THE UNIVERSITY OF CHICAGO

Electronic and structural order in oxides

Cargese August 9 2022

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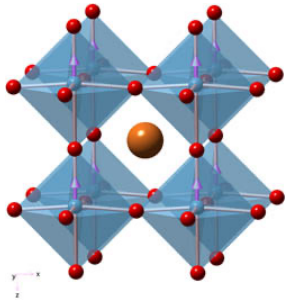
Simon Kimber (U Bourgogne)

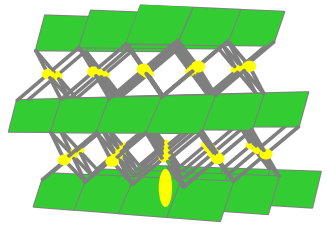
Kimber et al, arXiv:2202.05565
Guzman-Verri, Liang, PBL, arXiv:2205.14171
Guzman-Verri, Brierley, PBL, Nature 576, 429-432 (2019)

Functional materials often exploit broken symmetries induced by electronic correlations

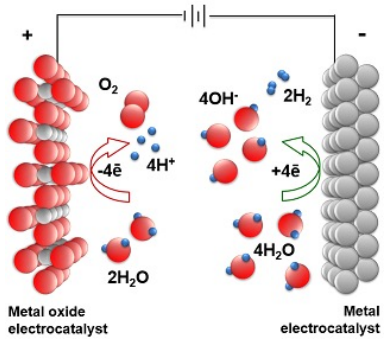
Ferroelectric memory

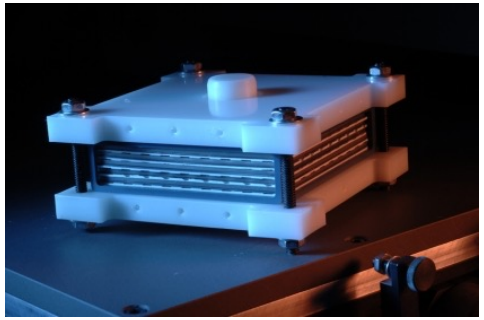


$LiMO_2$ battery cathode

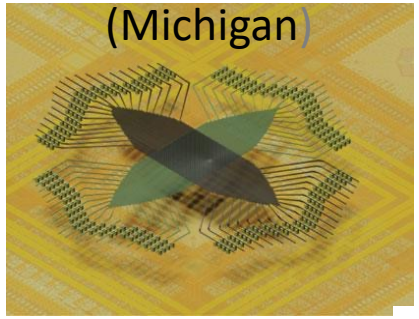


Electrocatalysis, fuel cells

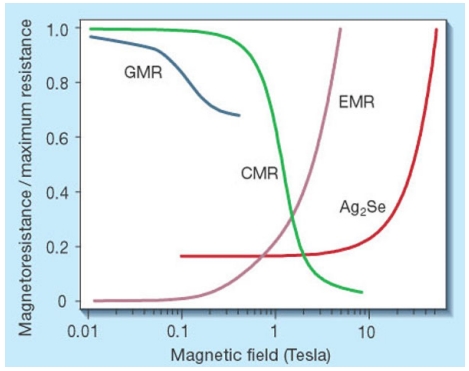




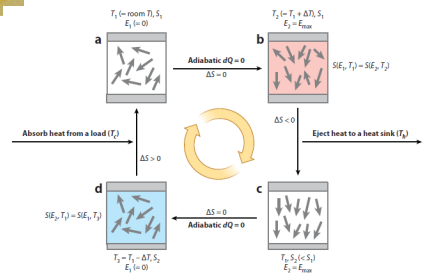
Memristor array (Michigan)



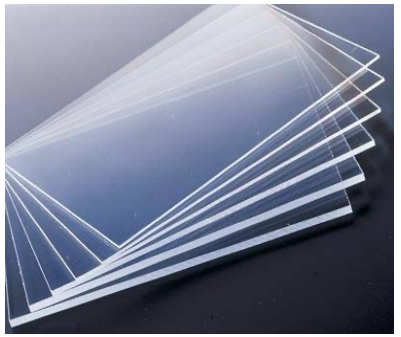
Magnetoresistive materials (Courtesy Soh, Aeppli)



Electrocalorics



Transparent conducting oxide



These are all very complicated systems

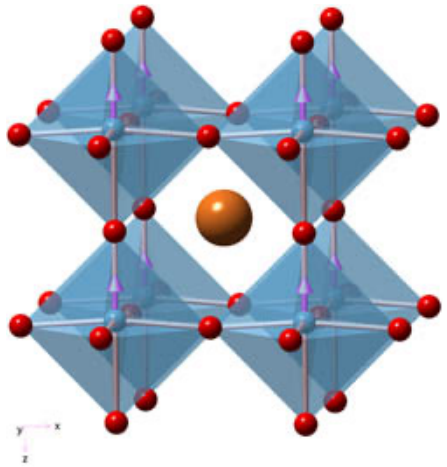
Each has their own Hamiltonian, different fluctuations, different order parameters

Anything systematic in common?

- Structural motifs
- Electronically driven phase transitions
- Tuning via chemical composition

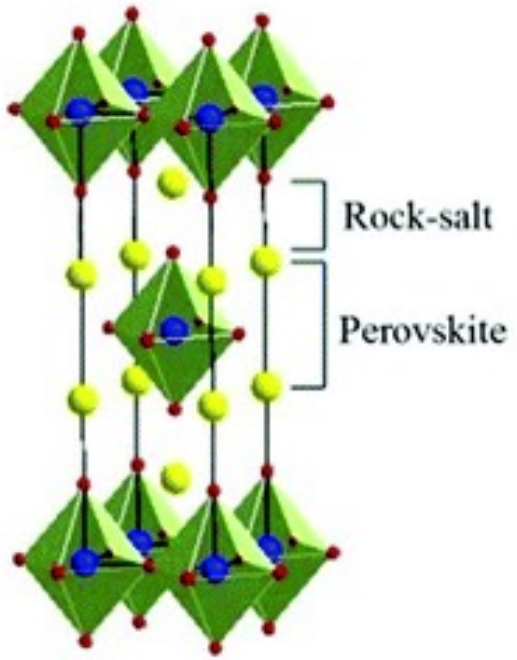
Structural motifs

Perovskite RMO_3



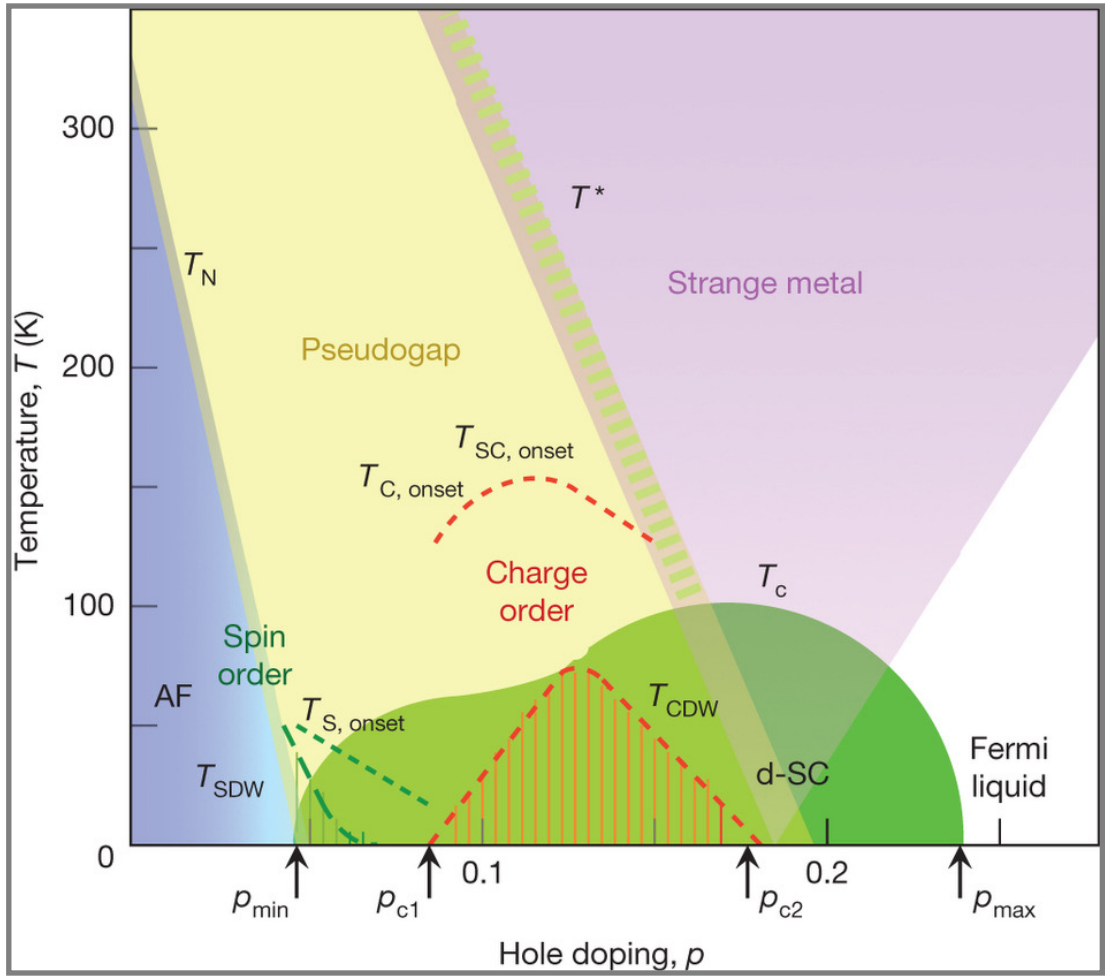
M = ‘active’ transition metal ion
R= Rare earth (3+); alkaline earth (2+); alkali (1+)

Layered RMO_4



With these simple ingredients, can mix and match superconductors, ferroelectrics, ferroelastics, ferromagnets, antiferromagnets, charge density waves, ion-transporting compounds, photoabsorbers, catalysts, cathodes, …

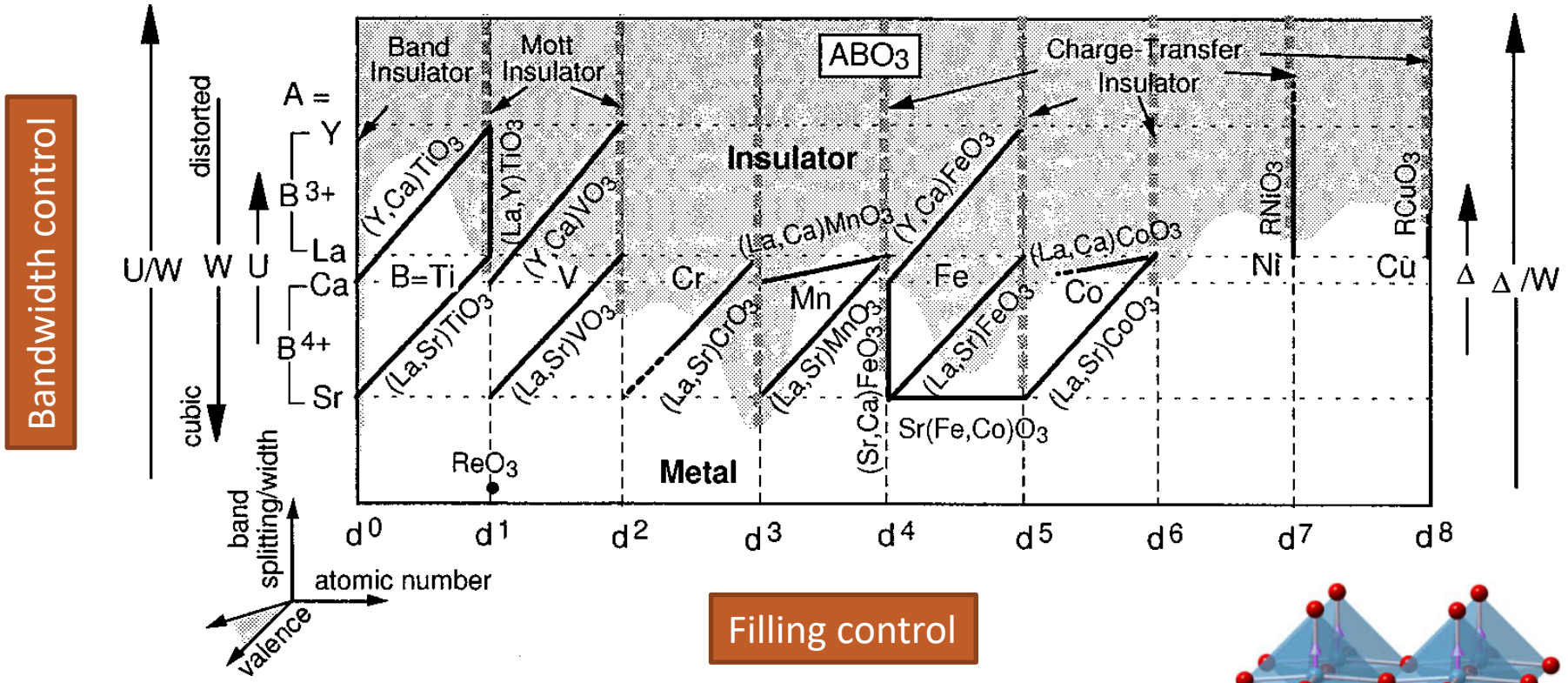
Routes to control - chemical doping - e.g. cuprate superconductors



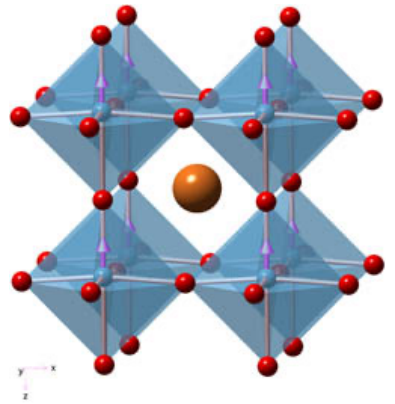
Keimer et al, Nature 518 (2015)

Control via ionic size

A= Rare Earth (3+) or Alkaline Earth (2+); B = transition metal; O = oxygen



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.



Phase transitions due to electron correlation

- 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

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

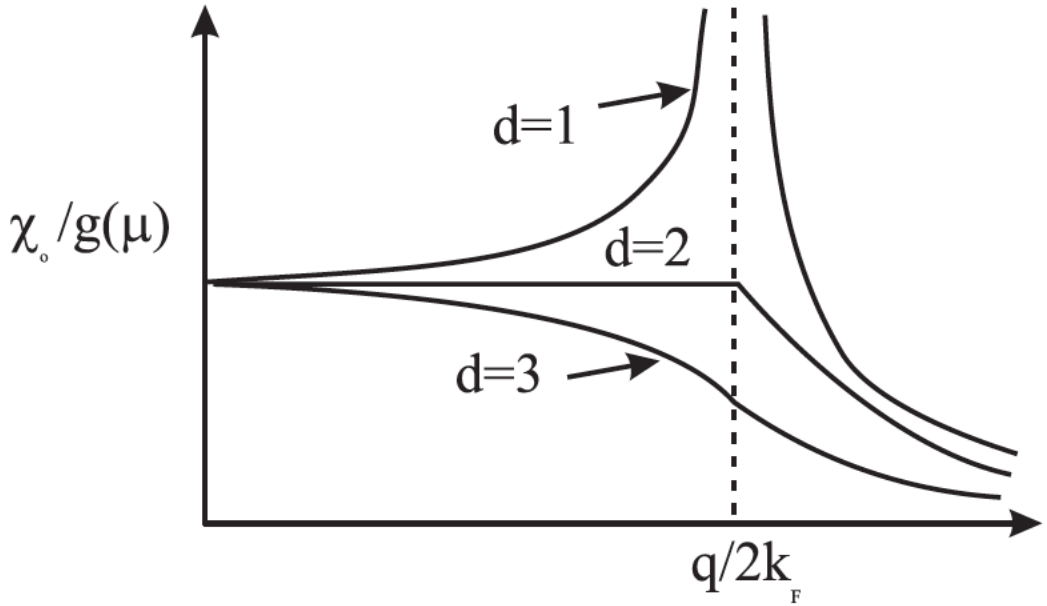
- Paradigm is the Hubbard model
  - But many possible broken symmetries, spin, orbit, lattice, charge etc.
- Central dogma is that the important parameters are all electronic
  - Ratio of interaction to bandwidth “U/W”
  - Number of carriers in the band
  - Coupling to lattice degrees of freedom is mostly irrelevant, or simply renormalizes parameters
- If the energy scales are all electronic, why isn’t T_c typically eV
  - There has to be some source of entropy that lowers T_c from electronic energy scales
  - All “Mott” transitions couple to elastic degrees of freedom.

Response function for free fermi gas

$$\delta\rho(\mathbf{q},\omega) = \chi(\mathbf{q}\omega)V(\mathbf{q},\omega) \qquad \chi_o(\mathbf{q},\omega) = \frac{\delta\rho(\mathbf{q},\omega)}{V(\mathbf{q},\omega)} = 2\sum_{k}\frac{n(\mathbf{k}) - n(\mathbf{k}+\mathbf{q})}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \hbar\omega}$$

$$\chi_{charge}(q,\omega) = \frac{\chi_0(q,\omega)}{1 + U_{charge}\,\chi_0(q,\omega)}$$

$$\chi_{spin}(q,\omega) = \frac{\chi_0(q,\omega)}{1 - U_{spin}\,\chi_0(q,\omega)}$$



Hubbard model: $U_{charge} = U_{spin} = U$
Repulsive interactions -> “spin density wave” (SDW)
Attractive interactions -> “charge density wave” (CDW)

Importance of low dimensionality – “nesting” of fermi surfaces
Implies CDW’s are always lattice-mediated – “Peierls” distortion

This is a good start but overly simplified

Weak to strong coupling in the Hubbard model with one electron per atom

$$\chi_\sigma(\mathbf{q},\omega) = \frac{\mu_B^2 \chi_o(\mathbf{q},\omega)}{1 - \frac{1}{2}U\chi_o(\mathbf{q},\omega)}$$

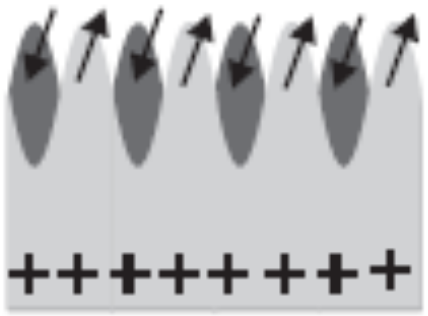
- Weak coupling: SDW at $q=2k_f$
- Intermediate coupling: SDW at $q=2k_f$;

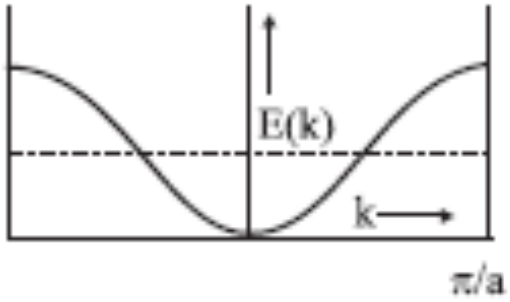
CDW at $4k_f$

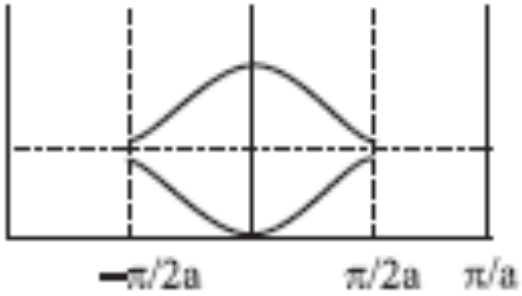
- Strong coupling

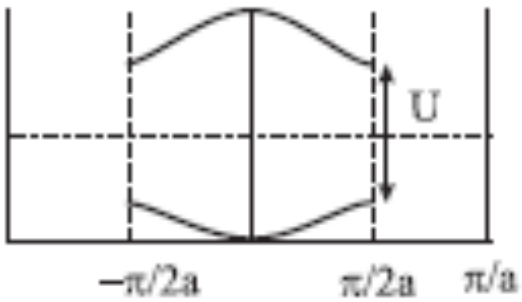
  Charge localised on site

  Spins weakly coupled by superexchange

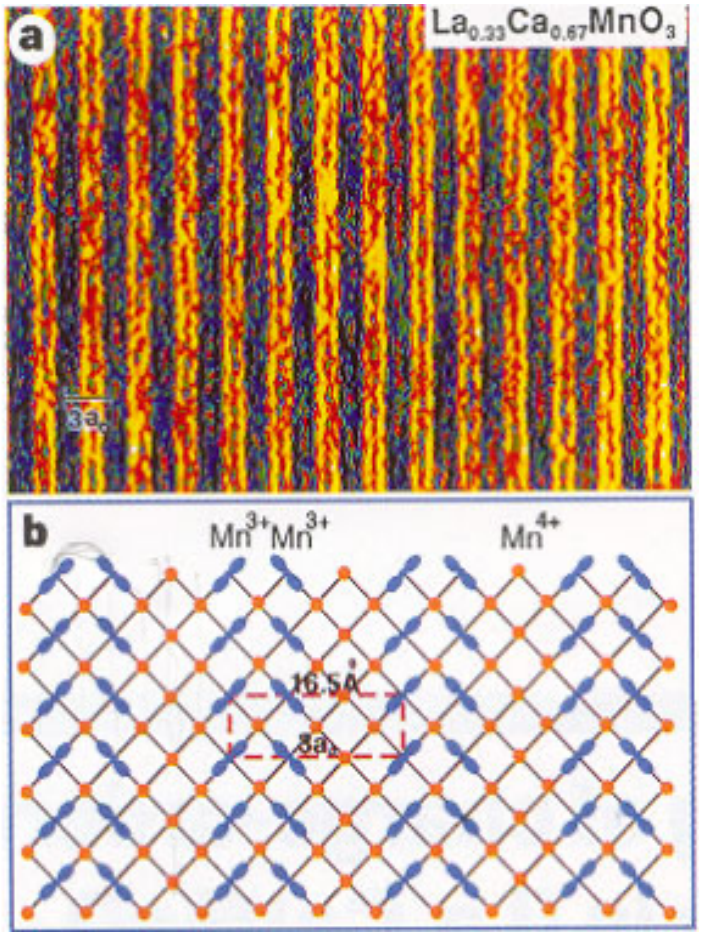








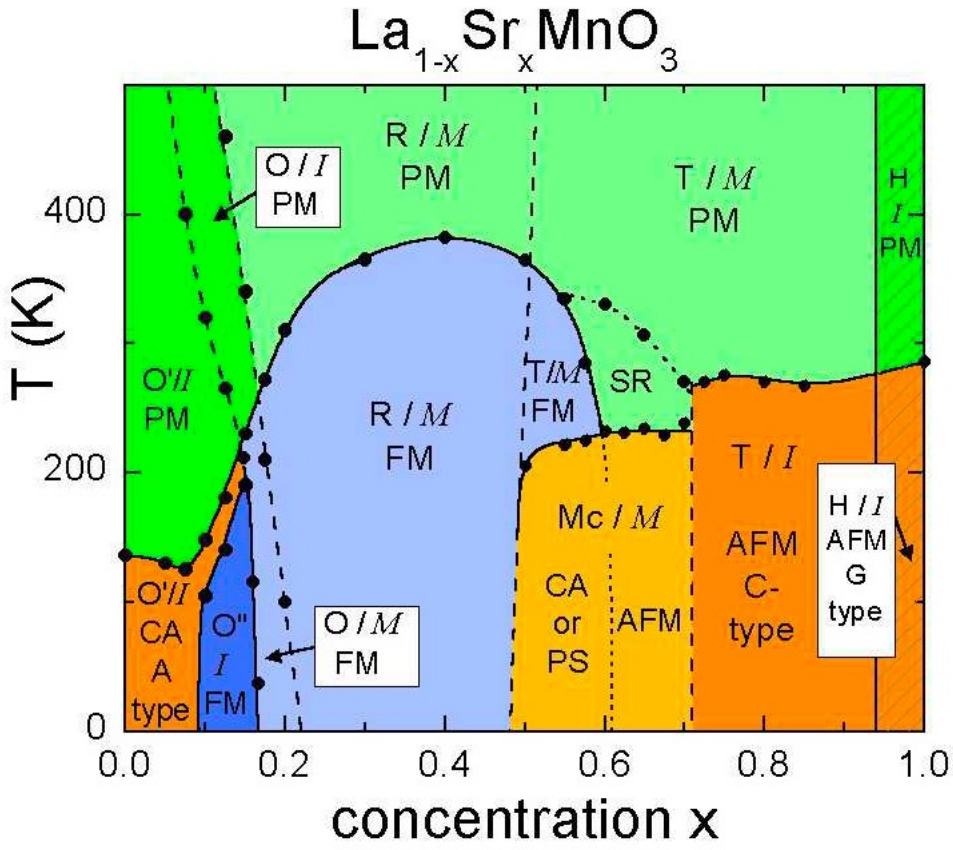
“Striped” phases of $La_{0.33}Ca_{0.67}MnO_3$



TEM image shows periodic ordered lattice

Interpreted as periodic array of 3+/4+ ions

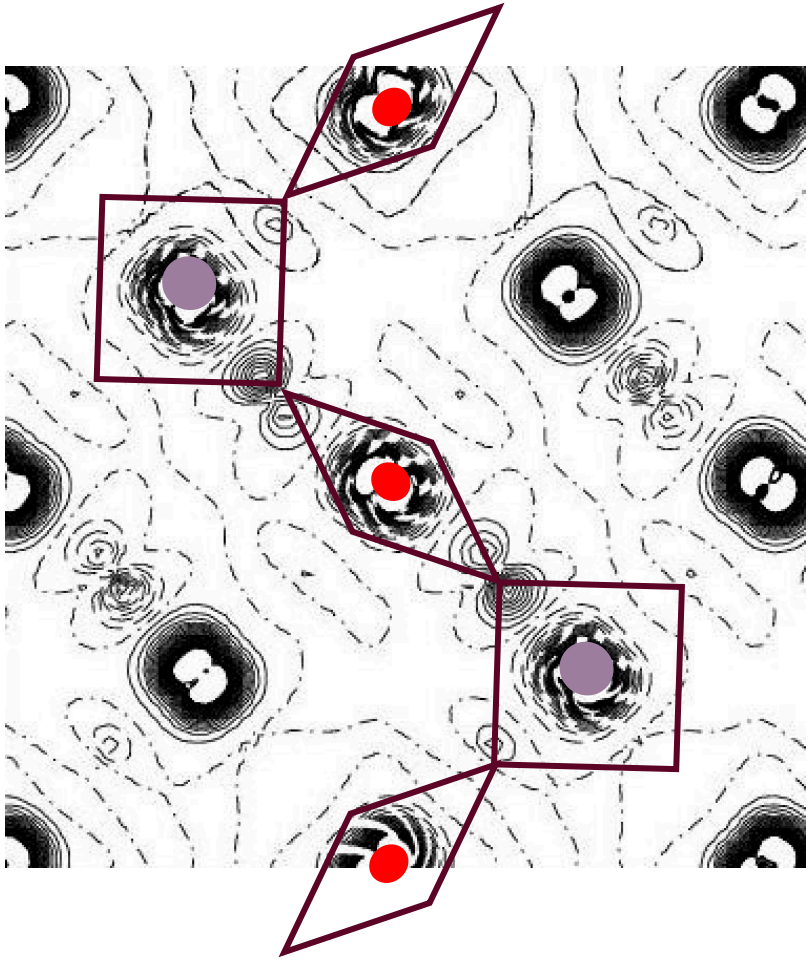
S Mori, CH Chen and S-W Cheong, Nature **392** (1998) 473

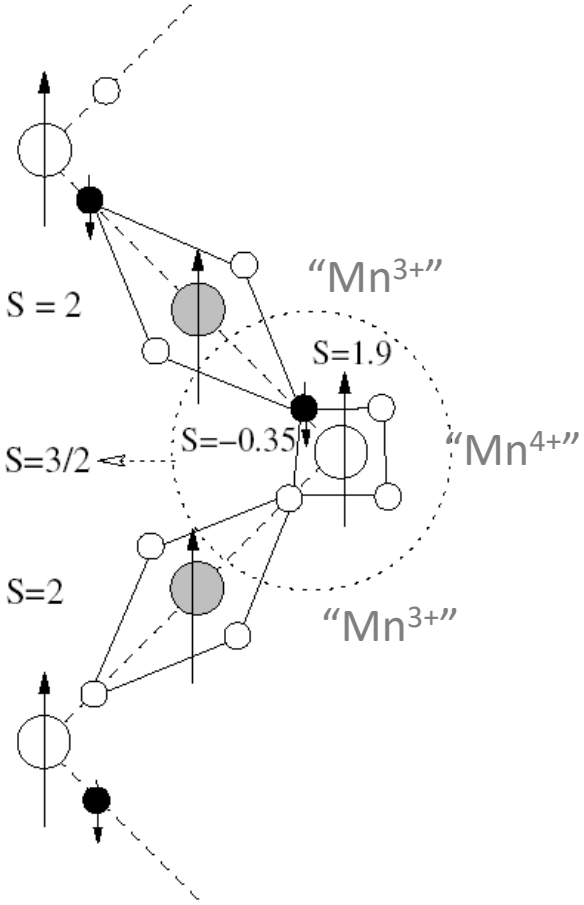


Hemberger et al Phys. Rev. B 66, 094410 (2002)

UHF spin density in $La_{0.5}Ca_{0.5}MnO_3$

V Ferrari et al, Phys. Rev. Lett. **91**, 227202 (2003)





Little true charge disproportionation – reapportionment between orbitals and screening

Strong coupling to lattice – here evident because Mn(III) is Jahn-Teller active

Why are the stripes straight? Are they always?

Message of this talk

Electronic phase transitions couple to structure at the atomic scale

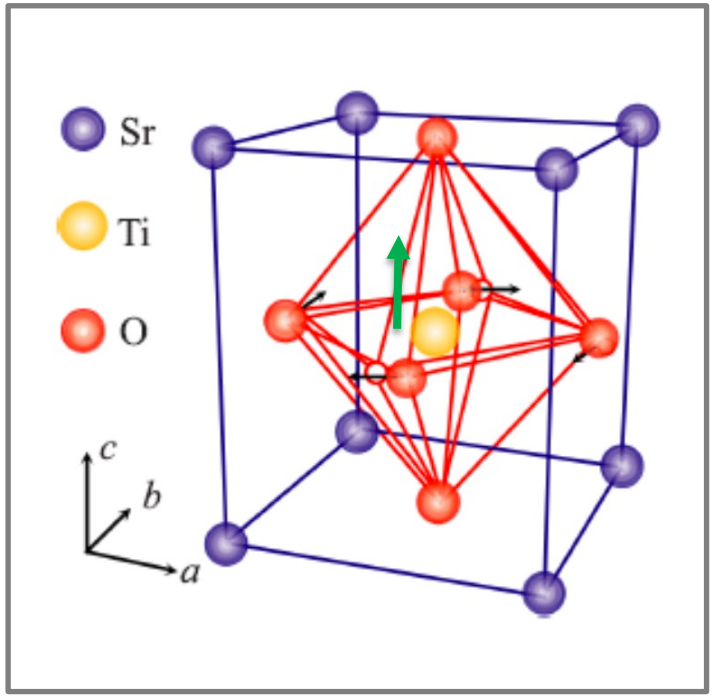
These local degrees of freedom interact via long range elastic forces

These long-range correlations profoundly change the nature of the phase transitions

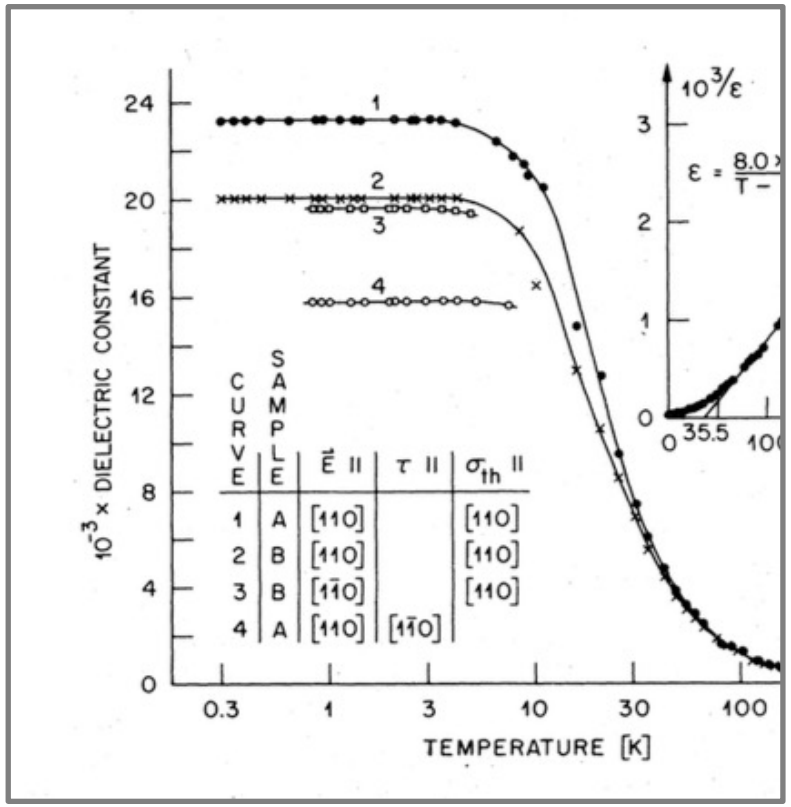
Examples

1. Dynamics of domain walls in ferroelectrics
2. Ferroelectric phase transition in GeTe
3. Tuning of phase transitions by atomic size in transition metal oxides
4. “Quantum paraelectricity” in $SrTiO_3$
5. Better batteries and refrigerators through control of strong correlation

SrTiO3 – nearly ferroelectric, very low carrier density superconductor



105K: cubic to tetragonal
37K: quantum paraelectric



Müller, PRB (1979)

Softening transverse optic phonon, Curie-law dielectric constant $\omega_{TO}^2 \propto 1/\epsilon \propto T - T_0$

Saturates below 35 K – quantum paraelectric?
Or something else?

Ferroelectricity couples to elastic strain

Primary order parameter – polarization P – couples to elastic strain ε

In a (nearly) cubic crystal

Electro-striction – εP^2

- Produces a non-linear long-range coupling between polarization fluctuations
- Macroscopic crystalline deformations at phase transition
- Expected to drive ferroelectric phase transition first-order

Flexoelectricity – ε dP/dx

- Coupling is harmonic – mixed optic (TO)/acoustic(TA) modes
- Coupling vanishes as q -> 0
- Softening TO mode hybridizes with TA – incommensurate fluctuations?

GG Verri, C Liang, PBL, unpublished

Landau theory for ferroelectric polarization *P* with electrostrictive coupling with a transition temperature T_0

$$F(P,\epsilon) = \int d^3r \left[a(T - T_0)P^2 + bP^4 + K\epsilon^2 + c\epsilon P^2 \right]$$

minimise F to eliminate strain variable ϵ gives $\epsilon \propto P^2$ and thus

$$F(P) = \int d^3r \left[a(T - T_0)P^2 + bP^4 - (K/c^2)P^2 \left\langle P^2 \right\rangle \right]$$

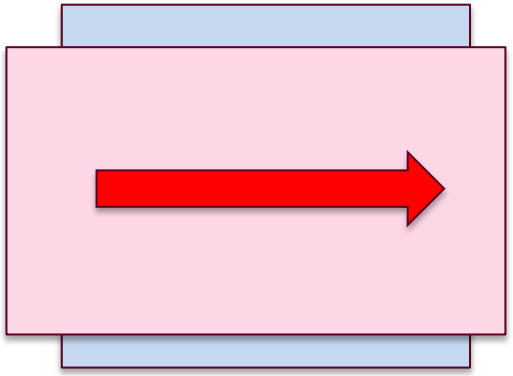
looks innocuous except the last term is infinitely long range

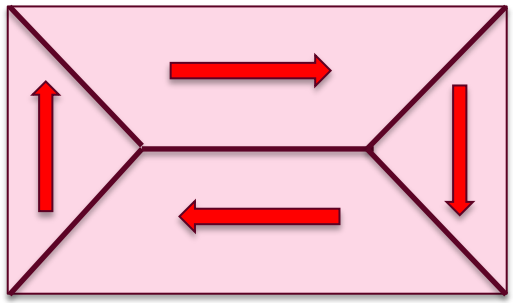
elastic strain is the metric of space and cannot be arbitrarily deformed

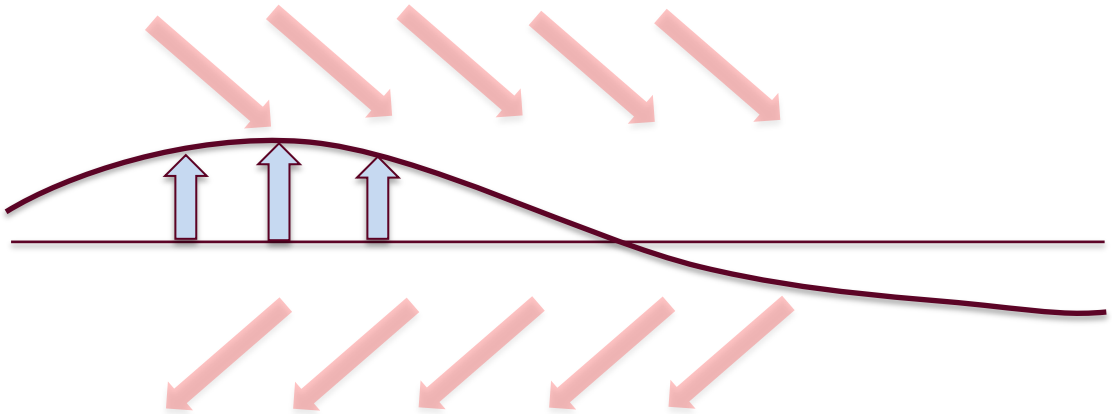
strain compatibility condition $\nabla \times (\nabla \times \epsilon)^T = 0$

Warm-up problem : a 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

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

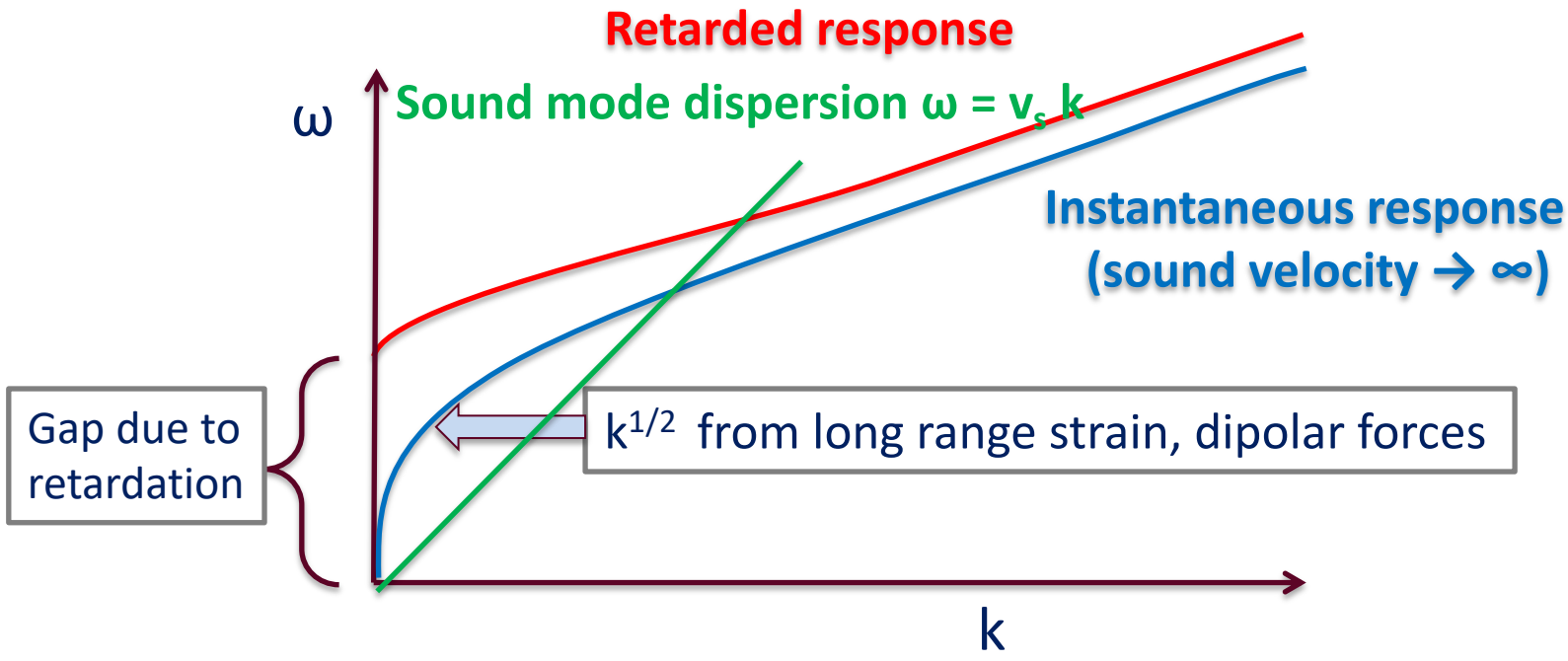
$$H(\mathbf{k}) = 1 - \frac{(D\Omega^4 + \Omega^2(k_x^2 + k_y^2) + \frac{4}{A} k_x^2 k_y^2)}{(k_x^2 + k_y^2)^2 + C k_x^2 k_y^2 + D\Omega^4 + \Omega^2 k_x^2 (1 + D)}$$

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

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

Mode dispersion for small amplitude, long wavelength displacements

Goldstone (sound) mode acquires a mass



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

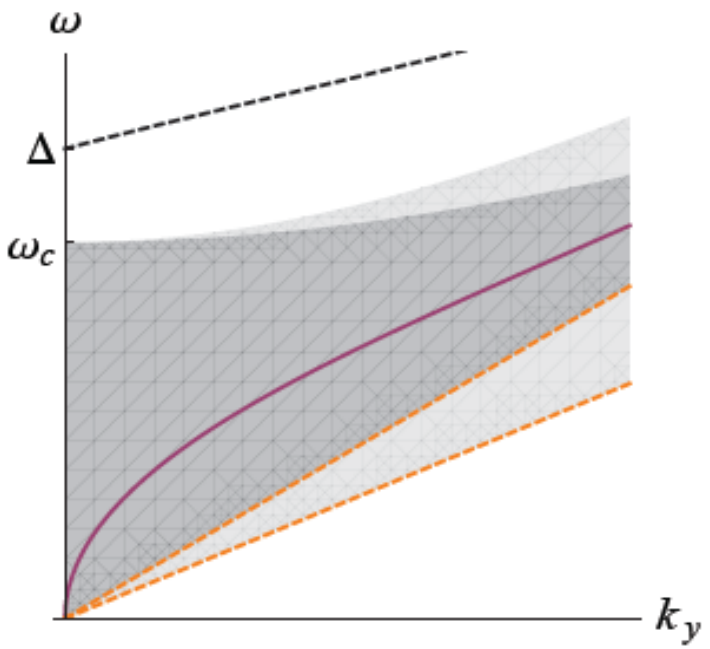
Gap is analogous to plasmon-polariton

Gap magnitude ~ shift in T_c by clamping of strain

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

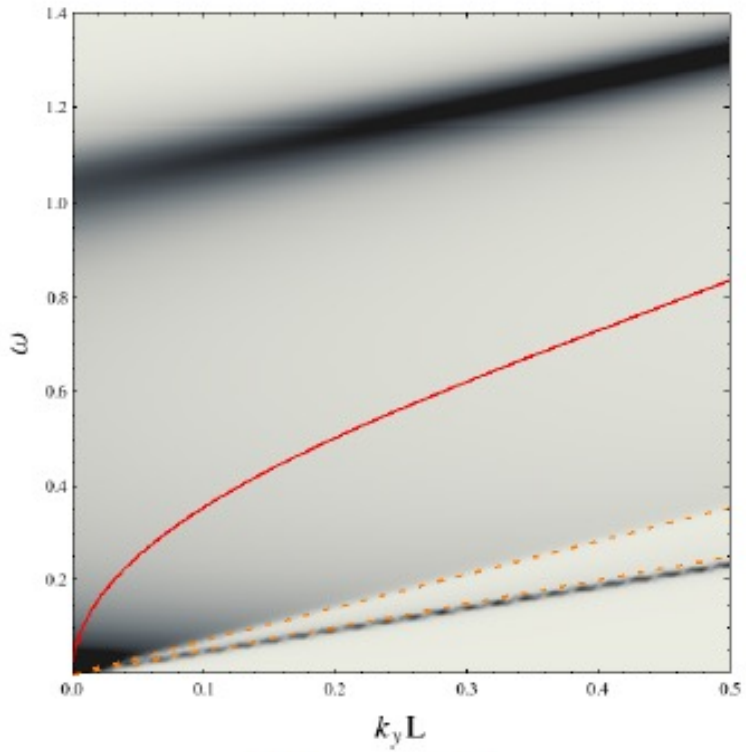
Slow phonons: response function depends on how efficiently gapped modes can decay into bulk phonons

- 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



$\Delta/\omega_c = 4$

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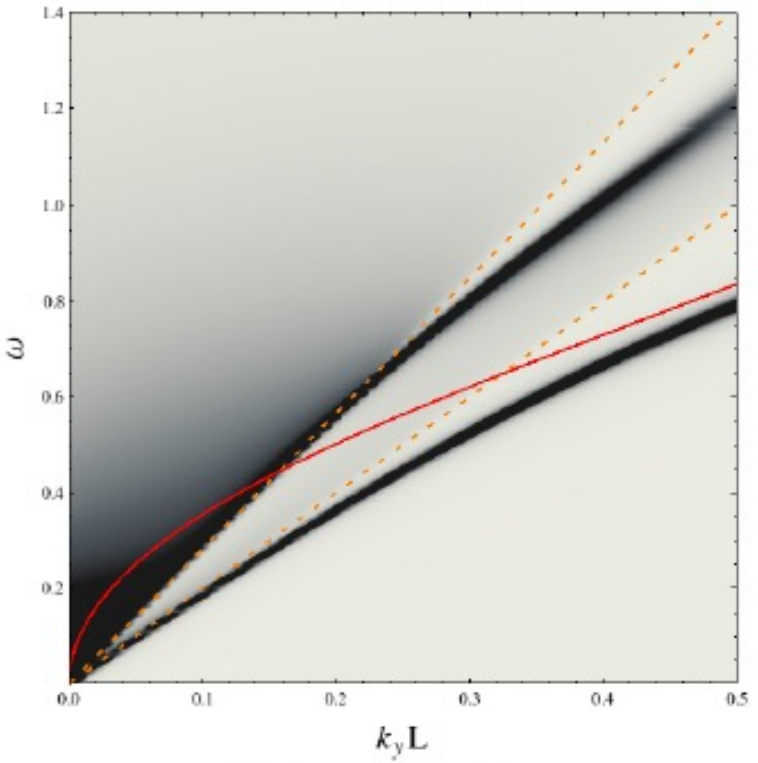
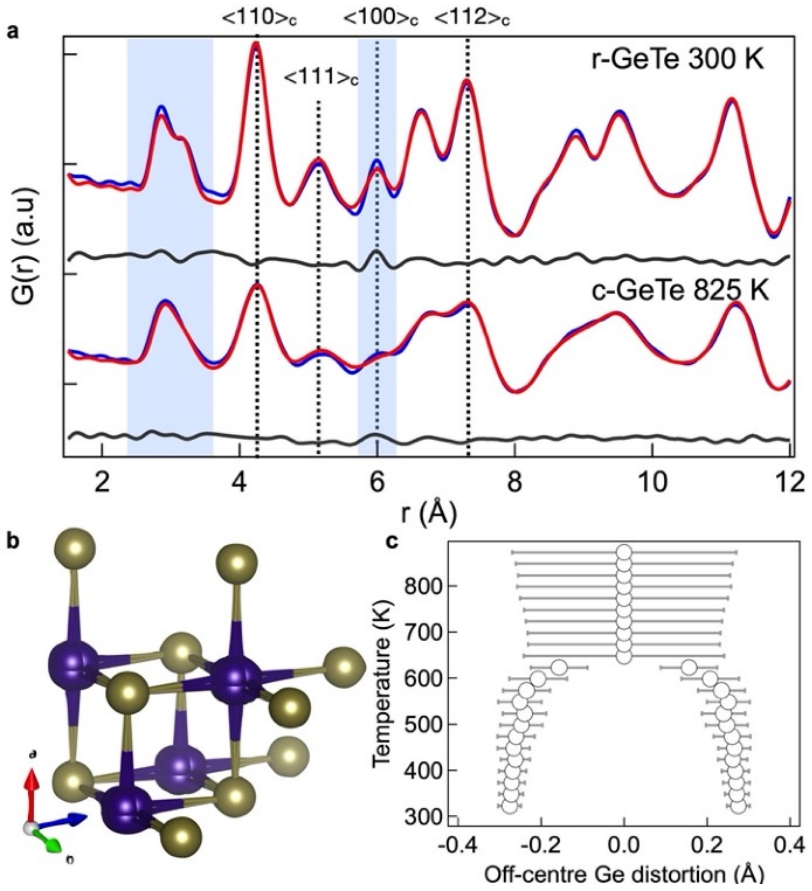


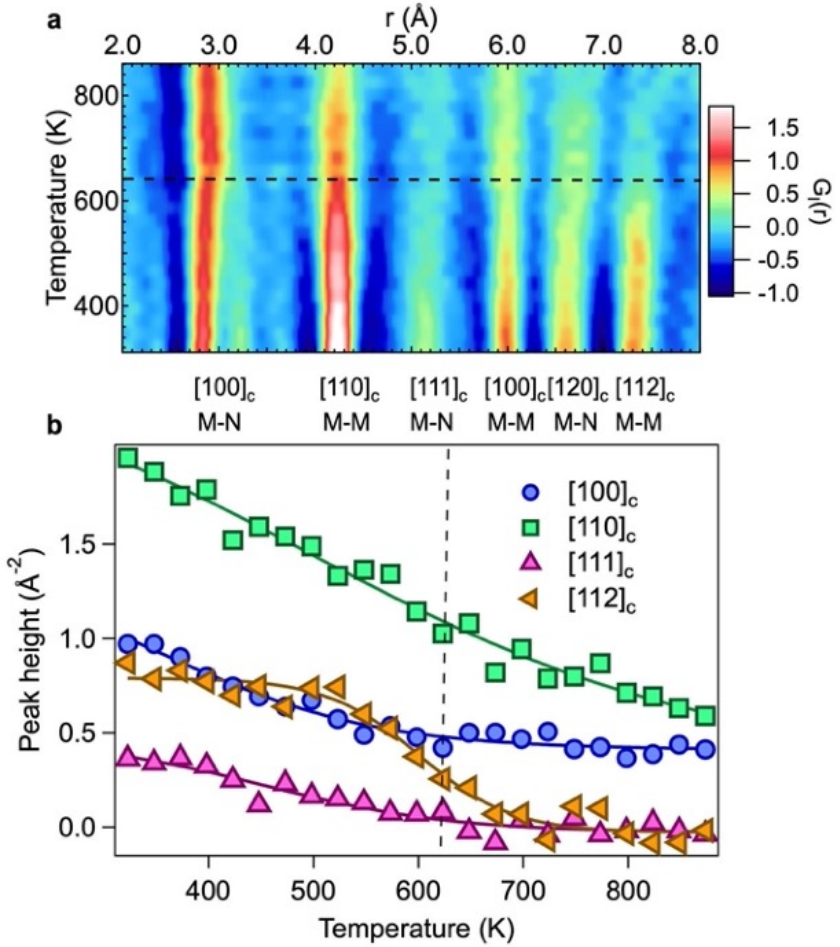
$$\Delta/\omega_c = 1/4$$

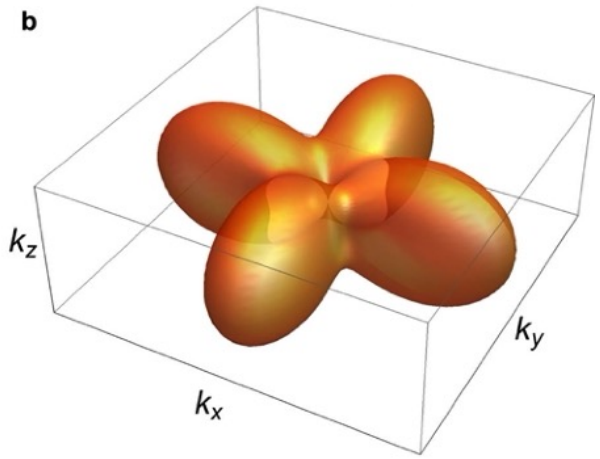
GeTe: cubic (rocksalt) to rhombohedral (ferroelectric) transition at 670 K

Measurement of pair correlation function – probability of finding two atoms a distance **r** apart



Correlations become strongly anisotropic above Tc – long-range in (100)



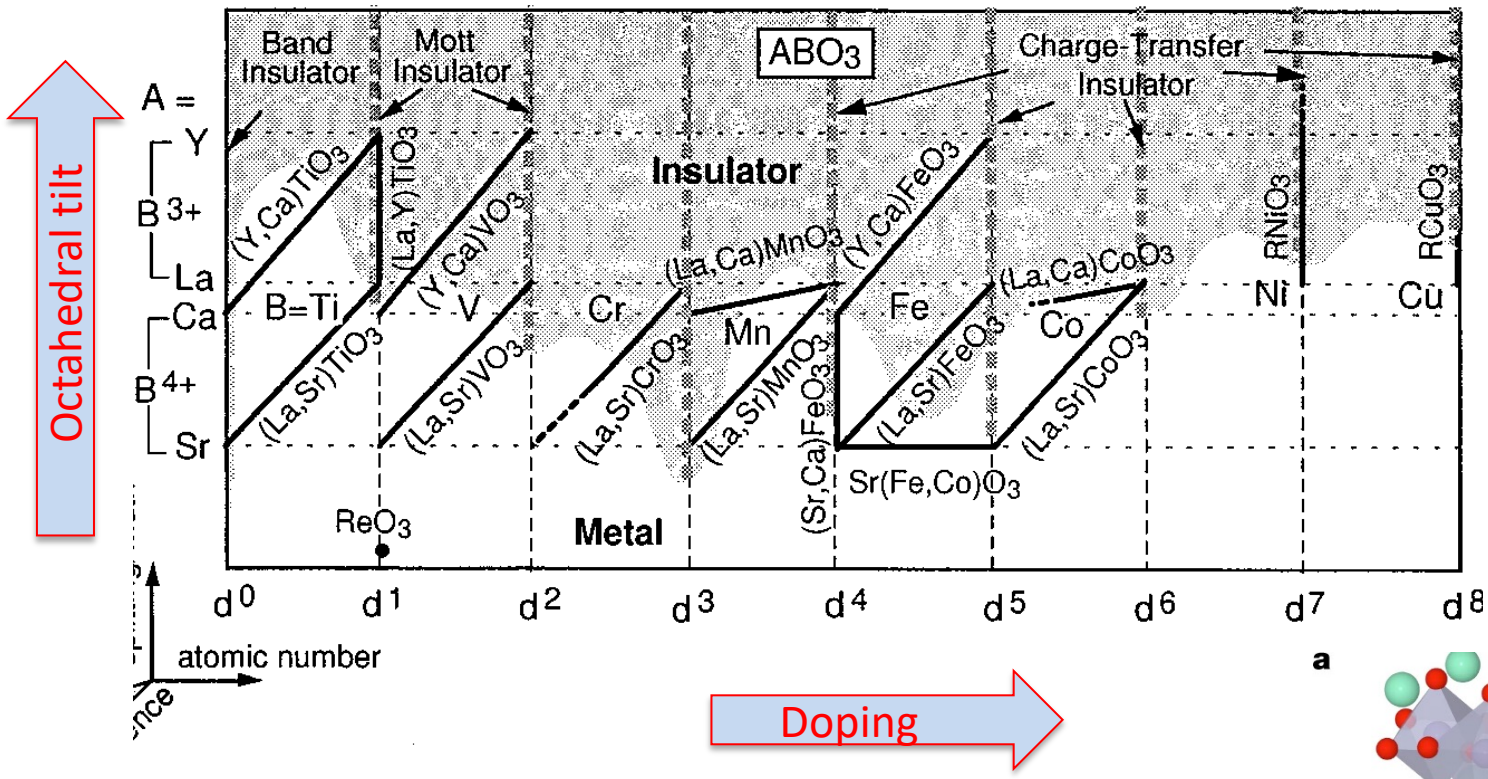


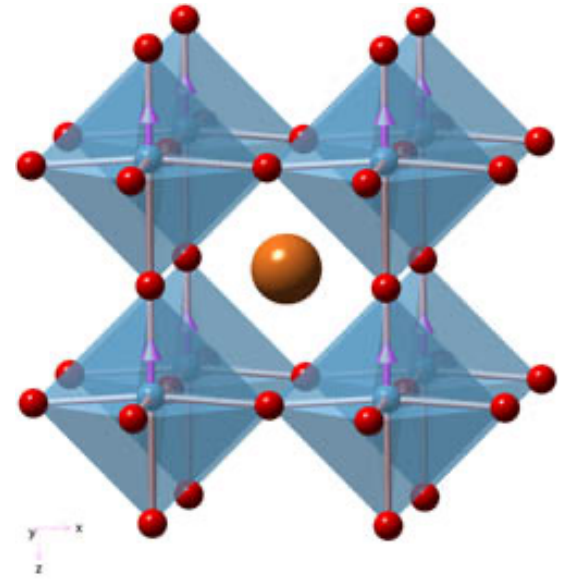
Predicted long-range kernel

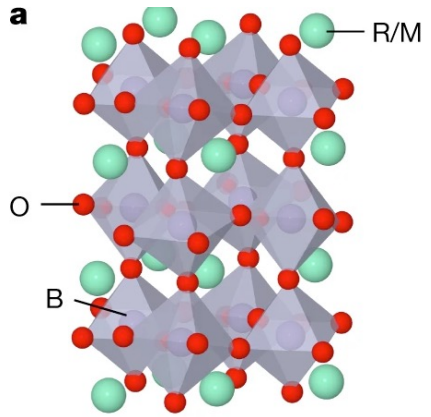
Kimber et al, arXiv:2202.05565

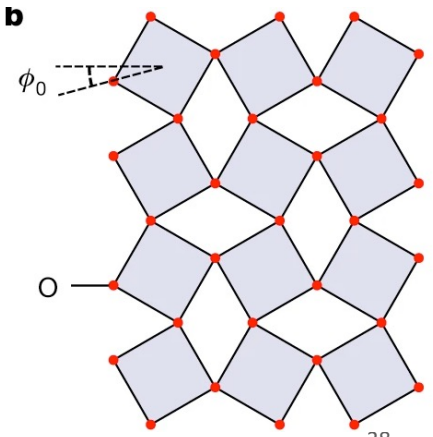
Ionic size effects in perovskite transition metal oxides ABO_3

A= Rare Earth (3+) or Alkaline Earth (2+); B = transition metal; O = oxygen





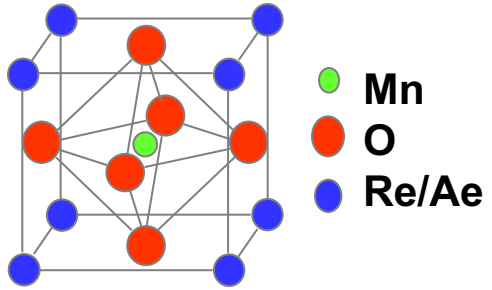




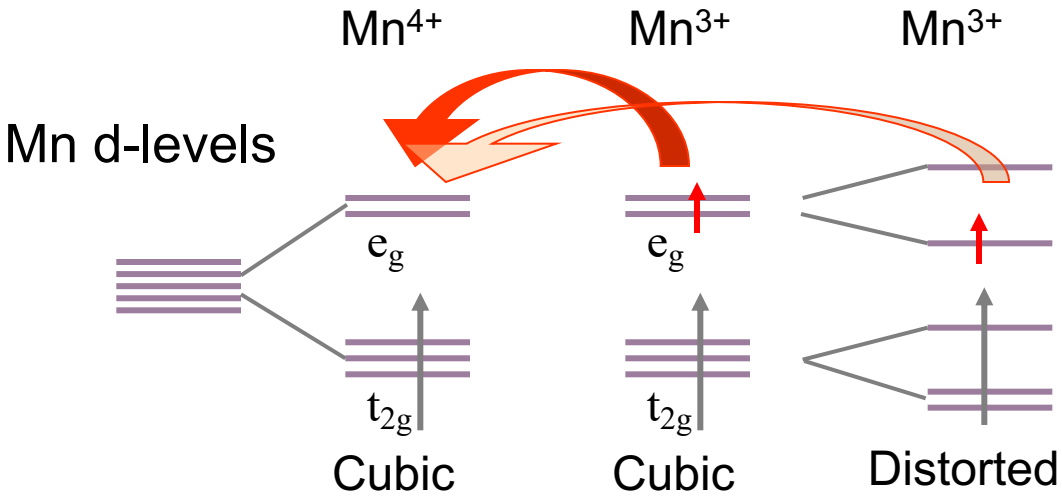
A schematic metal-insulator diagram for the filling-control (FC) and bandwidth-control (BC) 3*d* transition-metal oxides with perovskite structure. From Fujimori, 1992.

An example: Perovskite manganites

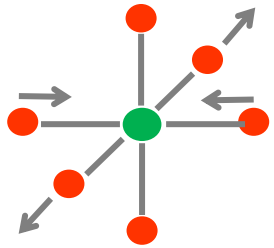
- A “doped” oxide - e.g. $La_{1-x}Ca_xMnO_3$ where the formal valence of Mn varies between Mn^{3+} and Mn^{4+}
- A “strongly correlated” electron system close to a (Mott) metal-insulator transition



Hopping - aligns core moments and leads to ferromagnetic metal

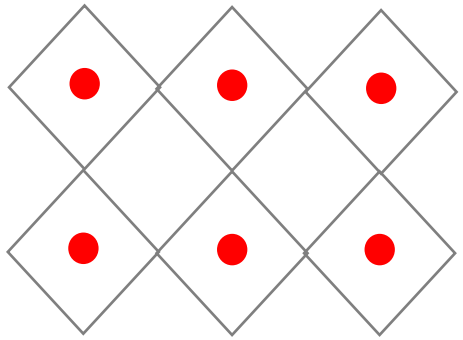


Jahn-Teller distortion suppresses hopping

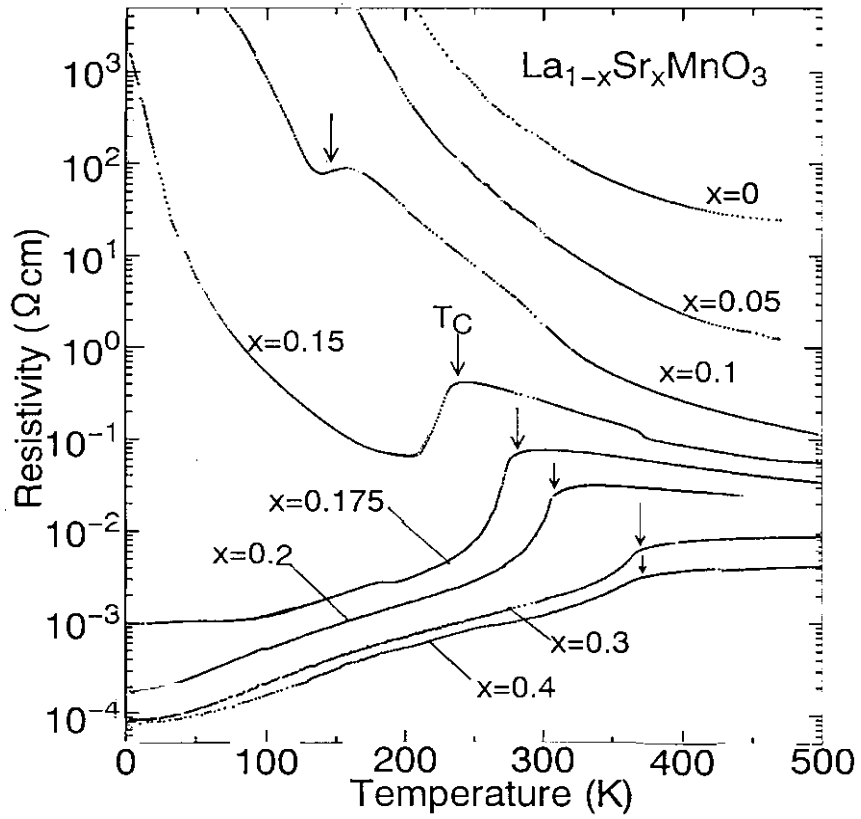


Leads to insulating state with orbital and/or charge order

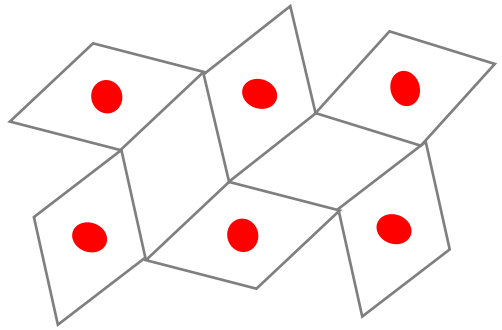
Doping dependence of transition



Uniform ferromagnetic metal

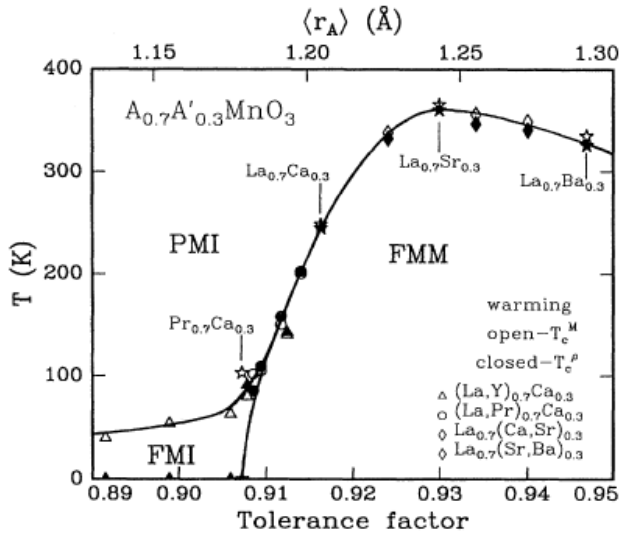


Urushibara et al 1995



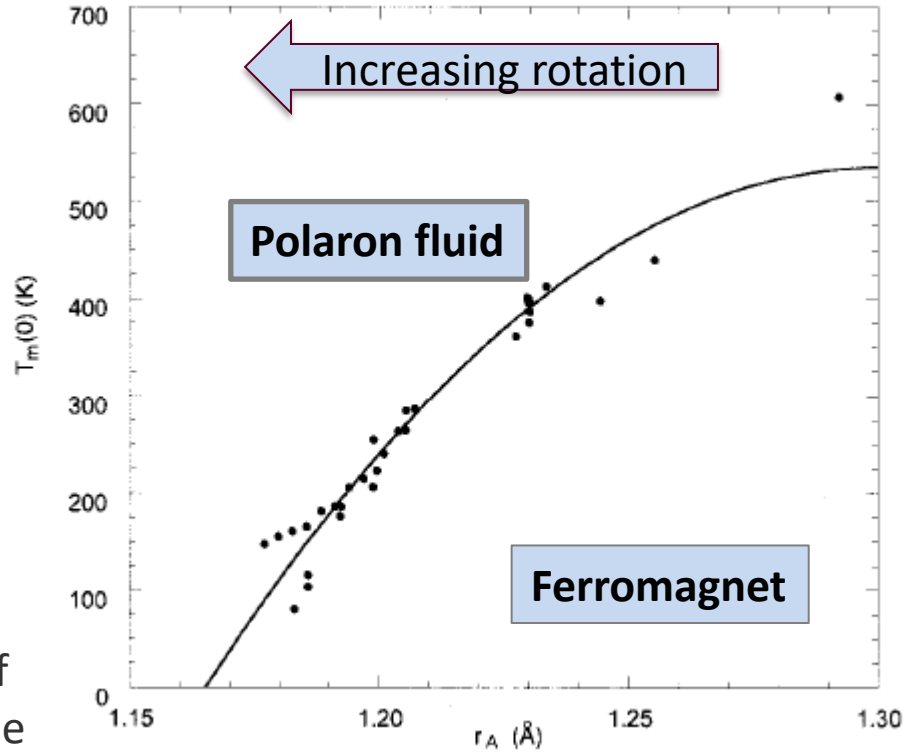
liquid of Jahn-Teller polarons

Atomic size dependence of the transition



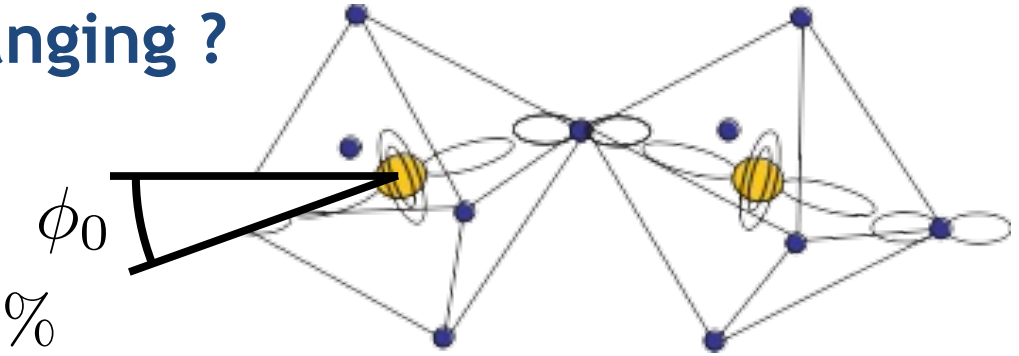
Hwang et al, PRL 75, 914 (95)

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



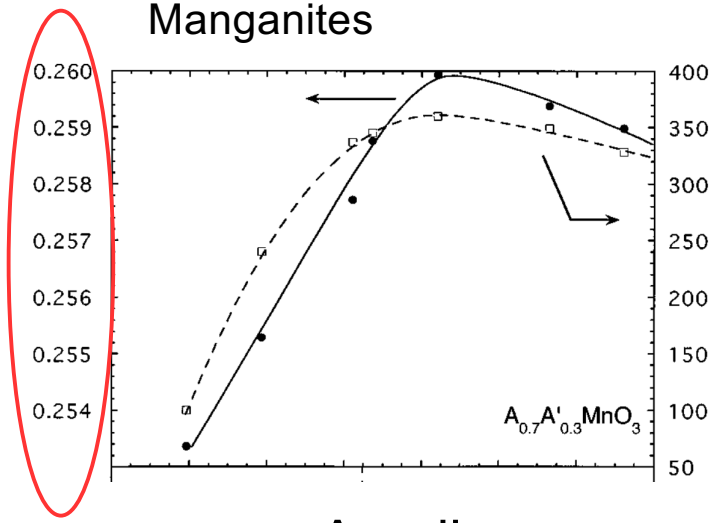
Rodriguez-Martinez and Attfield PRB 54 15622 (96)

Bandwidth control – is U/W changing ?



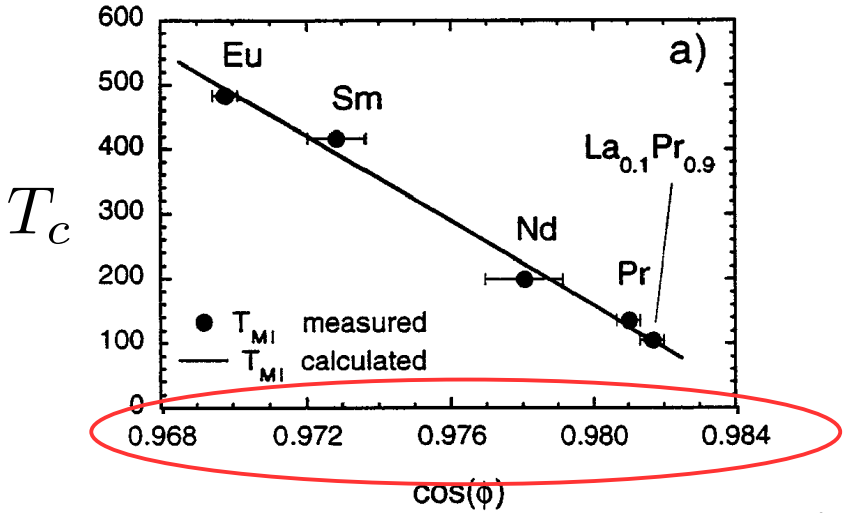
- Changes in W are $\sim 2\%$

Manganites



Radaelli et al, PRL (1997)

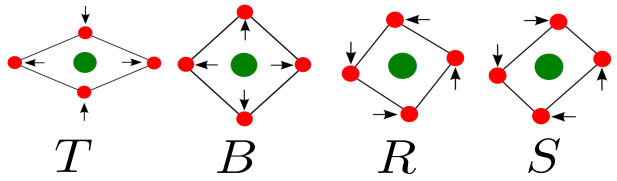
Nickelates



Medarde et al, PRL (1998)

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

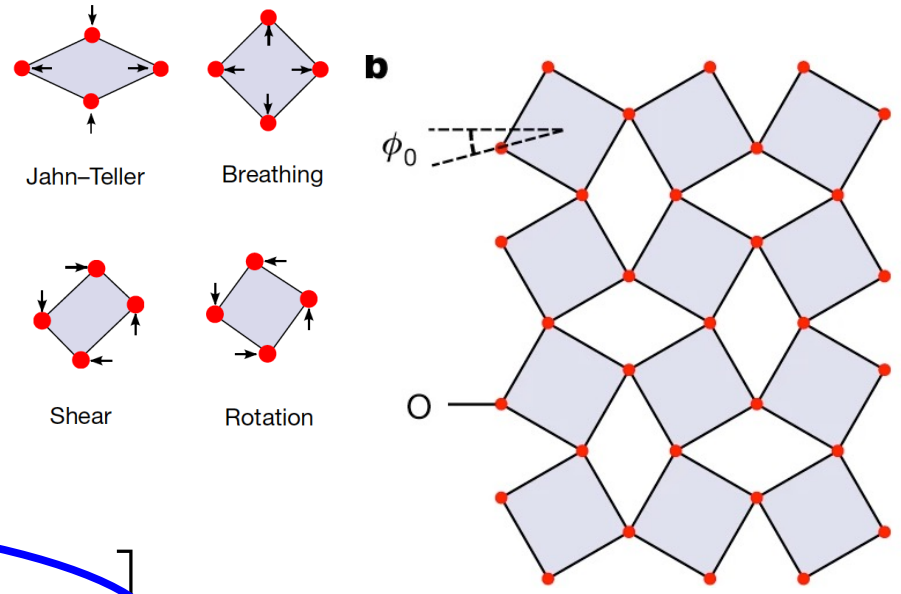
Cooperative Jahn Teller effect in perovskite manganites



Jahn-Teller Breathing Shear

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

In manganites, J-T is often a locally broken symmetry that produces a "bad metal" phase competing with ferromagnetic metal



As before, eliminate the other components while maintaining elastic compatibility

Local many-body physics Elastic interactions

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

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

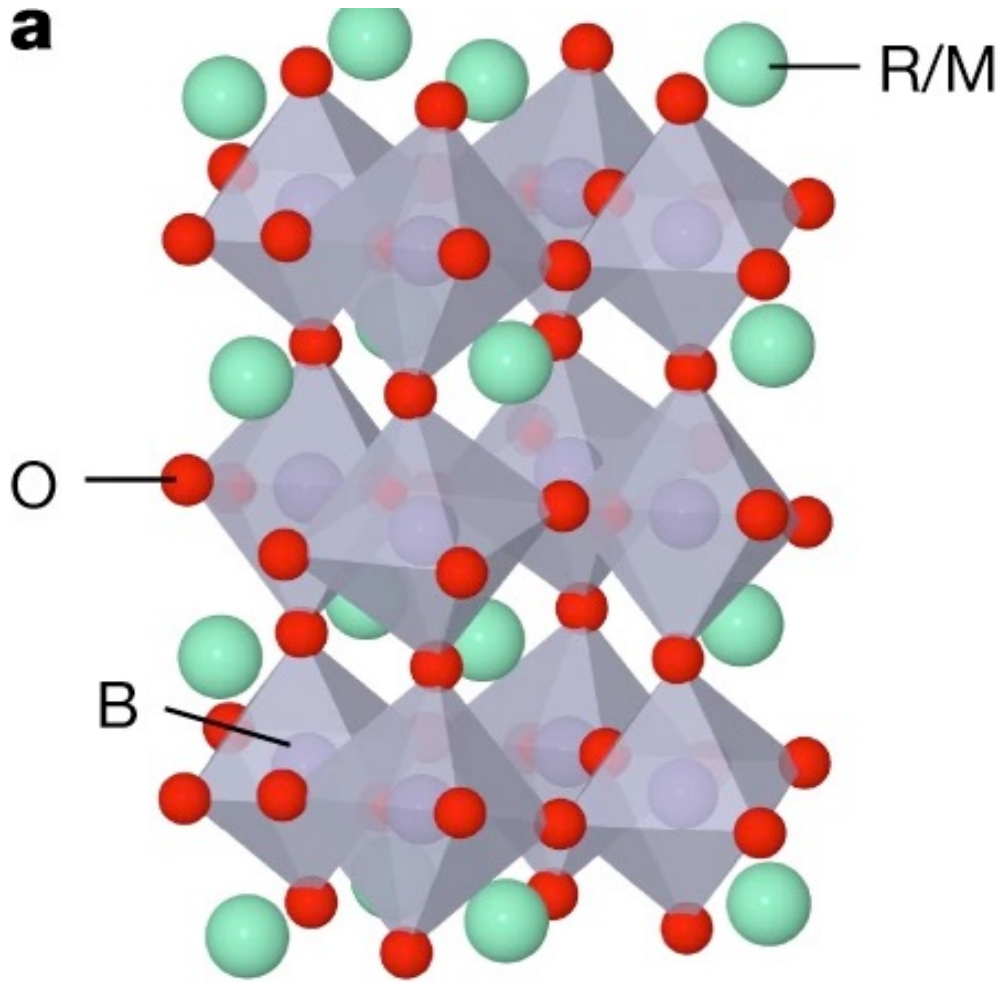
$V(\mathbf{k})$

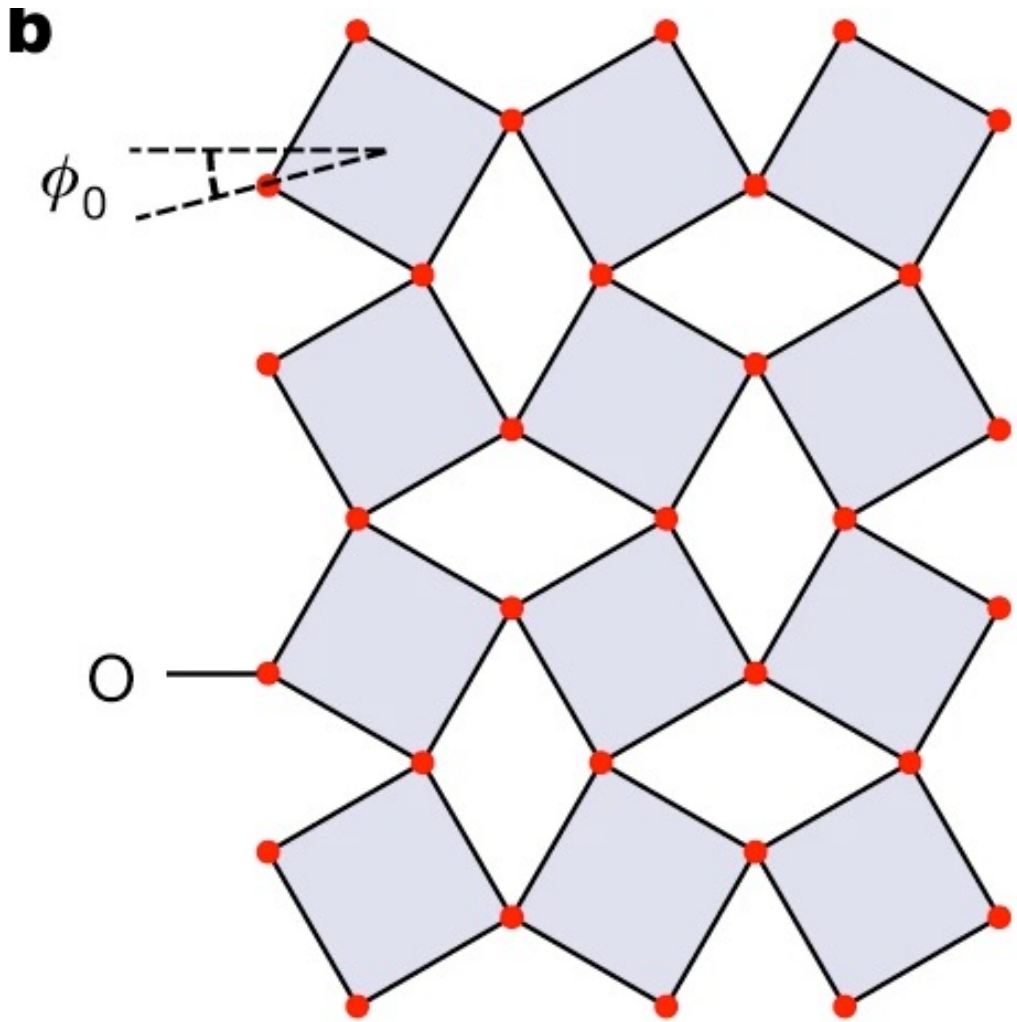
$$t_i = \tan \frac{k_i L}{2}$$

Interaction V(k) is moderated by rotation angle ϕ_0
Long-range coupling is quadratic (primary order parameter)

κ, γ, δh fixed

G Guzman-Verri et al, 2019


a
R/M
O
B

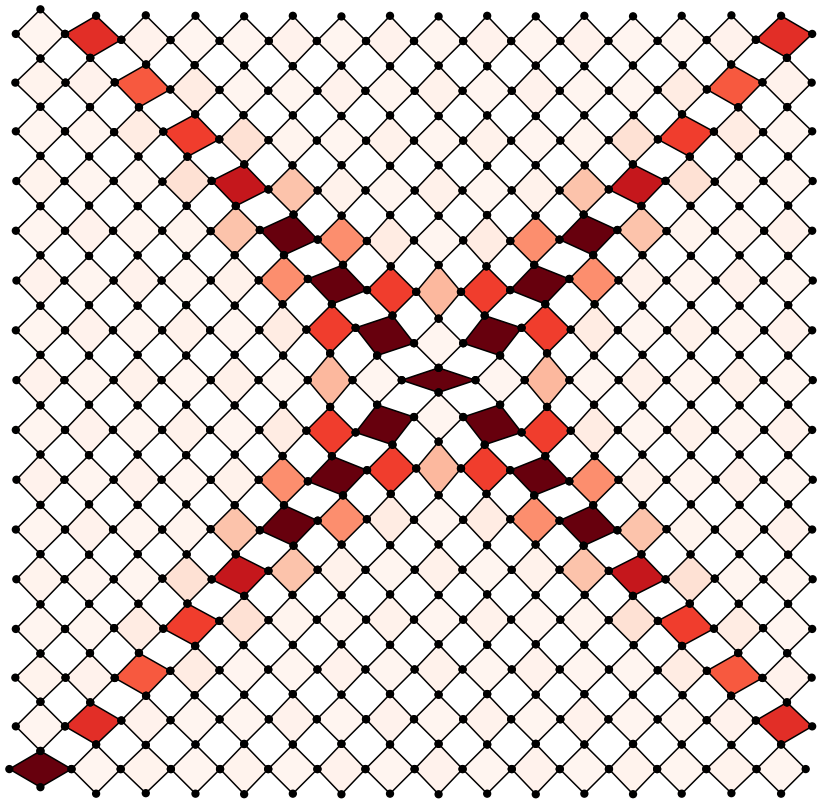

b
ϕ_0
O

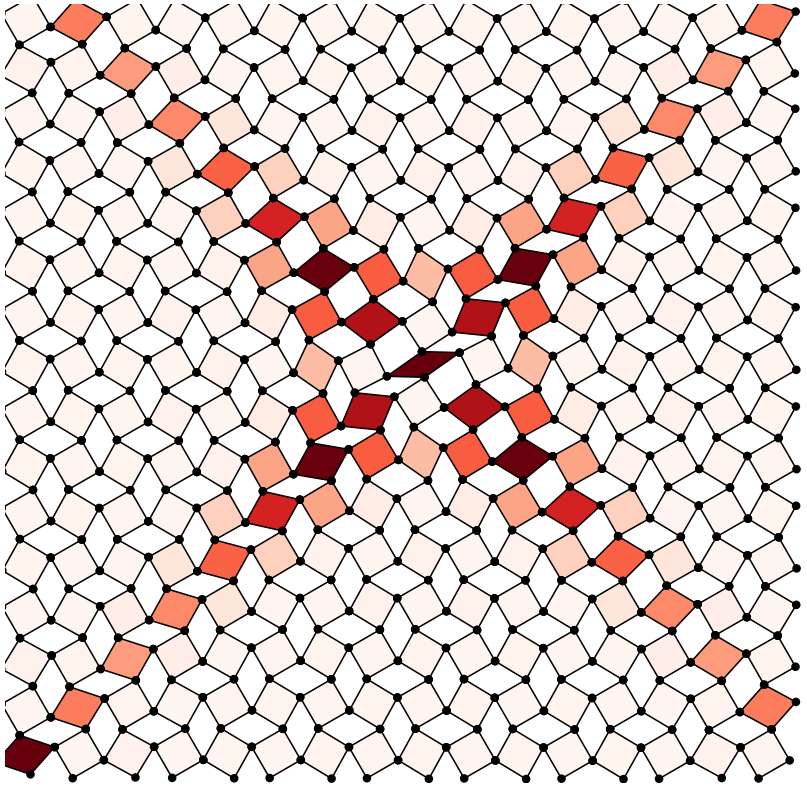
Cartoon of single Jahn-Teller polaron

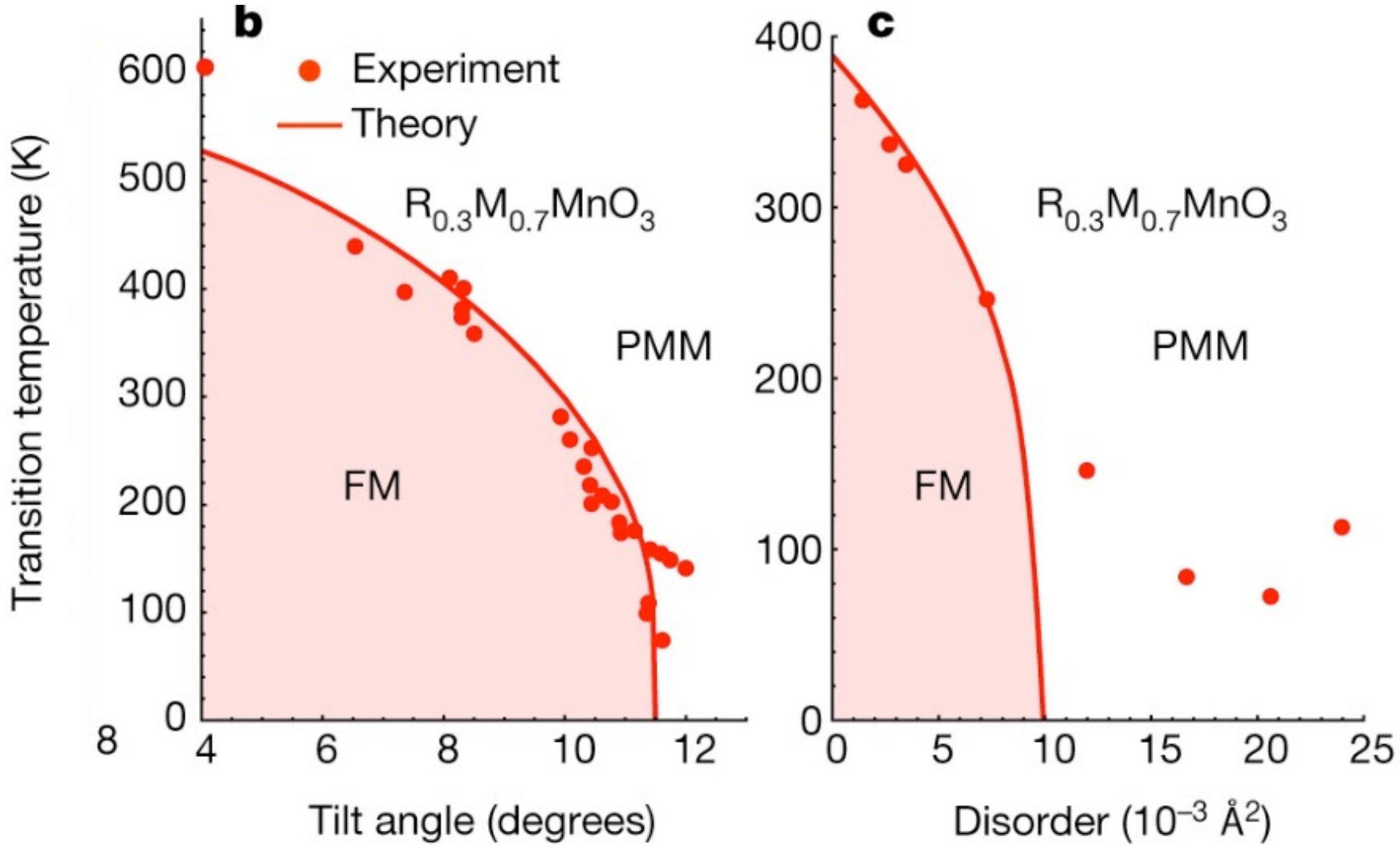
$a_T = 1, a_S = 15, a_B = 10^8$

$\phi_0 = 0$

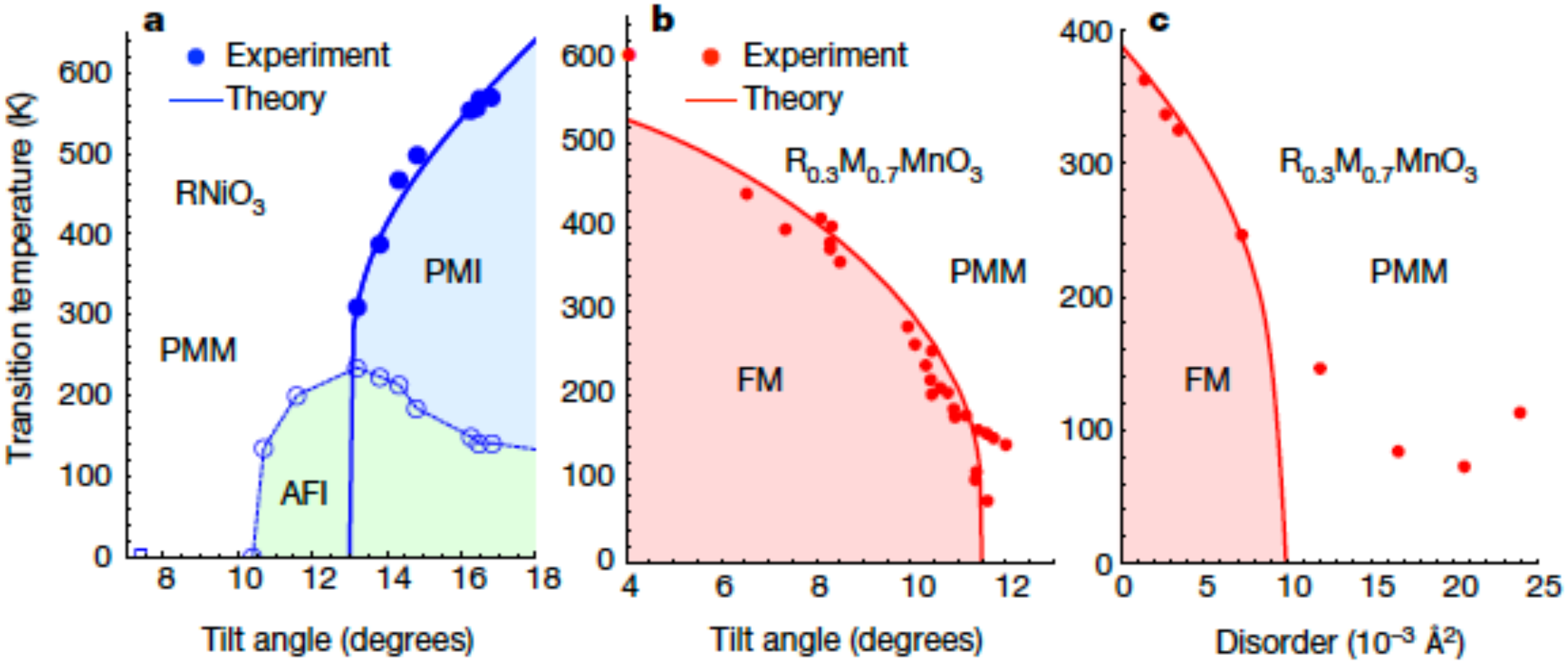
$\phi_0 = 15^o$





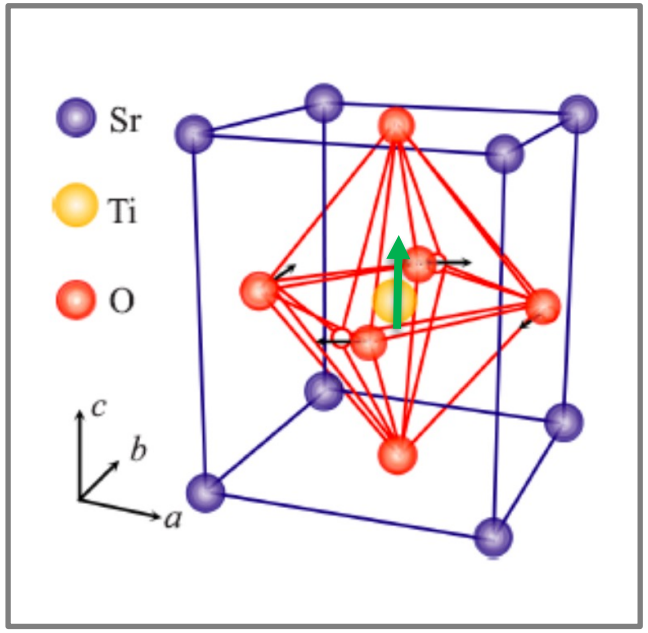


Data: Rodriguez-Martinez & Attfield, PRB (1996)

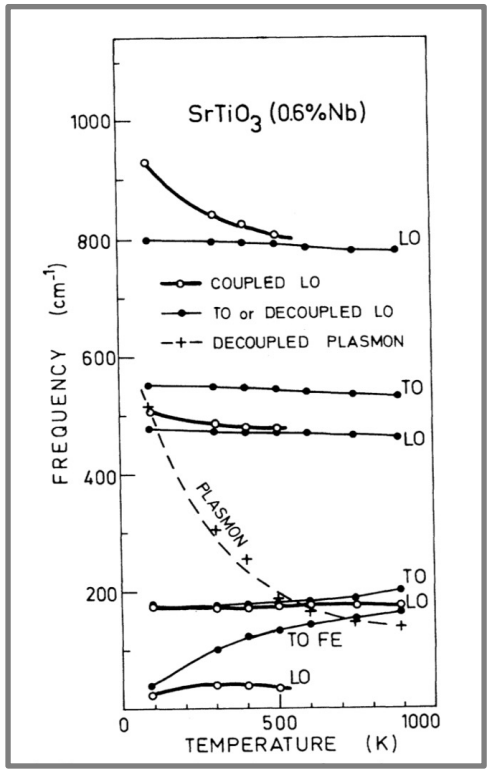


Guzman-Verri. Brierley and PBL Nature 2019

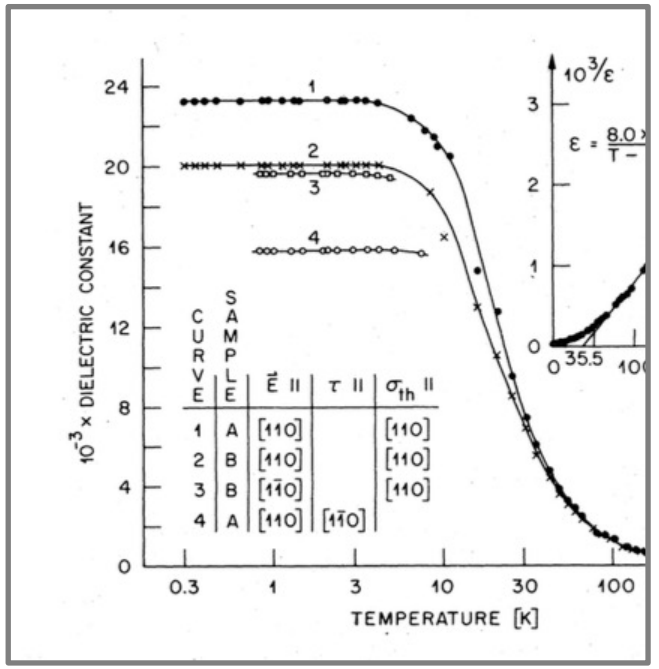
SrTiO3 – nearly ferroelectric, very low carrier density superconductor



105K: cubic to tetragonal
37K: quantum paraelectric



Gervais, PRB (1993)



Müller, PRB (1979)

Softening transverse optic phonon, Curie-law dielectric constant $\omega_{TO}^2 \propto 1/\epsilon \propto T - T_0$

Saturates below 35 K – quantum paralectric?
Or something else?

Ferroelectricity in STO couples to elastic strain

Primary order parameter – polarization P – couples to elastic strain ε

In a (nearly) cubic crystal

Electro-striction – εP^2

- Produces a non-linear long-range coupling between polarization fluctuations
- Macroscopic crystalline deformations at phase transition
- Expected to drive ferroelectric phase transition first-order

Flexoelectricity – ε dP/dx

- Coupling is harmonic – mixed optic (TO)/acoustic(TA) modes
- Coupling vanishes as q -> 0
- Softening TO mode hybridizes with TA – incommensurate fluctuations?

GG Verri, C Liang, PBL, arXiv:2205.14171

Harmonic Ginzburg-Landau theory for isotropic flexoelectric

polarization order parameter $P(\boldsymbol{q})$ elastic displacement $u(\boldsymbol{q})$

Optic | Acoustic | Flexoelectric coupling | Stabilising non-linearity

$$H = \int \frac{d^3q}{(2\pi)^3} \omega_{\mathrm{TO}}^2(\boldsymbol{q}) \left|P(\boldsymbol{q})\right|^2 + \omega_{\mathrm{TA}}^2(\boldsymbol{q}) \left|u(\boldsymbol{q})\right|^2 + (1/2)V(\boldsymbol{q}) \left[P(\boldsymbol{q})u^*(\boldsymbol{q}) + P^*(\boldsymbol{q})u(\boldsymbol{q})\right] + \frac{\gamma}{4}\int d^x P^4(\boldsymbol{x})$$

$$\omega_{\mathrm{TO}}^2(\boldsymbol{q}) = r + cq^2 + hq^4, \qquad r = r_0(T - T_0)$$

$$\omega_{\mathrm{TA}}^2(\boldsymbol{q}) = v_s^2 q^2, \qquad V(\boldsymbol{q}) = fq^2$$

Mean field ferroelectric transition at T_0

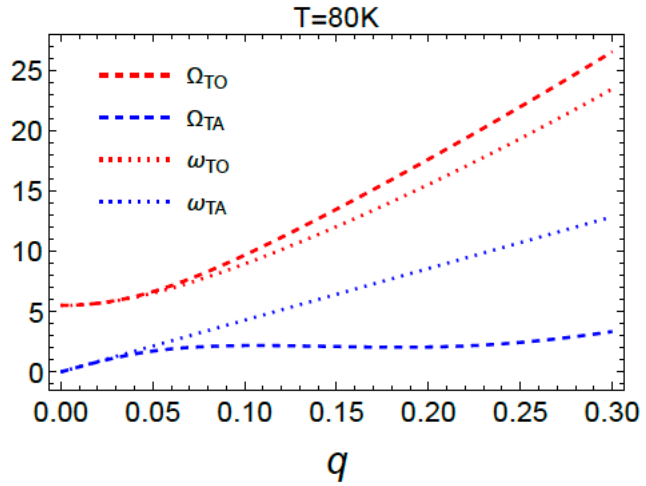
$$\Omega_{\mathrm{TO}}^2(\boldsymbol{q}) = \frac{1}{2}\left(\omega_{\mathrm{TA}}^2(\boldsymbol{q}) + \omega_{\mathrm{TO}}^2(\boldsymbol{q}) + \sqrt{V^2(\boldsymbol{q}) + \left[\omega_{\mathrm{TO}}^2(\boldsymbol{q}) - \omega_{\mathrm{TA}}^2(\boldsymbol{q})\right]^2}\right)$$

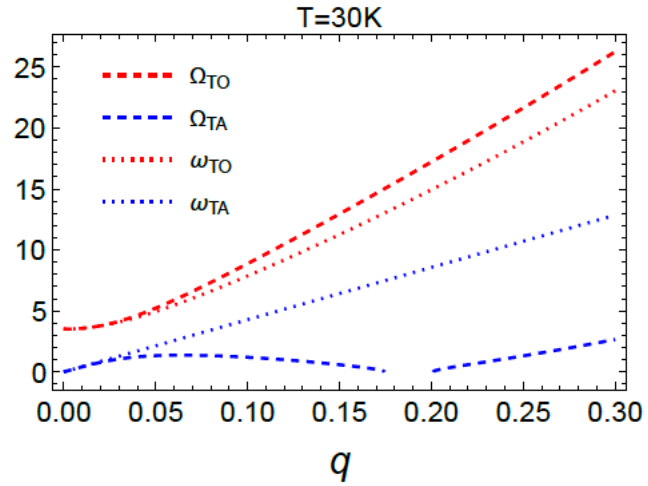
$$\Omega_{\mathrm{TA}}^2(\boldsymbol{q}) = \frac{1}{2}\left(\omega_{\mathrm{TA}}^2(\boldsymbol{q}) + \omega_{\mathrm{TO}}^2(\boldsymbol{q}) - \sqrt{V^2(\boldsymbol{q}) + \left[\omega_{\mathrm{TO}}^2(\boldsymbol{q}) - \omega_{\mathrm{TA}}^2(\boldsymbol{q})\right]^2}\right)$$

Coupled harmonic modes

$$(c - f^2/v_s^2) < 0$$

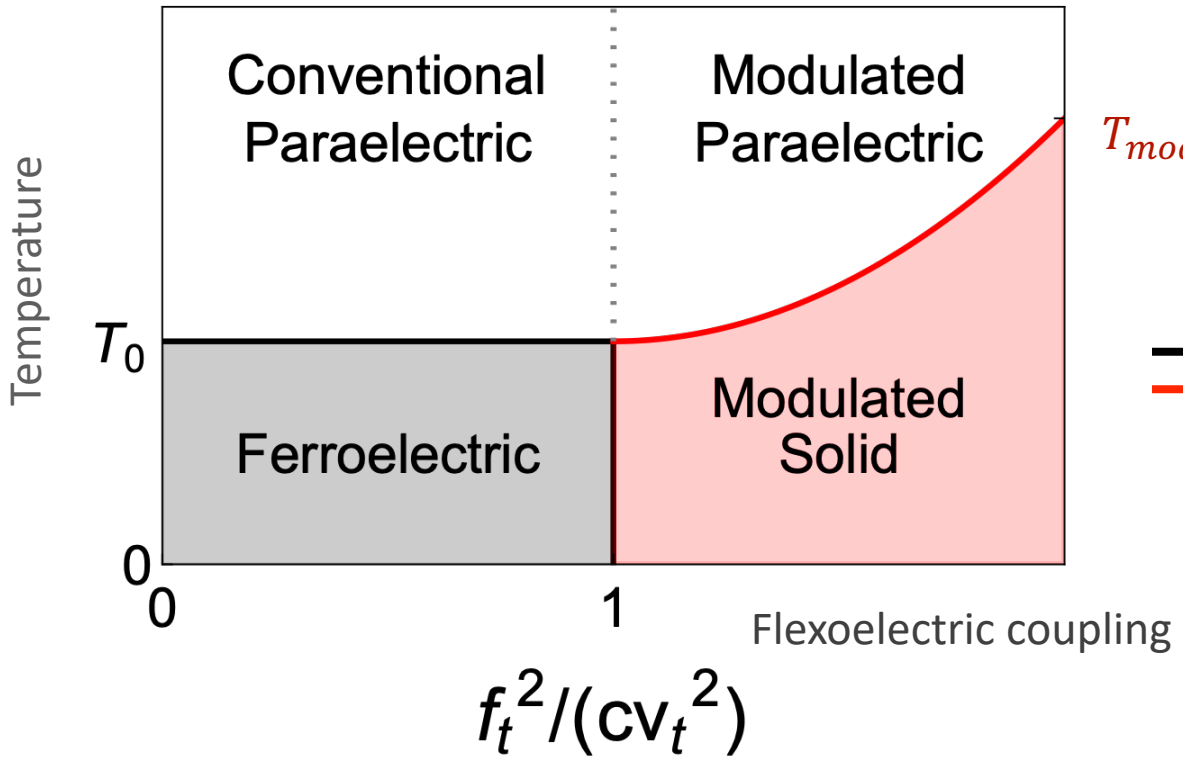
If satisfied, incommensurate transition at $T_{ic} > T_0$





Parameters approximate for KTaO3

Mean field phase diagram (harmonic)



$T_{mod} = T_0 + b^2/4h, b \equiv c - f_t^2/v_t^2$

Crossover

2nd order transition

Conventional Paraelectric = follows Curie-Weiss law, no modulation in the acoustic branch.

Modulated Paraelectric = follows Curie-Weiss law, modulated acoustic branch.

Modulated Solid = Acoustic branch has condensed @ finite q @ Tmod.

Self-consistent treatment of non-linearities - classical phonons

$$\frac{\gamma}{4}\int d^x P^4(\boldsymbol{x}) \to \frac{6\gamma}{4}\int d^3x \left\langle P(\boldsymbol{x})P(\boldsymbol{x})\right\rangle P^2(\boldsymbol{x}) = \frac{3\gamma}{2}\left(\underbrace{\left\langle P(\boldsymbol{x})P(\boldsymbol{x})\right\rangle}_{=\psi}\right)\left(\int d^3x P^2(\boldsymbol{x})\right)$$

4th order term treated at "Gaussian" level

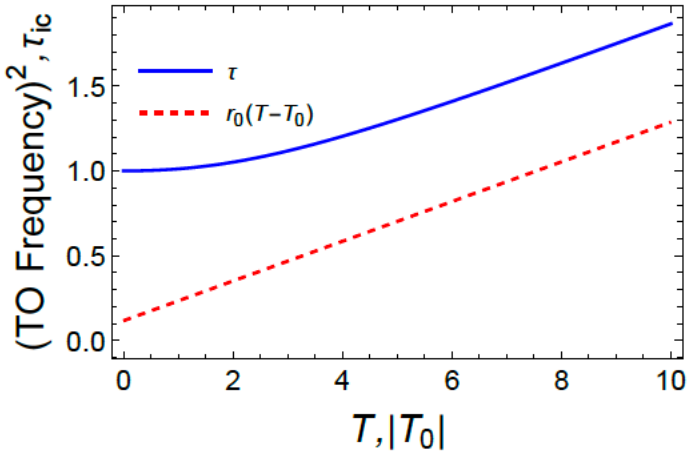
$$\psi(r) = \int \frac{d^3q}{(2\pi)^3}\left\langle |P(\boldsymbol{q})|^2\right\rangle = \int \frac{d^3q}{(2\pi)^3}\frac{T}{r+(c-f^2/v_s^2)\,q^2+hq^4}$$

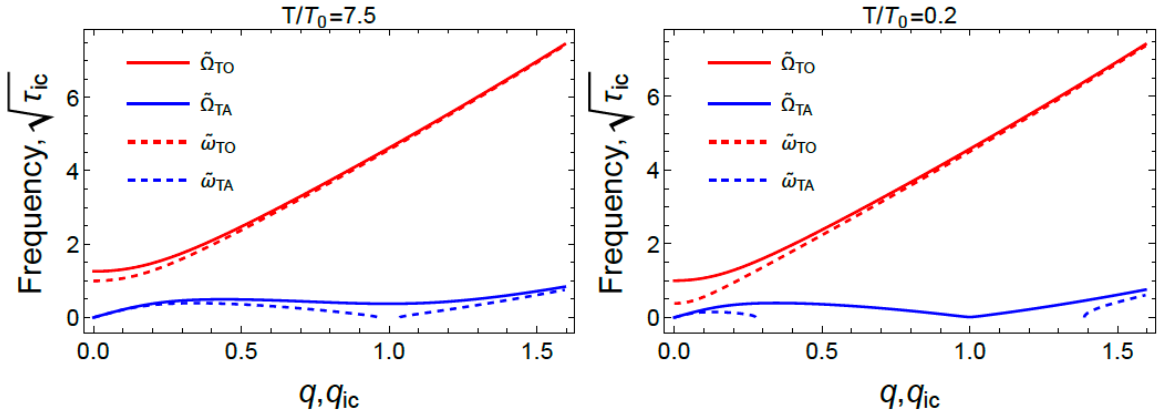
Diverges near T_{ic} in isotropic/cubic system – self-consistent theory necessary

$$\tilde{\omega}^2_{\mathrm{TO}}(\boldsymbol{q}) = \omega^2_{\mathrm{TO}}(\boldsymbol{q}) + 3\gamma\psi(r) = r + cq^2 + hq^4 + 3\gamma\psi(r),$$

$$\psi(\tau) = \int \frac{d^3q}{(2\pi)^3}\frac{T}{\tau+(c-f^2/v_s^2)\,q^2+hq^4}.$$

$$\tau \equiv \tilde{\omega}^2_{\mathrm{TO}}(0) = r + 3\gamma\psi(\tau).$$





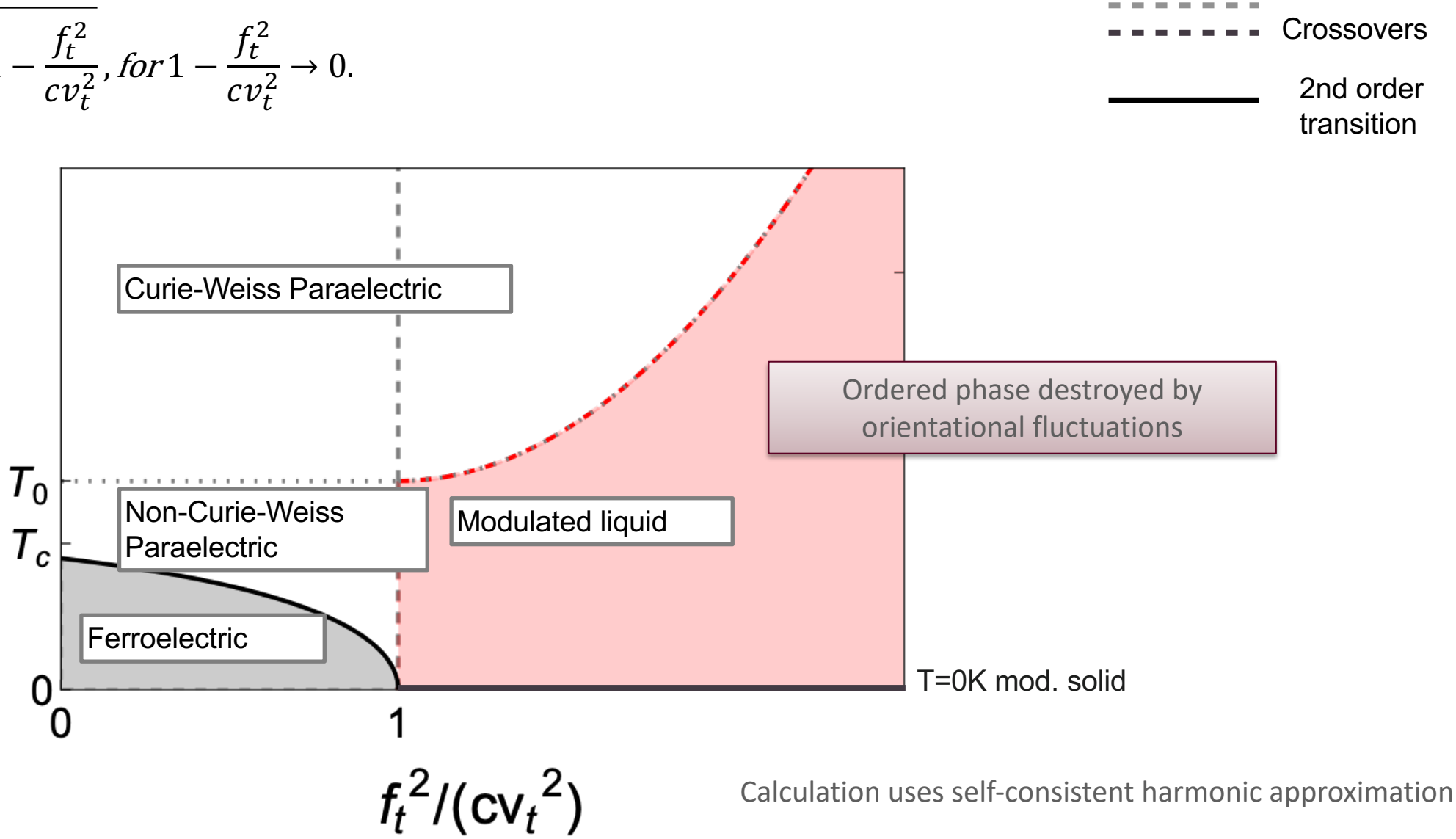
TO phonon stabilizes at $T >> T_0$

Incommensurate phase stable at $T < T_{ic} << T_0$

Brazovski S. A. Sov.Phys.JETP 41 85. (1975).

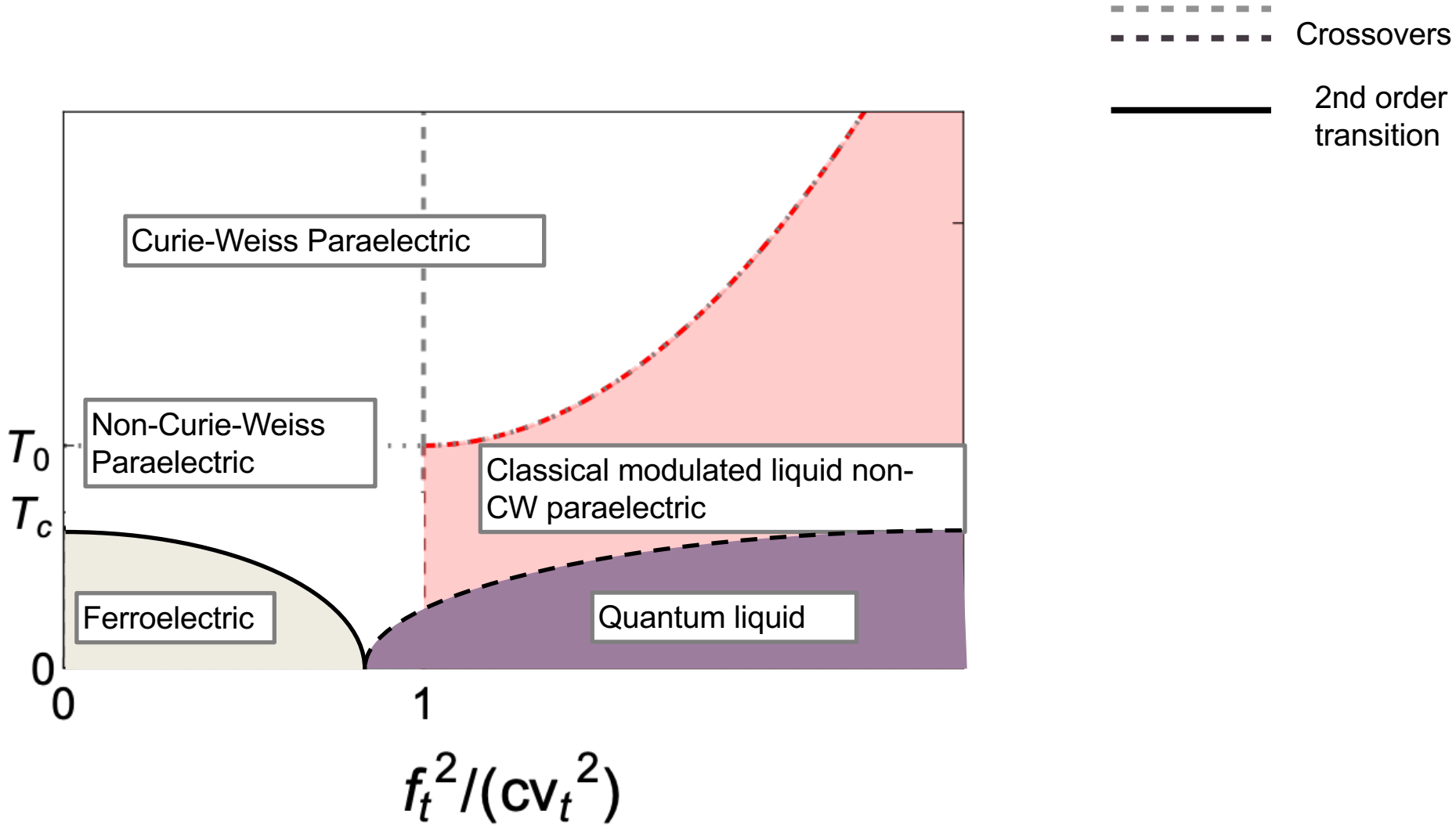
Phase diagram (classical thermal fluctuations only)

$$T_c \propto \sqrt{1 - \frac{f_t^2}{cv_t^2}}, for\, 1 - \frac{f_t^2}{cv_t^2} \to 0.$$



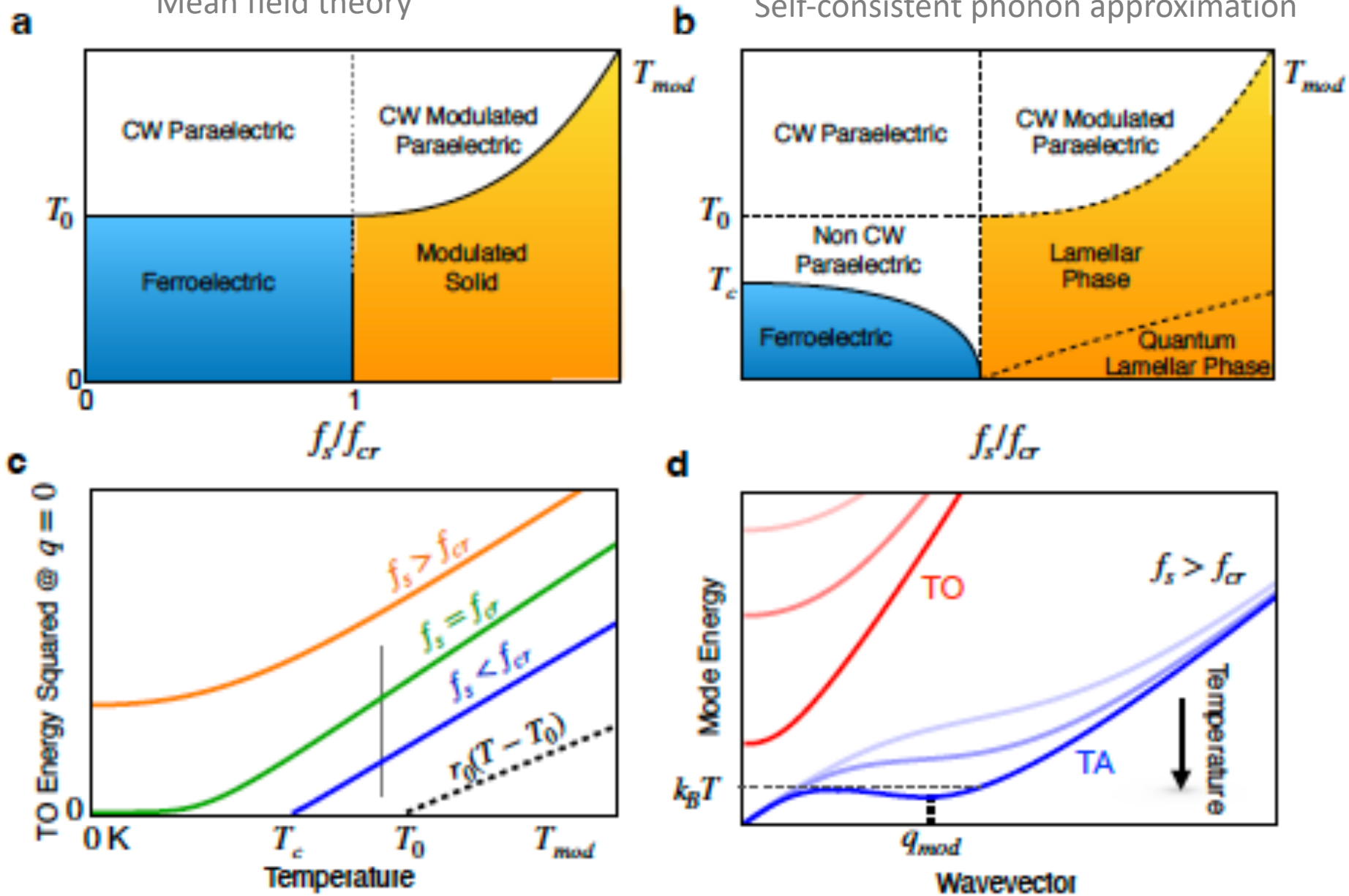
Calculation uses self-consistent harmonic approximation

Phase diagram (including quantum zero-point fluctuations)

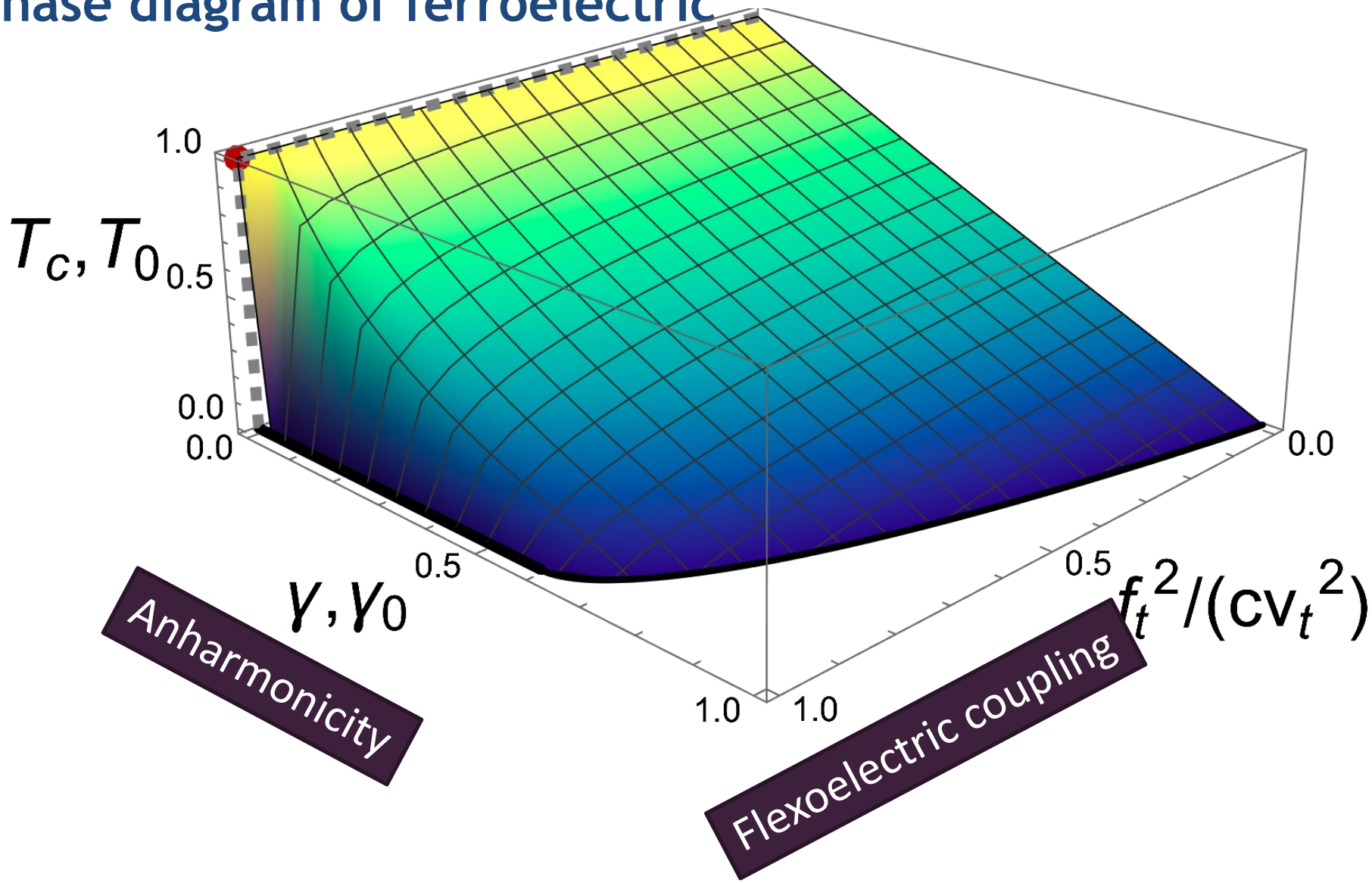


Mean field theory

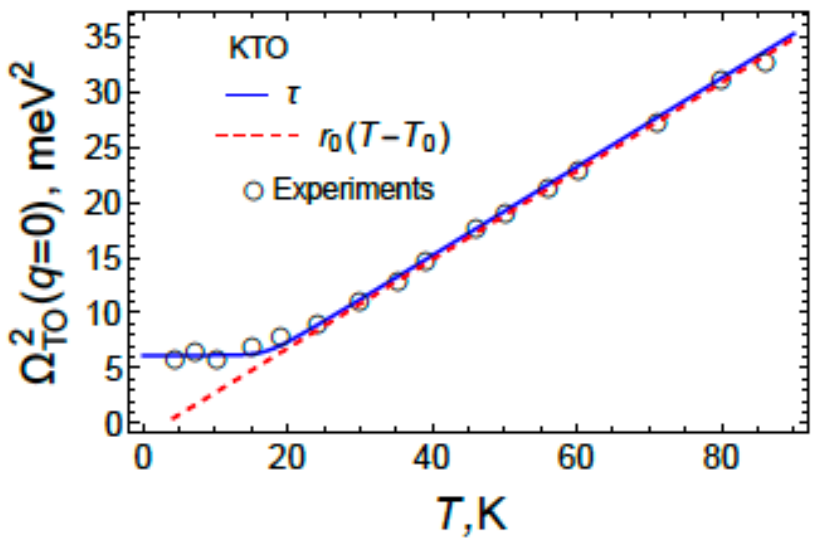
Self-consistent phonon approximation

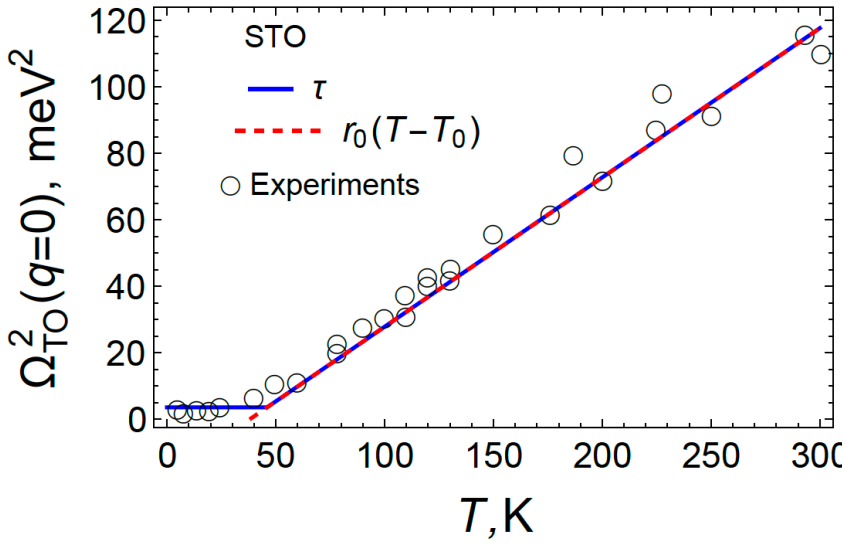


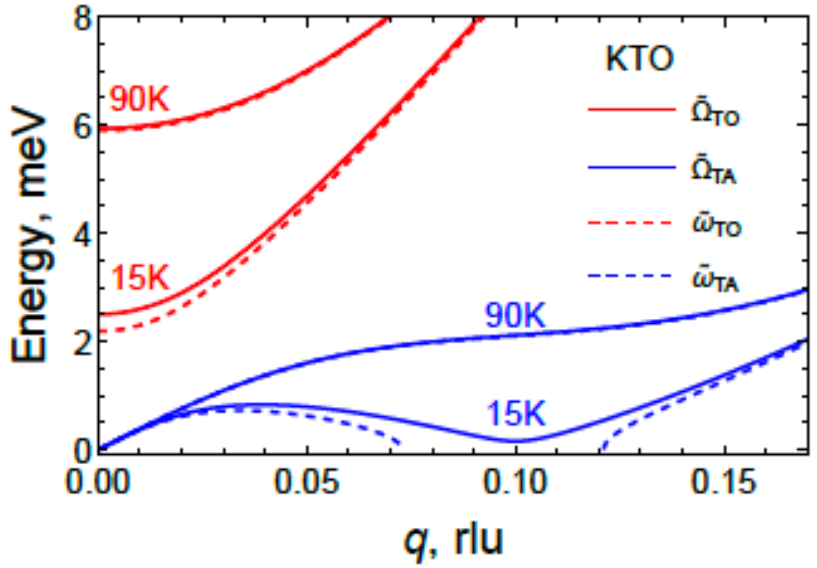
Phase diagram of ferroelectric

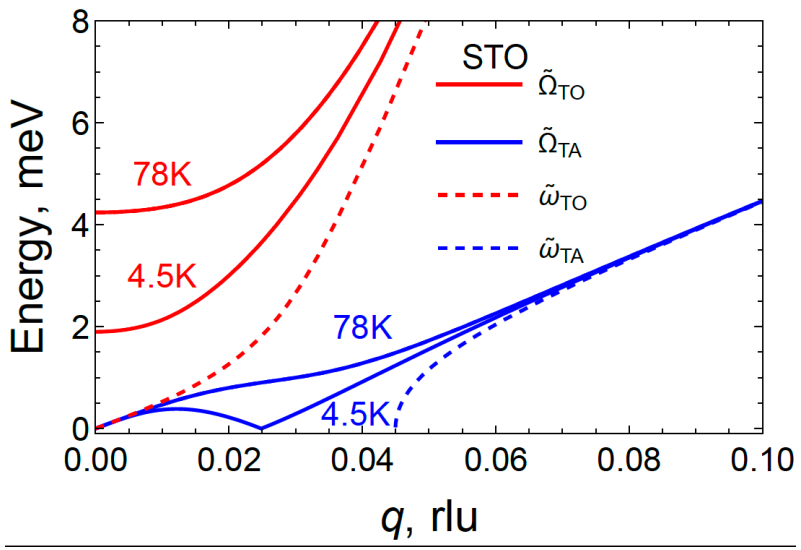


Estimates for $KTaO_3$ and $SrTiO_3$



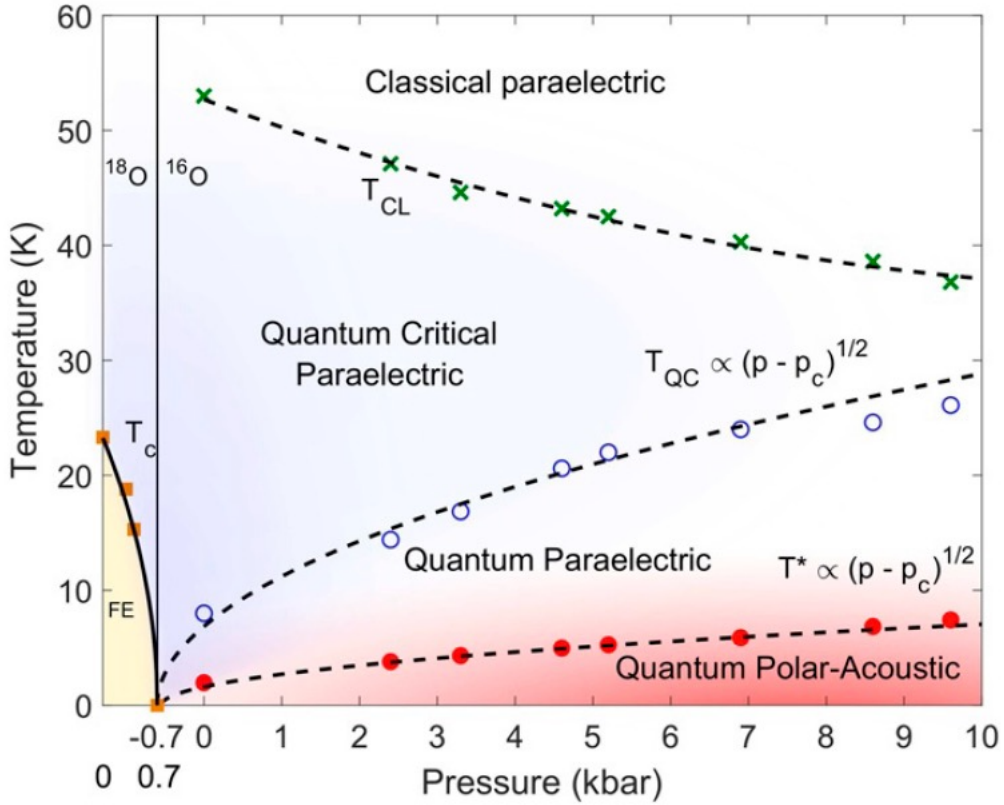




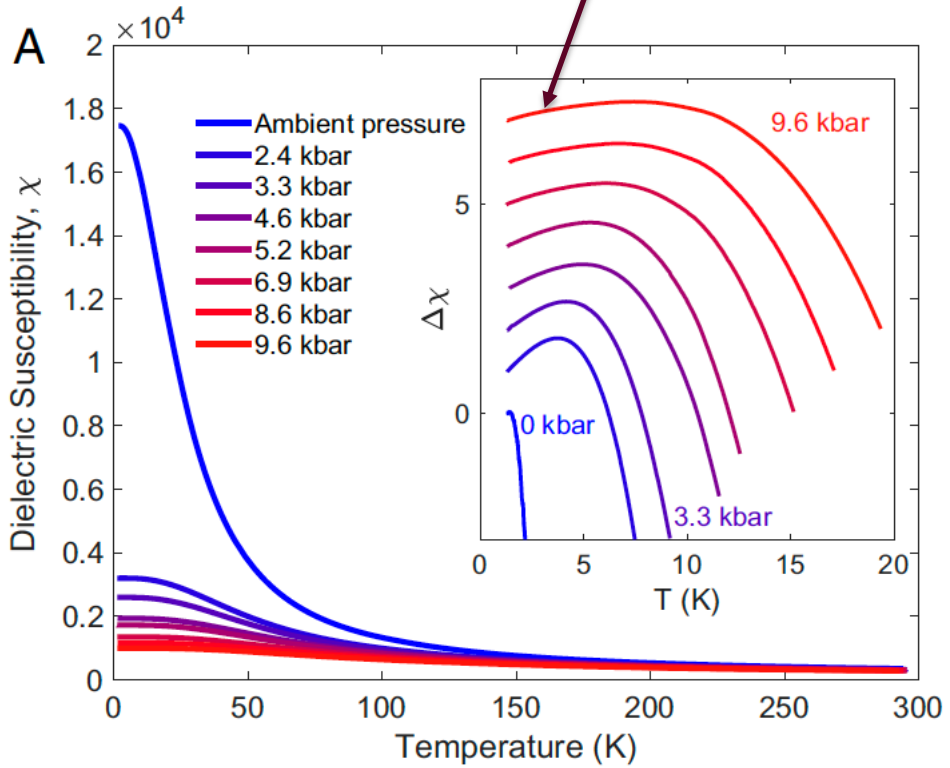


Quantum Criticality

Coak et al. PNAS June 9, 2020 117 (23) 12707-12712; https://doi.org/10.1073/pnas.1922151117



Linear T – some gapless mode?



Why are there so many cross-overs?

Evidence for modulated phase

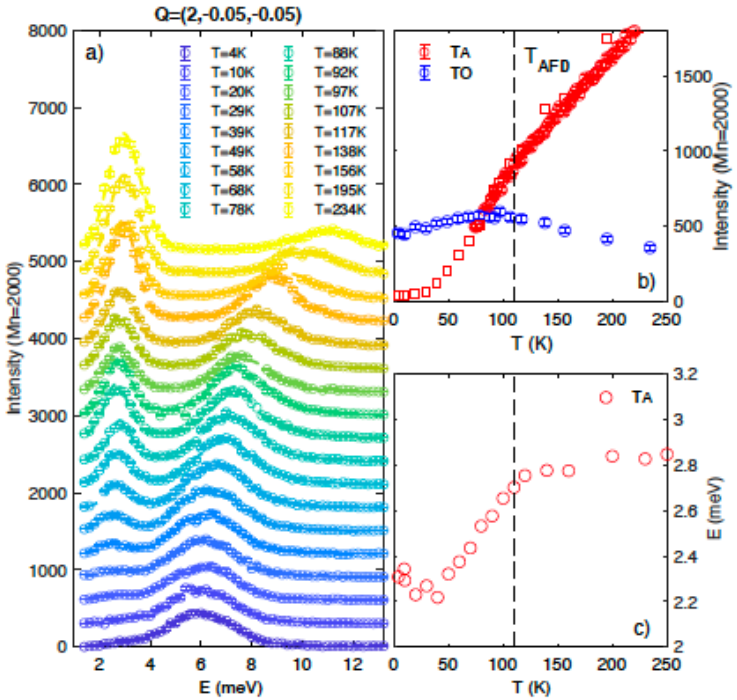
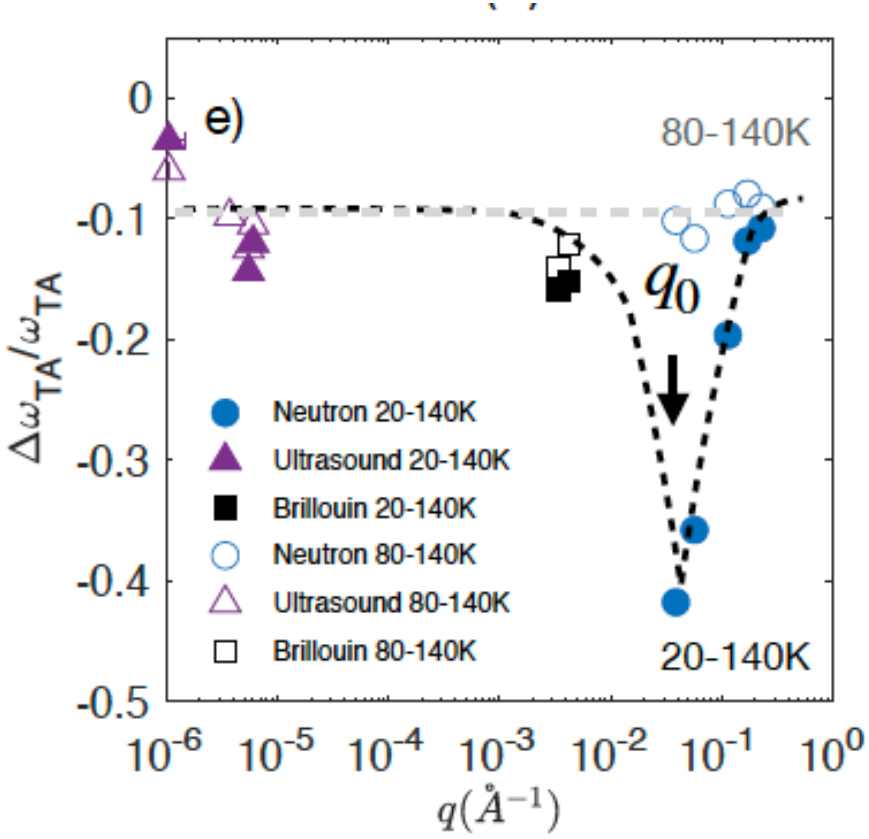


FIG. 2. **TA-TO coupling in the quantum paraelectric phase of $SrTiO_3$: a) Energy scans at Q = (2,-0.05,-0.05) for T = 250 K down to 4 K. Fits including a convolution with the experimental resolution are shown in dotted lines (see [29]). b) Intensity of the acoustic (in red) and optical modes (in blue) as a function of temperature. c) energy position of the acoustic mode deduced from a). We note a loss of intensity of the TA mode below T_{AFD} accompanied by a softening of the TA branch**

Mesoscopic tunneling in strontium titanate

Benot Fauqué,[1,*] Philippe Bourges,[2] Alaska Subedi,[3] Kamran Behnia,[4] Benot Baptiste,[5] Bertrand Roessli,[6] Tom Fennell,[6] Stéphane Raymond,[7] and Paul Steffens[8]



arxiv 2203.15495

Conclusions and caveats

Perhaps the “quantum paraelectric” in STO and KTO is a classical nematic

Evidence for soft mode (but no long-range order) at a few x 0.01 reciprocal lattice units

Nematic requires that flexoelectric coupling must exceed some critical value

Anisotropy (neglected here) will eventually win at low temperature and produce an ordered (striped) phase – large enough anisotropy will eat the quantum regime:

Two crossovers and one phase transition on cooling:

Curie-Weiss paraelectric -> classical nematic liquid -> quantum nematic -> striped phase

Electrostrictive coupling (neglected here) could preempt to force a first-order FE transition

Speculations and caveats

Have ignored anisotropy and electrostriction – both will in principle lead to ‘stripe’ order at low T

If flexoelectricity alone, incommensurate phase appears only if flexoelectric coupling *f* is large

$$(c - f^2/v_s^2) < 0$$

c is quadratic dispersion of TO mode, v_s is sound velocity

“bare” coupling – at least as calculated from ab initio methods – is too small (Stengel PRB 93, 245107 (2016)

Electrostriction drives v_s -> 0 at the mean-field ferroelectric transition T_0 so this condition is relaxed

In STO is the “quantum paraelectric” phase for T < 30K instead dominated by classical incommensurate fluctuations?

Might one identify the “quantum polar-acoustic” phase as a regime where quantum fluctuations of incommensurate domains are important?

Role of electrostriction will be to sharpen the directionality of the polar fluctuations to become oriented nanodomains?

Some recent ab initio calculations have found STO to be disordered at T=0 (Zhao et al, arXiv:2105.05231)

Conclusion: Soft matter physics in hard materials

Maintaining structural integrity through changes of state matters

The elastic strain field is literally the metric of space in which the electronic physics acts

Can subvert this rigidity by using local degrees of freedom (tilts, rotations) – sometimes even zero-point motion can be relevant

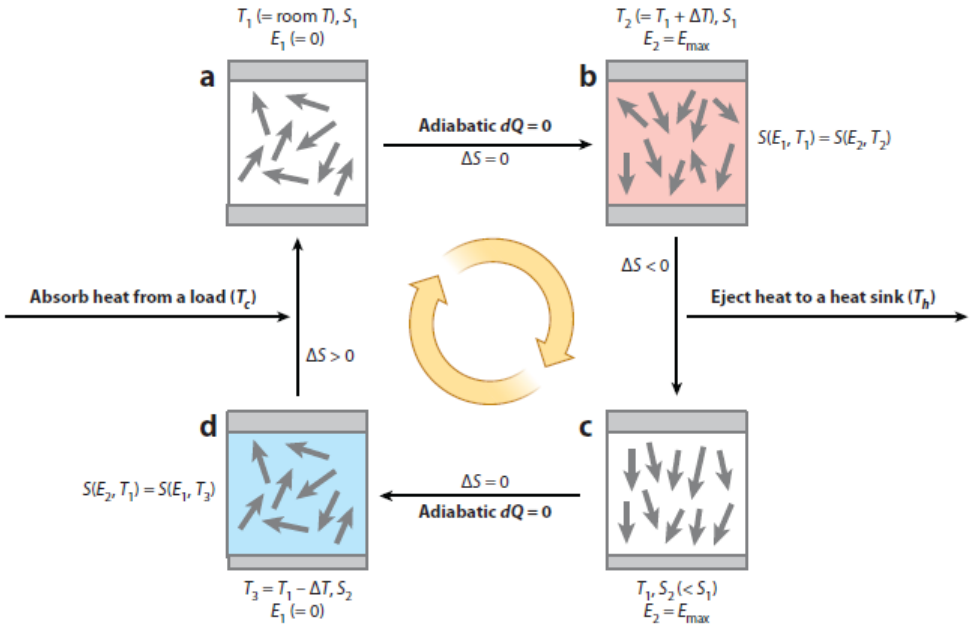
The need for soft correlated materials

Solid state refrigeration
Battery electrodes

Electro-caloric effect and refrigeration

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

Largest entropy changes if dipoles weakly coupled …. could then be of order k_B per unit cell … but in practice much smaller



Non-equilibrium effect so needs a model

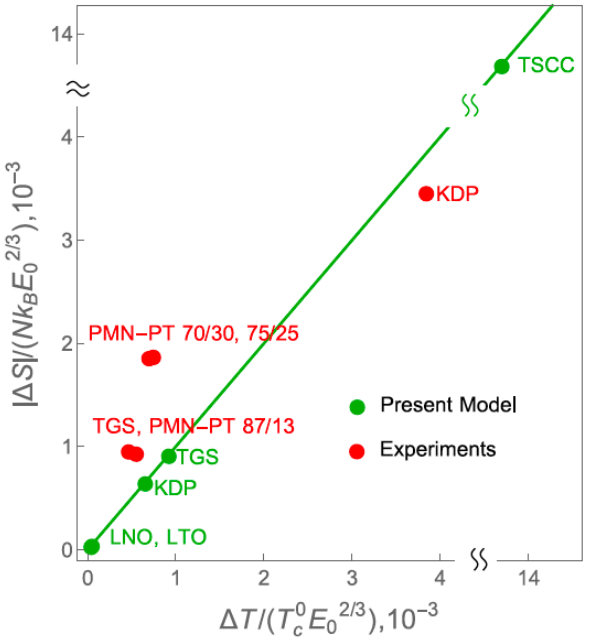
Here – relaxor dynamics from Guzman-Verri and Varma, arXiv:1212.3402

Entropy change depends on correlation length ξ in an electric field E_0

$$\frac{|\Delta S(T,E_0)|}{Nk_B} = \frac{3\zeta a^2}{8\pi}\left[\xi^{-2}(T,E_0) - \xi^{-2}(T,0)\right],$$

Elastic strain enforces long correlation lengths which reduce fluctuations …. need $a/\xi \sim 1$

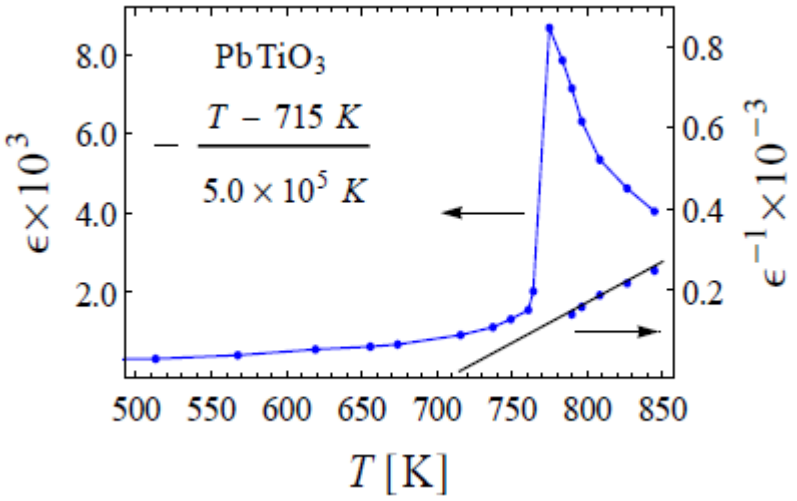
Can we find materials that are close to that limit?



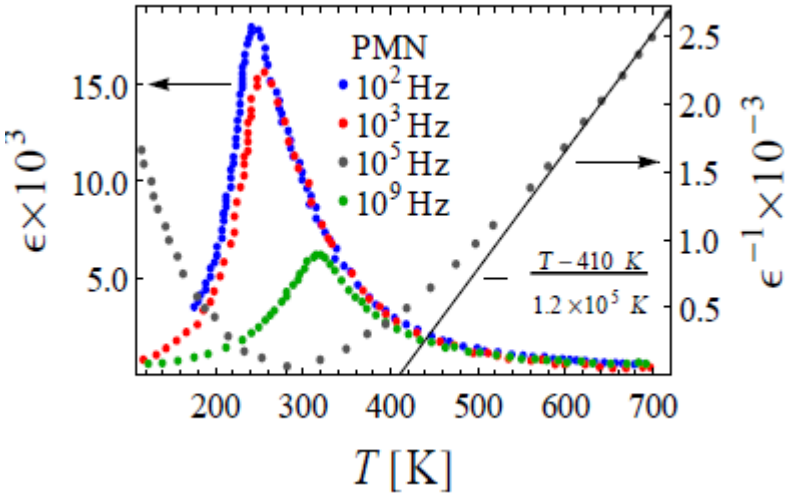
Guzman-Verri et al APL Mater, 4 , 064106 (2016)

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

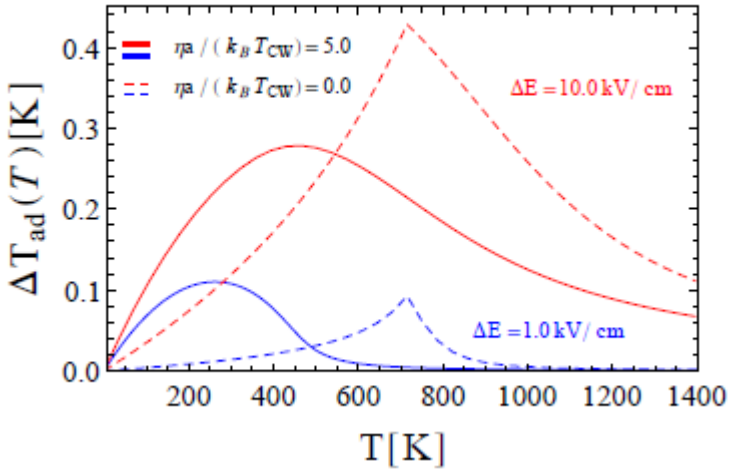
Ferroelectric



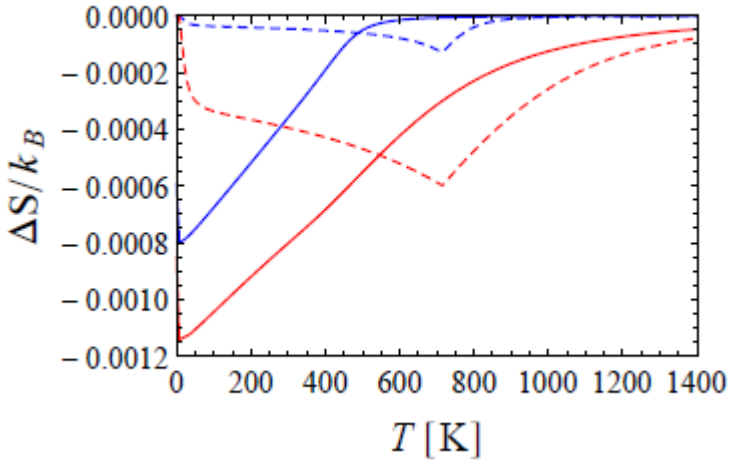
Relaxor



Adiabatic temperature change

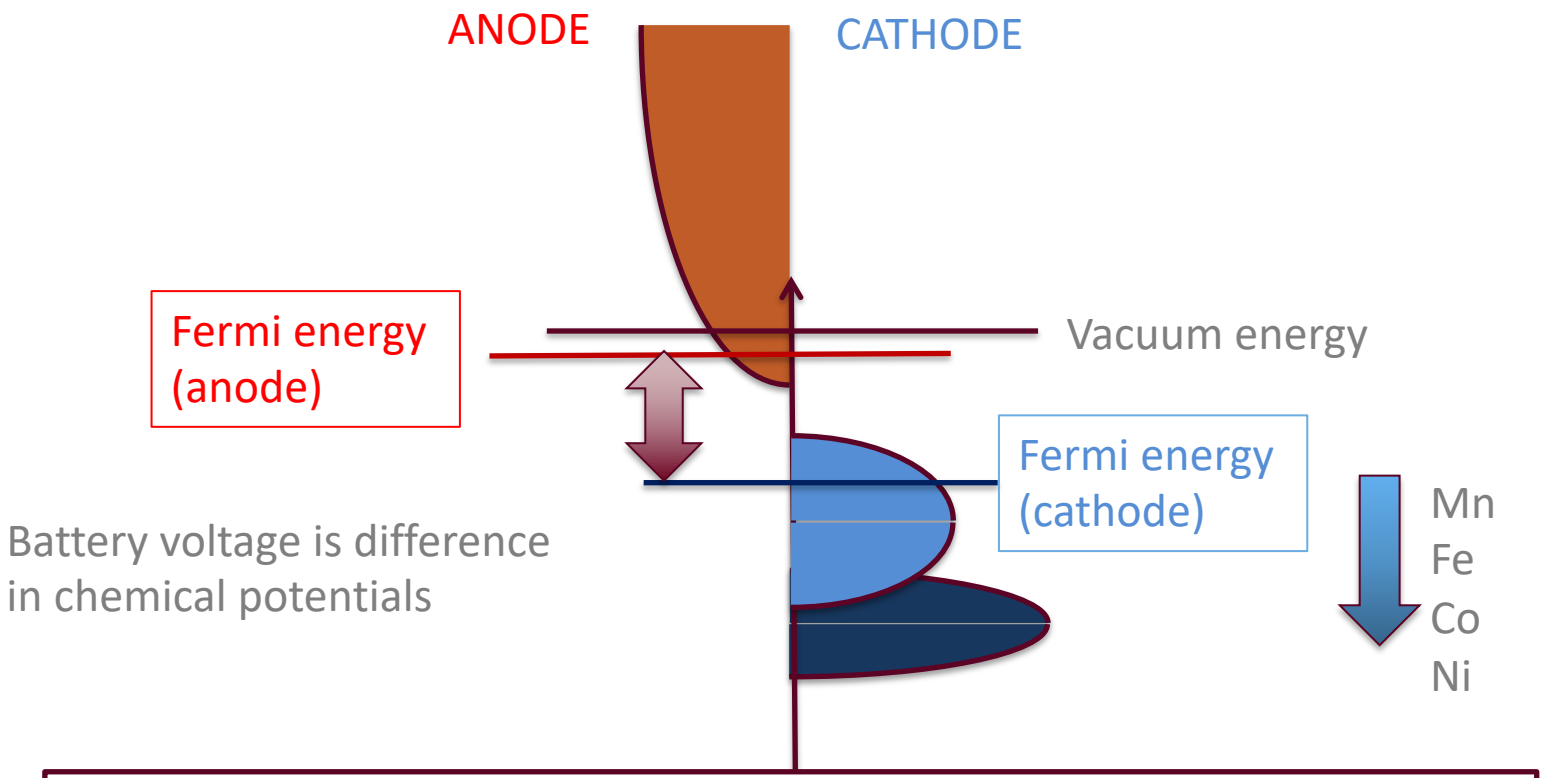


Isothermal entropy change



Patent 2017008234 GG Verri and PBL

Battery basics: electronic DOS vs. energy



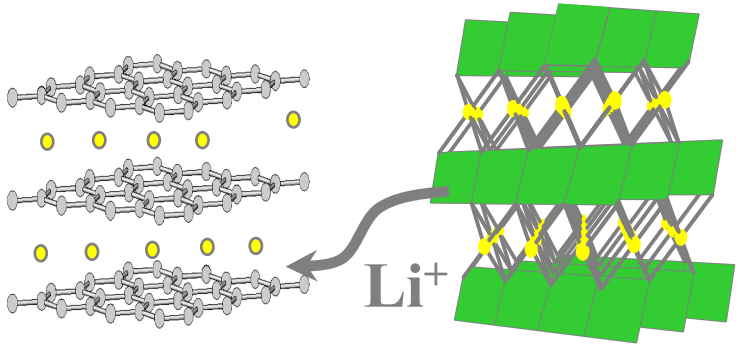
Want high density of states and deep levels (cathode)
- Use deep 3D states of transition metal (Mott physics?)

Want high density of states and shallow levels (anode)
- Move from graphite to nanotubes to Si to Li metal
- Use di- or tri-valent cation

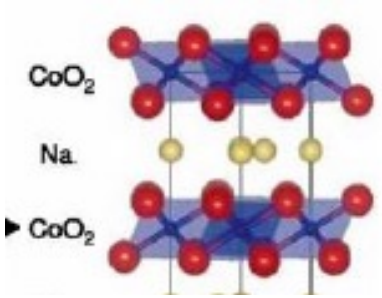
Need large band-gap stable electrolyte

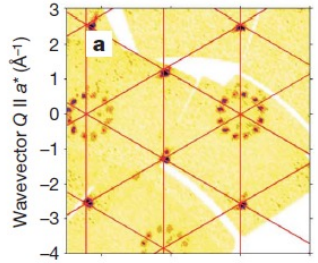
Tuning ionic mobilities in battery electrodes

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



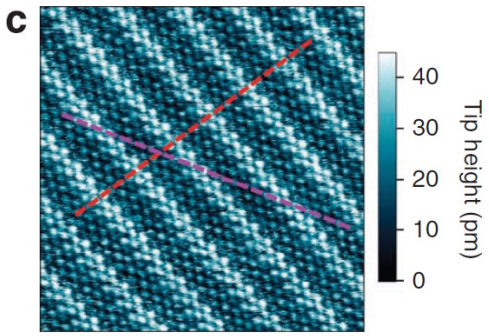
$Na_x CoO_2$
Enhanced thermopower, 5K superconductor
vacancy ordered phases

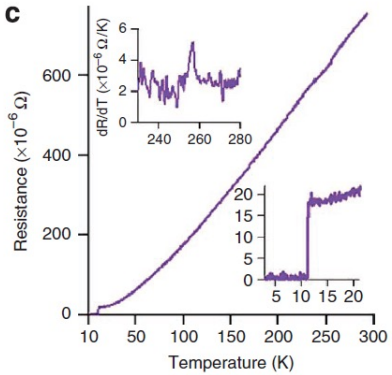




Roger et al. 2007 doi:10.1038/nature05531

CaC_6
12K superconductor; 250K CDW





Rahnejat et al 2011 DOI: 10.1038/ncomms1574

Some research targets that need softer correlated materials

Solid electrolyte materials

We would like insulating oxides(?) with high ionic mobility

There are many superionic conductors with Na, Hg, Ag, but not Li. Why?

Cathode materials for intercalation chemistry tend to be strongly correlated and have insulating phases driven by Coulomb interaction

A consequence in general of using deep d-levels. Can one find phases that are continuously metallic with substantial changes in doping?

THANK YOU