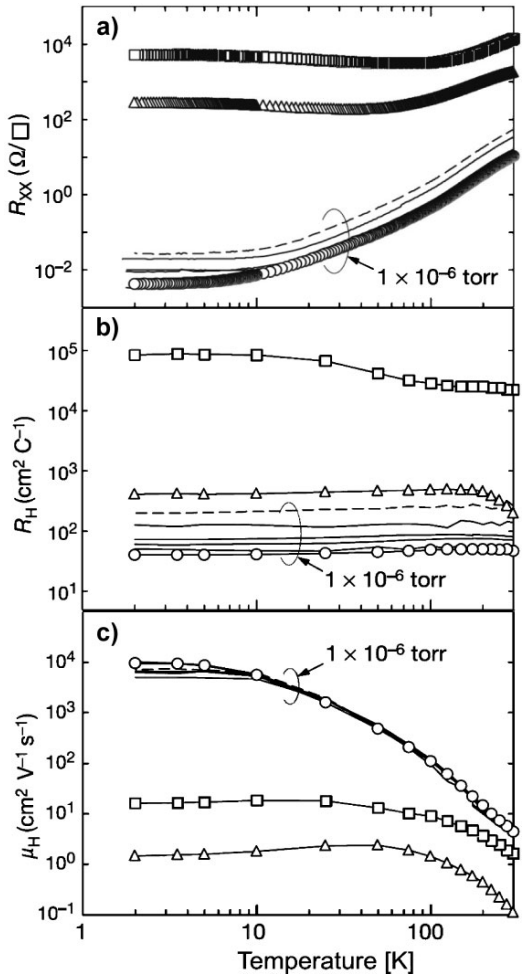
Problems:

- Strong dependence of carrier density on growth conditions (particularly oxygen pressure) – more metallic when grown in lower oxygen pressures
- Model critical thickness (>6 u.c.) > observed (<4 u.c.)
- No mobile holes seen at surface
- XPS measures no internal field
- HAXPS see electrons at interface before onset of conduction

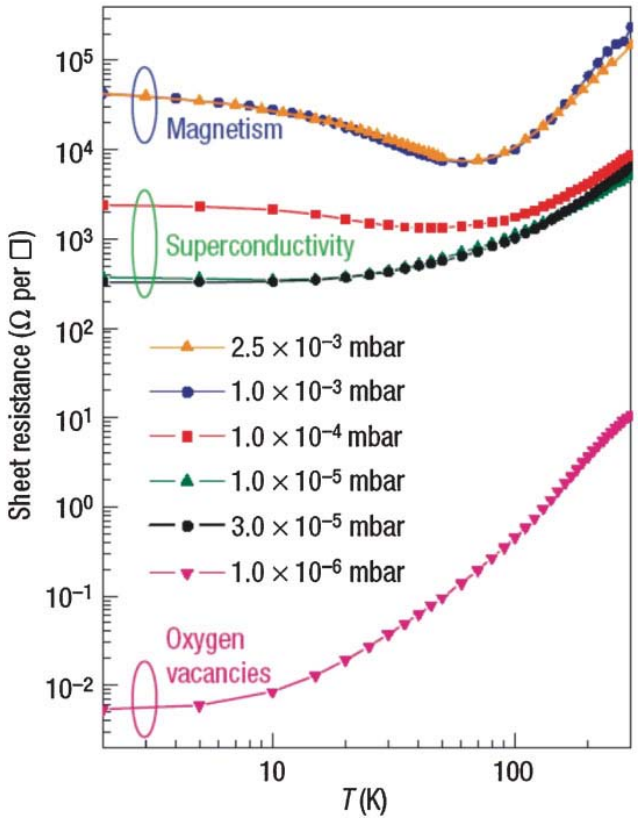
Resolution?

- Defects (bulk/surface) contribute to carriers ....

$LaAlO_3$ / $SrTiO_3$



Ohtomo and Hwang Nature 427, 423 2004



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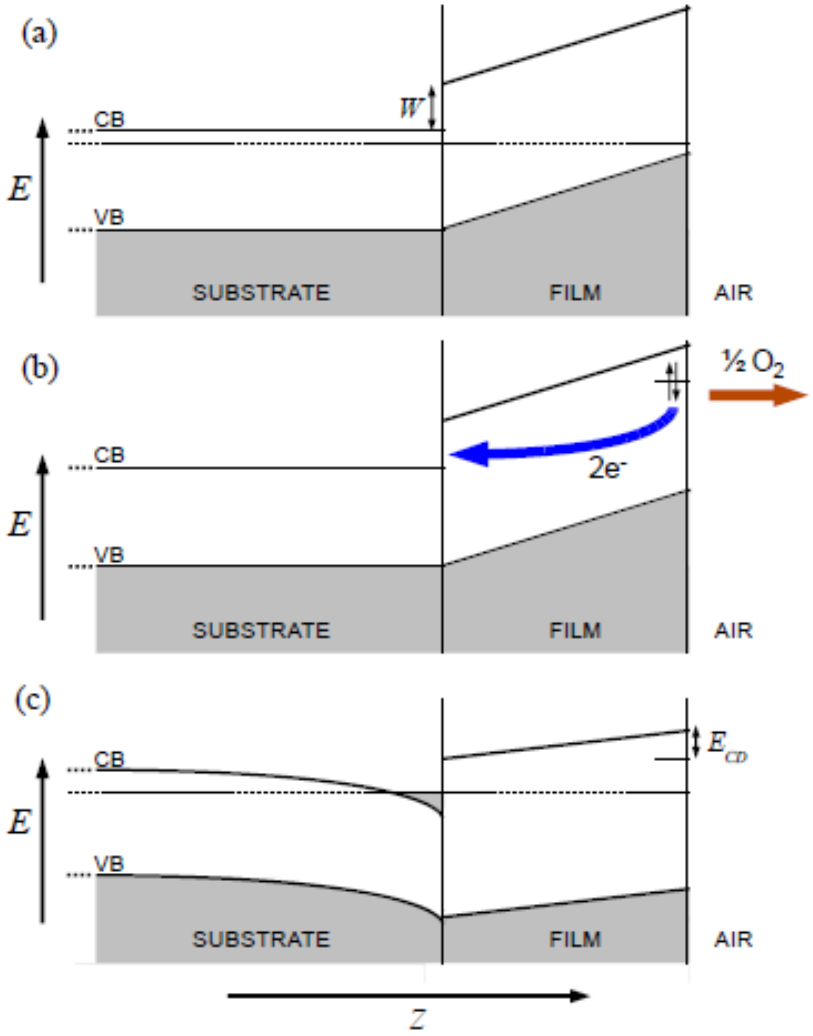
Surface redox reactions generated under growth conditions



E.g. Oxygen vacancy – creates (double) donor

Electrons transfer to interface

Thermodynamically stable for a thick enough layer – transferred charges lower capacitive energy that grows with thickness

Energy cost to create vacancy balanced against Coulomb

Surface donor states stabilised by Coulomb?

Free energy cost to create vacancy balanced against Coulomb

n = defect density
d = film thickness

Defect creation energy

Defect interactions

$$\Omega = Cn + \Omega_{\mathcal{E}}(n) + \frac{1}{2}\alpha n^2$$

Electrostatic energy

$$\Omega_{\mathcal{E}}(n) = \frac{d}{2\epsilon}\left[(\sigma_c - \sigma_v)^2 - \sigma_c^2\right]$$

Intrinsic charge density

$$\sigma_v = n(Ze)$$

Reconstructed charge density

$$n = \frac{d\,Ze\,\sigma_c - C\epsilon}{(Ze)^2 d + \alpha\epsilon}$$

$$d_c = C\epsilon/(Ze\sigma_c)$$

Critical separation

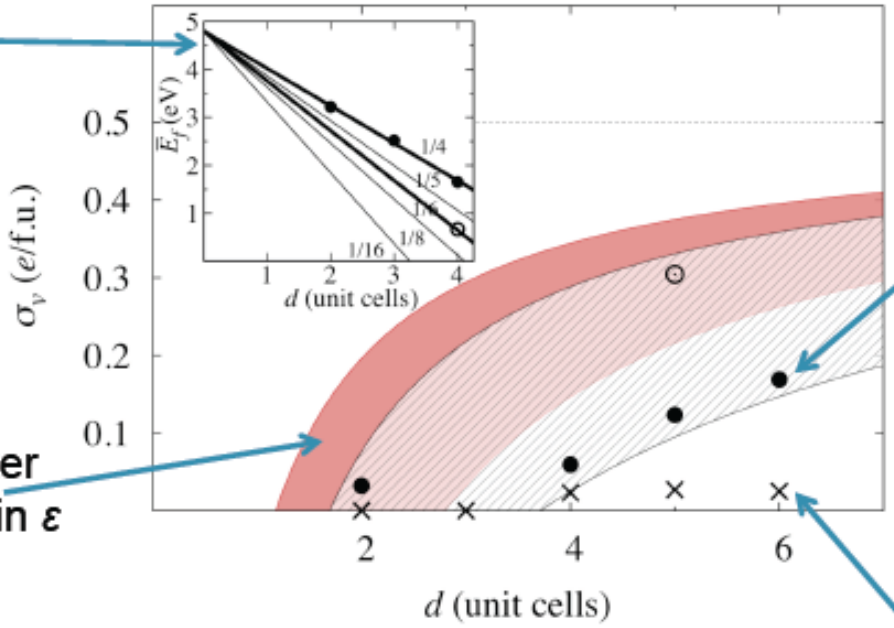
$$\Omega_{\mathcal{E}}(n) = \frac{d}{2\epsilon}(\sigma_c - \sigma_v)^2 - \frac{\sigma_c \Delta}{2}$$

Field energy if interface partially screened

Surface redox reactions and 2DEGs

Model vs DFT and experiments

Model (lines)
DFT (circles)
Li et al arXiv (2009)



Spectroscopic data
(HAXPS)
Sing et al PRL (2009)

Model using parameter range in C (red) and in ε and α (striped)

Transport data (Hall)
Thiel et al Science (2007)

Bristowe et al. PRB 83, 205405 (2011)

Surface polar adsorbates

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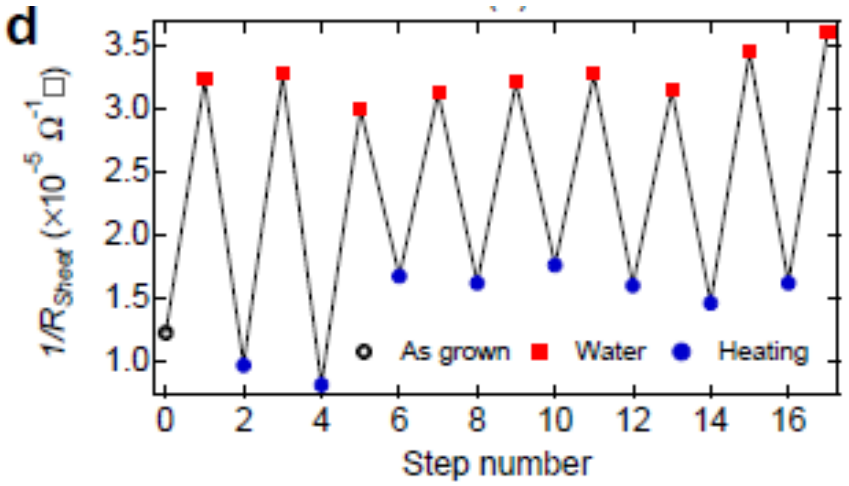
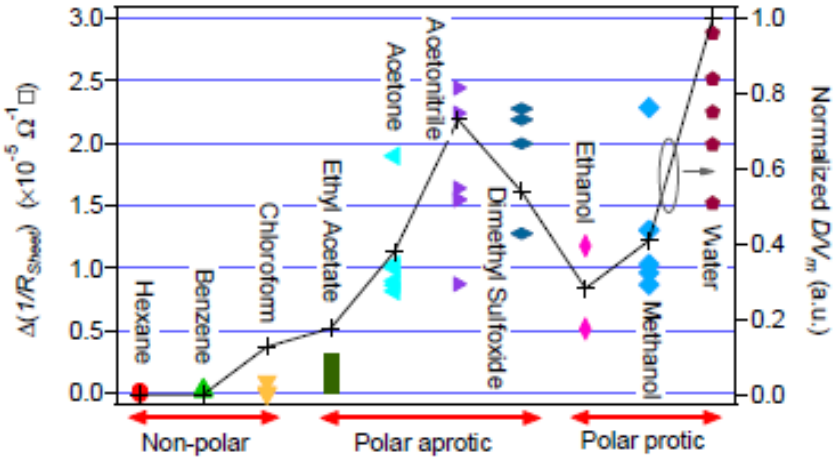




What is the origin of magnetism in defective $SrTiO_3$?

Lopez-Bezanilla, Ganesh and PBL arXiv:1408.3103

- Oxygen vacancy is a double donor (?)

  Two carriers / vacancy into large hydrogenic donor state – very low occcupancy of Ti d-band

  Conventional view, see Janotti et al PRB (2014)

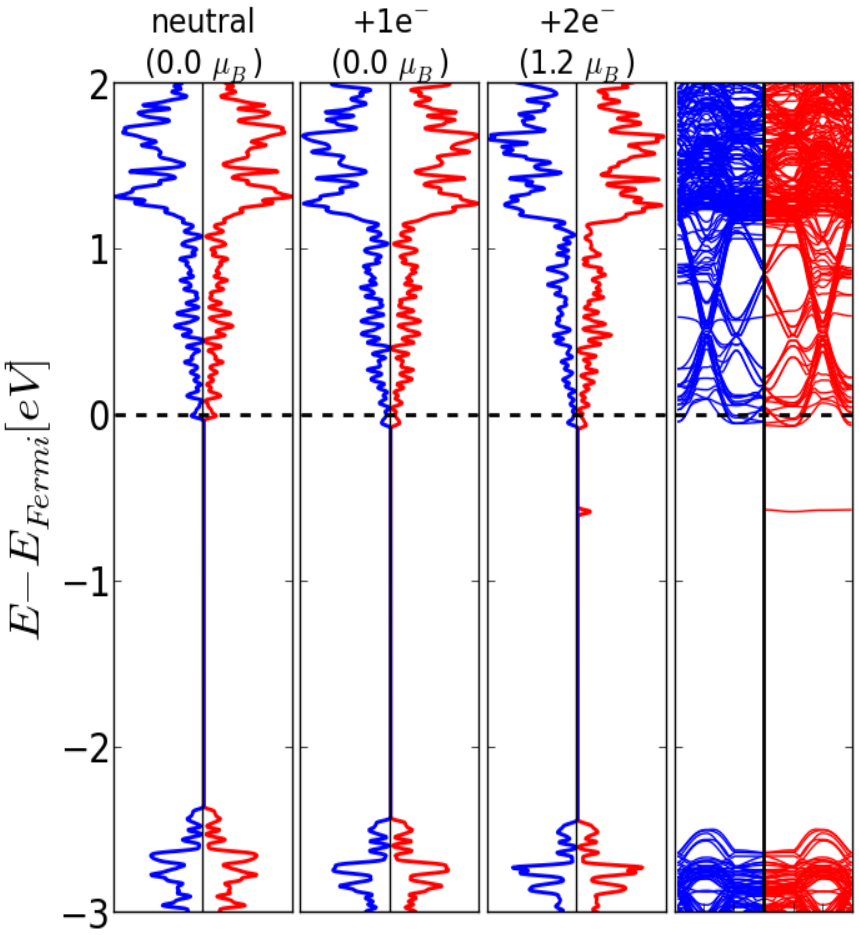
- Oxygen vacancy traps a single carrier (?)

  Paramagnetic local center coupled to another vacancy by remaining quasi-itinerant carrier

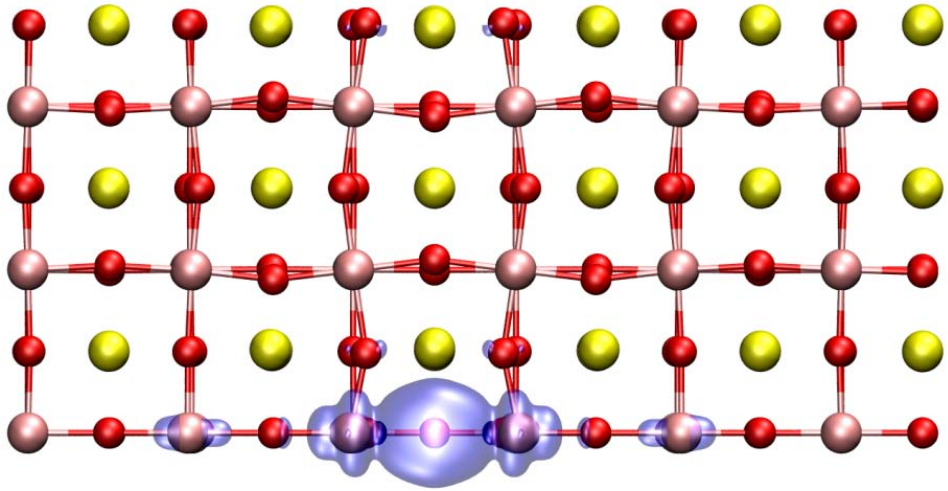
  Lin and Demkov PRL (2013)

An isolated vacancy: spin polarized LDA+U calculation

6 x 3 x 3 supercell
1 oxygen vacancy
Add further electrons

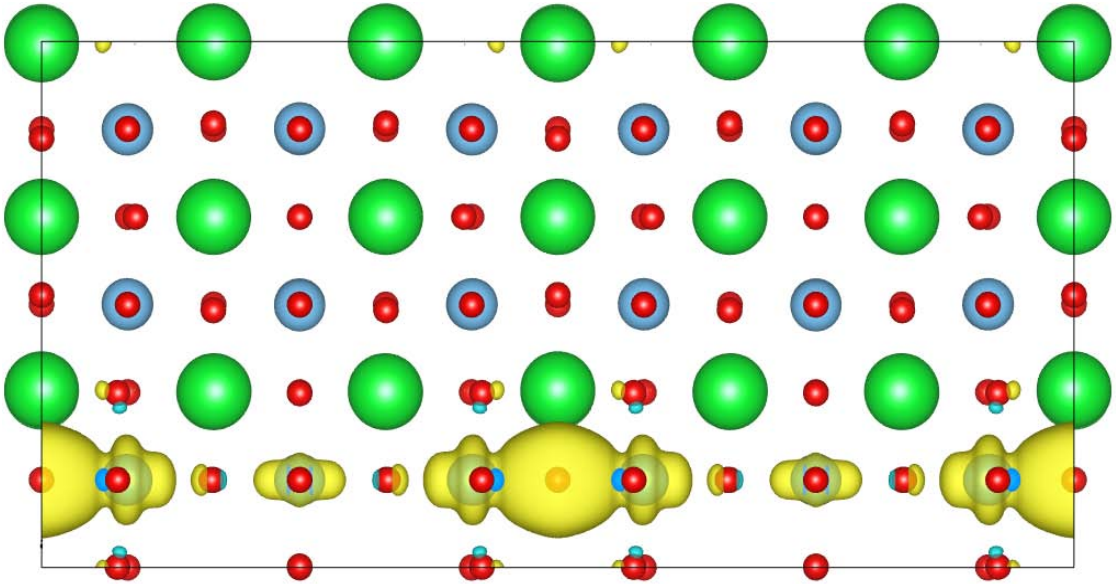


Localized paramagnetic center induced upon doping
Coupled to conduction band carrier by ferromagnetic exchange



2 extra electrons

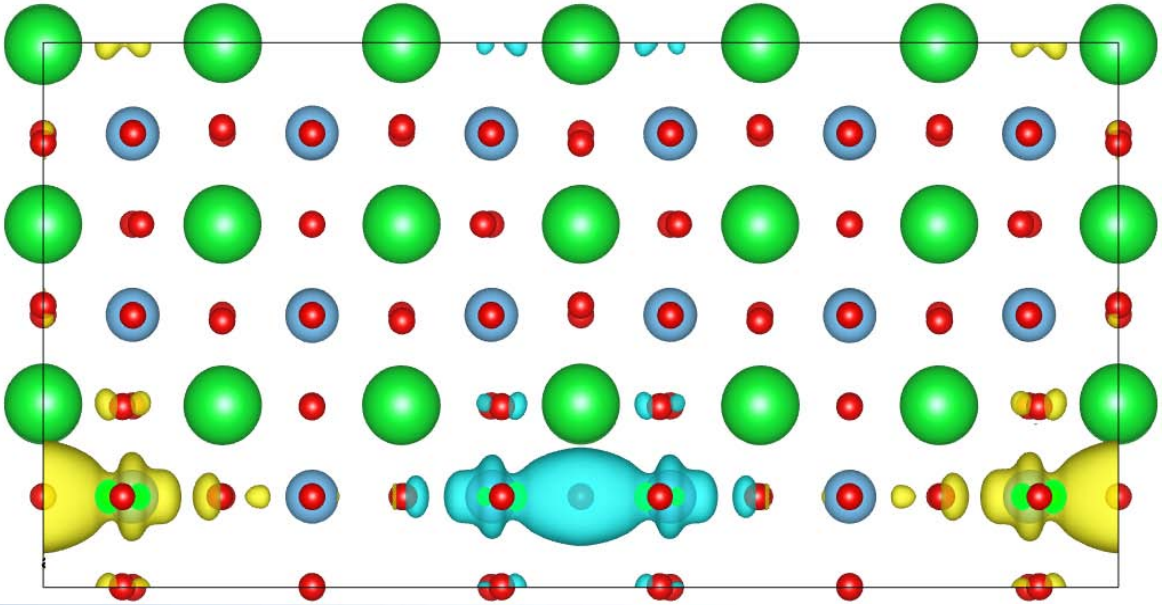
Vacancy clustering: FM stable by 220 meV



Ferromagnet

ΔE (triplet-singlet)=220 meV

Antiferro



- In-gap vacancy state is bound by small polaron physics (unrelaxed configuration does not bind)
- Partial occupancy of d-band enhances binding
- FM due to either vacancy clustering or due to electrostatic doping

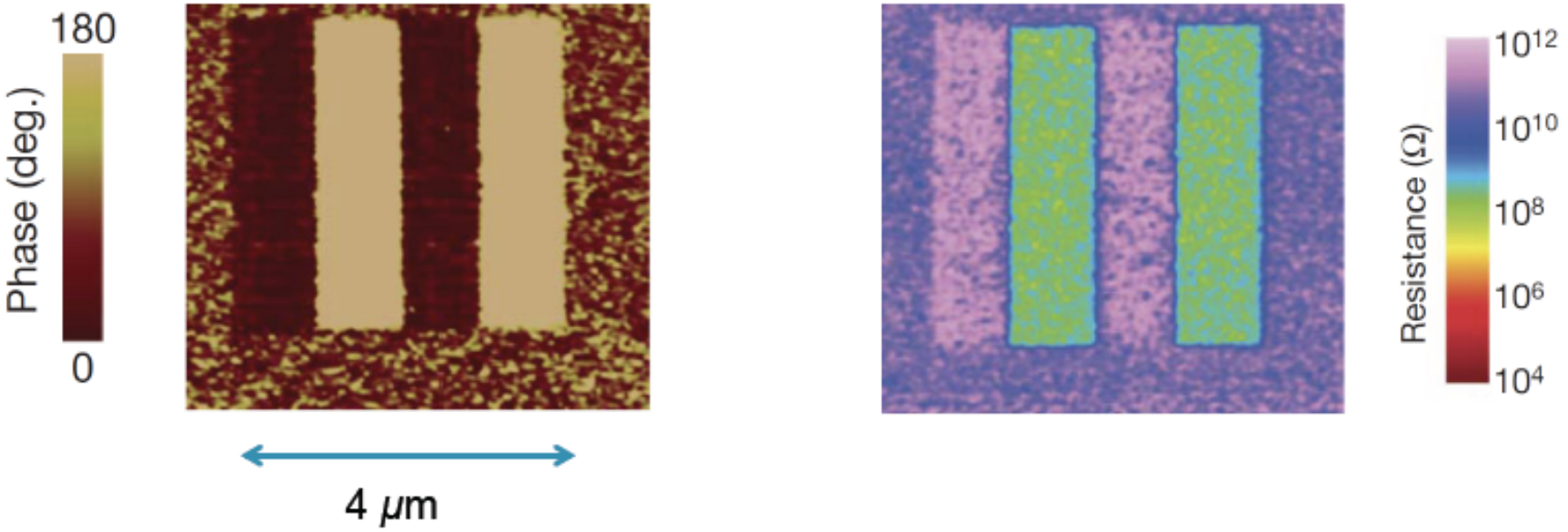
- $LaAlO_3/SrTiO_3$ (polar-insulator)
  - Introduction: interface 2DEG, “polar catastrophe” argument
  - Net interface charges – formal argument
  - Model test – n-p superlattices
  - Origin of 2DEG in reality – surface redox?

- $BaTiO_3/La_{0.7}Sr_{0.3}MnO_3$ (ferroelectric-half metal)
  - Introduction: ferroelectric screening
  - Redox calculations
  - Magnetoelectric and tunneling electroresistance

Surprising stability of domains in thin BTO films

Garcia et al Nature Letters (2009)

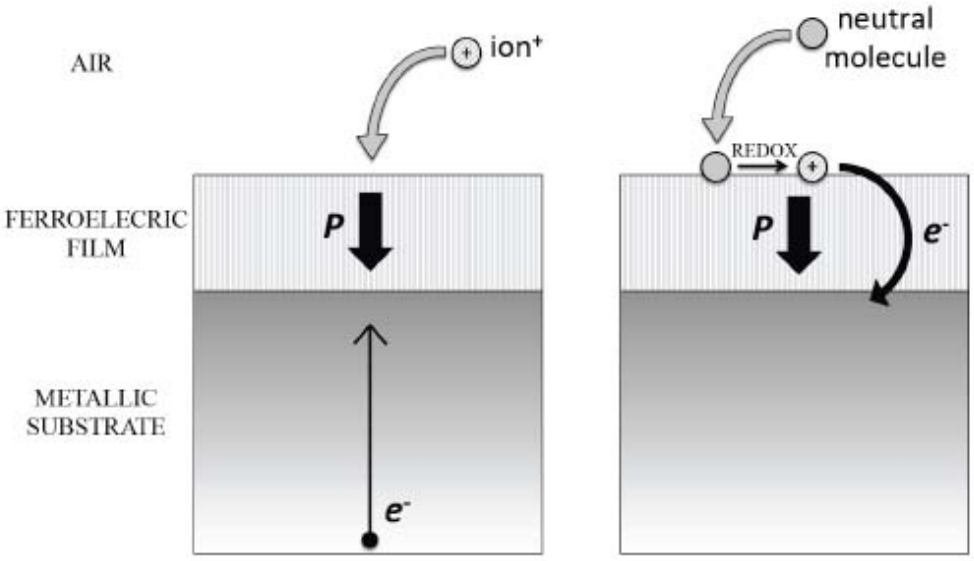
- Regions of stable, out-of-plane *P* written with biased AFM
- Read with PFM, and conductive-tip AFM
- 1nm thick BTO films! (on LSMO substrates)



Source of screening

- Conventional view : charged species and metallic screening -“accidental” charged species
- Redox reaction freeing charge to the interface ?

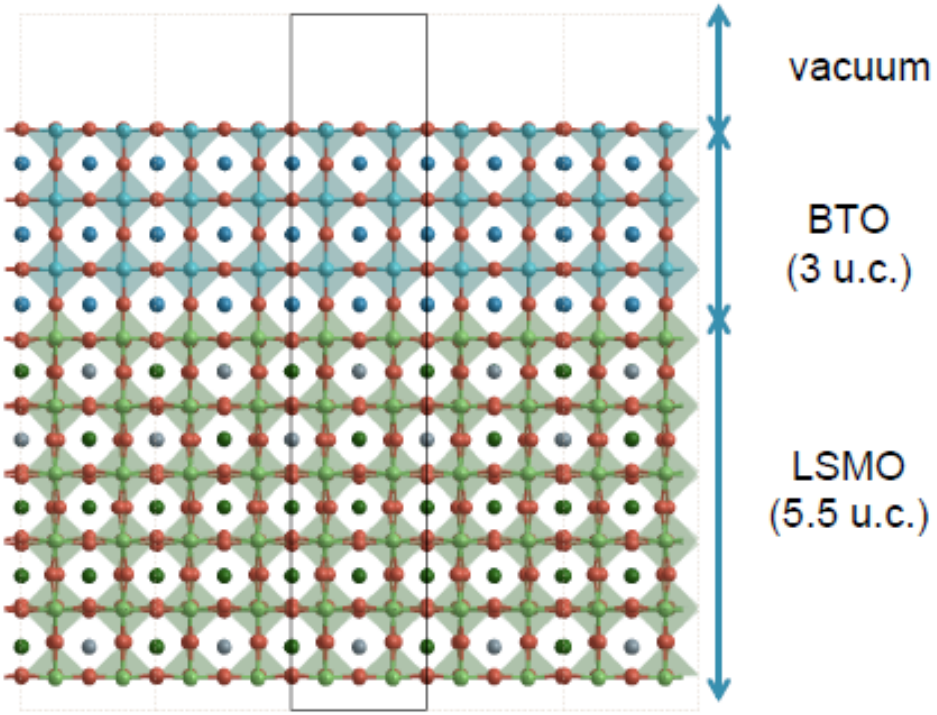
  thermodynamic equilibrium established in writing/growth



In context of ferroelectrics, see e.g. Stephenson and Highland, arXiv:1101.0298

Methods

- DFT calculations (GGA PBE)
- Dipole correction in vacuum
- Search for ferroelectric distortion
- Surface O vacancies/adatoms

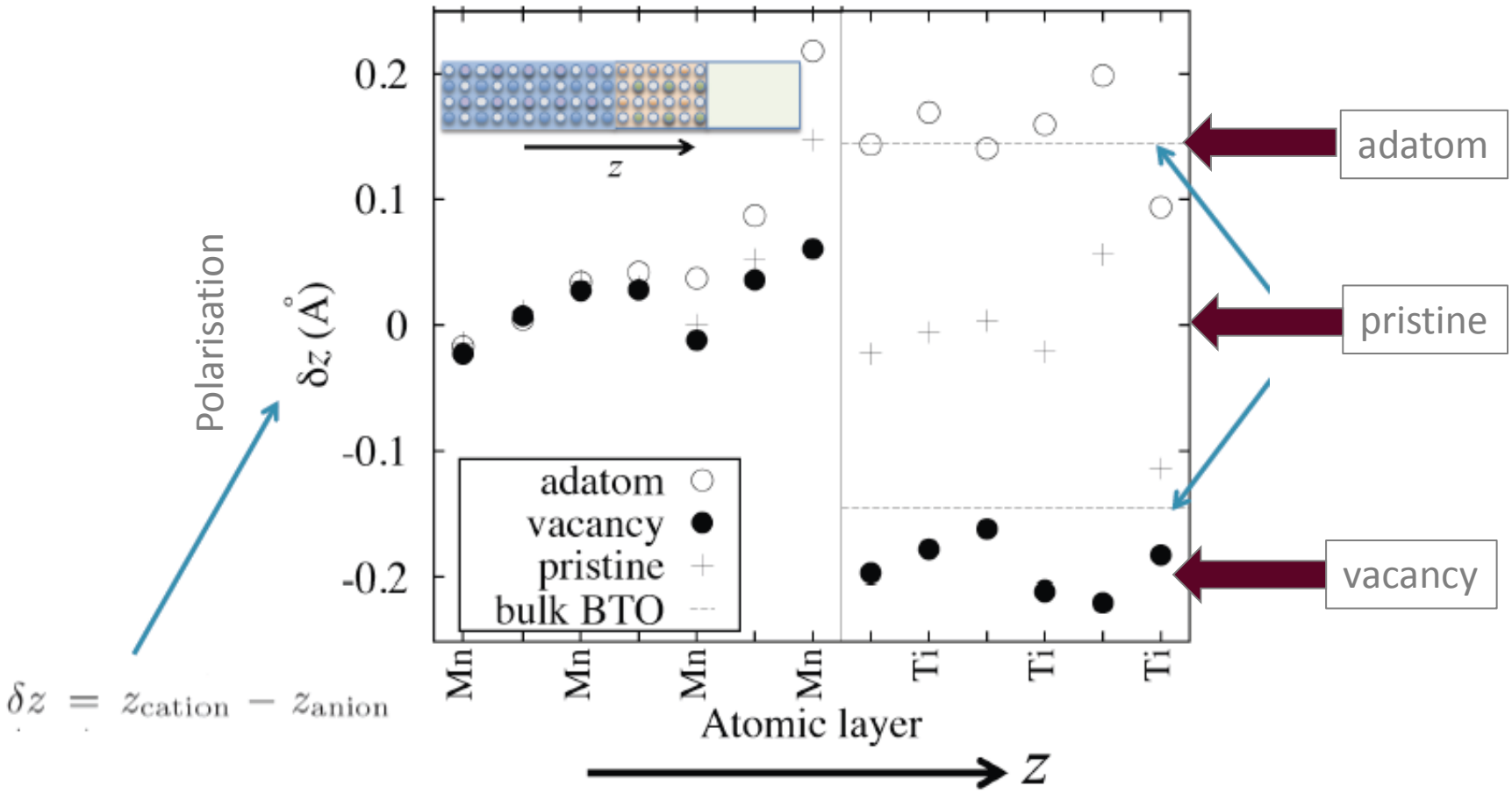


Bristowe et al PRB 85, 024106 (2012)

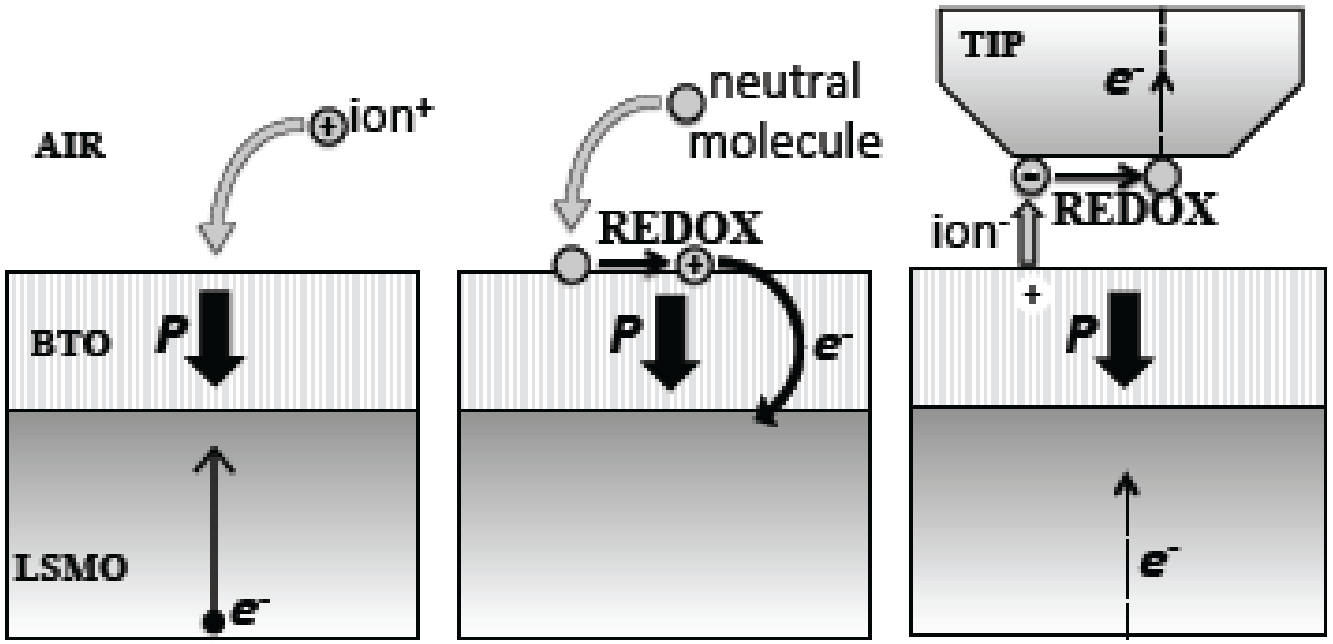
Atomic displacements

Pristine film non-ferroelectric

Surface species stabilise polarised film near the bulk distortions

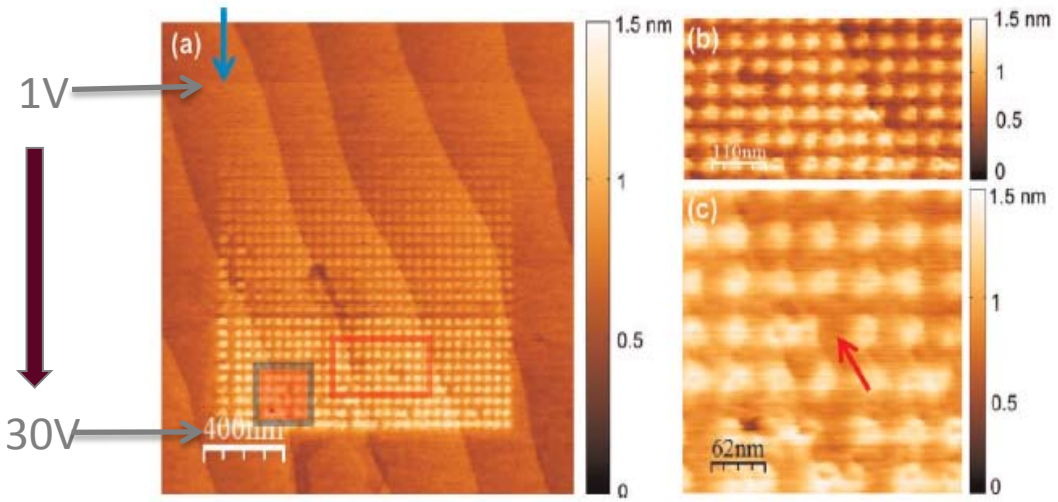


Electrochemistry?

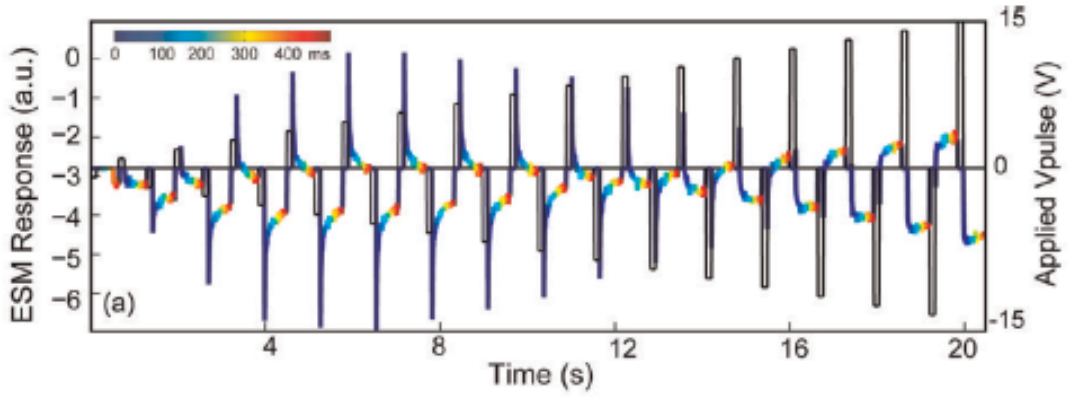


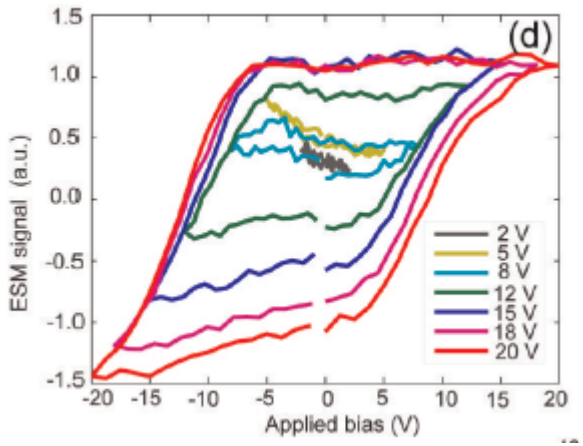
Electrochemical Strain Microscopy on LAO/STO

KUMAR *ET AL.* VOL. 6 ▪ NO. 5 ▪ 3841–3852 ▪ 2012 ACSNANO



Apply a tip bias, and measure both the topographic changes and the elastic response – ramp up voltage in a sequence





Screening of strain-mediated interactions in ferroelastic and ferroelectric materials

Richard Brierley, Cambridge University -> Yale
Gian Guzmán-Verri, Argonne National Lab
Peter Littlewood, Argonne and University of Chicago

thanks to K Ahn, T Lookman, A Saxena, & J F Scott

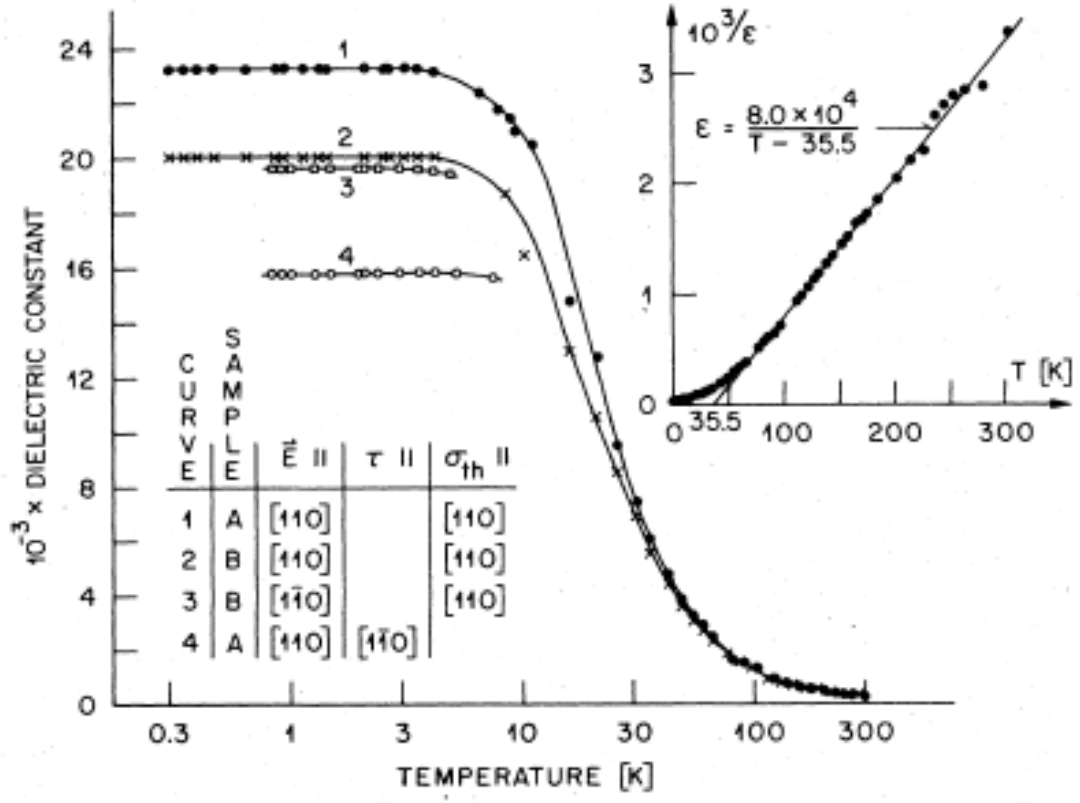
Quantum paraelectricity in $SrTiO_3$

PHYSICAL REVIEW B VOLUME 19, NUMBER 7 1 APRIL 1979

$SrTiO_3$: An intrinsic quantum paraelectric below 4 K

K. A. Müller
IBM Zürich Research Laboratory, 8803 Rüschlikon, Switzerland
H. Burkard *
Laboratory of Solid State Physics, ETH 8093 Zürich, Switzerland

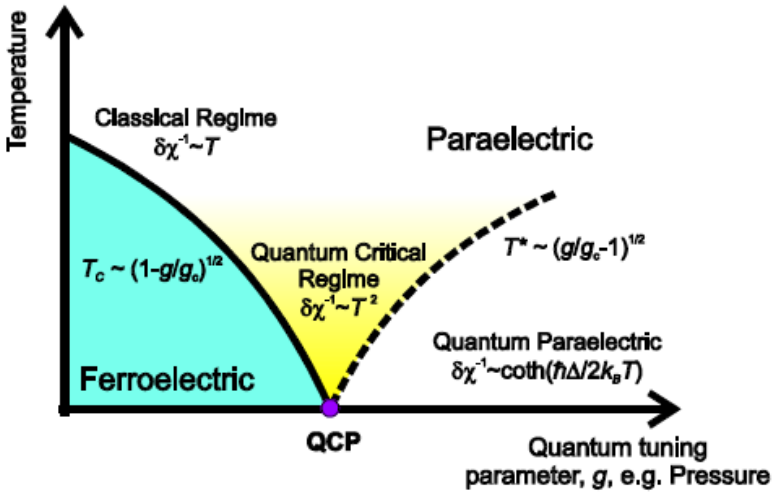
(Received 19 July 1976; revised manuscript received 14 August 1978)

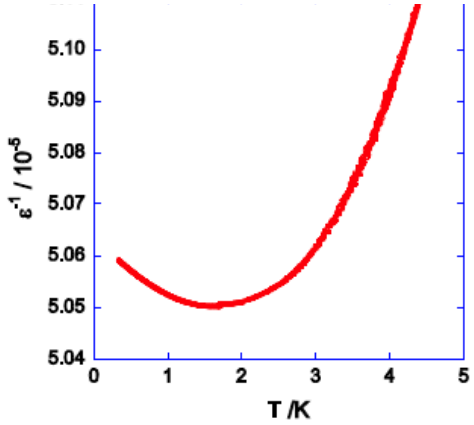


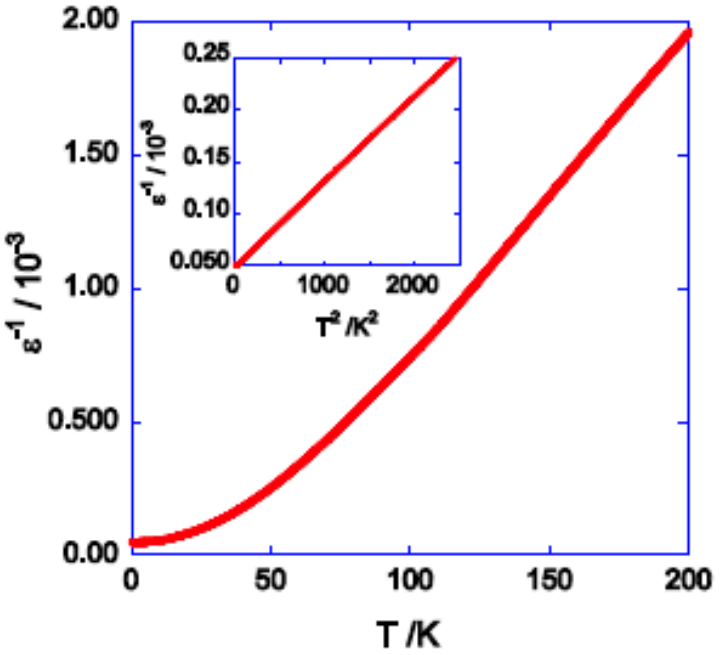
Quantum Criticality?

S.E. Rowley[1], L.J. Spalek[1], R.P. Smith[1], M.P.M. Dean[1], G.G. Lonzarich[1], J.F. Scott[2] and S.S. Saxena[1]

ArXiv:0903.1445







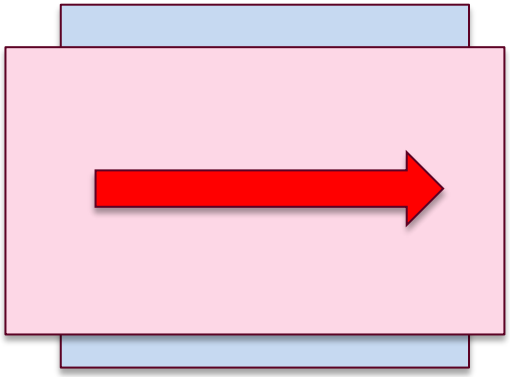
Outline

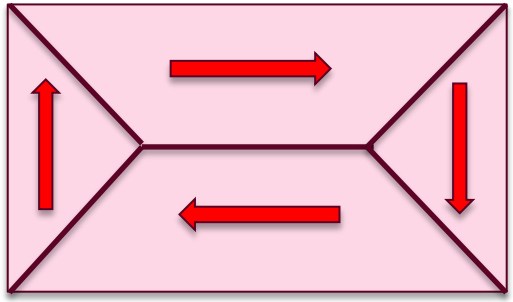
- Elastic strain is a subsidiary order parameter in many phase transitions, particularly ferroelectrics and multiferroics
- Strain abhors inhomogeneity
  - Elastic compatibility conditions enforce domain patterns,
  - Fluctuations are suppressed by long-range strain-induced couplings
- Charge- or dipole forces can be screened (carriers, defects, etc) - is there an analogy for strain fields?

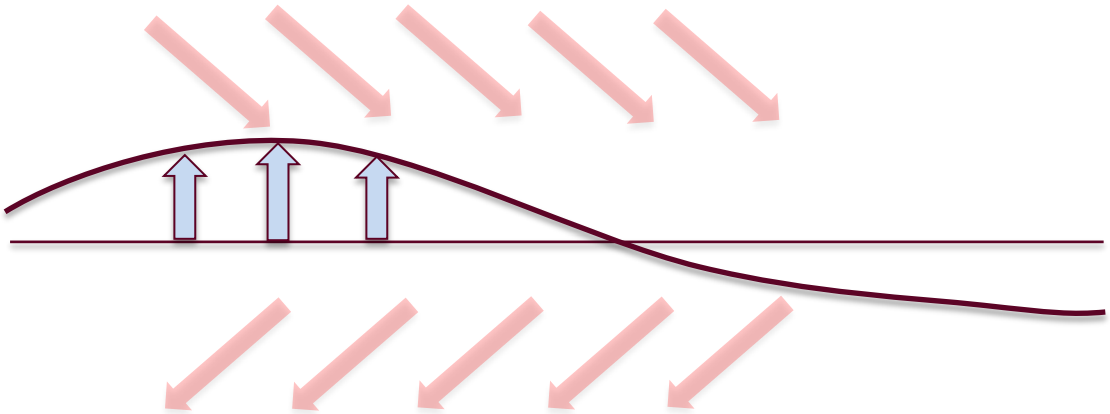
1. What is the spectrum of the “surface waves” of a domain wall?
2. Can you screen long range strain-induced interactions, and how?
3. Can you design a good electrocaloric material ?
4. Does this have any relevance to quantum paraelectrics?

The 90 degree domain wall in a pseudo-cubic ferroelectric

90°and 180° domain walls have
no polarisatIon charge and no elastic stress







Domain wall tilting/curvature induces both Coulomb forces and elastic stress

What is the dispersion curve ω(k) of displacements of the wall?

2D elastic theory from Ginzburg-Landau ….

$$S = \int d\mathbf{r} \left[\overbrace{-(\partial_t \mathbf{P})^2 + \gamma(\nabla \mathbf{P})^2 + r|\mathbf{P}|^2 + u|\mathbf{P}|^4}^{\text{Polarization}} + \underbrace{\frac{a_1}{2}\phi_1^2 + \frac{a_2}{2}\phi_2^2 + \frac{a_3}{2}\phi_3^2}_{\text{Strain}} + \overbrace{q_2\phi_2(P_x^2 - P_y^2)}^{\text{Strain coupling}} \right]$$

$$+ \underbrace{\sum_{\mathbf{q}} \sum_{\alpha,\beta} \tilde{P}_\alpha \left(f_\alpha q_\alpha^2 \delta_{\alpha\beta} + g_{\alpha\beta} \frac{q_\alpha q_\beta}{q^2} + h_{\alpha\beta} q_\alpha q_\beta \right) \tilde{P}_\beta}_{\text{Dipolar interactions}}$$

$$\phi_1 = (\epsilon_{xx} + \epsilon_{yy})/\sqrt{2}, \quad \phi_2 = (\epsilon_{xx} - \epsilon_{yy})/\sqrt{2} \quad \phi_3 = \epsilon_{xy}$$

$$\nabla^2 \phi_1 - (\partial_x^2 - \partial_y^2)\phi_2 - 2\sqrt{2}\partial_x \partial_y \phi_3 = 0 \Rightarrow$$

Elastic compatibility condition

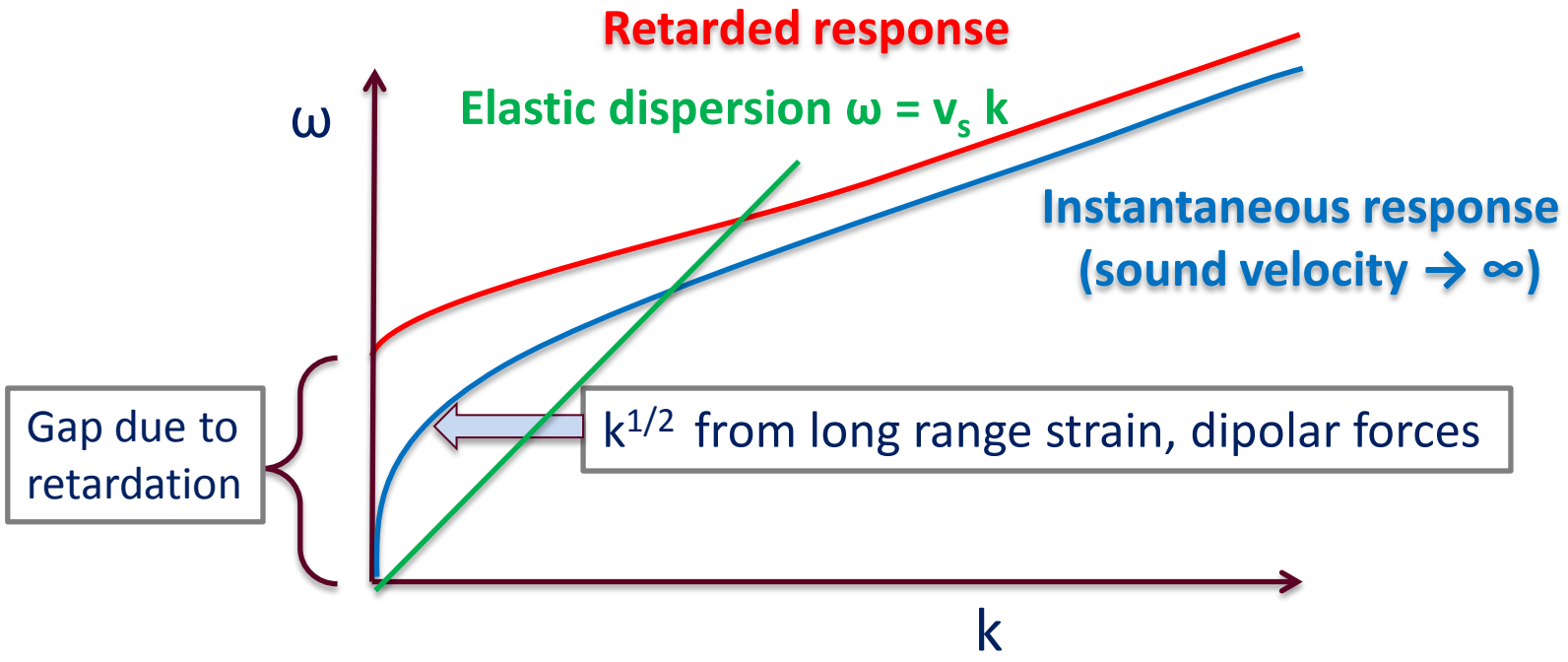
$$S = \int d\mathbf{r} \left[\gamma(\nabla \mathbf{P})^2 + r|\mathbf{P}|^2 + u|\mathbf{P}|^4 \right] - \frac{m_2}{2} \int d\mathbf{k} |\Gamma(k)|^2 H(\mathbf{k}) + \sum_{\alpha,\beta} \tilde{P}_\alpha \left(g \frac{q_\alpha q_\beta}{q^2} + h_{\alpha\beta} q_\alpha q_\beta \right) \tilde{P}_\beta$$

$$H(\mathbf{k}) = 1 - \frac{(D\Omega^4 + \Omega^2(k_x^2 + k_y^2) + \frac{4}{A}k_x^2 k_y^2)}{(k_x^2 + k_y^2)^2 + C k_x^2 k_y^2 + D\Omega^4 + \Omega^2 k_x^2 (1 + D)}$$

$$\Gamma(\mathbf{k}) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} (P_x(\mathbf{r})^2 - P_y(\mathbf{r})^2)$$

$\Rightarrow$ Infinite range, retarded, strain-mediated coupling

Mode dispersion for small amplitude, long wavelength displacements



$k^{1/2}$ dispersion is analogous to 2D plasmon

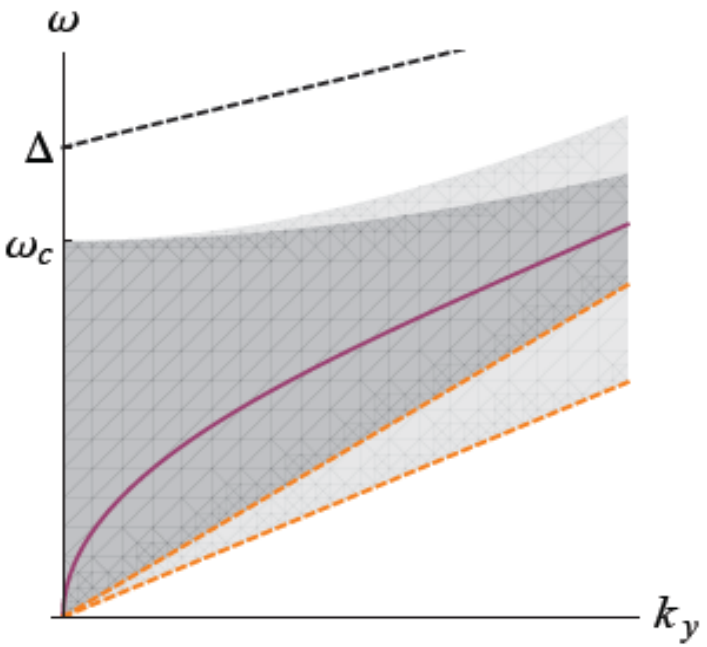
Gap is analogous to plasmon-polariton

Gap magnitude ~ shift in T_c by clamping of strain

Brierley & Littlewood, ArXiv:1307.7886

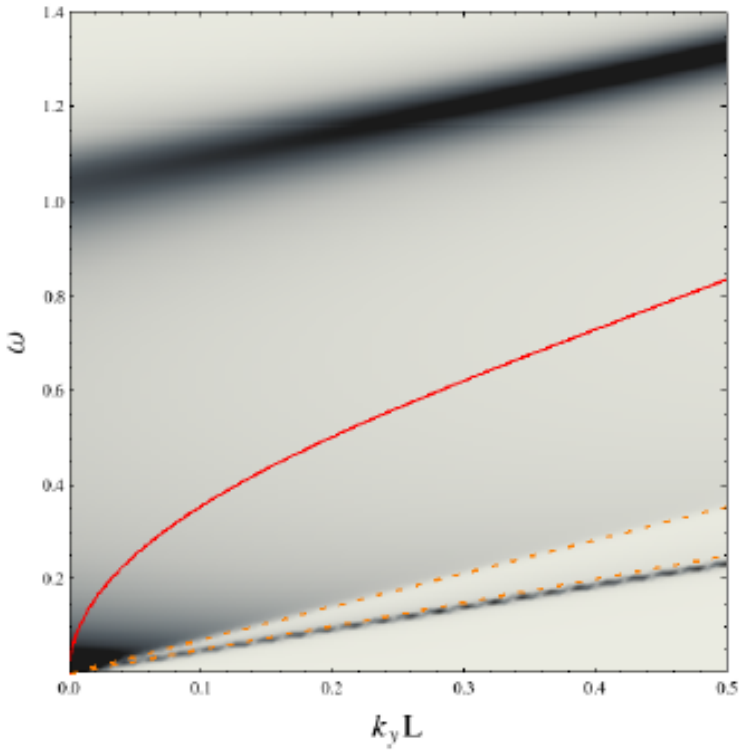
Slow phonons: response function depends on how efficiently gapped modes can decay into bulk phonons

- For finite v_s, strain interaction is retarded
- $v_s \to 0 \implies$ static strain potential, energy gap $\Delta \sim \sqrt{\eta |P_0|^2} \sim 10\text{meV}$
- Wall is coupled to phonons with $k_x < k_c \sim 1/L$; $\omega_c = v_s k_c \sim 10\text{meV}$
- Excitations can decay if $v_s k_y < \omega < \sqrt{\omega_c^2 + v_s^2 k_y^2}$



Large elastic “gap”

- Coupling to low $|\mathbf{k}|$ phonons introduces response at $\omega \sim v_s k_y$
- Fast excitations with $\omega > \omega_{\text{acoustic}}$ are damped
- For faster v_s, larger ω_c, gapped mode is absorbed by phonon continuum



$\Delta/\omega_c = 4$

Small elastic “gap”

- Coupling to low $|\mathbf{k}|$ phonons introduces response at $\omega \sim v_s k_y$
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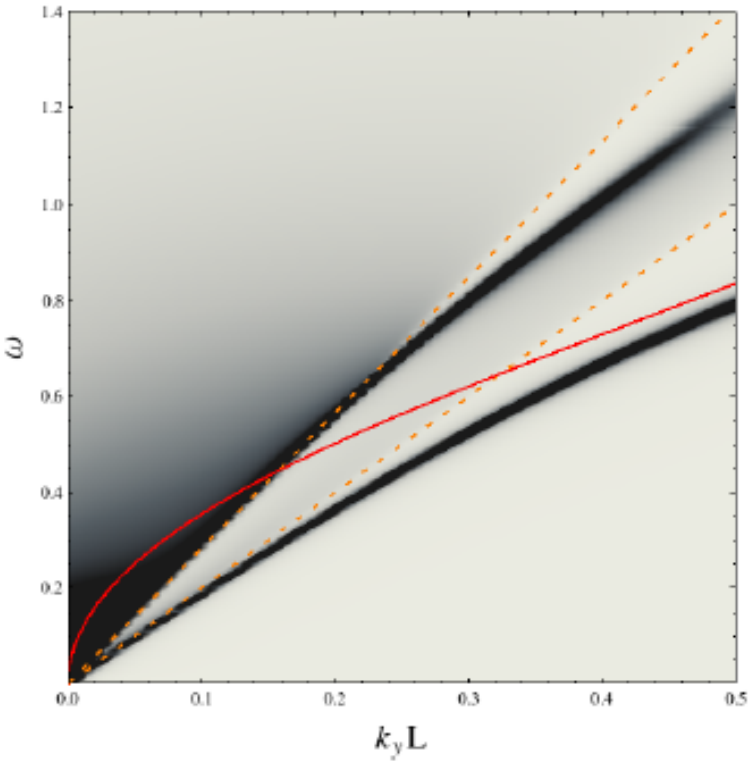
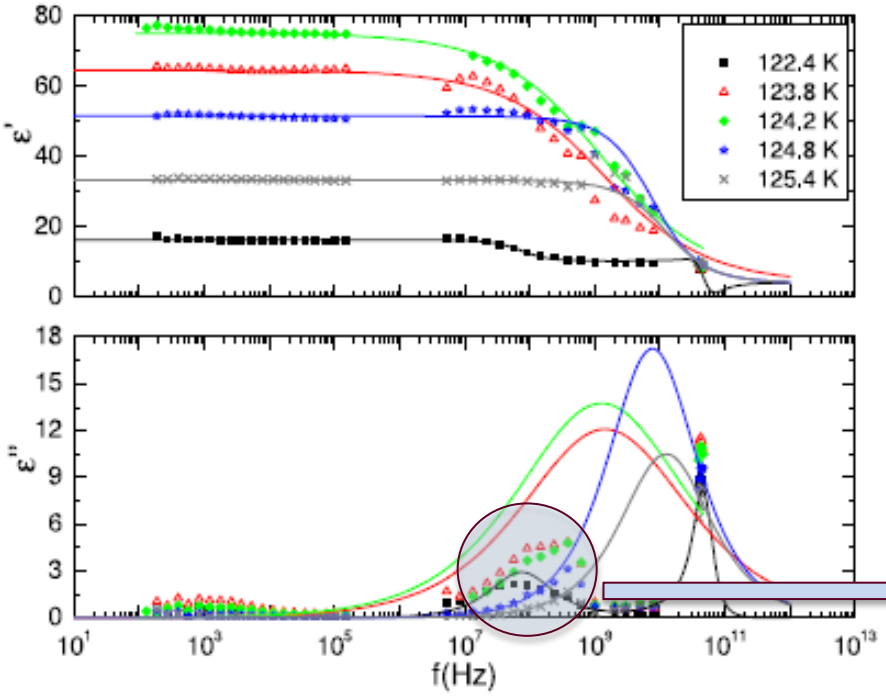


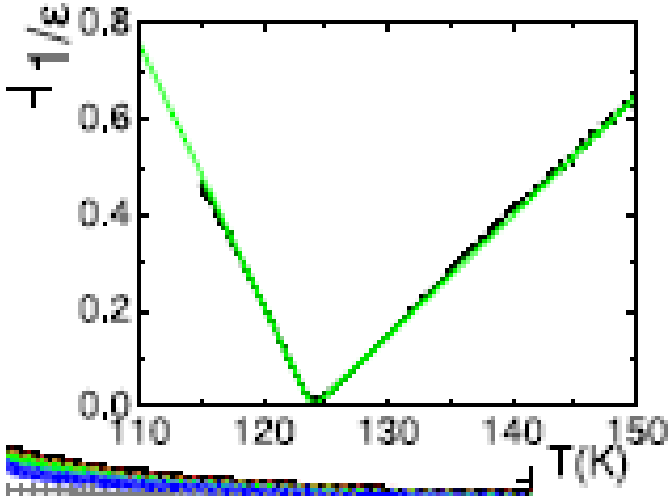
$$\Delta/\omega_c = 1/4$$

Soft mode dynamics in TSCC

R Mackeviciute[1], M Ivanov[1], J Banys[1], Nikola Novak[2], Zdravko Kutnjak[2], Magdalena Wencka[3] and J F Scott[4]

J. Phys.: Condens. Matter **25** (2013) 212201





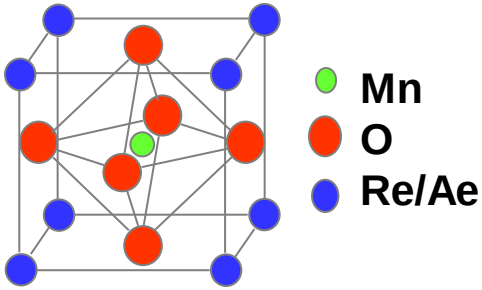
"Below T_C a strong relaxational process is observed at frequencies from 100 MHz to 1 GHz. This is almost certainly related to domain wall dynamics."

Is there a way to screen strain fields, analogous to screening charges?

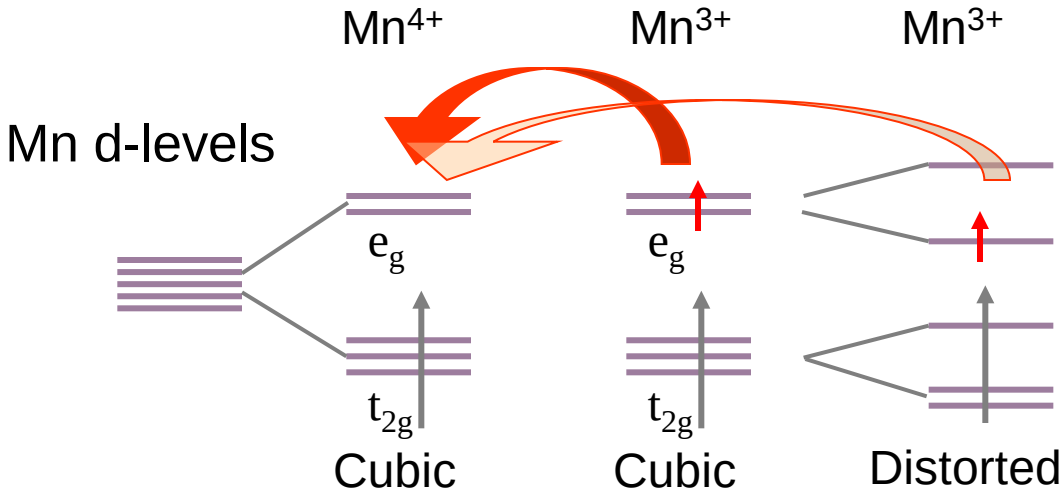
Case study: perovskite manganites and size control of colossal magnetoresistance (CMR)

Perovskite manganites

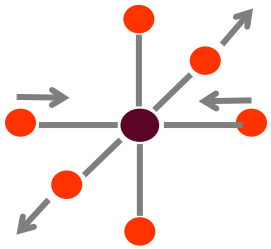
- A “doped” oxide - e.g. $La_{1-x}Ca_xMnO_3$ where the formal valence of Mn varies between Mn^{3+} and Mn^{4+}
- A “strongly correlated” electron system close to a (Mott) metal-insulator transition



Hopping - aligns core moments and leads to ferromagnetic metal

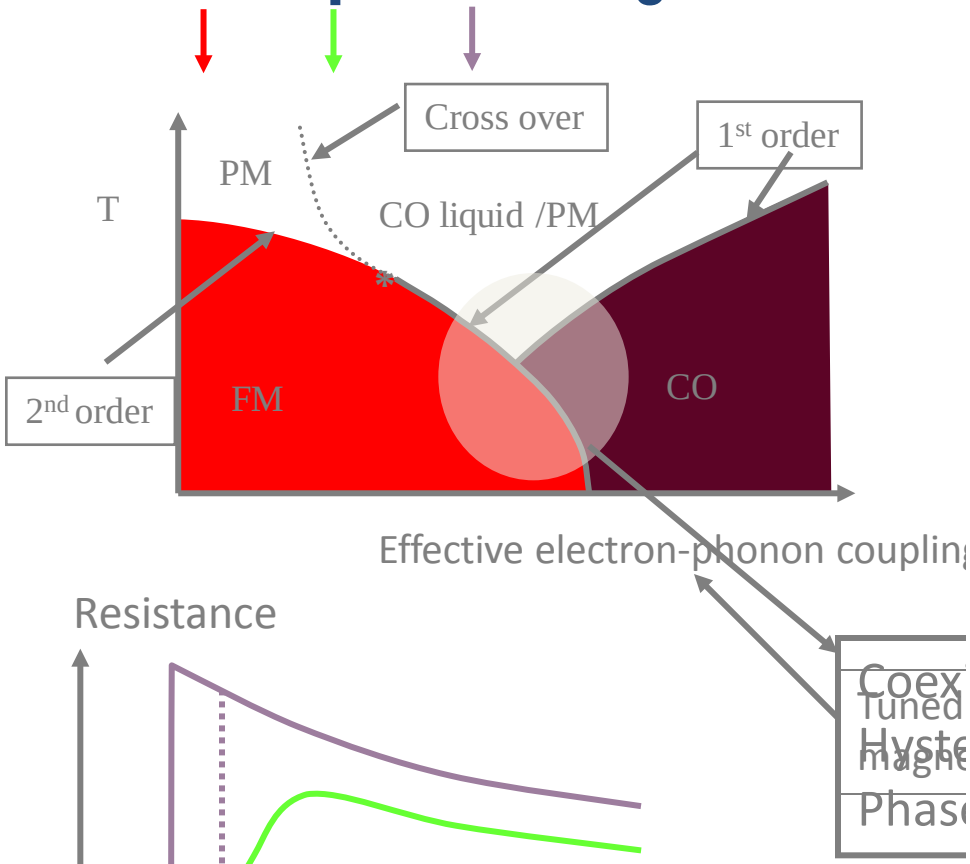


Jahn-Teller distortion suppresses hopping

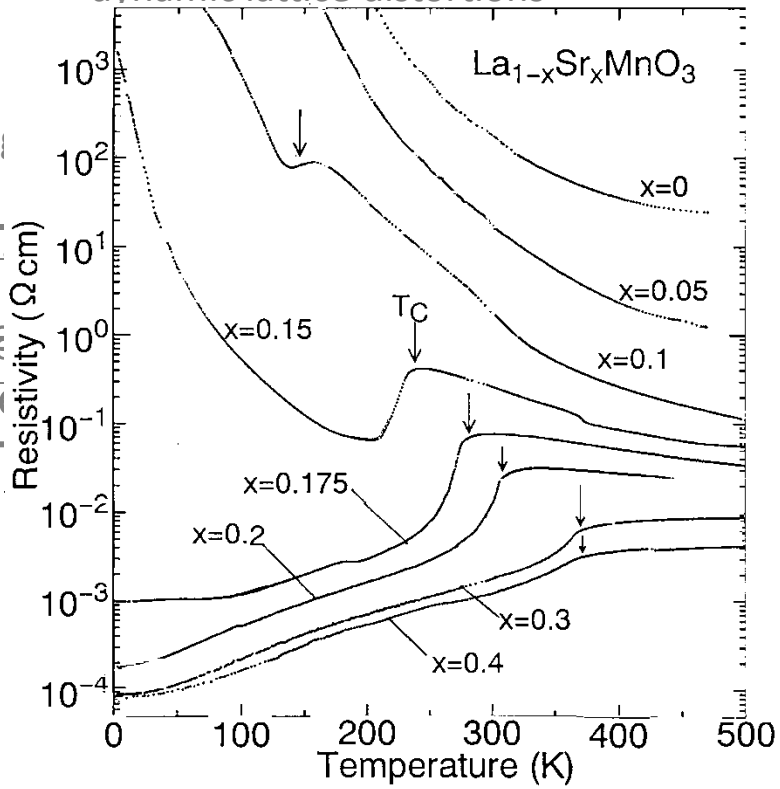


Leads to insulating state with orbital and/or charge order

Generic phase diagram

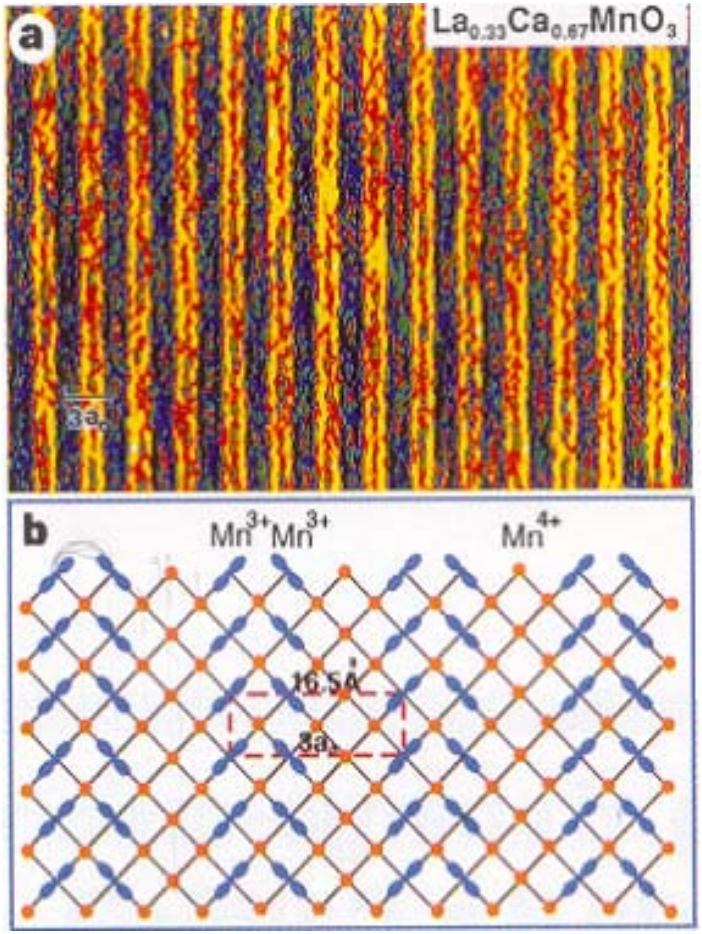


- Ferromagnetic metal
  degenerate electron plasma
  suppressed lattice distortions
- Charge/orbital ordered solid
  ordered insulating array of 3+/4+
- Polaronic liquid
  dynamic lattice distortions



Urushibara et al 1995

"Striped" phases of $La_{0.33}Ca_{0.67}MnO_3$



TEM image shows periodic ordered lattice

Interpreted as periodic array of 3+/4+ ions
???

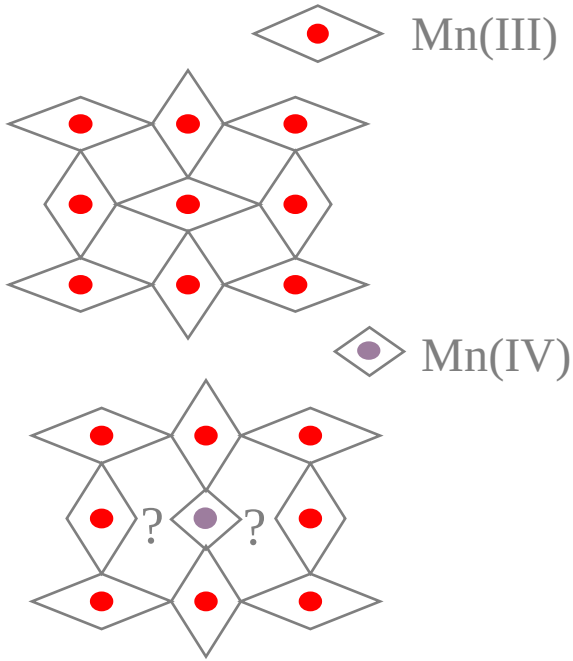
S Mori, CH Chen and S-W Cheong, Nature **392** (1998) 473

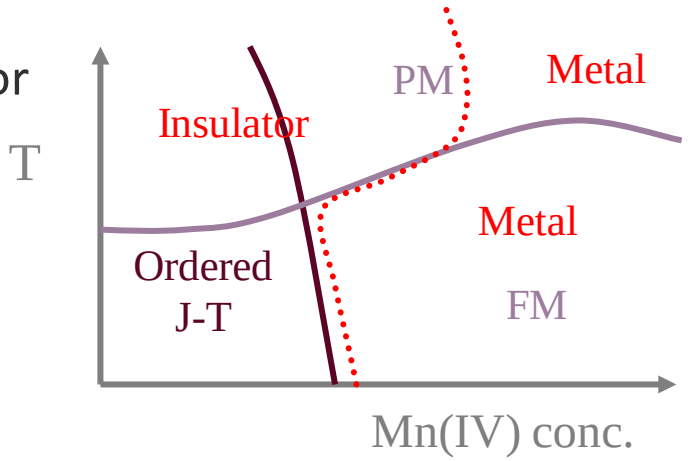
Jahn-Teller distortions and CMR

Doped $La_{1-x}Ca_xMnO_3$ has mixed-valent Mn^{3+}/Mn^{4+}

Mn^{3+} in octahedral environment is a Jahn-Teller ion, and octahedron distorts

- Charge distributed homogeneously – a metallic ferromagnet
- Charge distributed inhomogeneously – either an ordered solid (insulating stripes) or a polaron liquid (bad metal)

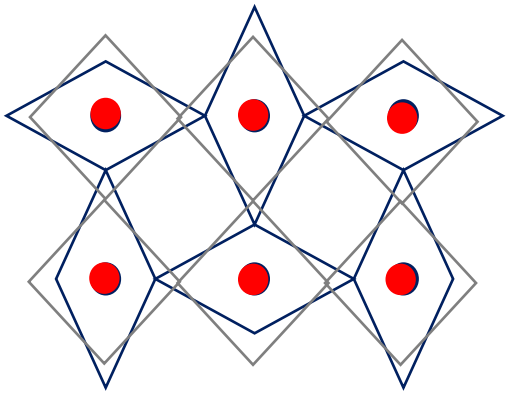


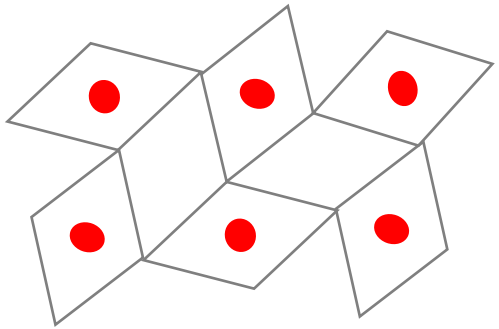


Millis et al., PRL 74, 5144 (1995); PRB 54, 5389 (1996)
Roder, Zang & Bishop PRL 76, 1356 (1996)

How do you make a polaron liquid?

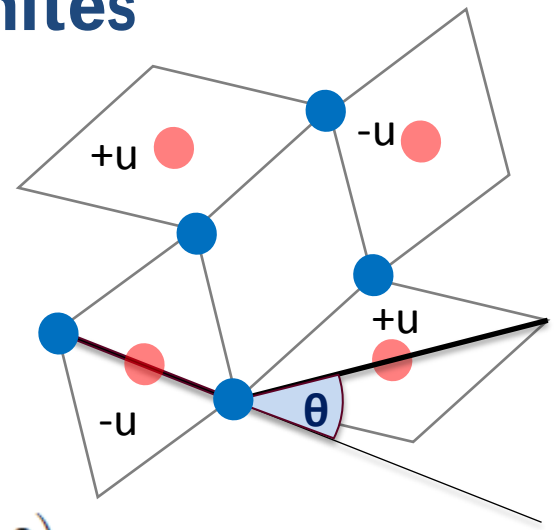
- In a cubic system, a local J-T distortion propagates to infinity ... can this be screened?
- With rotations of octahedra inhomogeneous patterns are allowed





“Jamming” transition in manganites

(staggered) Jahn-Teller order parameter **u**
Bond angle deviation on Oxygen **θ**
Allow for equilibrium rotation θ_0
Other degrees of freedom rigid
Consider volume strain only



$$F = \int d\mathbf{r} \left(\frac{1}{2}\alpha u^2 + \frac{1}{4}\beta u^4 + \frac{1}{2}\gamma(\nabla u)^2 + \frac{1}{2}K(\theta - \theta_0)^2 \right)$$

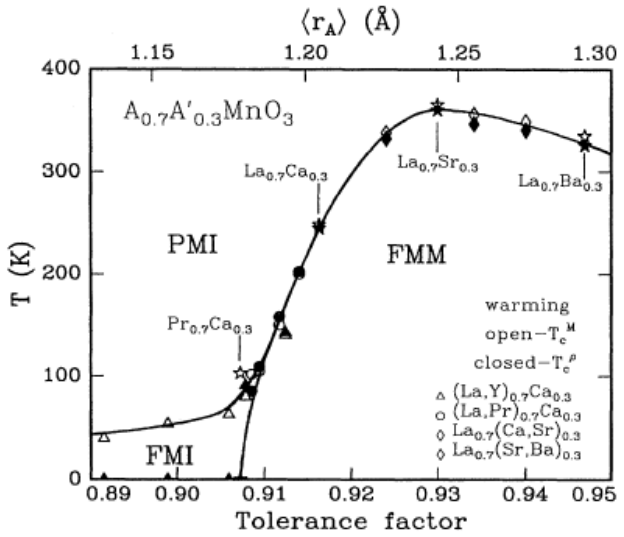
$$\phi_1 = \epsilon_{xx} + \epsilon_{yy} = \theta^2 + \frac{\partial u}{\partial x} + \frac{\partial u}{\partial y} \Rightarrow$$ Volume strain

$$\nabla^2 \left[\theta^2 + \partial_x u + \partial_y u \right] = 0 \Rightarrow$$ Elastic compatibility condition

$$\rightarrow \quad \nabla^2 \left[\theta + \frac{\partial_x u + \partial_y u}{2\theta_0} \right] = 0 \Rightarrow \gamma \rightarrow \gamma + \frac{K}{2\theta_0^2}$$

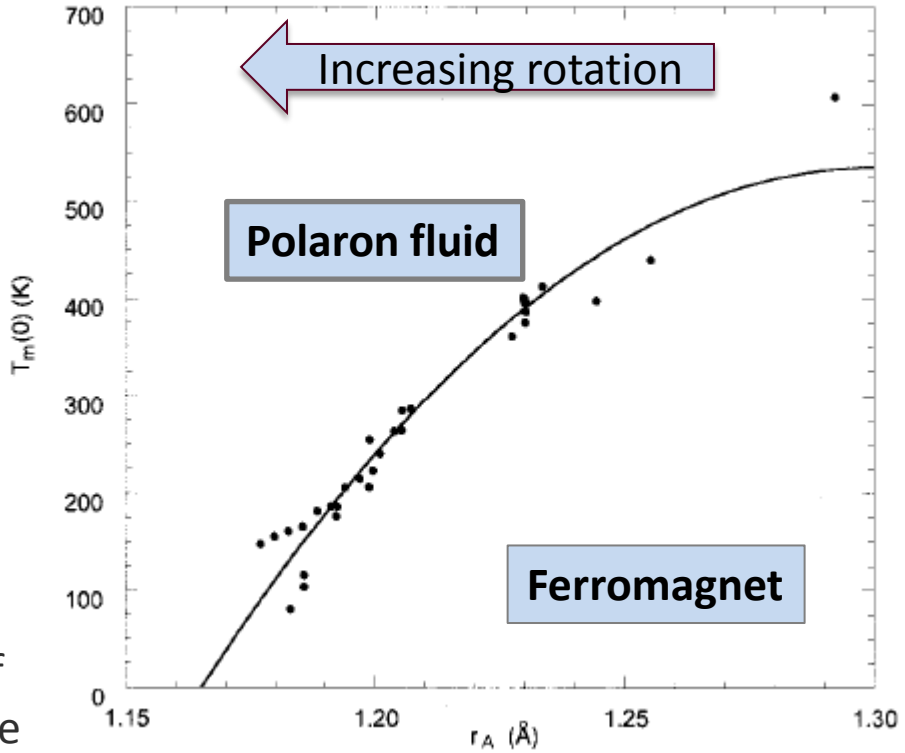
(linear) rigidity diverges as equilibrium rotation → 0

Colossal magnetoresistance in manganites controlled by size of A-site cation

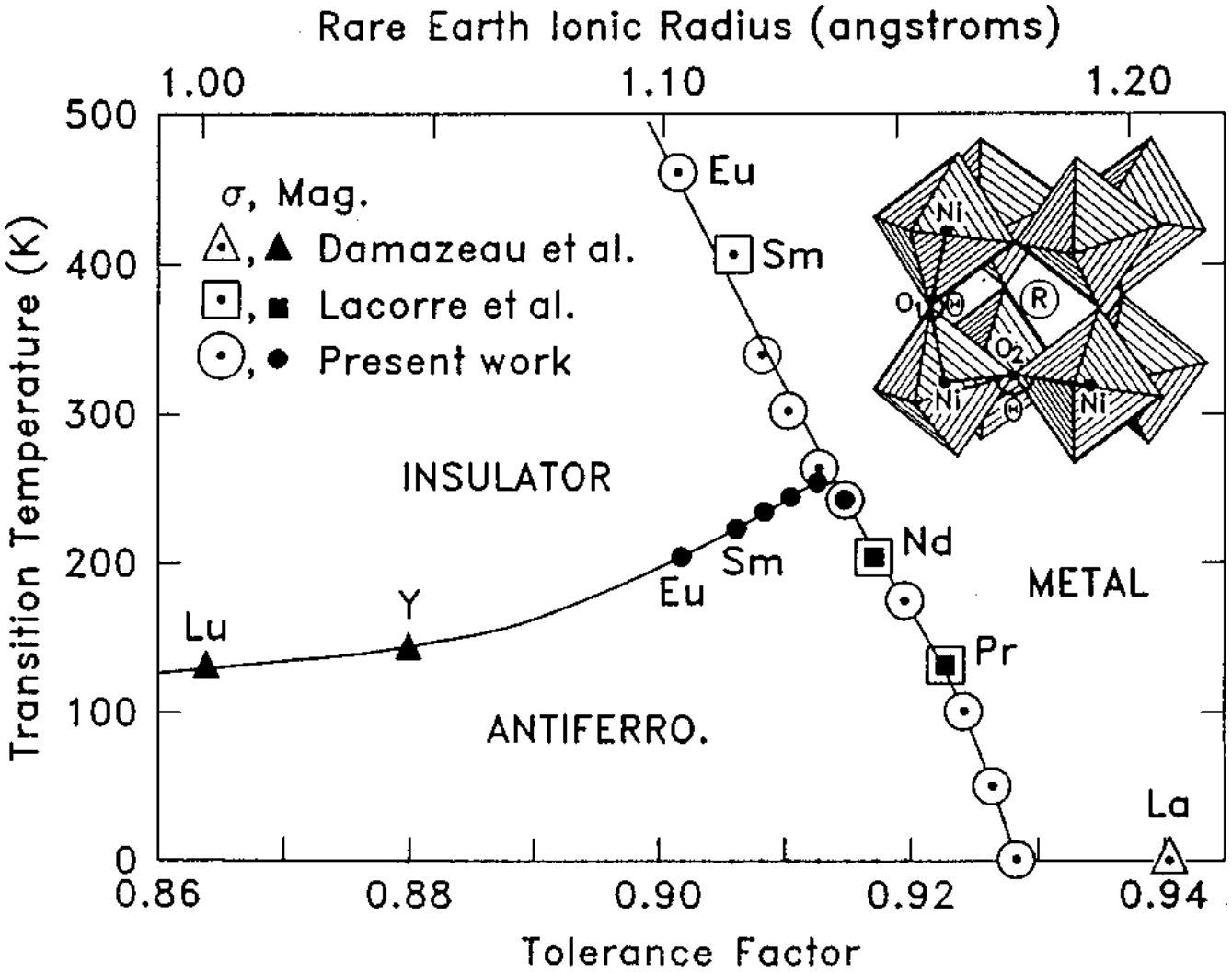


Hwang et al, PRL 75, 914 (95)

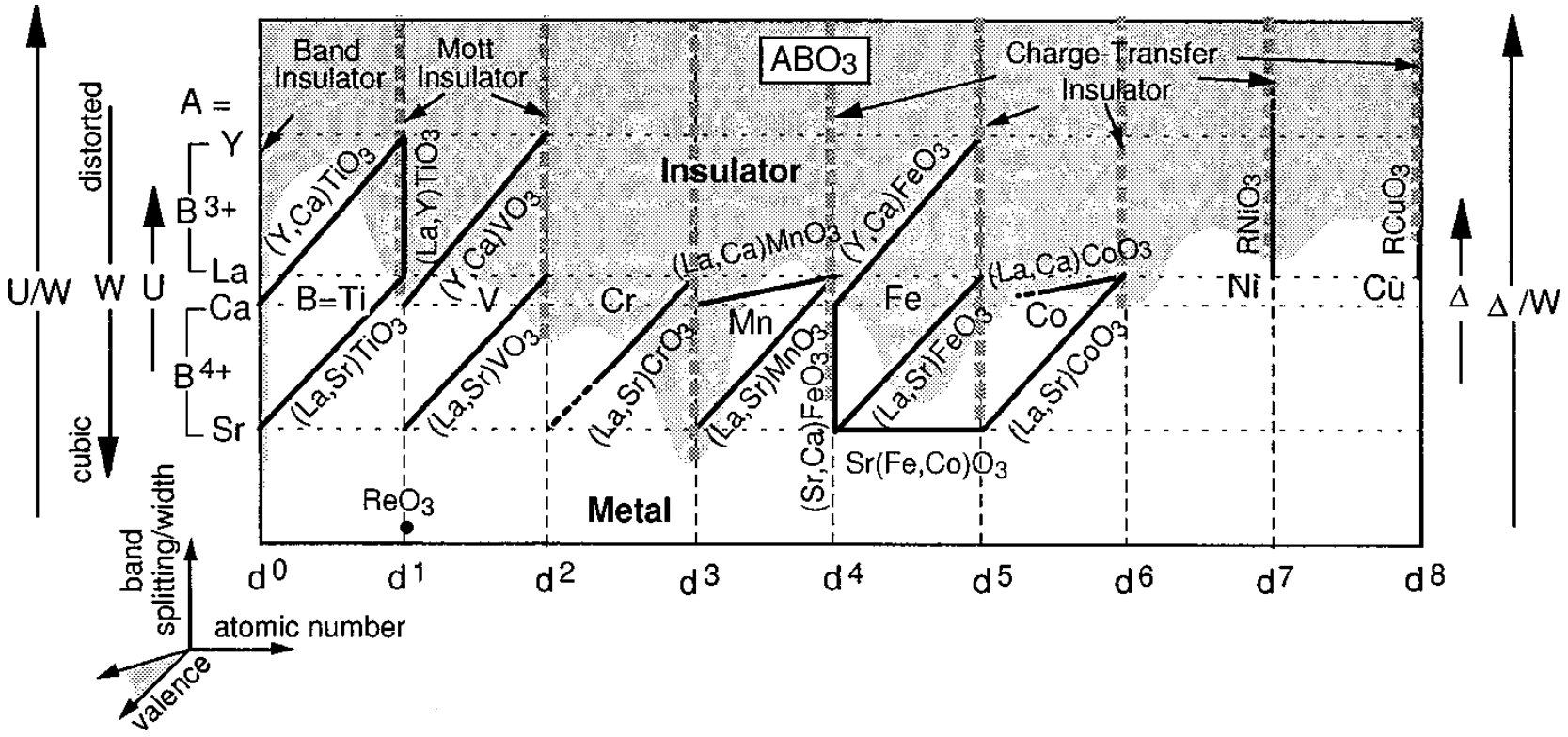
Magnetic transition temperature of $Ln_{0.7}M_{0.3}MnO_3$ varying size of the A-site cation at fixed doping



Rodriguez-Martinez and Attfield PRB 54 15622 (96)



Electronic phase diagram of *R*NiO3 (Torrance *et al.*,1992).



A schematic metal-insulator diagram for the filling-control (FC) and bandwidth-control (BC) 3*d* transition-metal oxides with perovskite structure. From Fujimori, 1992.

Conclusions (2)

- Gap in (linear) spectrum of wall-wandering modes
- Strain interactions in GL theories can be screened by intra-cell degrees of freedom – requires explicit inclusion of further auxiliary fields to treat them
- CMR: straightforward explanation of size-control of ferromagnetic phase transition
- NB: straightforward extension to $ReNiO_3$

Can one get thermodynamic control over local structural degrees of freedom?

How much entropy can you control?

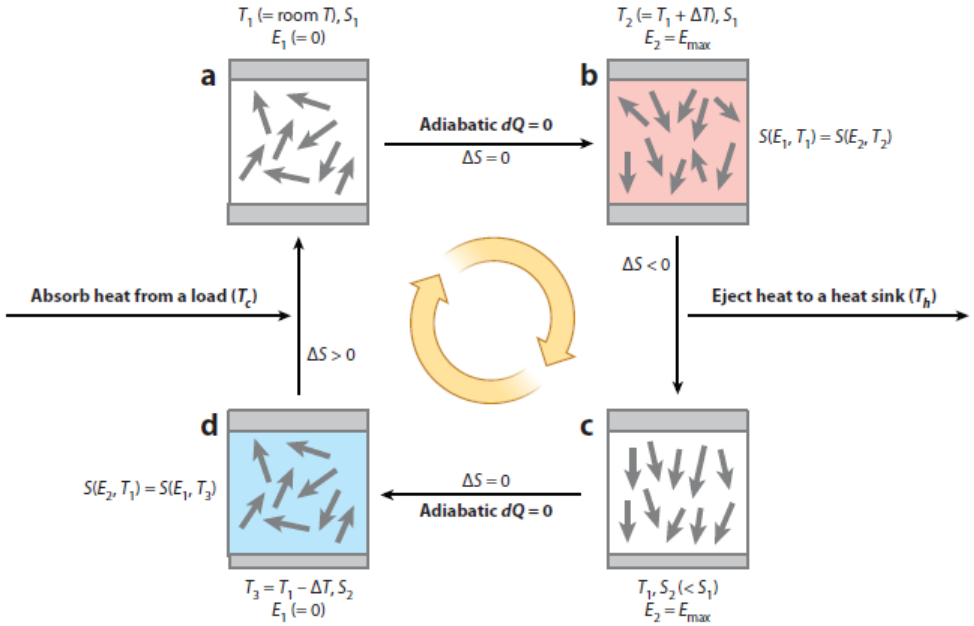
The Electrocaloric Effect

Electro-caloric effect and refrigeration

Electrocaloric effect = change in temperature in response to an electric field

Largest entropy changes if dipoles weakly coupled ….

…. but then one needs to apply electric fields to overcome thermal energies at high T

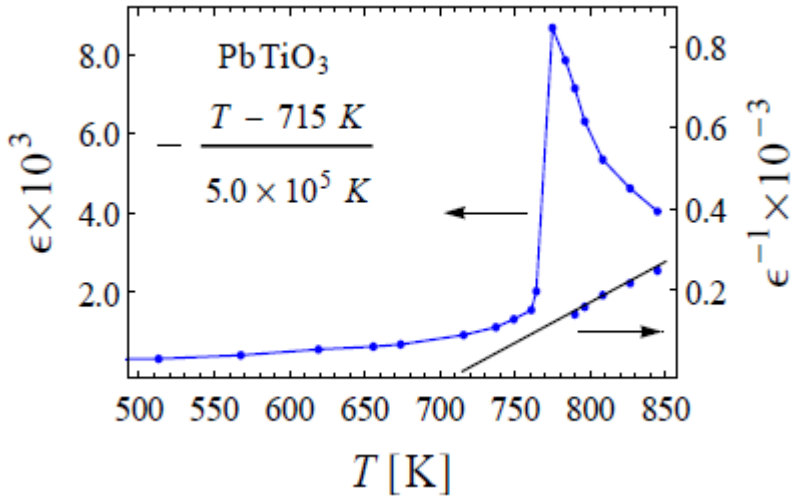


Non-equilibrium effect so needs a model

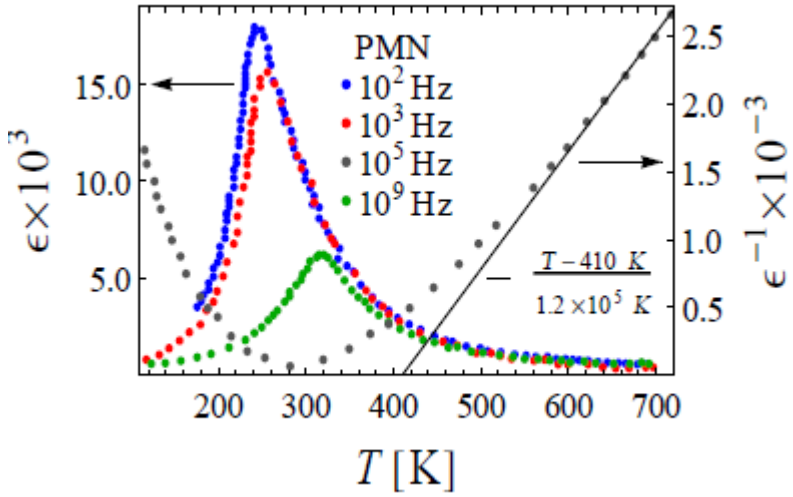
Here – relaxor dynamics from Guzman-Verri and Varma, arXiv:1212.3402

From ferroelectrics to relaxors? – broadening and modest enhancement at low fields

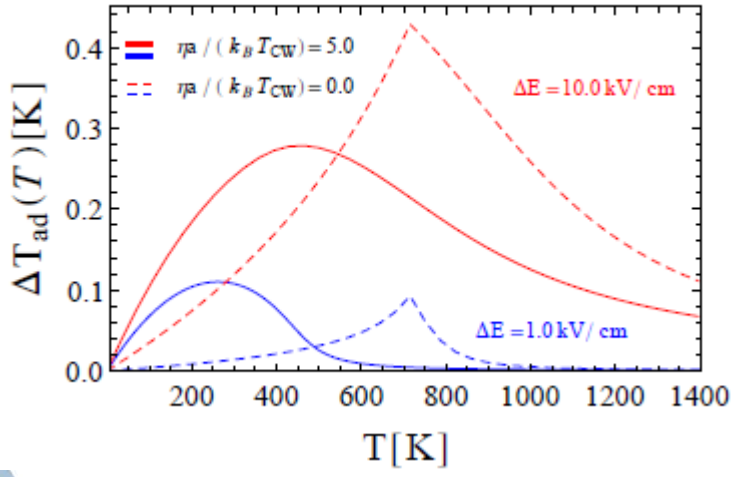
Ferroelectric



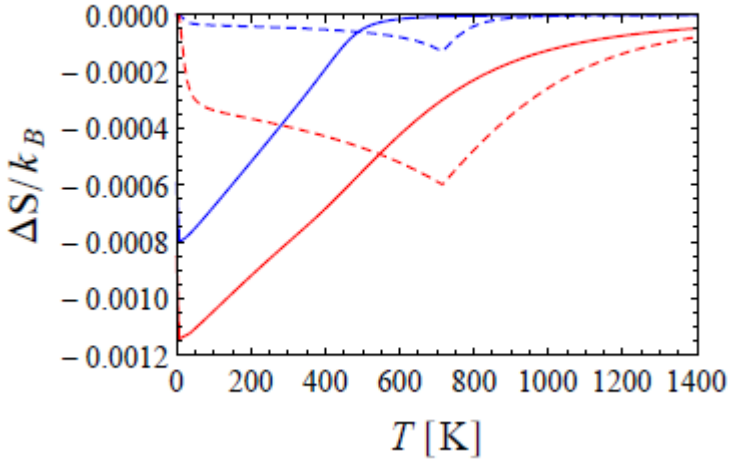
Relaxor



Adiabatic temperature change



Isothermal entropy change



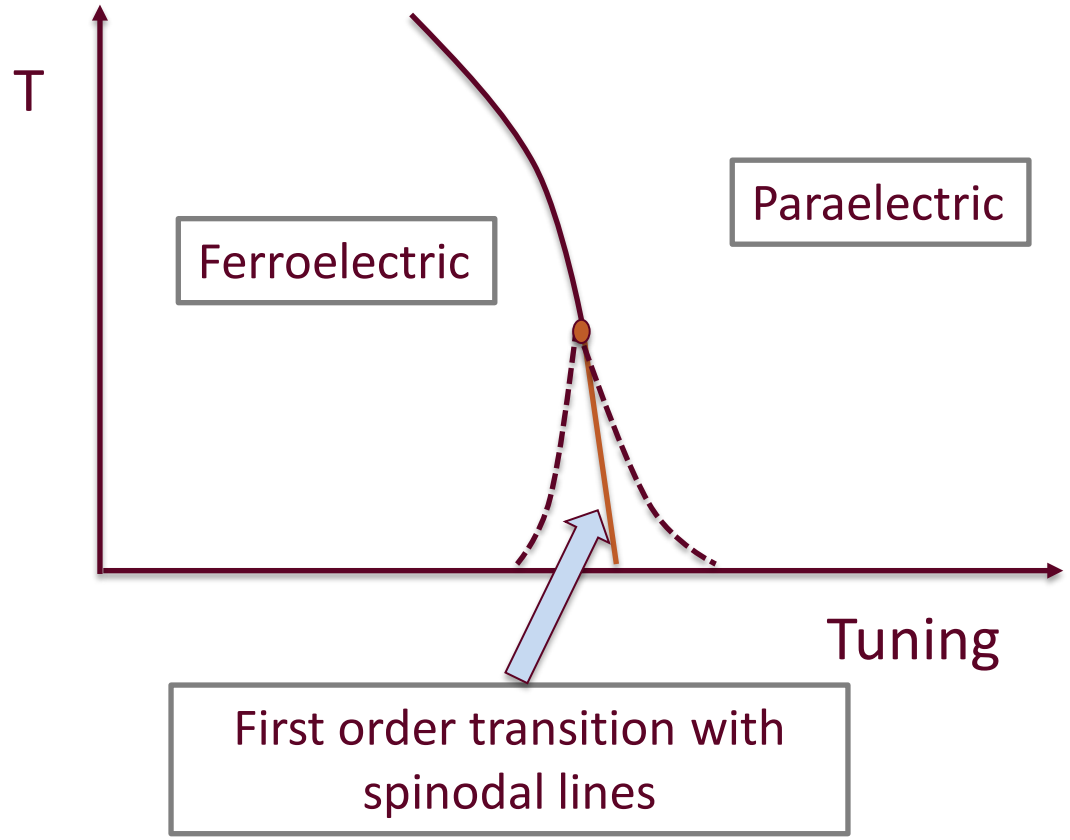
Outlook

Are there systematic ways to make structurally (and electronically) “soft” phases in oxides, for example

- negative thermal expansion materials
- fragile glasses
- polaronic liquids, nematics, smectics, ...
- electrocaloric materials
- low coercivity ferroelectrics
- phase change materials
- strong quantum fluctuations near critical points and high T_c conventional superconductors

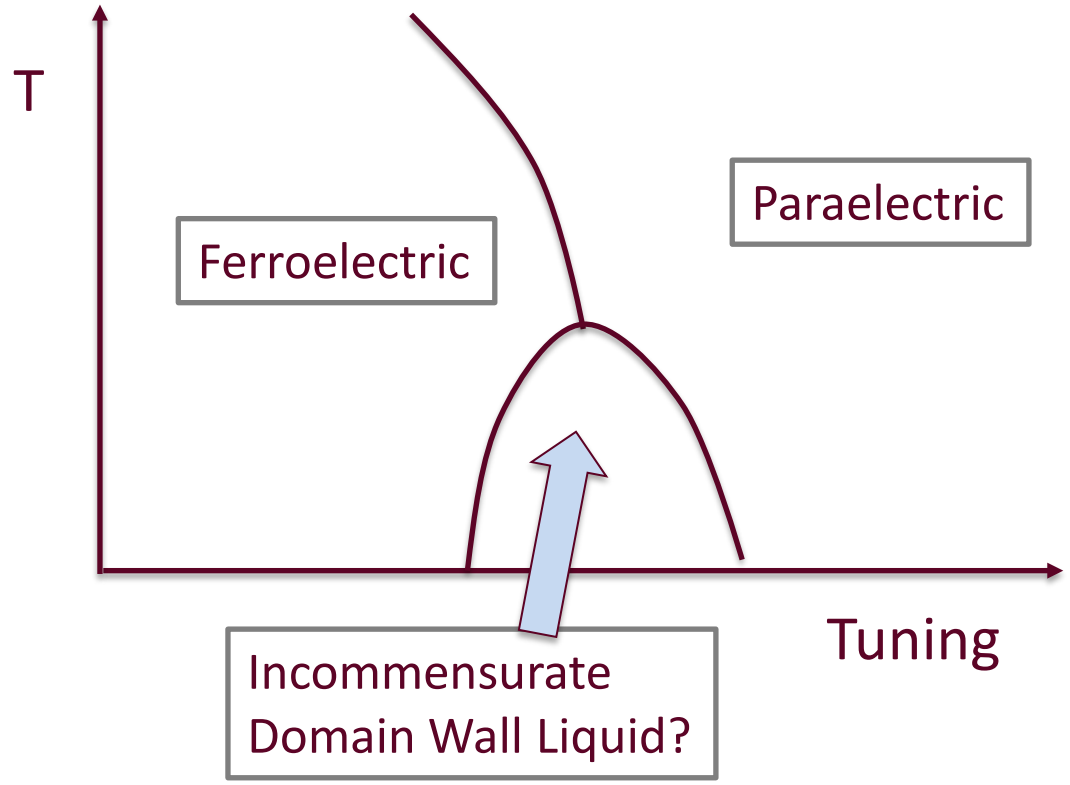
Quantum paraelectrics – possible phase diagram

Expect first order transition with critical point at low T



Quantum paraelectrics – possible phase diagram

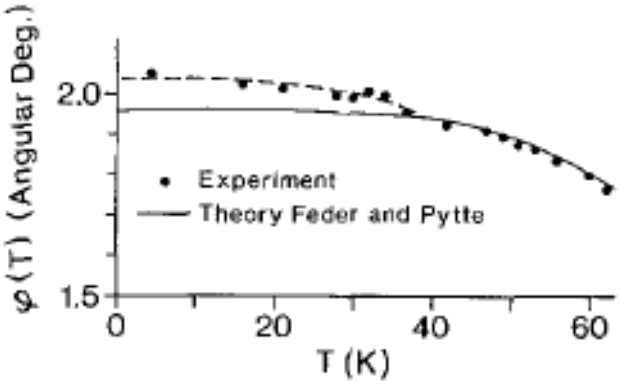
Octahedral rotations can screen the strain fields set up by DW fluctuations – subverts expected 1st order transition

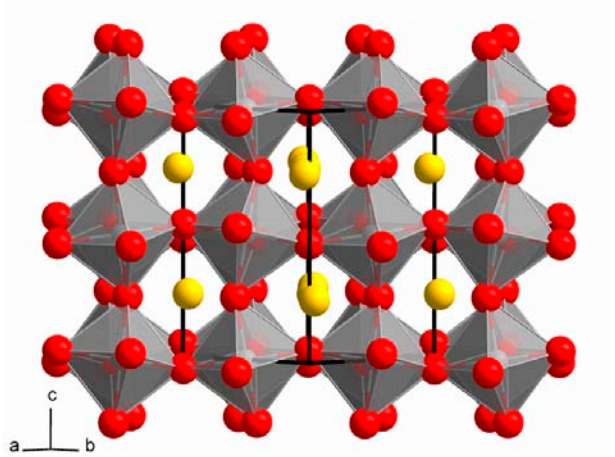


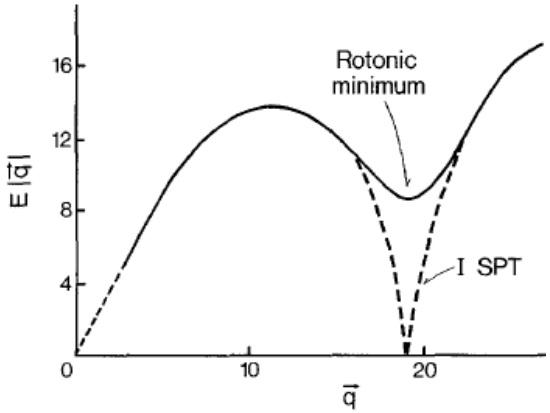
Indication for a novel phase in the quantum paraelectric regime of $SrTiO_3$

K. Alex Müller[1], W. Berlinger[1,†], and E. Tosatti[2]

Z. Phys. B – Condensed Matter 84, 277–283 (1991)







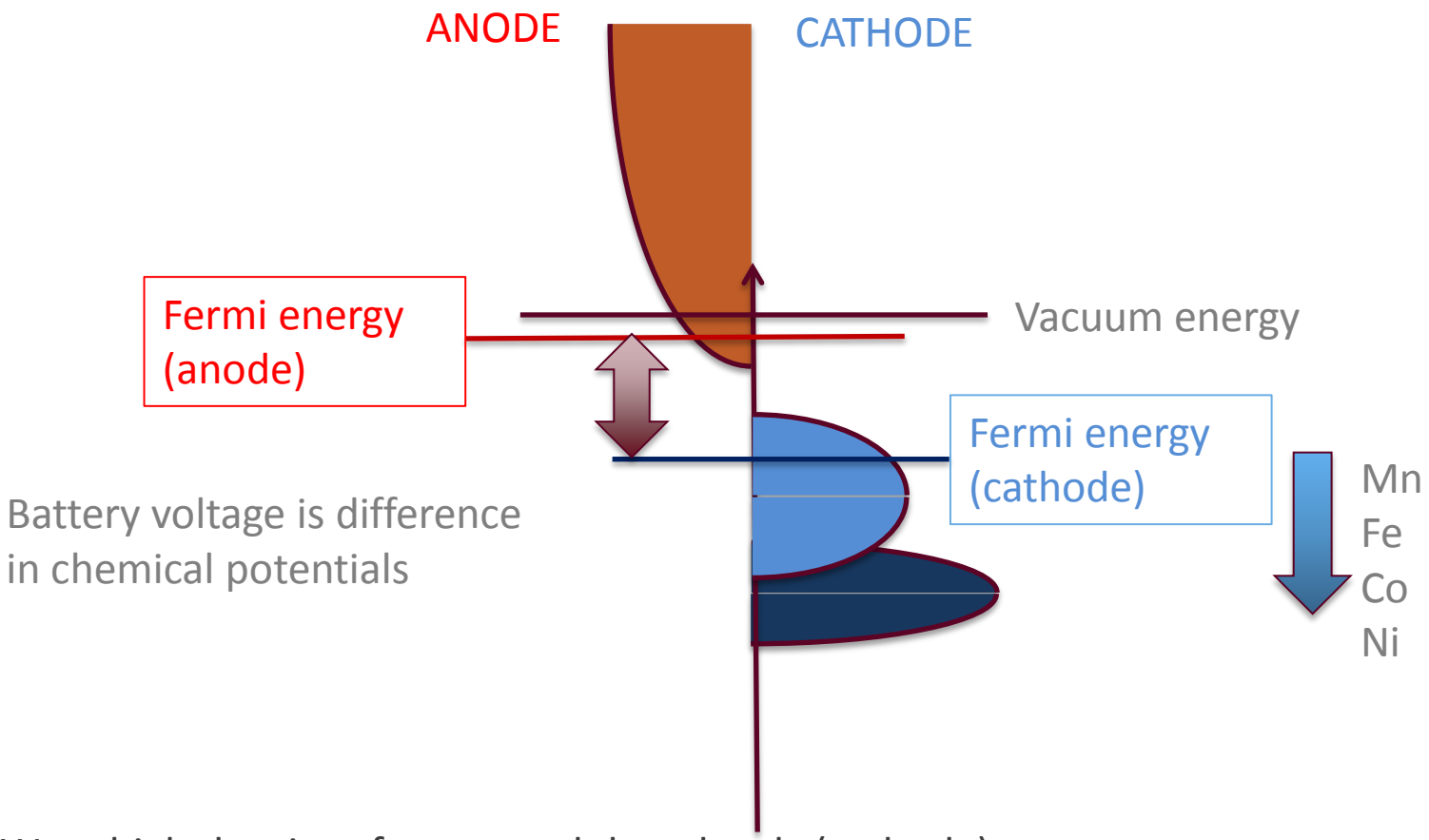
PHYSICAL REVIEW B VOLUME 49, NUMBER 18 1 MAY 1994

Path-integral Monte Carlo study of a model two-dimensional quantum paraelectric

R. Martoňák and E. Tosatti*

And why this matters for batteries …..

Battery basics



Want high density of states and deep levels (cathode)

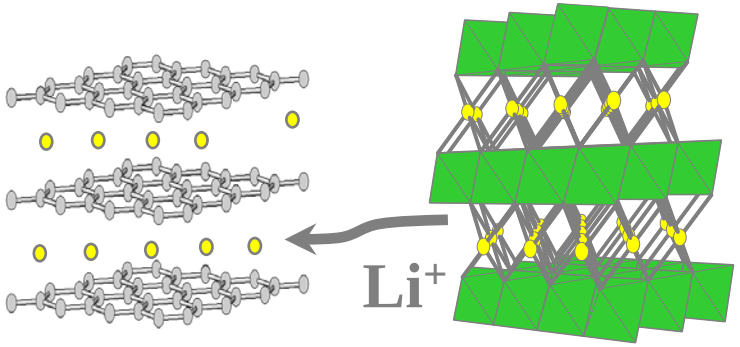
Want high density of states and shallow levels (anode)

Must be able to reversibly shift chemical potentials by ion transport (Li^+)

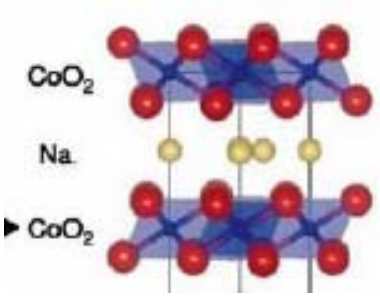
Non-reactive electrolyte

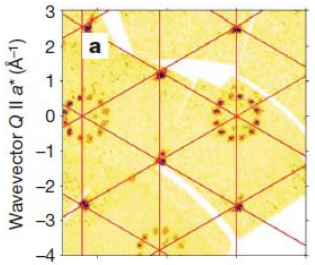
Energy dense materials are strongly correlated

Li-ion battery, commercialised by Sony in 1991
$Li_x C_6$ (anode) / $Li_{1-x} CoO_2$ (cathode)
x limited to ~ 0.5



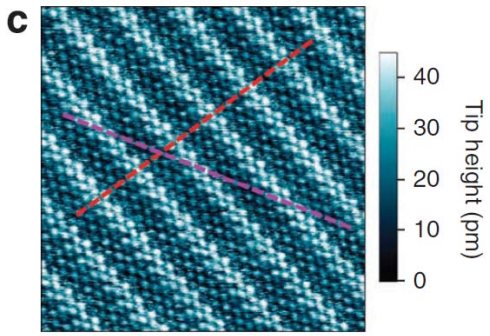
$Na_x CoO_2$
Enhanced thermopower, 5K superconductor
vacancy ordered phases

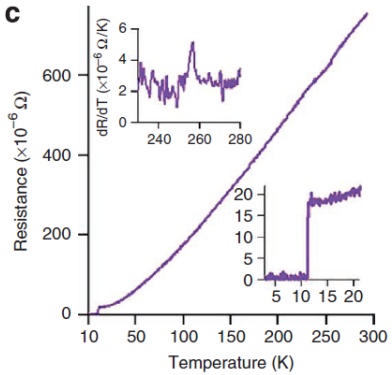




Roger et al. 2007 doi:10.1038/nature05531

CaC_6
12K superconductor; 250K CDW

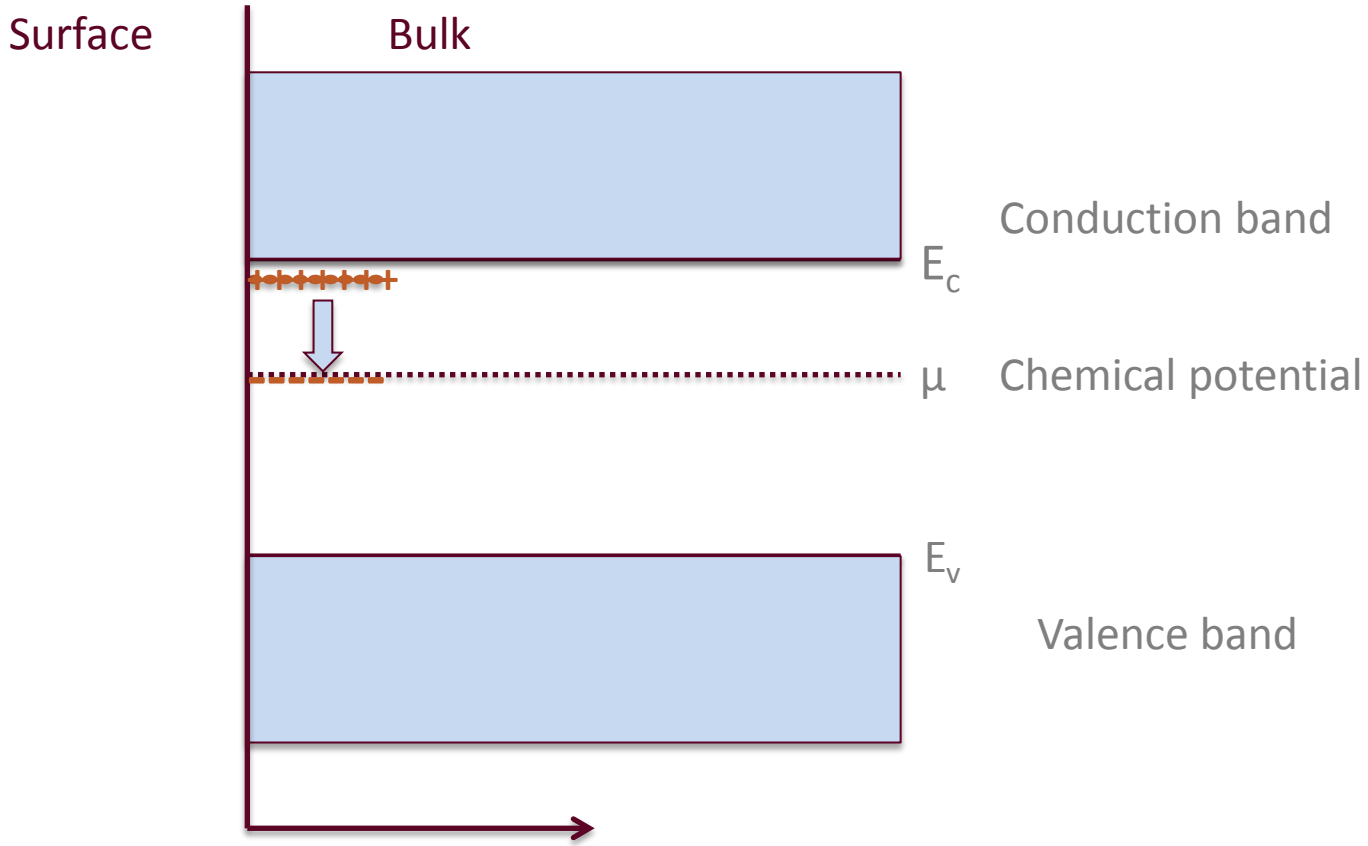




This is not an accident!

Rahnejat et al 2011 DOI: 10.1038/ncomms1574

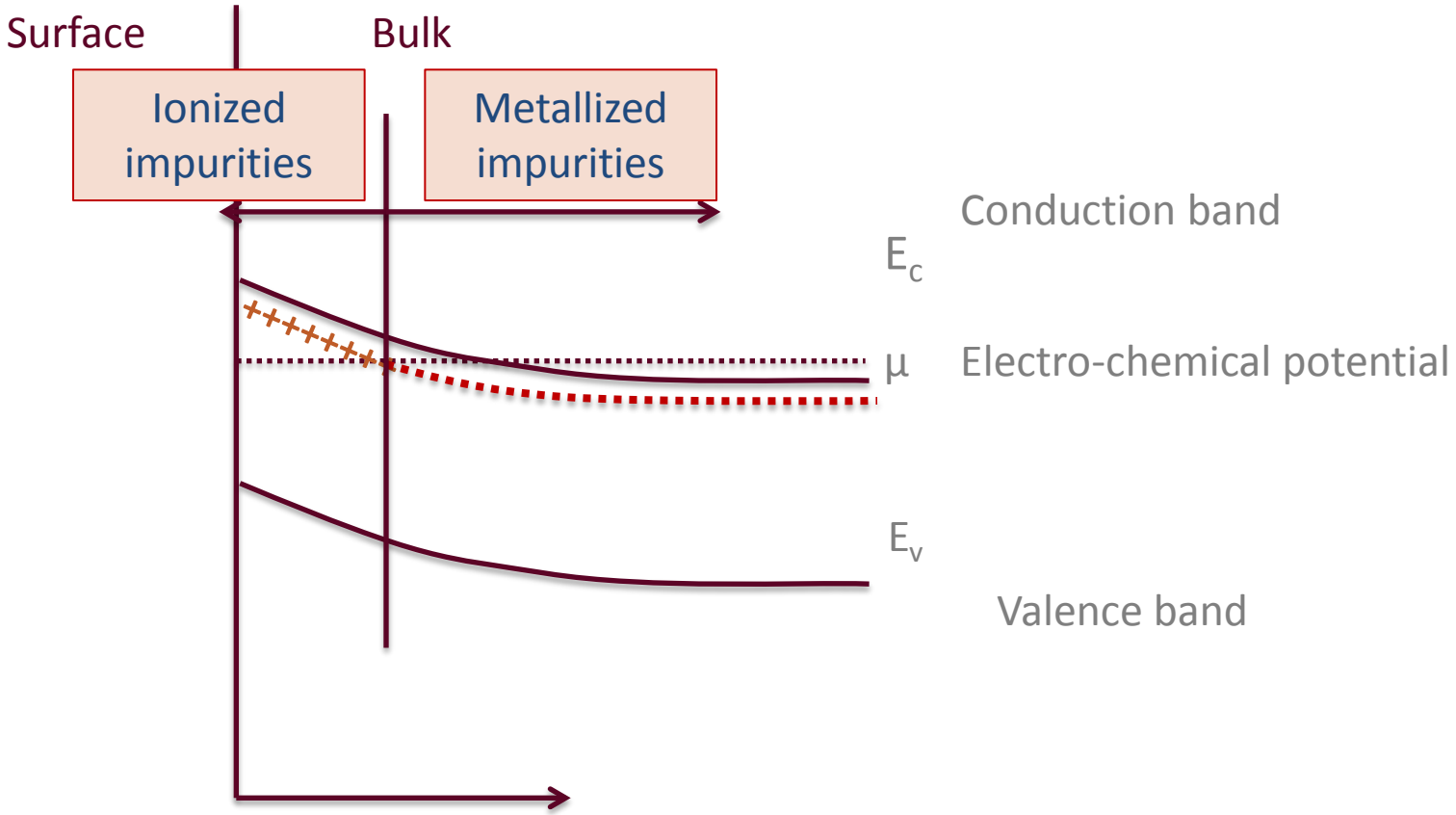
Doping of conventional semiconductor



Add dopant (including associated electron) near the interface

Dopants ionize and electrons delocalise

Doping of conventional semiconductor



Charge separation introduces electrical potential which shifts the band edge

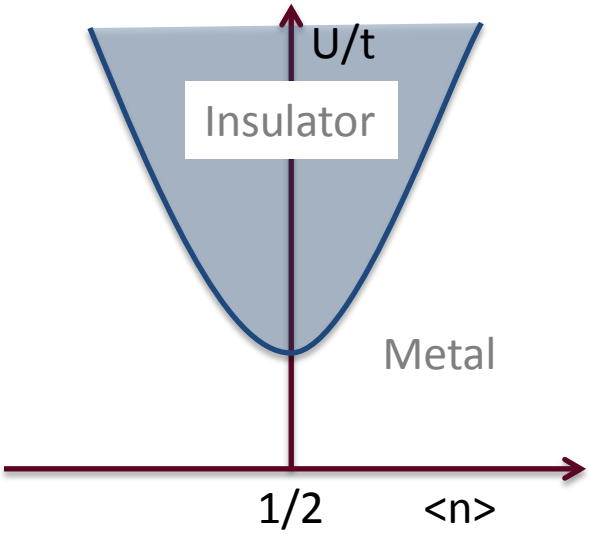
Weakly bound carriers metallize , depletion layer at interface

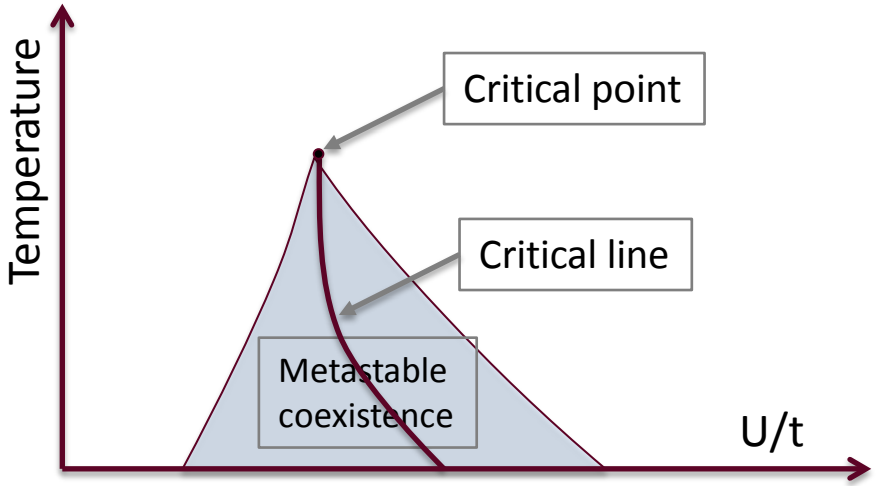
Mott insulator

- Generic model due to Mott, Hubbard --- competition between hopping “t” and Coulomb “U”

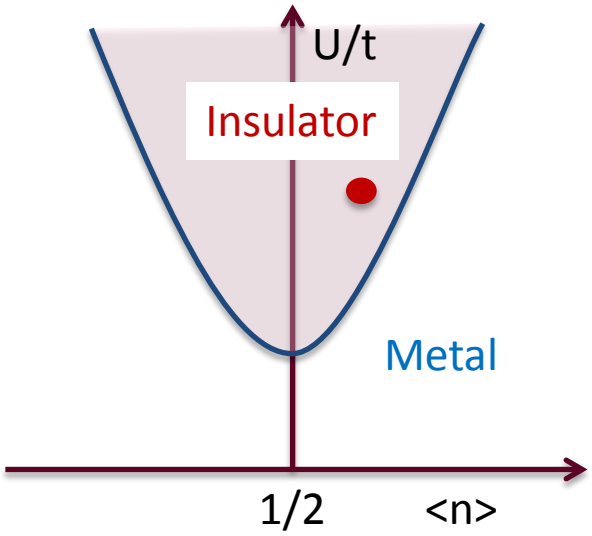
$$H = \sum_{ij} t_{ij} \hat{c}_i^\dagger \hat{c}_j + \sum_i U \hat{n}_{i\uparrow} \hat{n}_{j\downarrow}$$

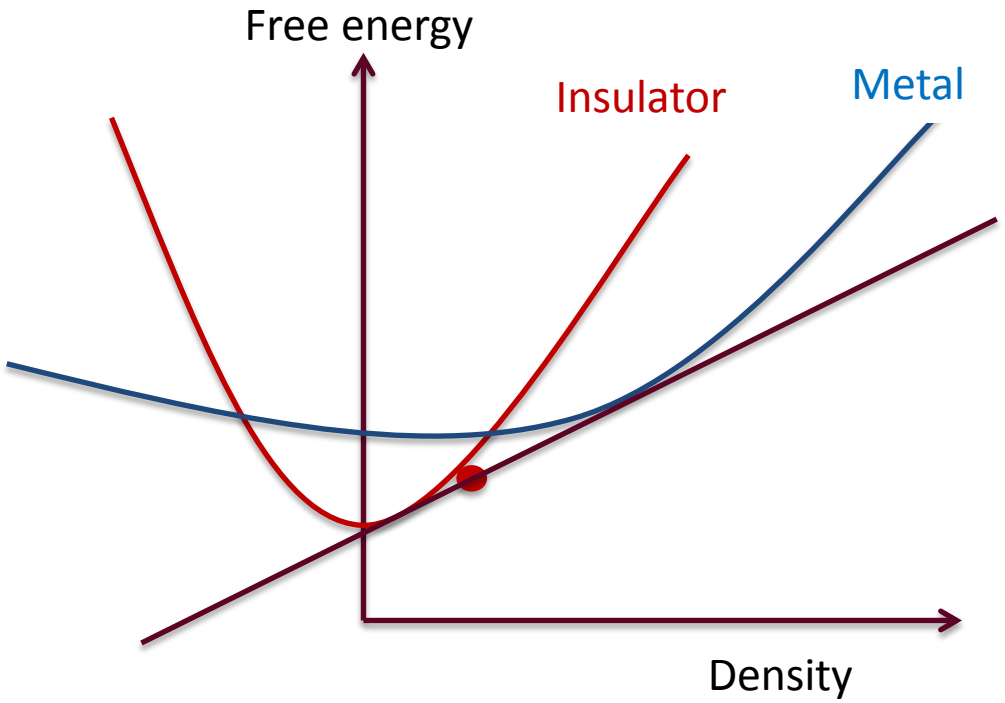
- Near half-filling, induces insulating/magnetic states by a discontinuous first-order phase transition





Doping of a Mott insulator

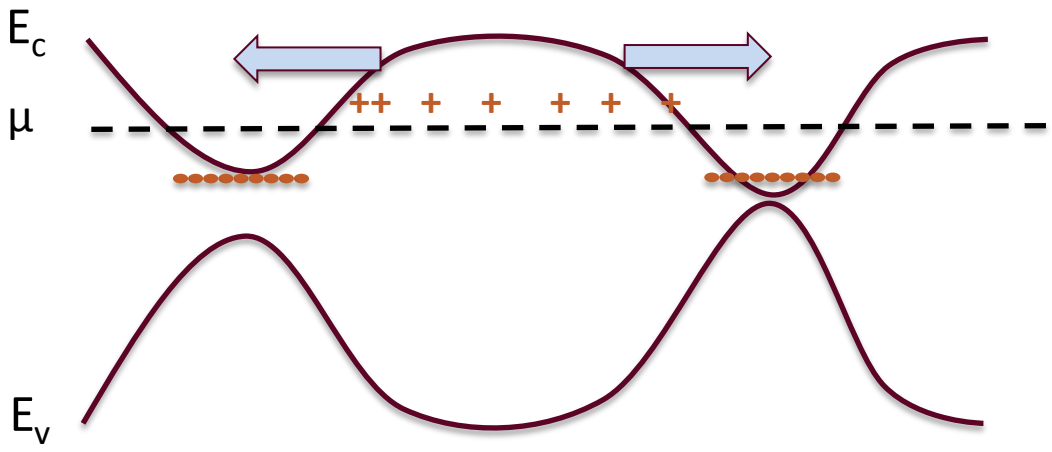




Expect phase separation and an inhomogeneous state
“Frustrated” by Coulomb interaction

Inhomogeneous phases in Mott systems

Mobile donors diffuse to form metallic puddles and screen Coulomb repulsion of phase-separating carriers

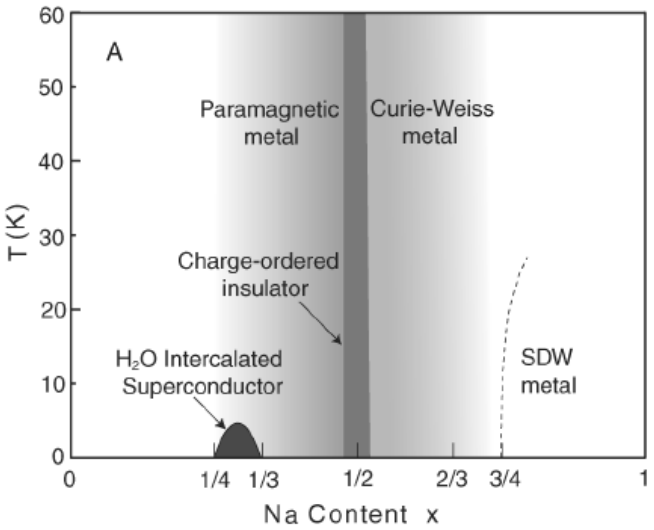


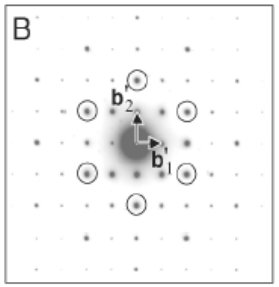
This is a generic feature of any system with a first-order phase transitions separating stable phases of differing electron density

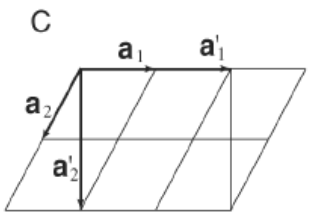
Particularly prevalent when dopant species are highly mobile – e.g. O vacancies and Li ions

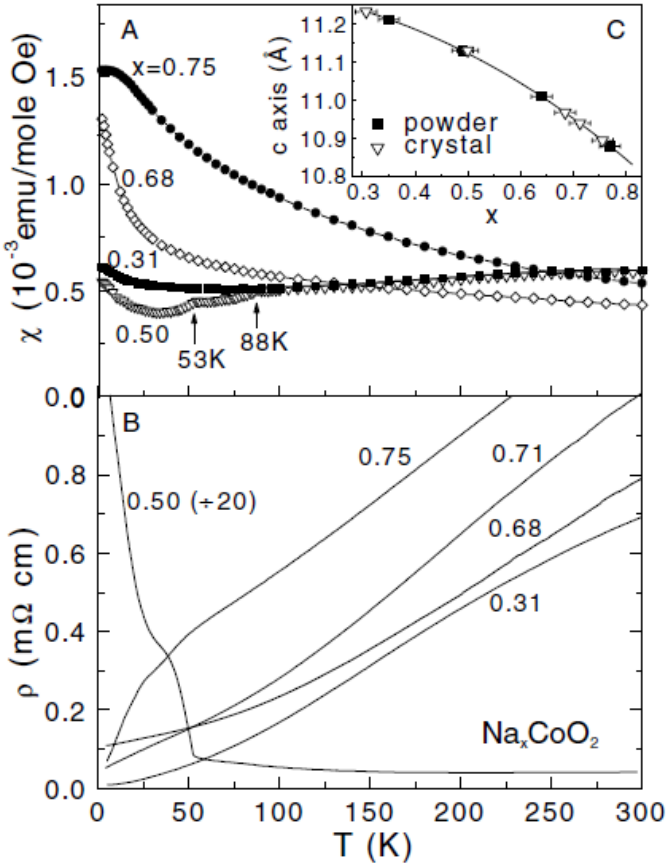
Charge Ordering, Commensurability, and Metallicity in the Phase Diagram of the Layered Na_xCoO_2

Maw Lin Foo,[1] Yayu Wang,[2] Satoshi Watauchi,[1,*] H.W. Zandbergen,[3,4] Tao He,[5] R. J. Cava,[1,3] and N. P. Ong[2,3]





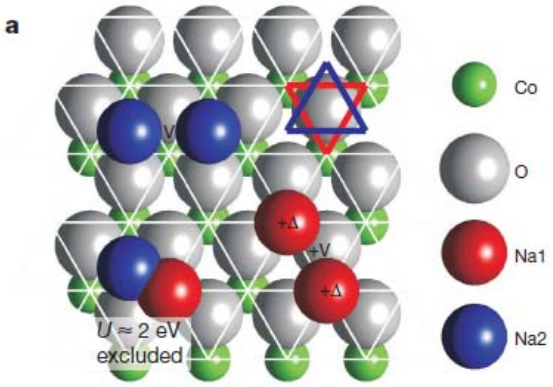




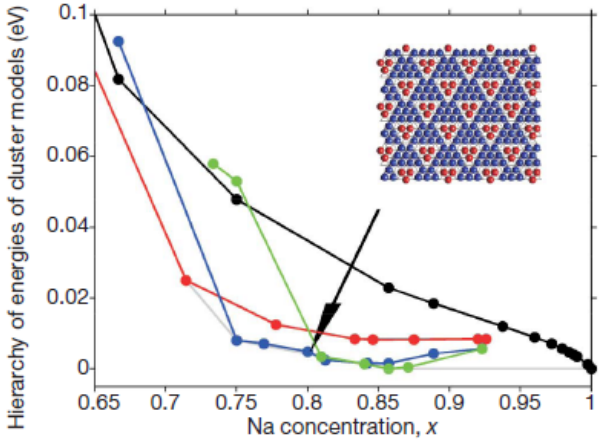
Patterning of sodium ions and the control of electrons in sodium cobaltate

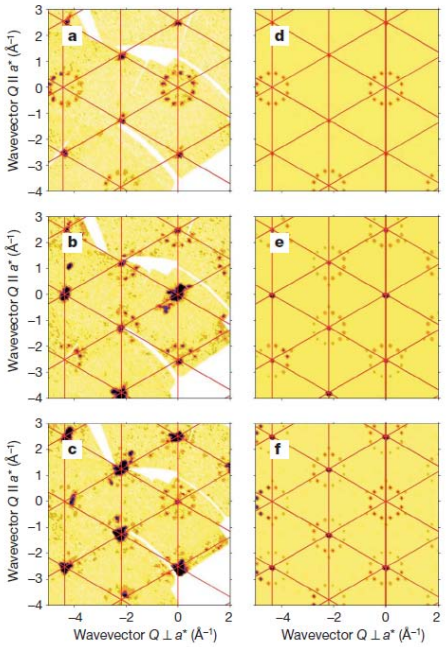
Vol 445 | 8 February 2007 | doi:10.1038/nature05531

M. Roger[1], D. J. P. Morris[2], D. A. Tennant[3,4], M. J. Gutmann[5], J. P. Goff[2], J.-U. Hoffmann[3], R. Feyerherm[3], E. Dudzik[3], D. Prabhakaran[6], A. T. Boothroyd[6], N. Shannon[7], B. Lake[3,4] & P. P. Deen[8]



Ordered trivacancy phase of $Na_{0.8}CoO_2$



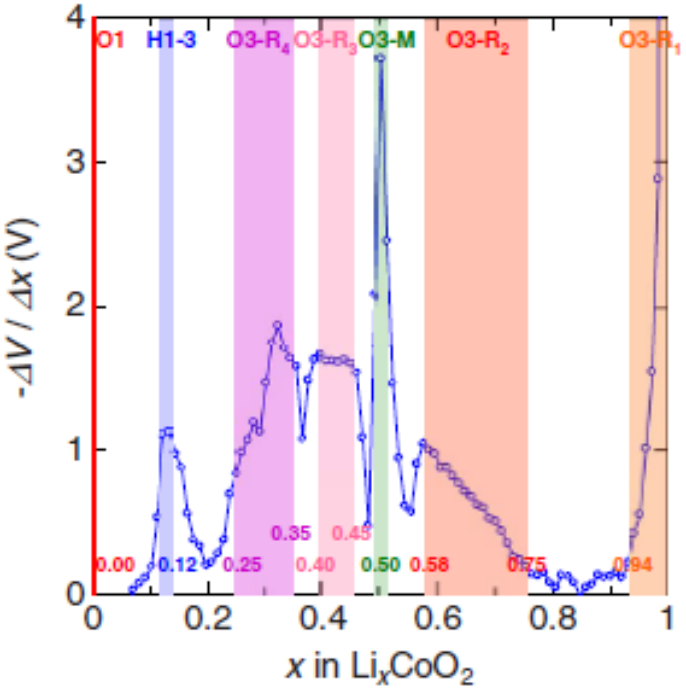


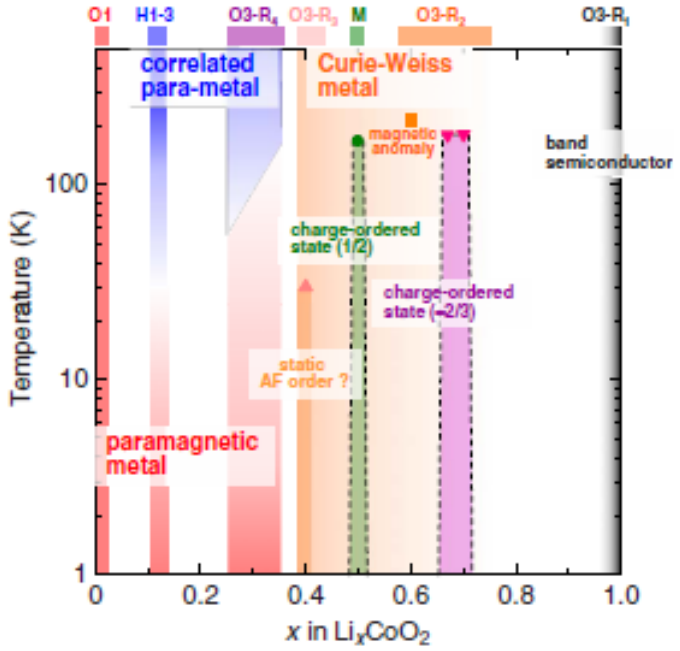
PHYSICAL REVIEW B 80, 165114 (2009)

Electronic phase diagram of the layered cobalt oxide system Li_xCoO_2 $(0.0 \leq x \leq 1.0)$

T. Motohashi,[1,2] T. Ono,[2,3] Y. Sugimoto,[1] Y. Masubuchi,[1] S. Kikkawa,[1] R. Kanno,[3] M. Karppinen,[2,4] and H. Yamauchi[2,3,4]

Derivative of open cell voltage dV/dx indicates biphasic regions





Acknowledgements

Electrostatic charging and redox effects in oxide heterostructures

Nick Bristowe (Cambridge, Liege) , Emilio Artacho (Cambridge, CIC Nanogune, San Sebastian), Miguel Pruneda and Massimiliano Stengel (Barcelona) Sergei Kalinin (Oak Ridge), Alejandro Lopez Bezanilla (Argonne)

Bristowe et al., PRB 80, 45425 (2009); 83,20545 (2011); 85, 021406 (2012); JPCM 23, 081001 (2011); PRL 108, 166802 (2012); Lopez-Bezanilla et al, Arxiv:1408.3103

Strain physics in ferroics

Richard Brierley (Yale) and Gian Guzman-Verri (Argonne)

Avadh Saxena, Turab Lookman, (Los Alamos) Ken Ahn (NJIT)

Seman et al, arXiv:1208.2304 ;
Brierley and Littlewood, arXiv:1307.7886
Guzmán-Verri, Littlewood, Varma, arXiv:1309.2816