Elastic control of the Mott transition

Richard Brierley, Cambridge University -> Yale -> Nature
Gian Guzmán-Verri, Argonne National Lab -> U Costa Rica
Peter Littlewood, Argonne and University of Chicago
Alex Edelman, University of Chicago

thanks to K Ahn, T Lookman, A Saxena, J F Scott, S S Saxena, J H Hancock

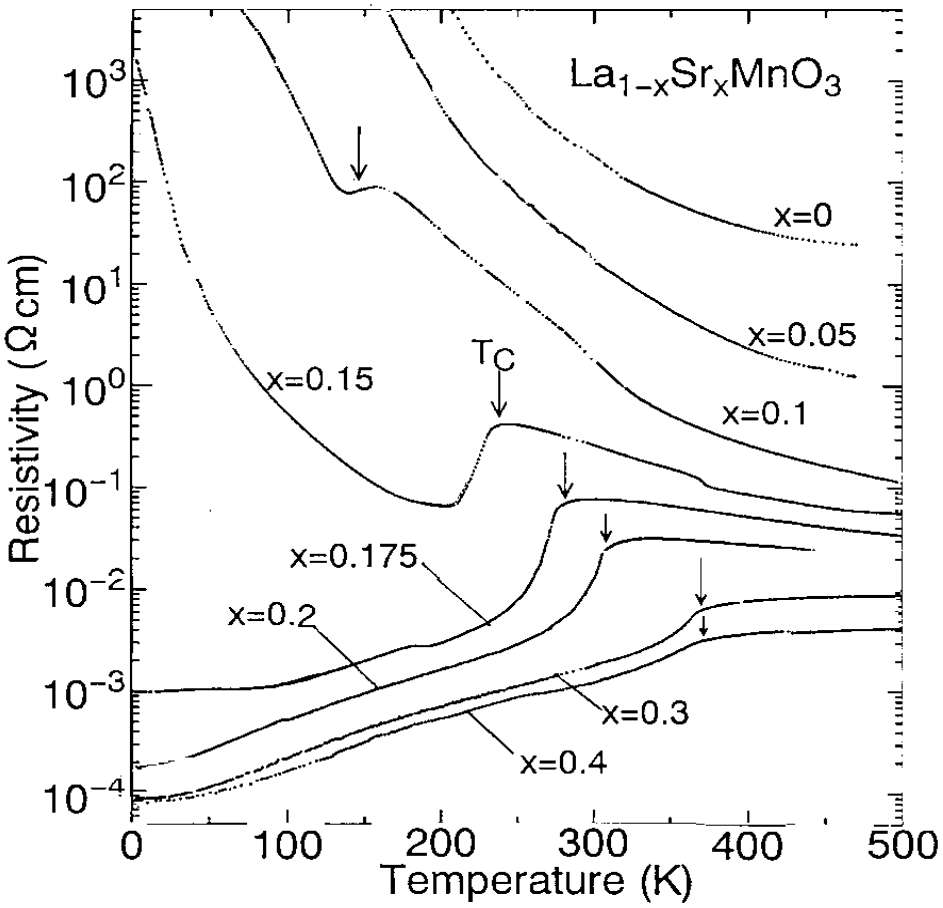
The "Mott" transition

- There are many classes of materials where Coulomb correlations cause a phase transition from a high temperature disordered metallic phase to a low temperature ordered insulating phase
- Paradigm is the Hubbard model

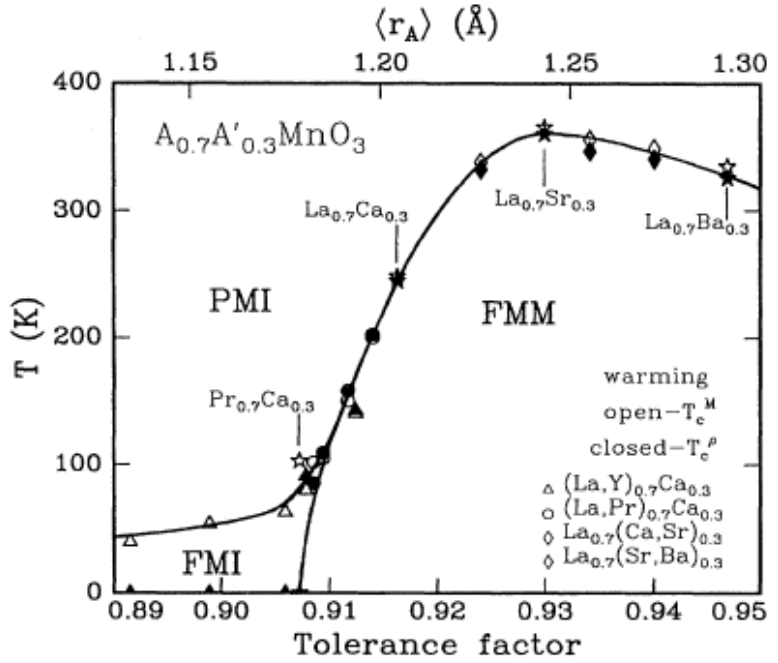
$$H = \sum_{ij} t_{ij} \hat{c}_i^\dagger \hat{c}_j + \sum_i U \hat{n}_{i\uparrow} \hat{n}_{j\downarrow}$$

  - But many possible broken symmetries, spin, orbit, lattice, charge etc.
- Central dogma is that the important parameters are all electronic
  - Ratio of interaction to bandwidth "U/W"
  - Number of carriers in the band
  - Coupling to lattice degrees of freedom is mostly irrelevant, or simply renormalizes parameters

Cation size effect: Colossal magnetoresistance in manganites



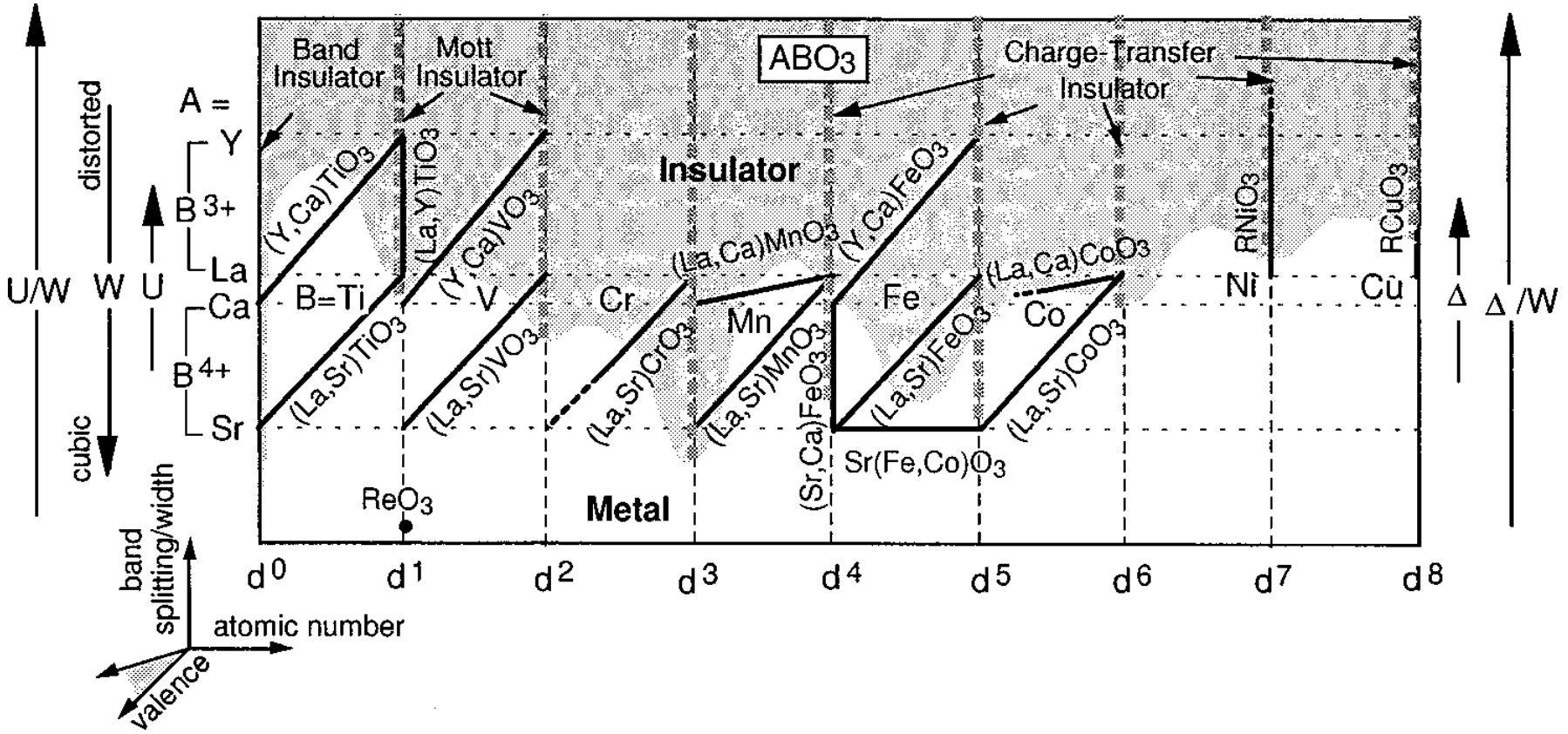
Urushibara et al 1995



Hwang et al, PRL 75, 914 (95)

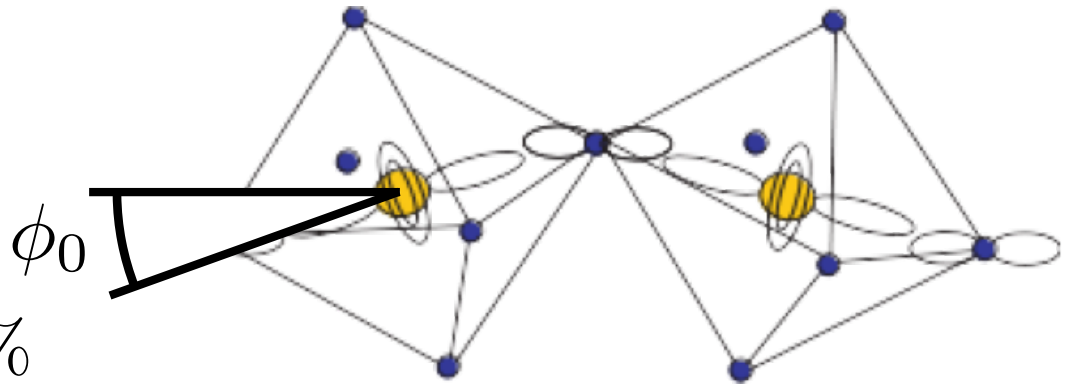
Magnetic transition temperature of $Ln_{0.7}M_{0.3}MnO_3$ varying size of the A-site cation at fixed doping

“Bandwidth control” of the Mott transition



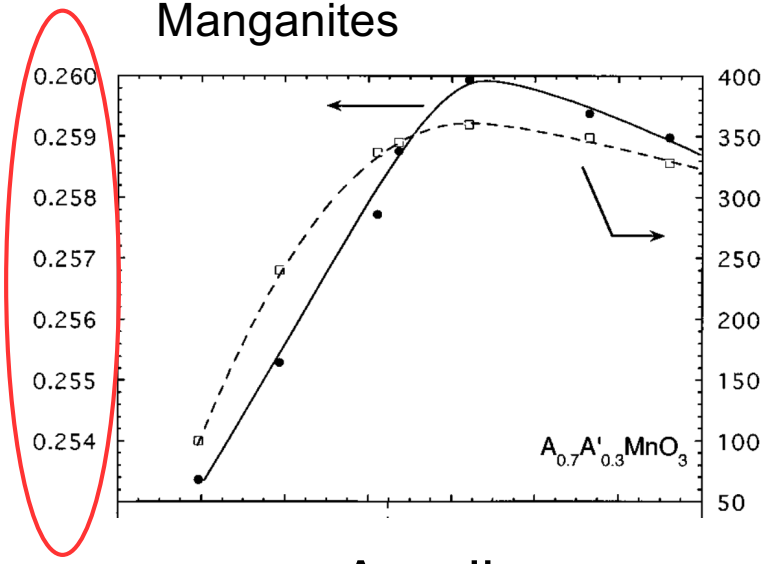
A schematic metal-insulator diagram for the filling-control (FC) and bandwidth-control (BC) 3*d* transition-metal oxides with perovskite structure. From Fujimori, 1992.

Bandwidth control



- Changes in W are $\sim 2\%$

Manganites



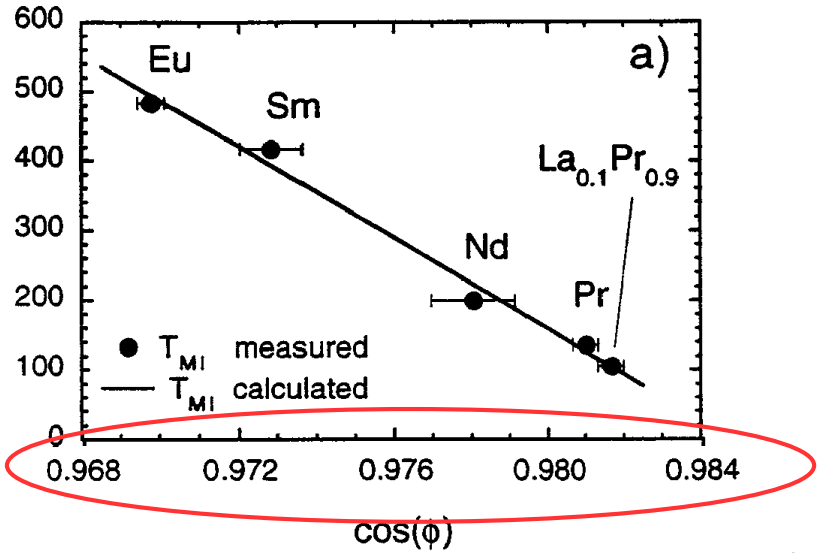
W T_c

A radius

Radaelli et al, PRL (1997)

Nickelates

T_c



Medarde et al, PRL (1998)

- Is there another mechanism that can contribute to the tilt dependence?

Outline

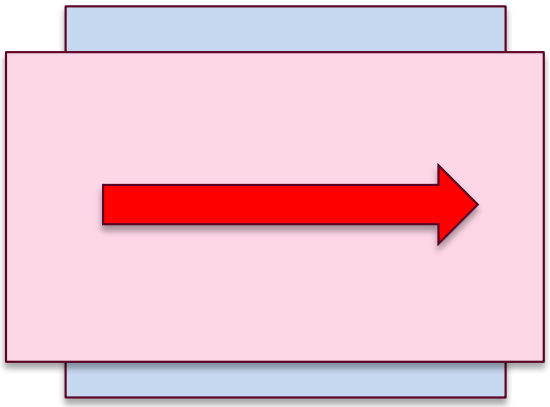
With few exceptions, all electronic phase transitions in solids are coupled to the lattice

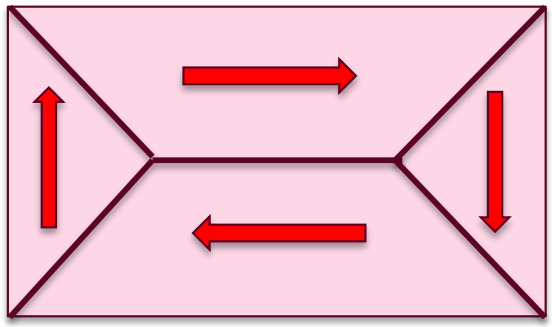
Does this matter? Yes, in principle…

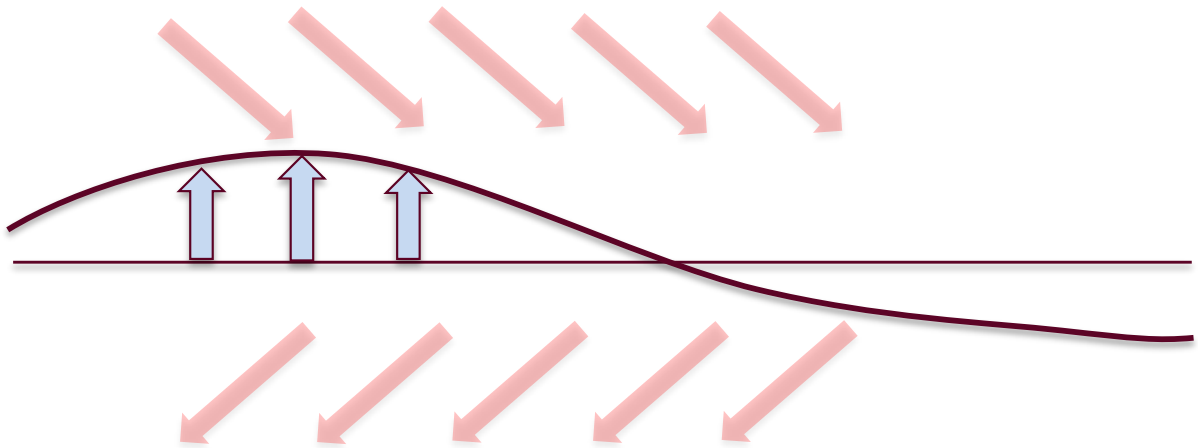
1. View from Ginzburg-Landau: Elastic interactions generate long-range couplings of the primary order parameter
   - toy example – domain walls in ferroelectrics
2. Can the strain be 'screened' by yet another coupled field
   - 'concertina' rotations
   - Cooperative Jahn-Teller in manganites
   - Mott transition in nickelates
   - revision of 'bandwidth-tuning' of the Mott transition
3. $SrTiO_3$ as a polaronic metal
   - See poster by Alex Edelman

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 ....

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

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

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

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

Elastic compatibility condition

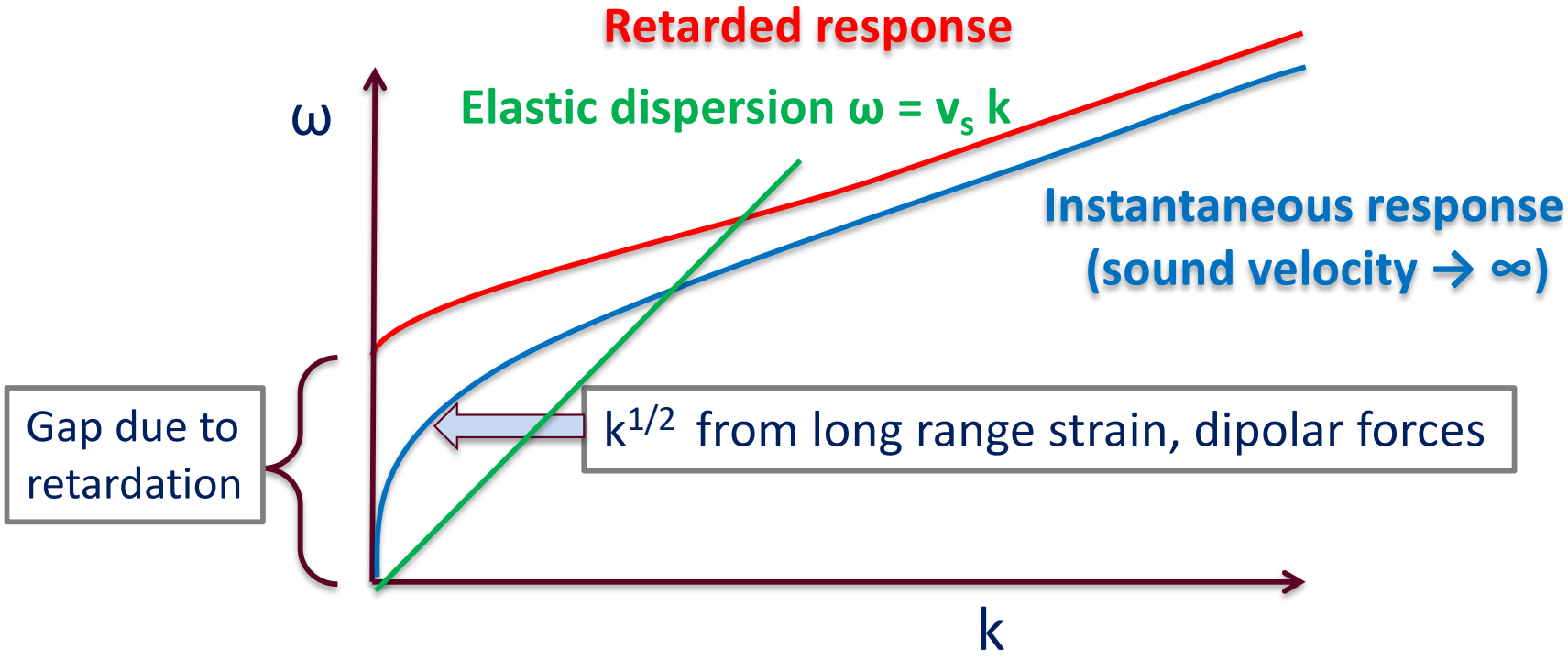
$$S = \int d\mathbf{r} \left[\gamma(\nabla \mathbf{P})^2 + r|\mathbf{P}|^2 + u|\mathbf{P}|^4 \right] - \frac{m_2}{2} \int d\mathbf{k} |\Gamma(k)|^2 H(\mathbf{k}) + \sum_{\alpha,\beta} \tilde{P}_\alpha \left(g \frac{q_\alpha q_\beta}{q^2} + h_{\alpha\beta} q_\alpha q_\beta \right) \tilde{P}_\beta$$

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

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

$\Rightarrow$ 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

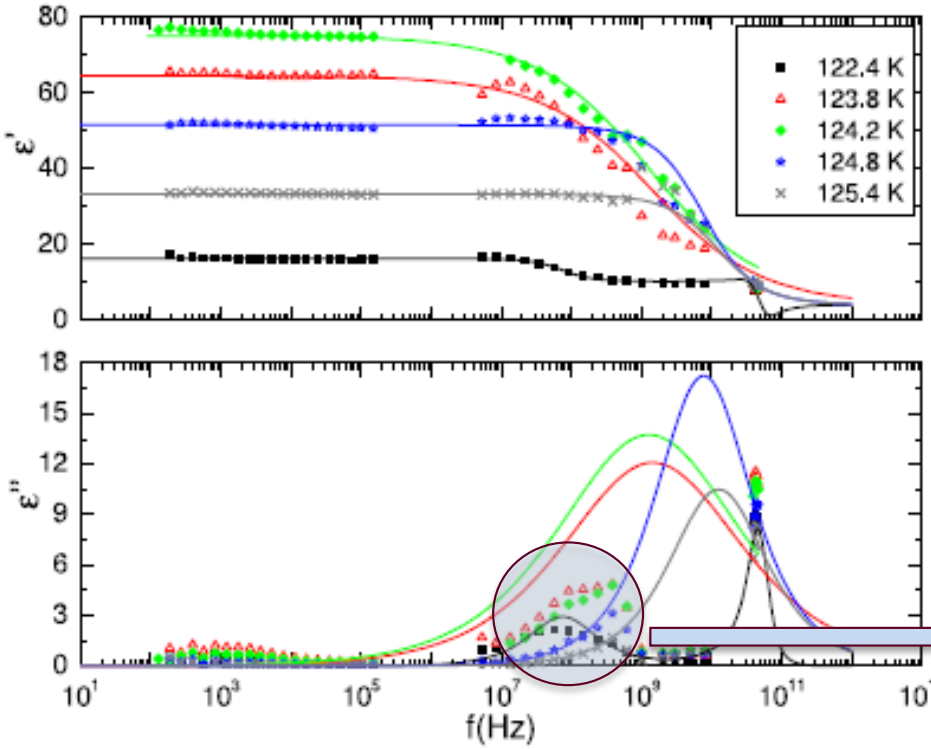
Gap magnitude ~ shift in T_c by clamping of strain

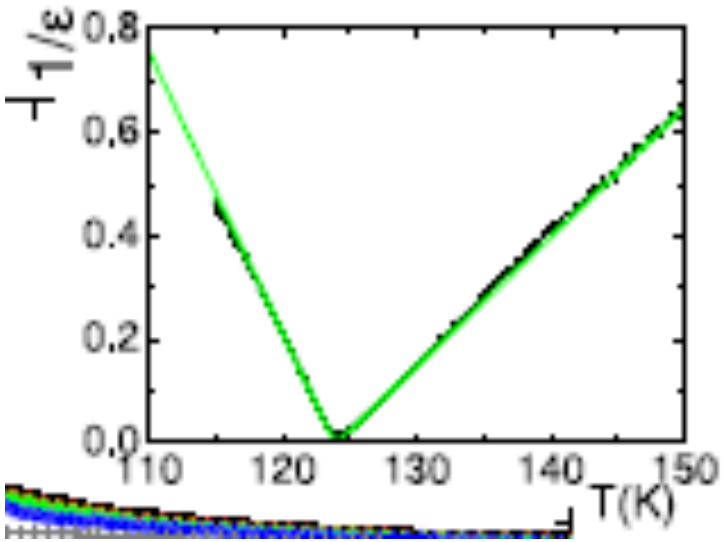
Brierley & Littlewood, *PhysRevB.89.184104 (2014)*

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





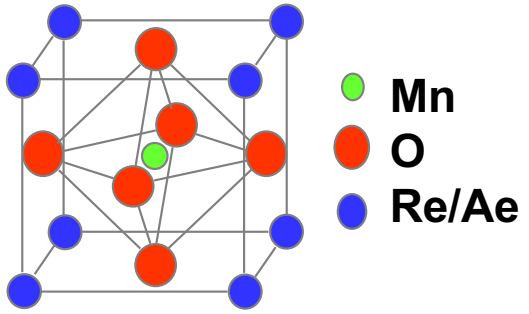
"Below T_C a strong relaxational process is observed at frequencies from 100 MHz to 1 GHz. This is almost certainly related to domain wall dynamics."

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

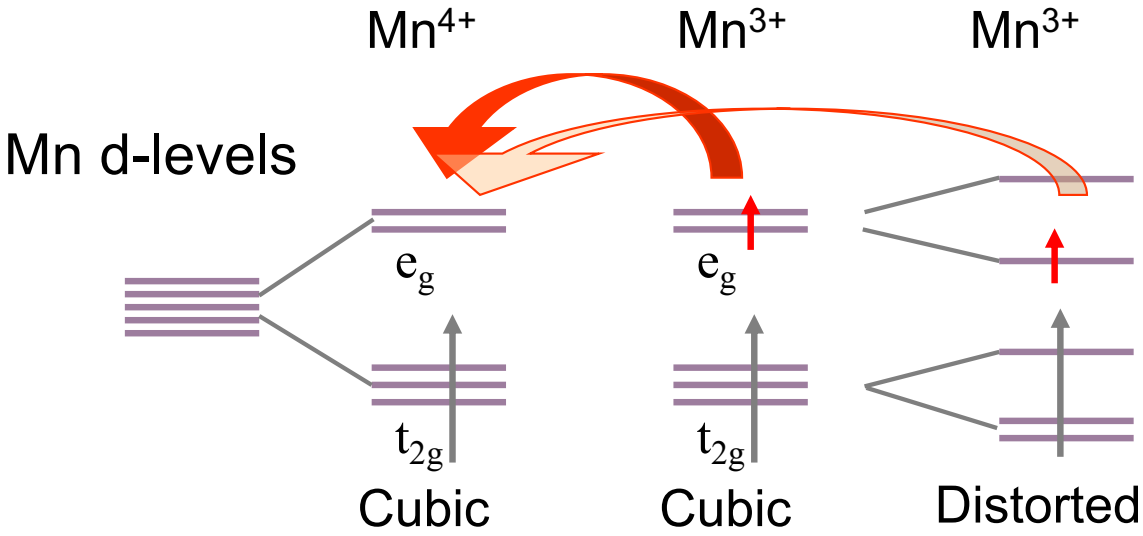
Case study: perovskite manganites and size control of colossal magnetoresistance (CMR)

Perovskite manganites

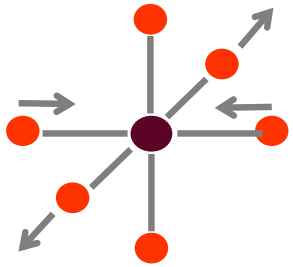
- A “doped” oxide - e.g. $La_{1-x}Ca_xMnO_3$ where the formal valence of Mn varies between Mn^{3+} and Mn^{4+}
- A “strongly correlated” electron system close to a (Mott) metal-insulator transition



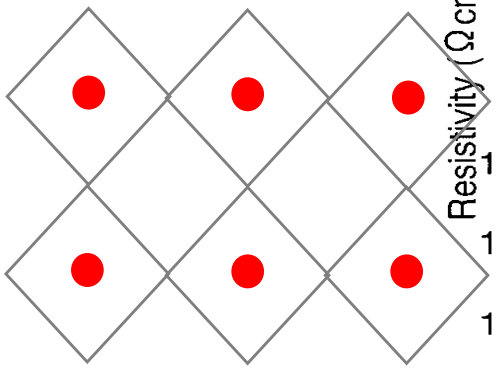
Hopping - aligns core moments and leads to ferromagnetic metal

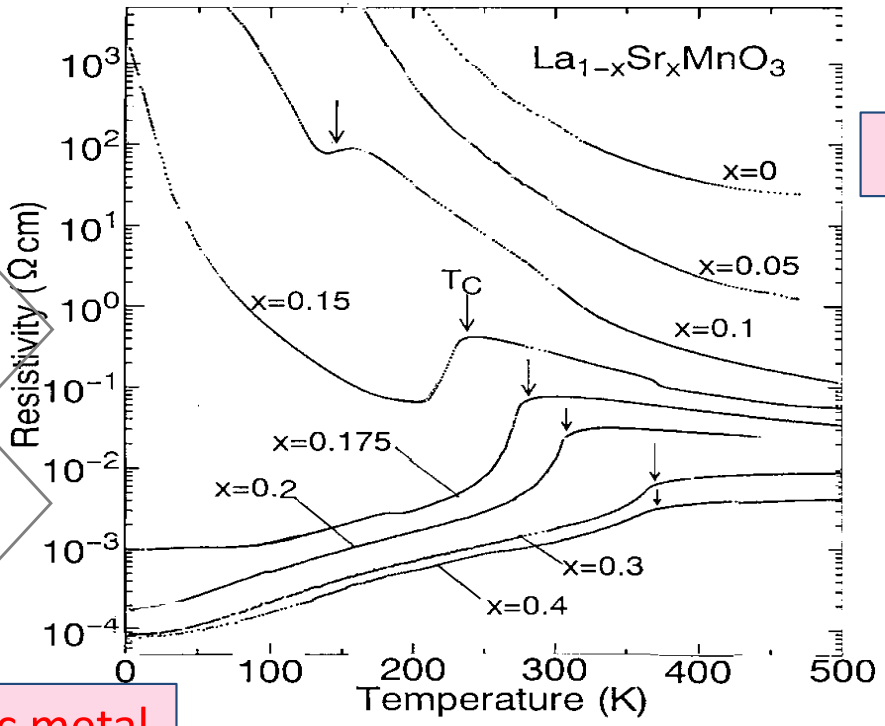


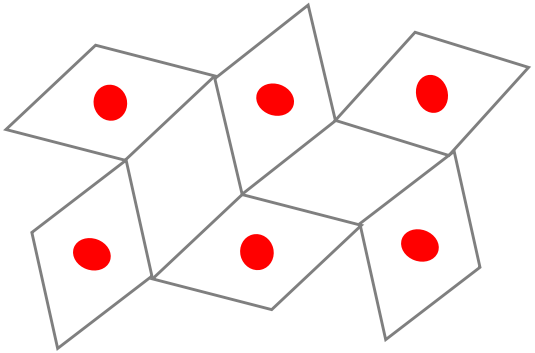
Jahn-Teller distortion suppresses hopping



Leads to insulating state with orbital and/or charge order





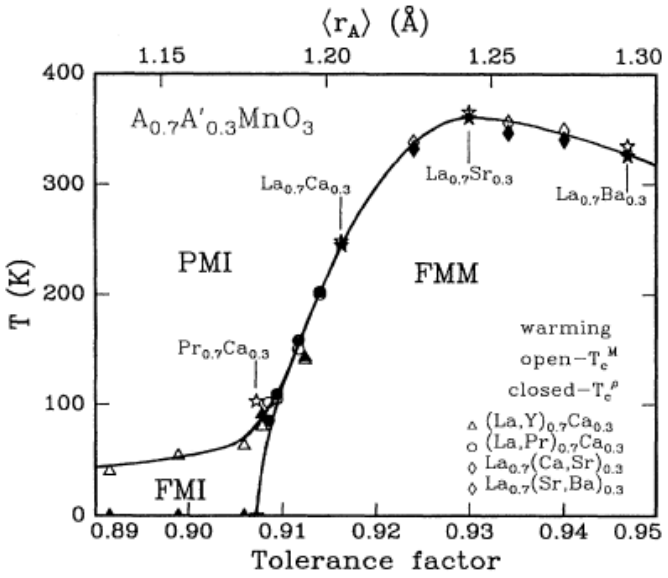


Uniform ferromagnetic metal

liquid of Jahn-Teller polarons

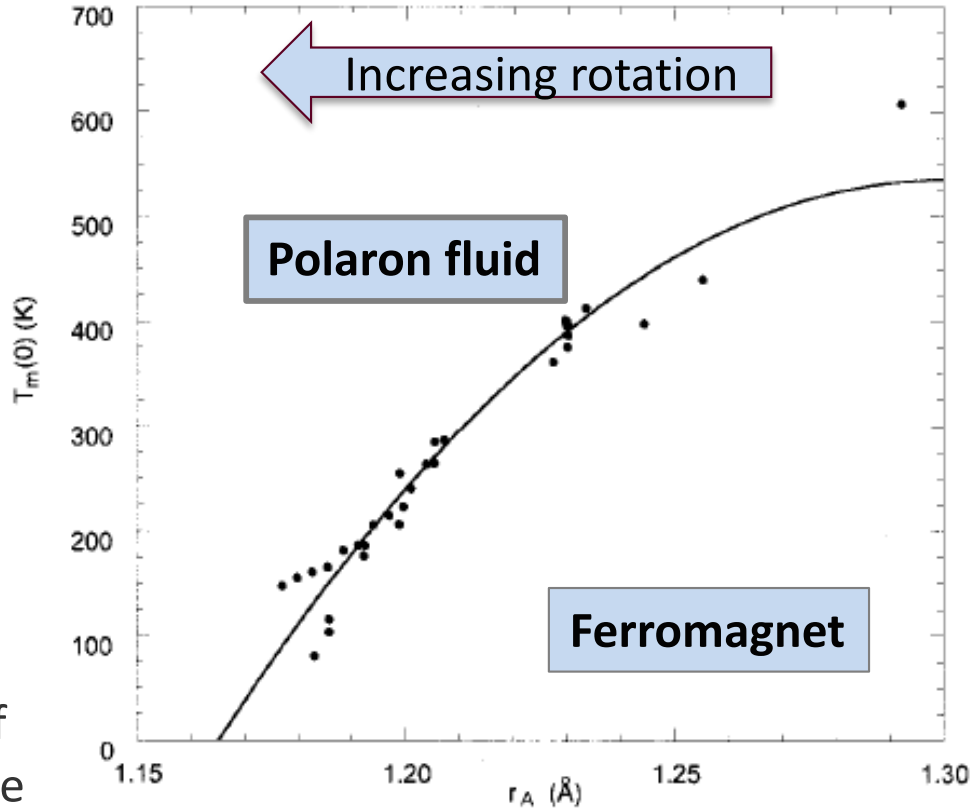
shibara et al 1995

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



Hwang et al, PRL 75, 914 (95)

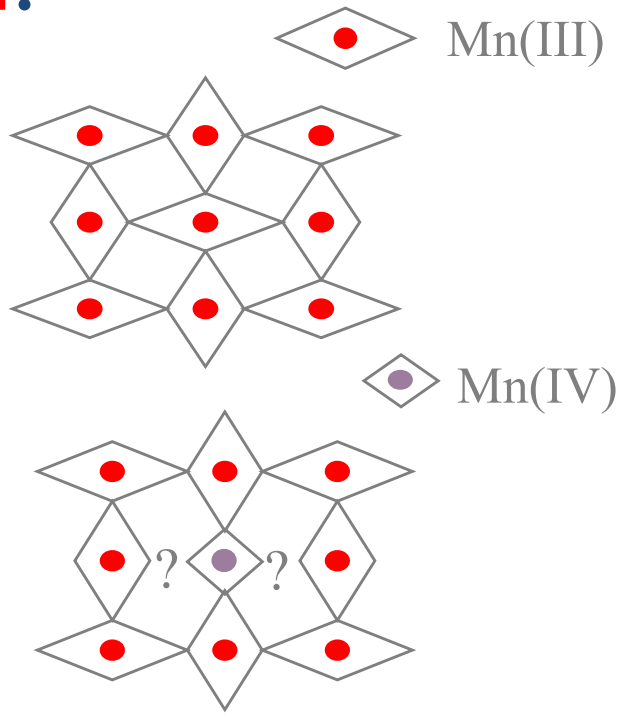
Magnetic transition temperature of $Ln_{0.7}M_{0.3}MnO_3$ varying size of the A-site cation at fixed doping

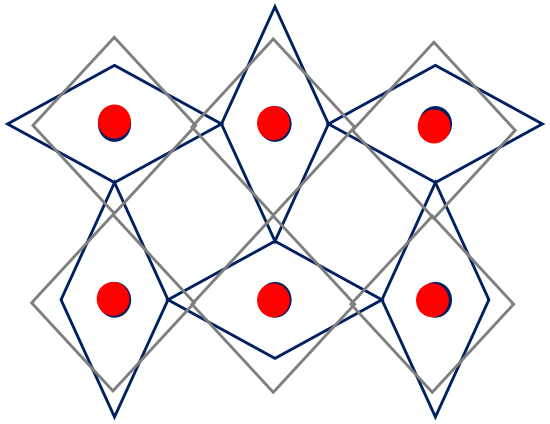


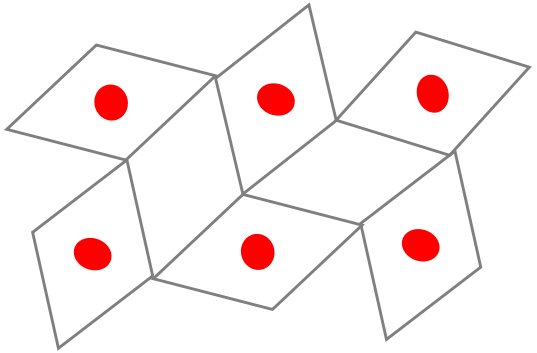
Rodriguez-Martinez and Attfield PRB 54 15622 (96)

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

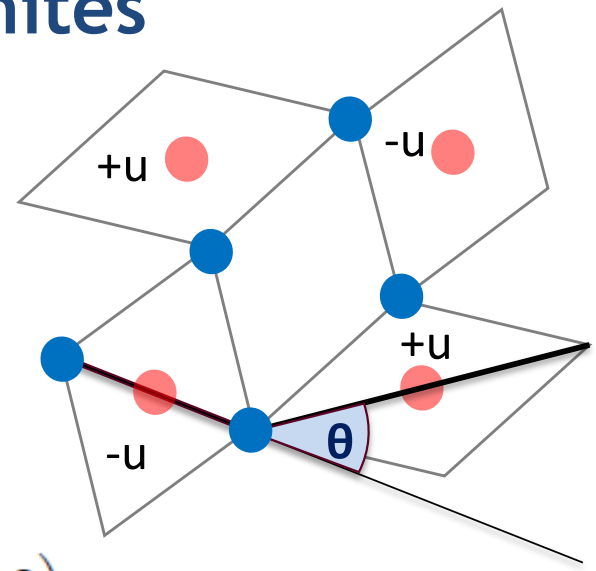






“Jamming” transition in manganites

(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



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

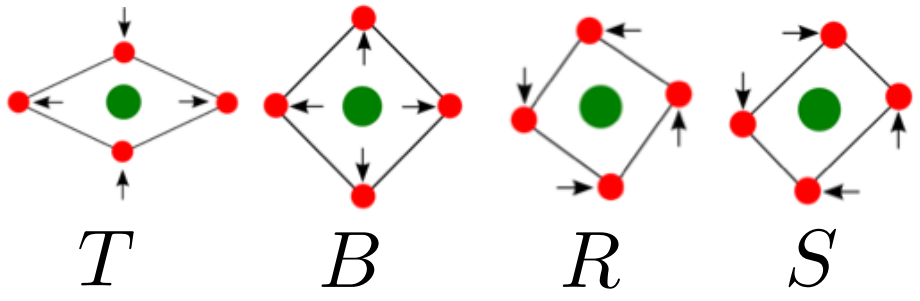
$$\phi_1 = \epsilon_{xx} + \epsilon_{yy} = \theta^2 + \frac{\partial u}{\partial x} + \frac{\partial u}{\partial y} \Longrightarrow$$ Volume strain

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

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

(linear) rigidity diverges as equilibrium rotation → 0

Microscopic theory of effective interaction



- Decompose elastic interaction into local modes

$$H = \sum_{\mathbf{k}} a_T |T_{\mathbf{k}}|^2 + a_B |B_{\mathbf{k}}|^2 + a_S |S_{\mathbf{k}}|^2$$

- Optimize with one other variable to give effective interaction
- Increase in ϕ_0 changes strength of strain interaction

$$H_{\mathrm{Ni}} = \sum_{\mathbf{k}} \left[a_B + \frac{a_S a_T (t_x^2 + t_y^2)^2}{4 a_T t_x^2 t_y^2 + a_S (t_x^2 - t_y^2)^2 + (a_T - a_S)(t_x^2 - t_y^2)^2 \sin^2 2\phi_0} \right] |B_{\mathbf{k}}|^2$$

$$H_{\mathrm{Mn}} = \sum_{\mathbf{k}} \left[a_T + \frac{a_B a_S \cos^2 2\phi_0 (t_x^2 - t_y^2)^2}{4 a_B t_x^2 t_y^2 + a_S (t_x^2 + t_y^2)^2 + a_B (t_x^2 - t_y^2)^2 \sin^2 2\phi_0} \right] |T_{\mathbf{k}}|^2$$

$V(\mathbf{k})$

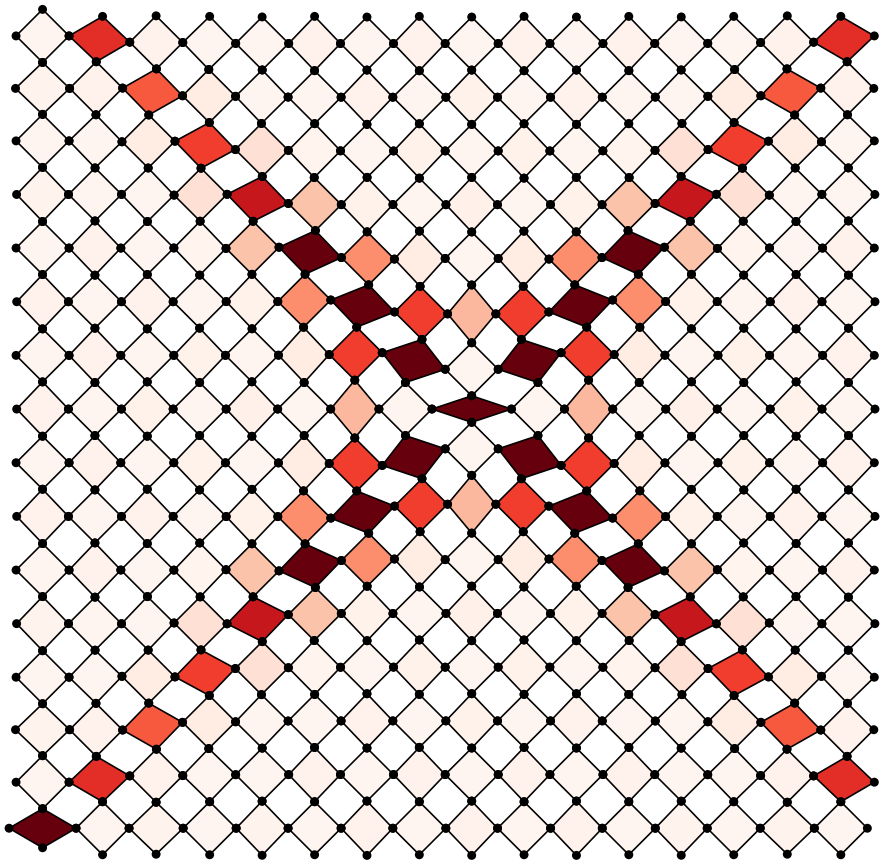
$$t_i = \tan \frac{k_i L}{2}$$

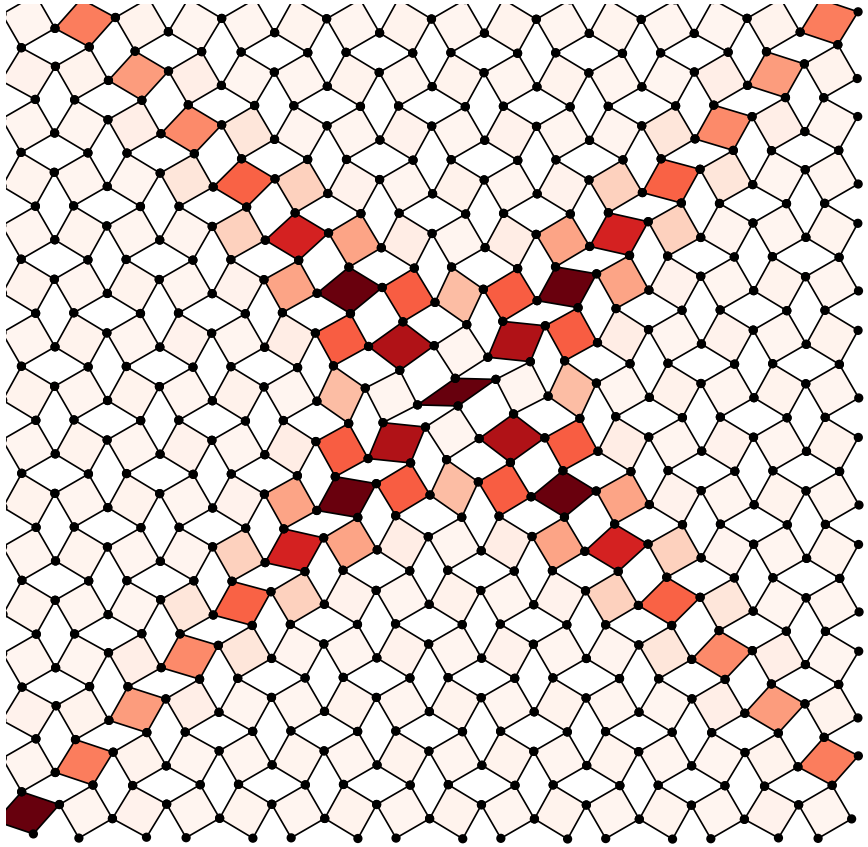
Cartoon of single Jahn-Teller polaron

$a_T = 1,\ a_S = 15,\ a_B = 10^8$

$\phi_0 = 0$

$\phi_0 = 15^o$





Model for transition

- Self-consistent phonon model

$$H = \sum_i -\kappa T_i^2 + \gamma T_i^4 + h_i T_i + \sum_{\mathbf{k}} V(\mathbf{k}) |T_{\mathbf{k}}|^2$$

- Estimate free energy variationally

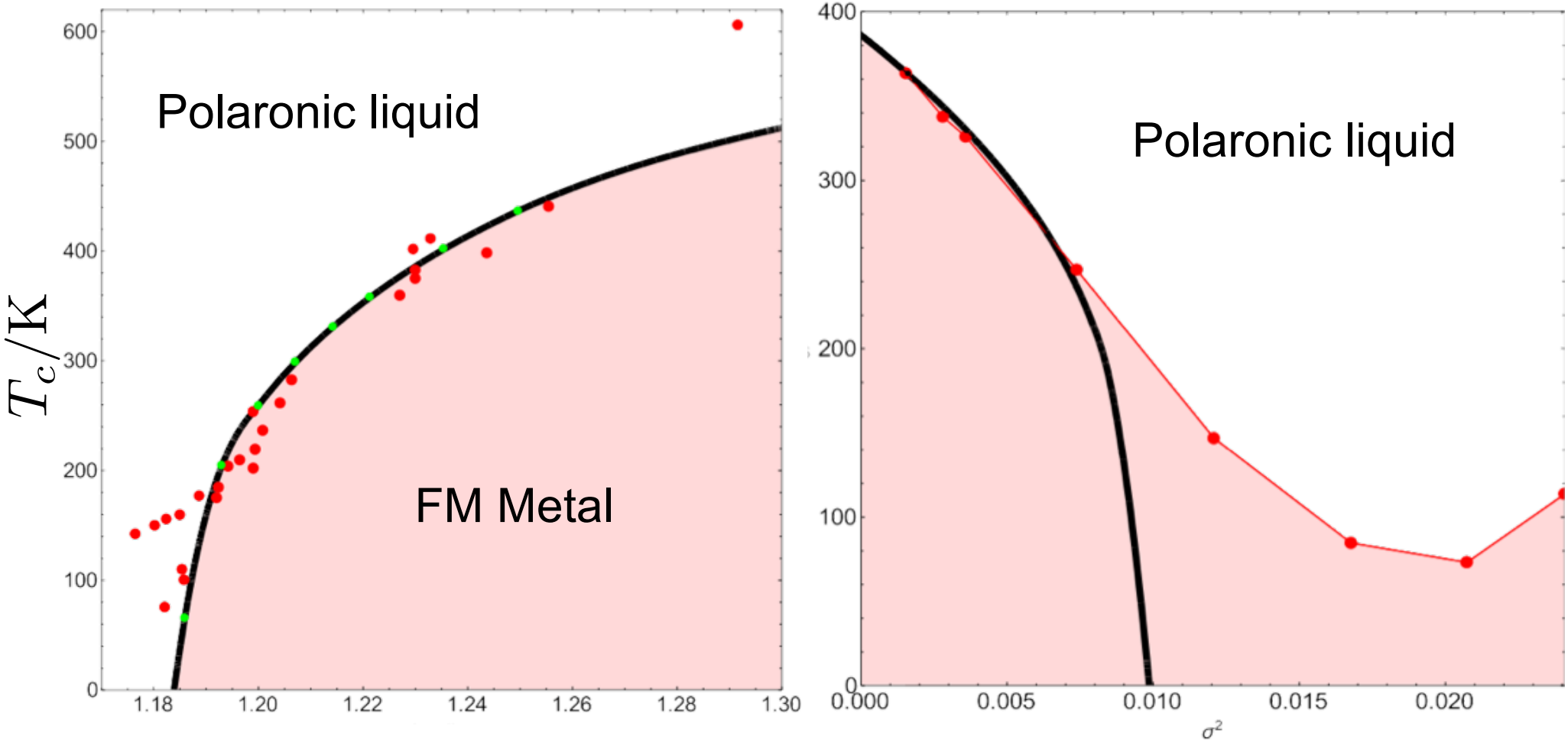
$$\overline{F}_{\mathrm{var}} = \overline{\langle H \rangle} + T \overline{\langle k_B \ln \rho_{\mathrm{var}} \rangle}$$

$$\rho_{\mathrm{var}} \propto \exp\left[-\frac{\beta}{2} \left(\sum_{\mathbf{k}} \frac{\Pi_{\mathbf{k}}^2}{2M} + \frac{1}{2M} \Omega(\mathbf{k}) |T_{\mathbf{k}}|^2 - \sum_i h_i T_i \right) \right]$$

Gillis et al, Phys. Rev. (1968)

Guzman-Verri et al, PRB (2013)

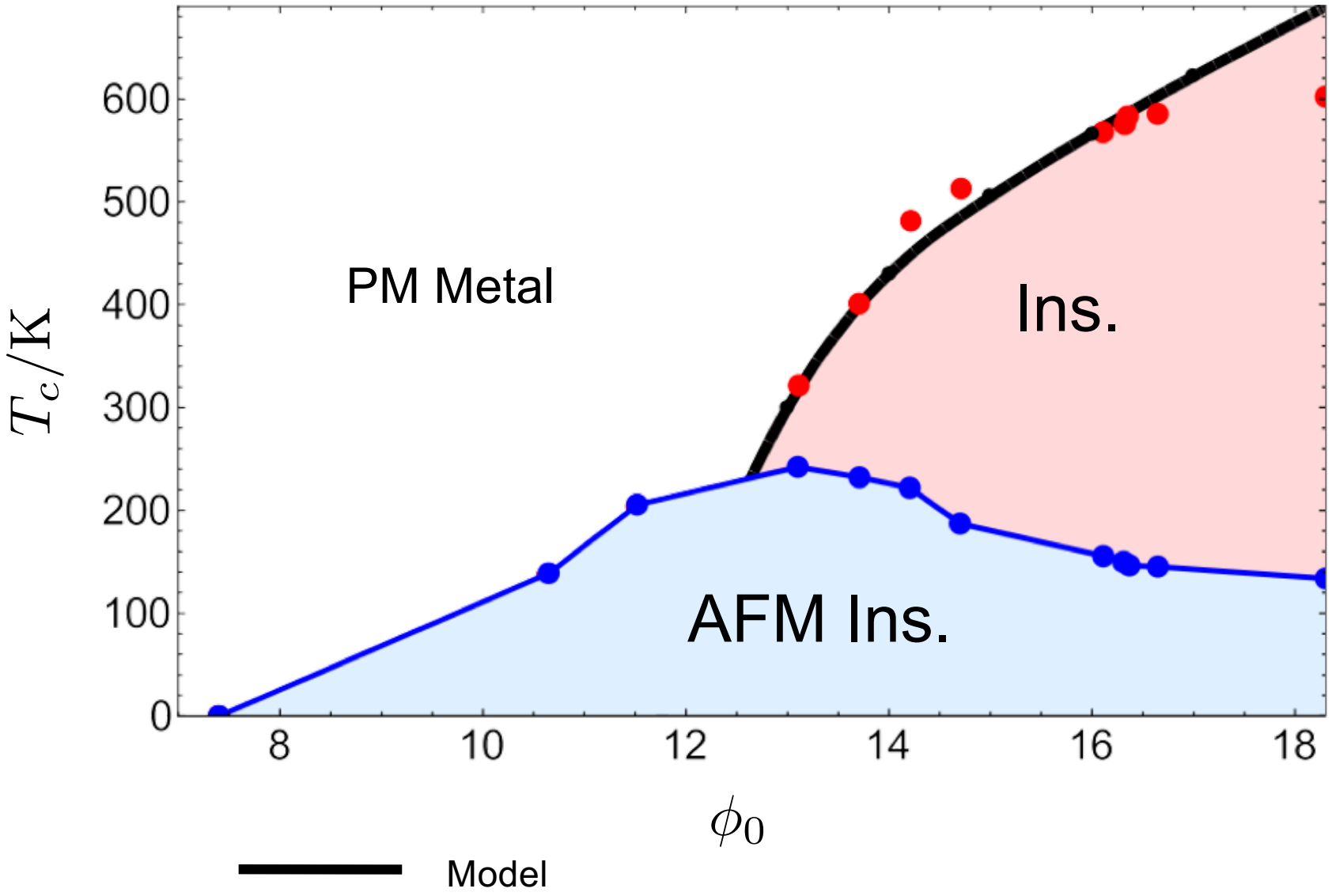
Manganites: Tc variation with both average rotation and disordered rotation



Model

Rodriguez-Martinez & Attfield, PRB (1996)

Rare-earth Nickelates $ReNiO_3$



Practical advantages – where this matters?

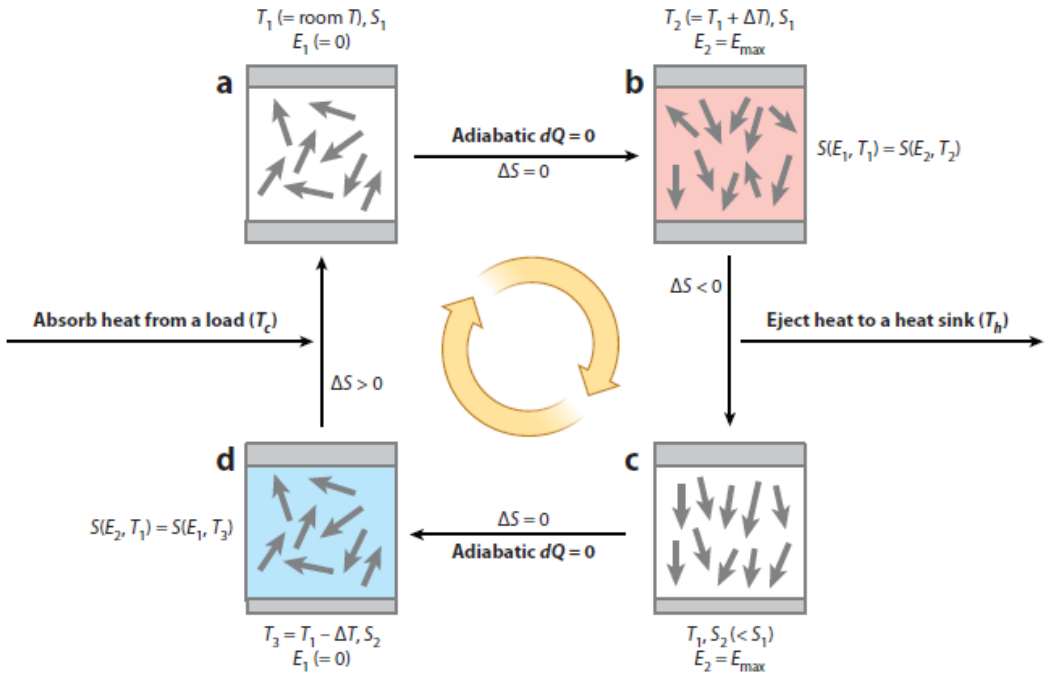
- Solid state refrigeration
- Battery electrodes
- Superconductivity

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

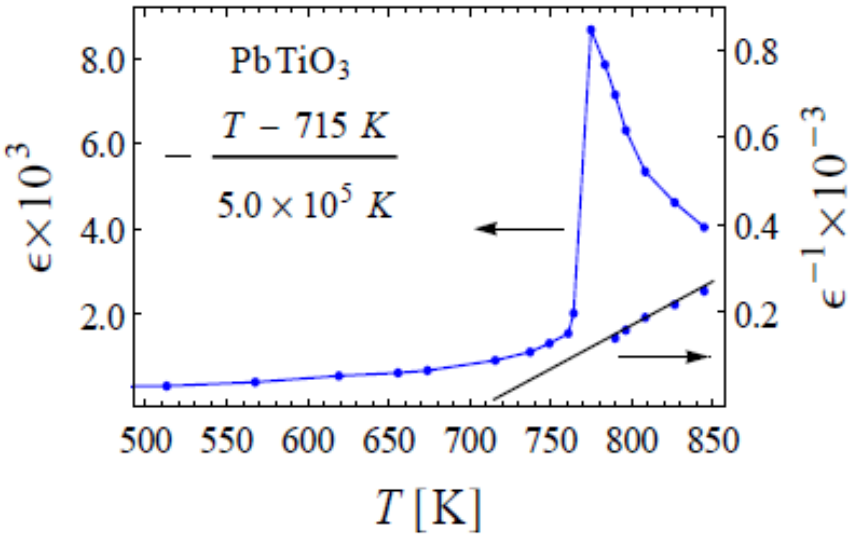


Non-equilibrium effect so needs a model

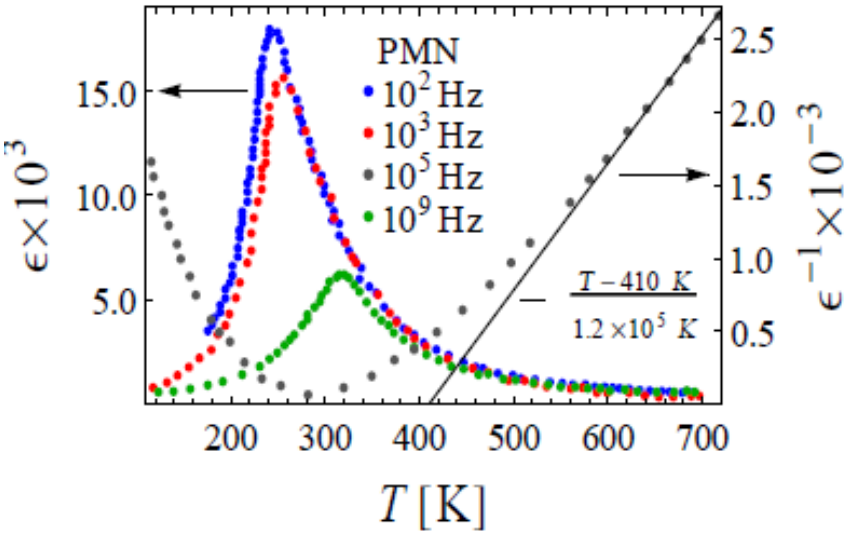
Here – relaxor dynamics from Guzman-Verri and Varma, arXiv:1212.3402

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

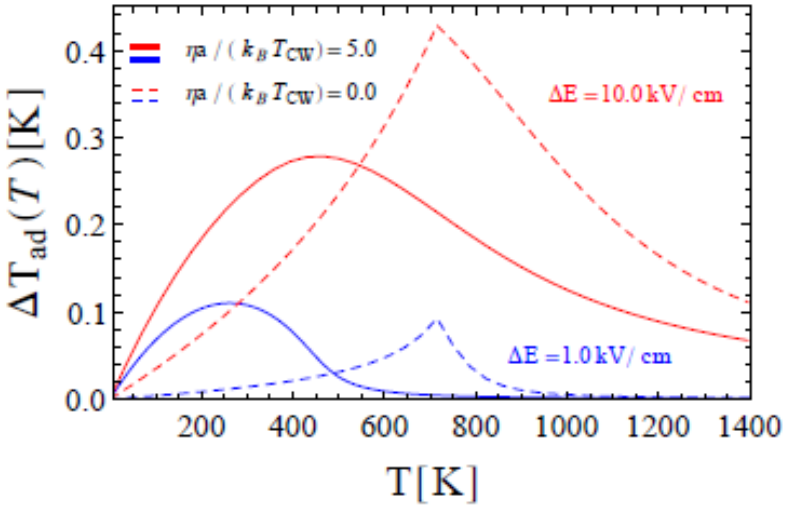
Ferroelectric



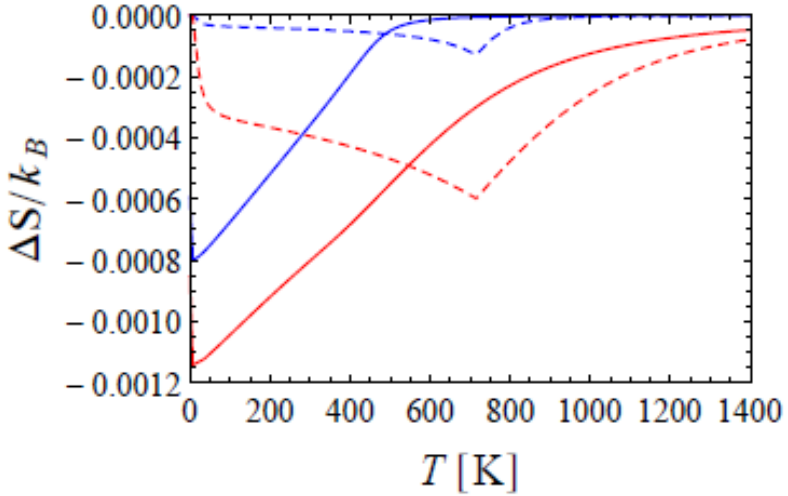
Relaxor



Adiabatic temperature change



Isothermal entropy change

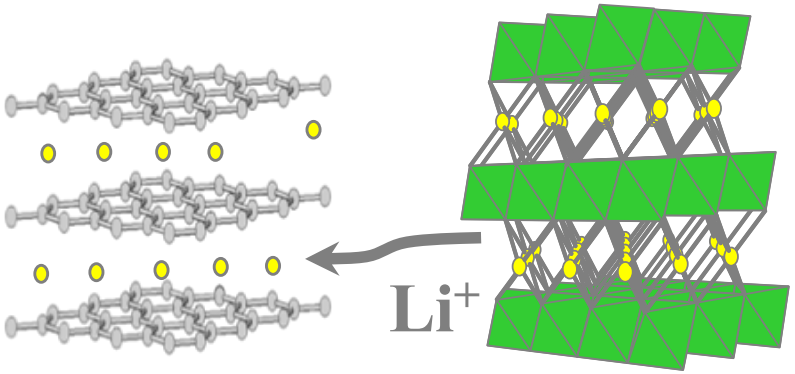


Tuning ionic mobilities in battery electrodes

Li-ion battery, commercialised by Sony in 1991

$Li_x C_6$ (anode) / $Li_{1-x} CoO_2$ (cathode)

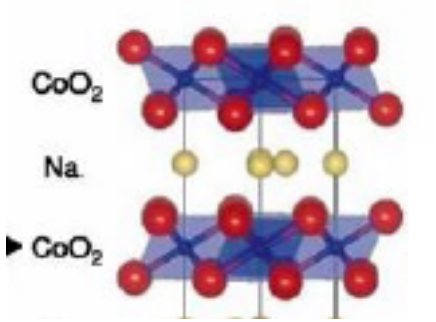
x limited to ~ 0.5

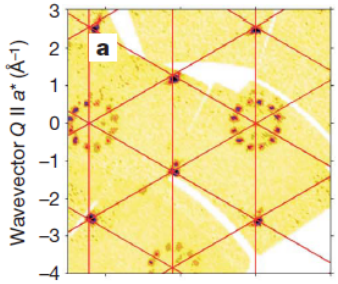


$Na_x CoO_2$

Enhanced thermopower, 5K superconductor

vacancy ordered phases

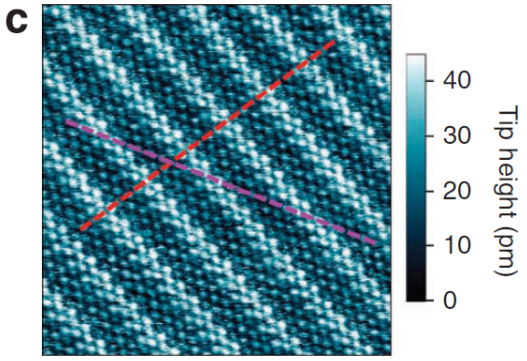


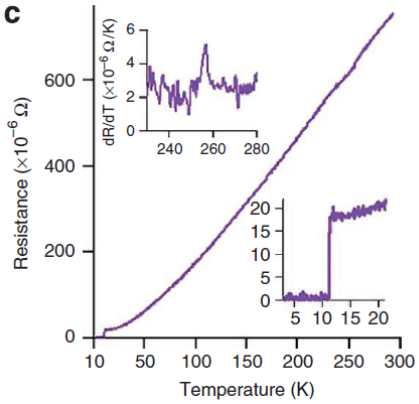


Roger et al. 2007 doi:10.1038/nature05531

CaC_6

12K superconductor; 250K CDW

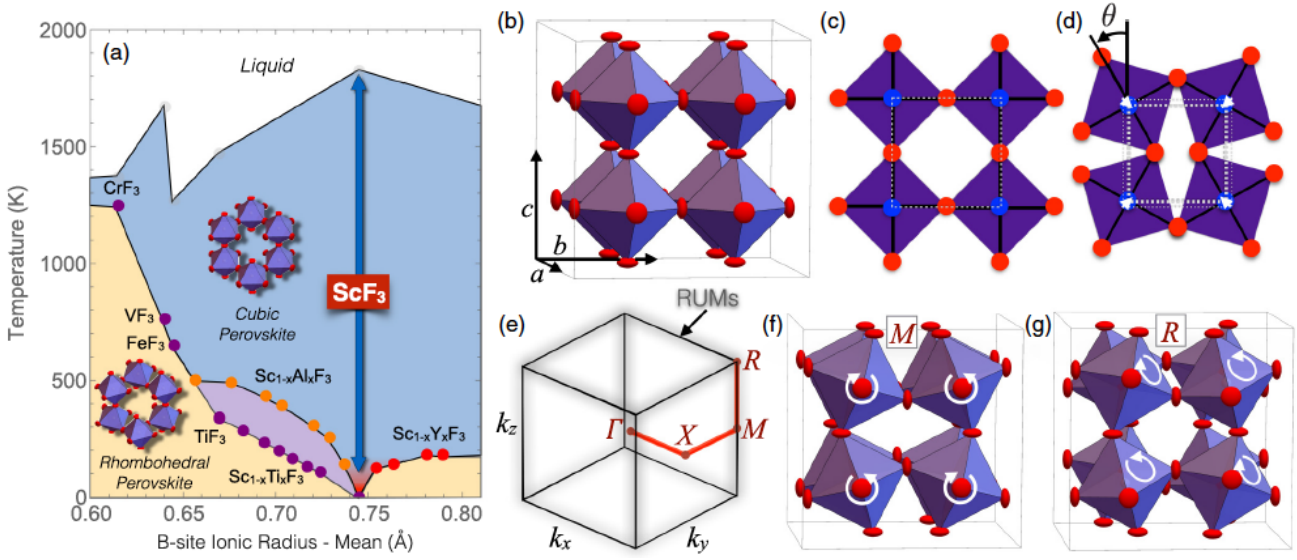


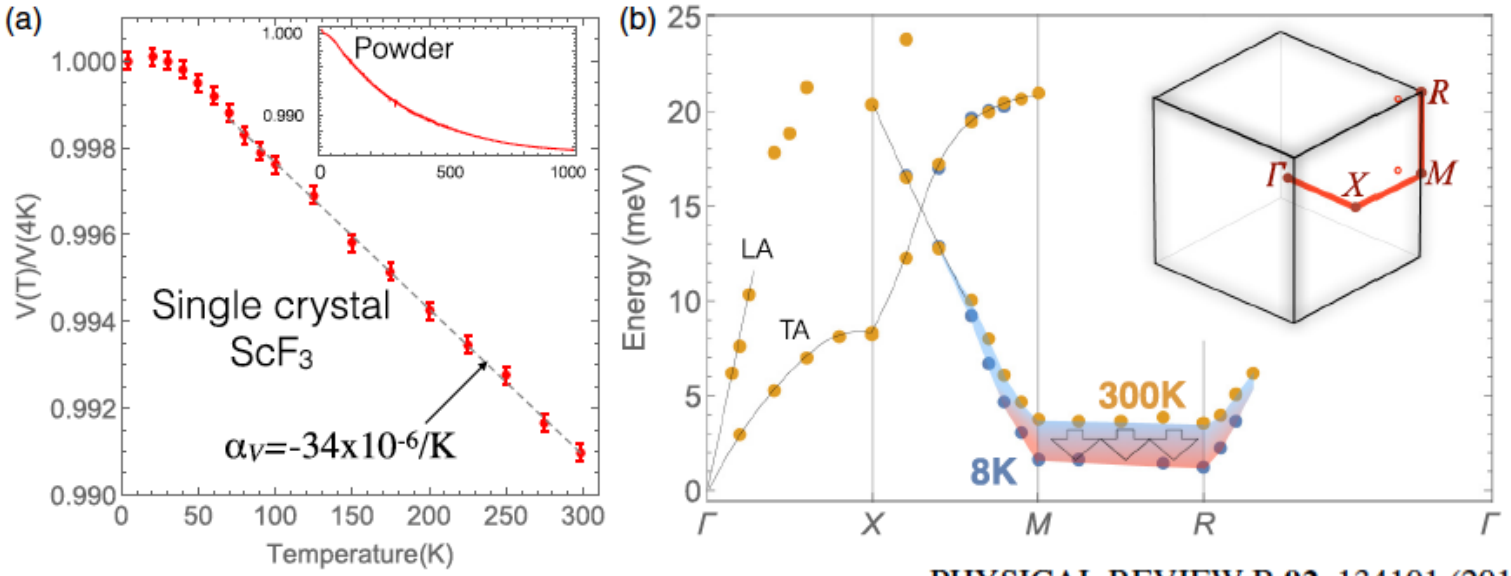


Rahnejat et al 2011 DOI: 10.1038/ncomms1574

ScF_3 - quantum criticality for phonons

Sahan U. Handunkanda,[1] Erin B. Curry,[1] Vladimir Voronov,[2] Ayman H. Said,[3] Gian G. Guzmán-Verri,[4,5]
Richard T. Brierley,[6] Peter B. Littlewood,[7,8] and Jason N. Hancock[1,*]





PHYSICAL REVIEW B 92, 134101 (2015)

ScF_3 predicted to have substantial barocaloric effect

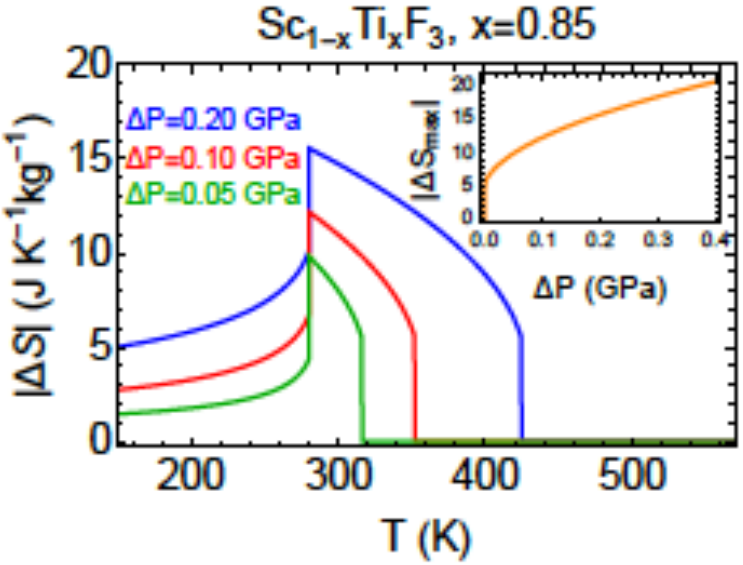


TABLE II. Transition temperatures (T_c), isothermal entropy changes (ΔS), isothermal heats ($Q = T_c\Delta S$), pressure changes (ΔP), caloric strengths ($\Delta S/\Delta P$), refrigerant capacity (RC), and $T - P$ slope (dT_c/dP) of giant barocaloric materials.

Compound	T_c [K]	ΔS [$JK^{-1}kg^{-1}$]	Q [$kJkg^{-1}$]	ΔP [GPa]	$\frac{\Delta S}{\Delta P}$ [$JK^{-1}kg^{-1}GPa^{-1}$]	RC [Jkg^{-1}]	$\frac{dT_c}{dP}$ [$KGPa^{-1}$]	Ref.
$Ni_{49.26}Mn_{36.08}In_{14.66}$	293	24	7.0	0.26	92	120	18	28
$LaFe_{11.33}Co_{0.47}Si_{1.2}$	237	8.7	2.0	0.20	43.5	81	73	29
$(NH_4)_3MoO_3F_3$	297	55	16.3	0.5	110	5200	202	30
$Gd_5Si_2Ge_2$	270	11	2.9	0.20	55	180	32	31
$Fe_{49}Rh_{51}$	308	12.5	3.8	0.11	114	105	54	32
Mn_3GaN	285	21.6	6.2	0.09	240	125	65	33
$(NH_4)_2SO_4$	219	60	13.2	0.10	600	276	45	34
$BaTiO_3$	400	1.6	0.64	0.10	16	10	−58	35
[TPrA] [Mn(dca)$_3$]	330	35.1	11.6	0.00689	5094	62	231	36
$Sc_{1-x}Ti_xF_3$ ($x = 0.85$)	283	12	3.4	0.10	120	406	723	This work

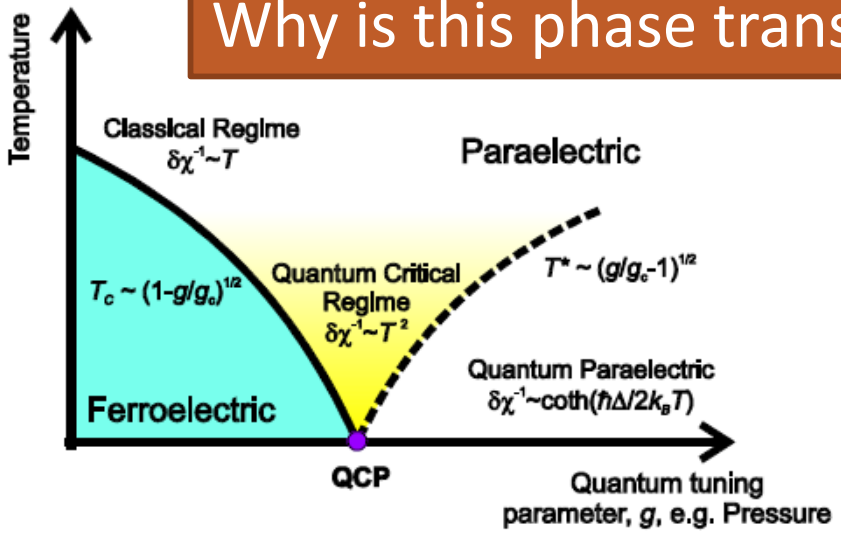
A. Corrales-Salazar, R. T. Brierley, P. B. Littlewood, G. G. Guzmán-Verri
Phys. Rev. Materials 1, 053601 (2017)

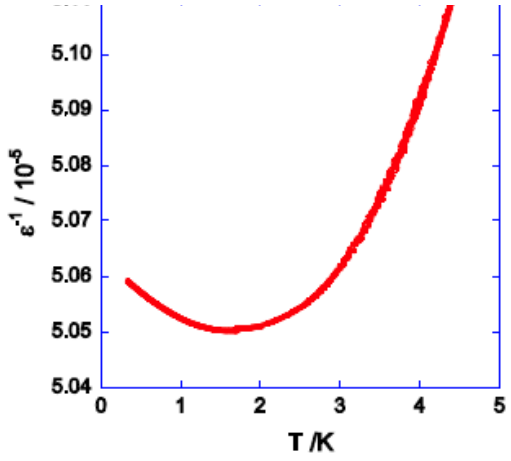
Quantum Criticality in ferroelectrics

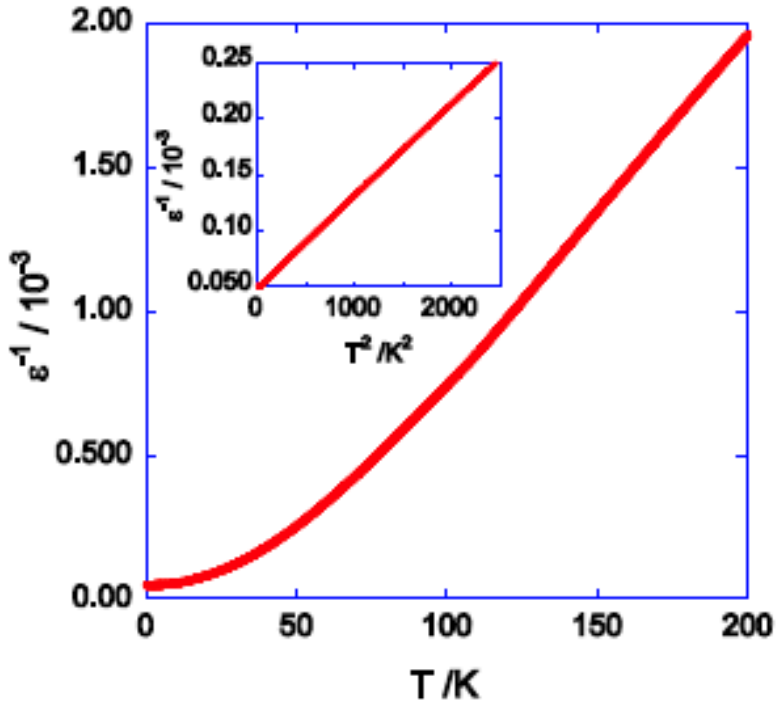
S.E. Rowley[1], L.J. Spalek[1], R.P. Smith[1], M.P.M. Dean[1], G.G. Lonzarich[1], J.F. Scott[2] and S.S. Saxena[1]

ArXiv:0903.1445

Why is this phase transition not first order?

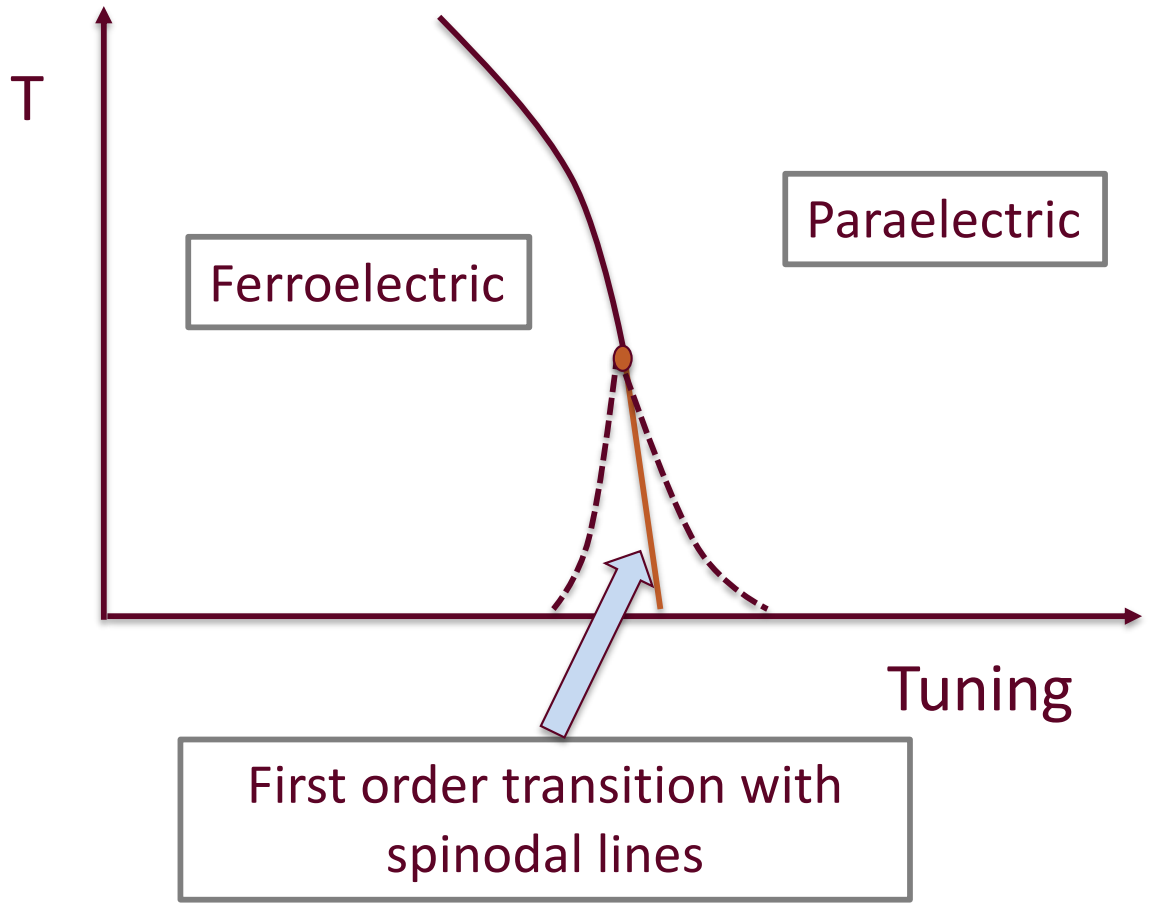






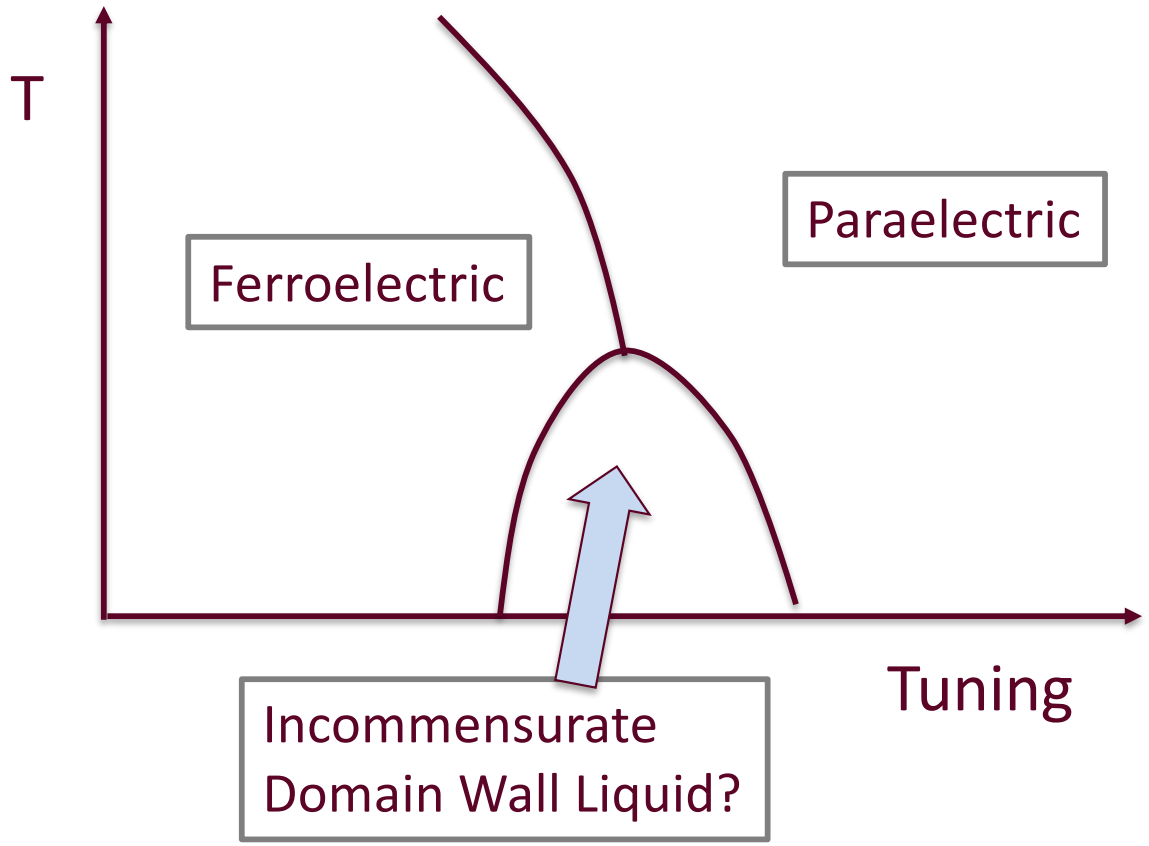
Quantum paraelectrics - possible phase diagram

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



Domain walls: instanton gas

1D strip: elastic constraints make DW parallel and particle-like
Competition between (quantum) entropy and energy cost