





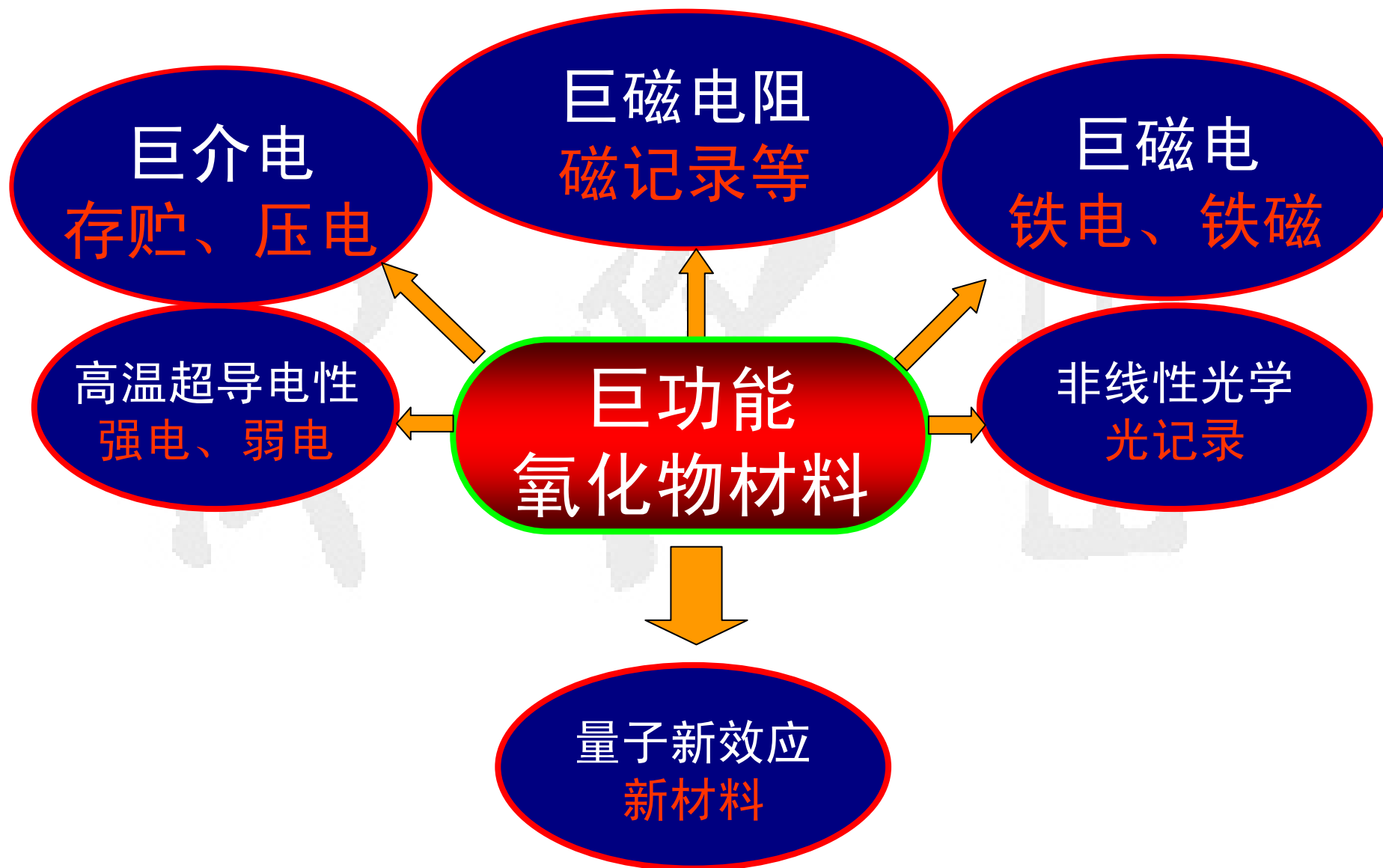
Functional transition metal oxides: effects, challenges, and opportunities

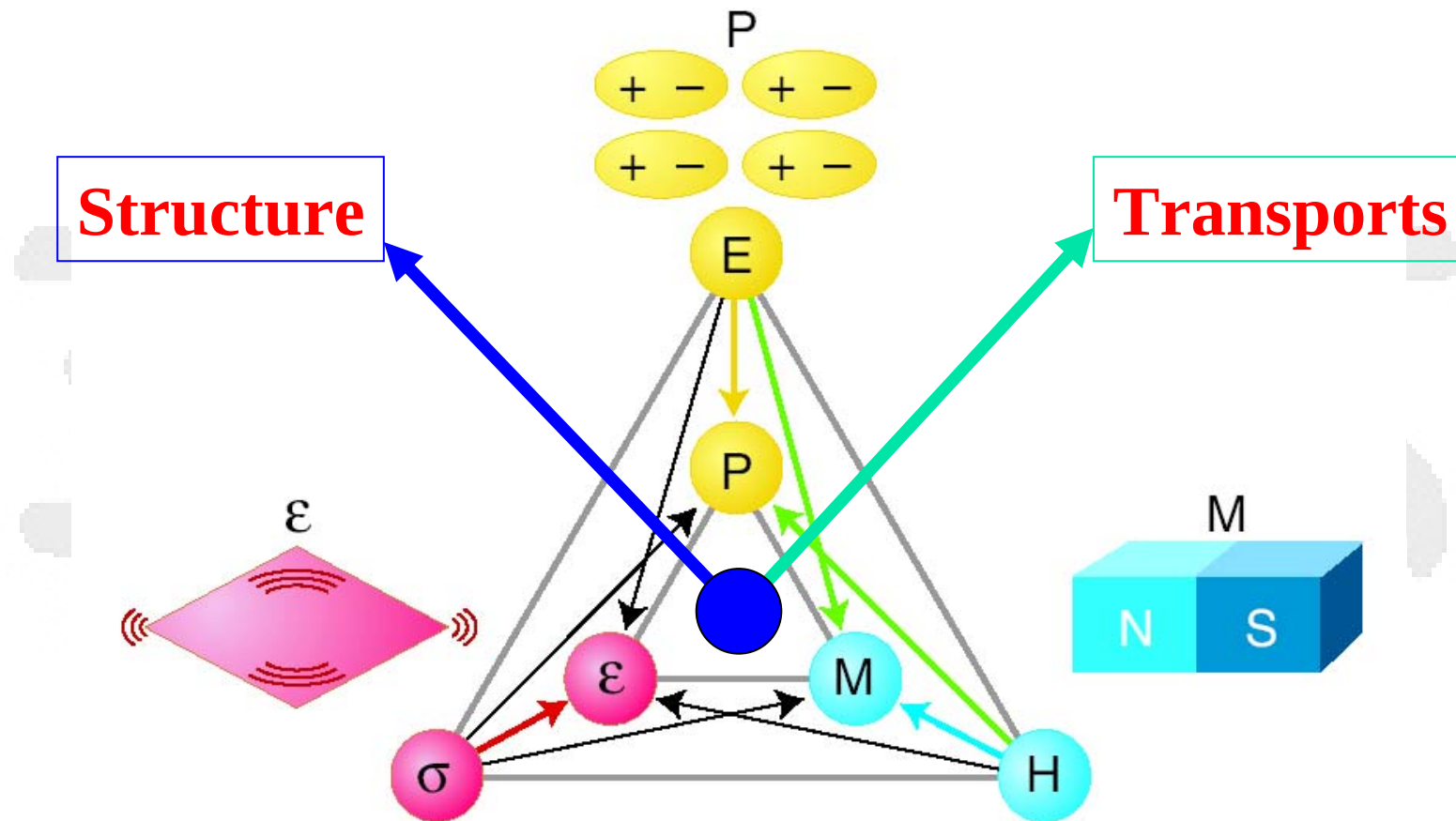
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Group page <http://pld.nju.edu.cn/>







Content

1. What we learn from chemists
2. CMR manganites
3. 4d/5d multifunctional oxides
4. Multiferroic oxides
5. Spin liquids and spin ices
6. Perspectives and challenges



What we learn from chemists

Transition metal oxides embedded in the periodical chart of elements

PERIODIC CHART OF THE ELEMENTS

IA IIA IIIB IVB VB VIB VIIB VIII IB IIB IIIA IVA VA VIA VIIA

INERT GASES

1 H 1.00797																	1 H 1.00797	2 He 4.0026					
3 Li 6.939	4 Be 9.0122																	5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312																	13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.9	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80						
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 14.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30						
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 78.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 95.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)						
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)												

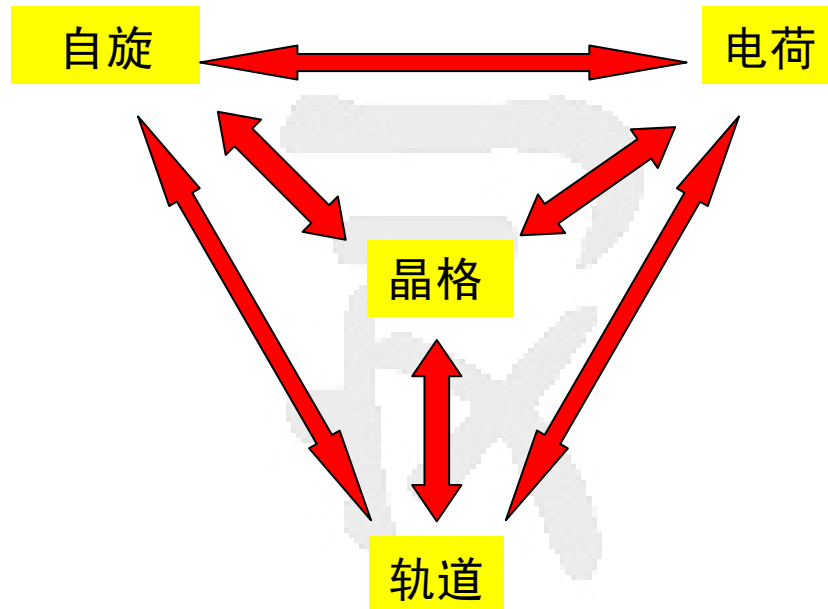
3d, 4d, & 5d transition metals

Th	1	Pa	2	U	3	Np	4	Pu	5	Am	6	Cm	7	Bk	8	Cf	9	Es	10	Fm	11	Md	12	No	13	Lr	14
← 5f →																											

From Wikipedia & GC, Kentucky



What we learn from chemists



- Structure determines the interactions
- The interactions determine the orders
- Quantum theory on charges, spins, orbitals, and phonons

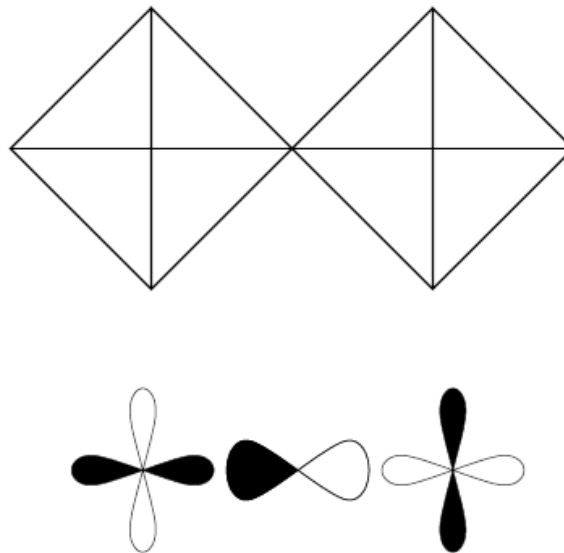
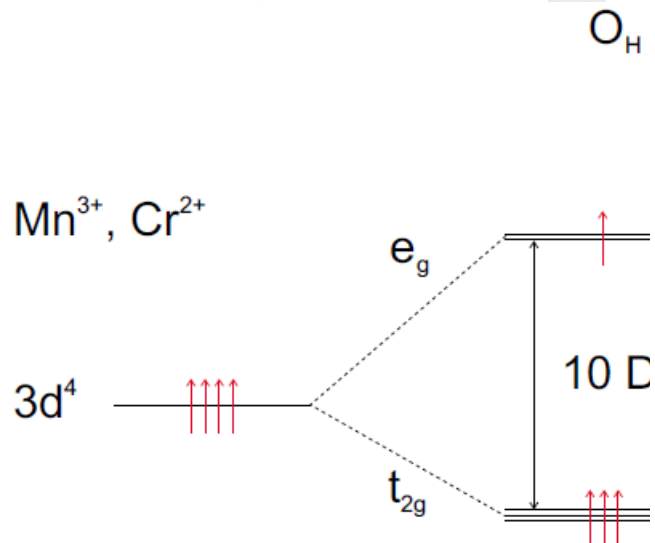


- Goodenough-Kanamori rules
- Tolerance factor

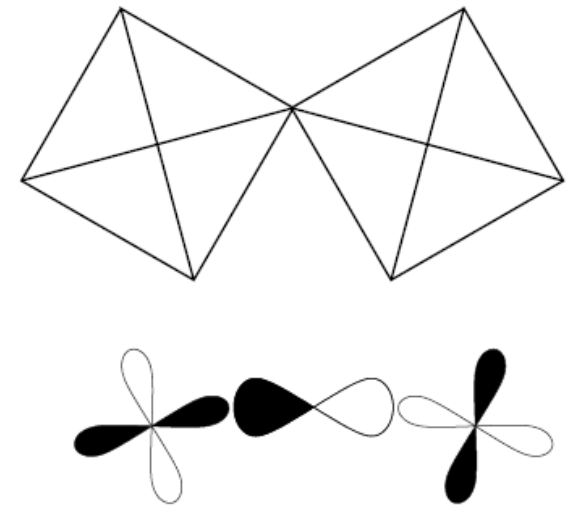


What we learn from chemists: Goodenough-Kanamori rules

- ❑ Semi-empirical rules applied to predict magnetic and electronic interactions in transition metal oxides.
- ❑ Extended rules to more complex transition metal oxides.



M-O-M bond angle $\sim 180^\circ$

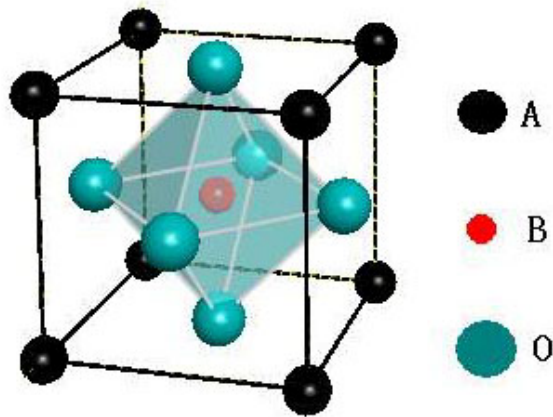


M-O-M bond angle $< 180^\circ$



What we learn from chemists: Tolerance factor

- A structural factor to measure the mismatch between AO layer and BO_2 layer in ABO_3 -type oxides.
- It has been extended to other transition metal oxides.

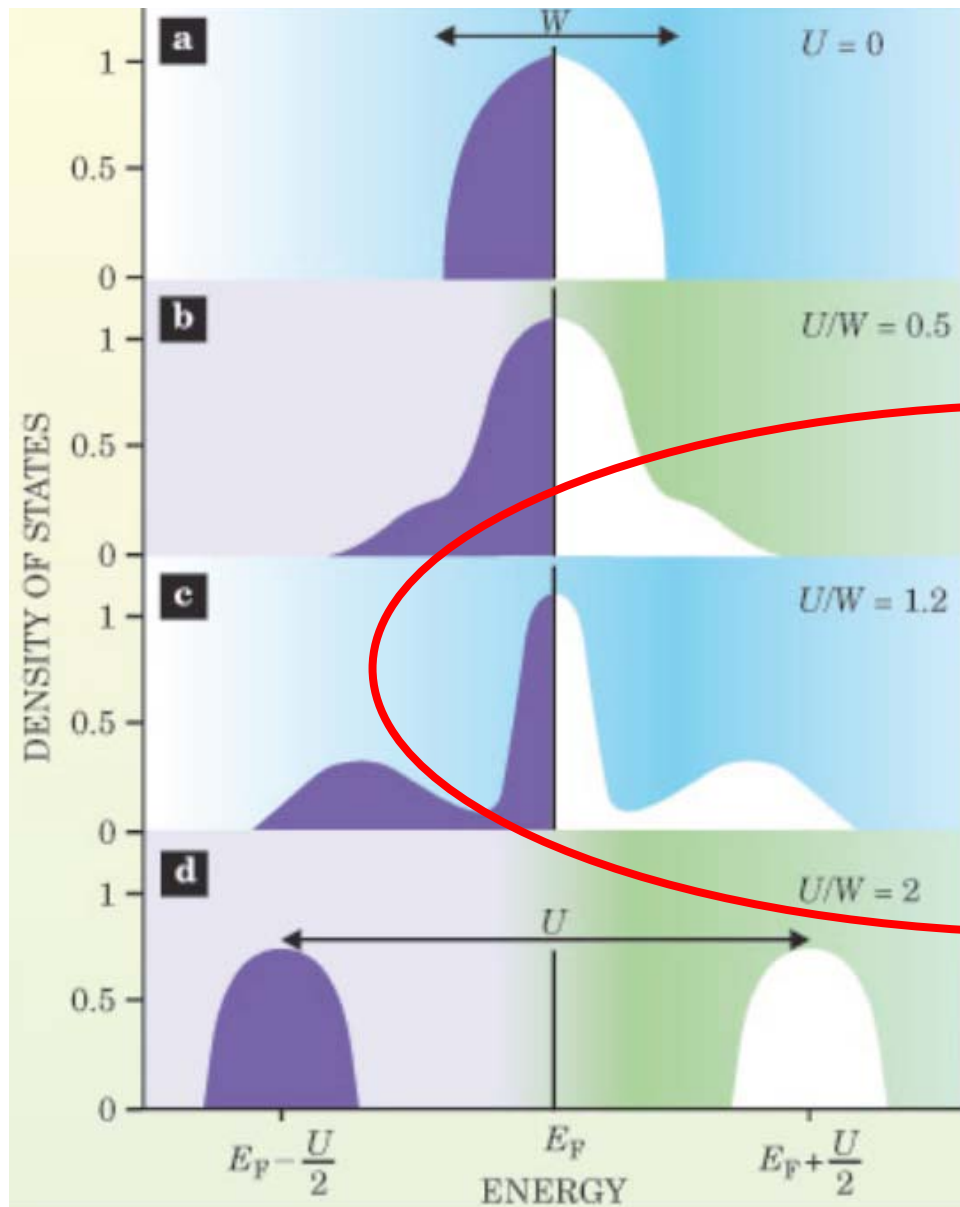


- $f=1.0 \Rightarrow$ ideal cubic
- $f=0.96 \sim 1.0 \Rightarrow$ rhombohedral & tetragonal
- $f=0.75 \sim 0.96 \Rightarrow$ orthorhombic
- $f > 1.0 \Rightarrow$ hexagonal

$$f = (\langle r_A \rangle + r_O) / \sqrt{2}(r_B + r_O) = d_{A-O} / (\sqrt{2}d_{Mn-O})$$



What we learn from chemists: strong correlation



Metals: $U < W$

*Free electrons (a) or
nearly free electrons (b).*

Stable ground state

Metals or Insulator: $U \sim W$

*Strongly correlated
electrons.*

*On the verge of
metal-insulator transition*

Unstable ground state

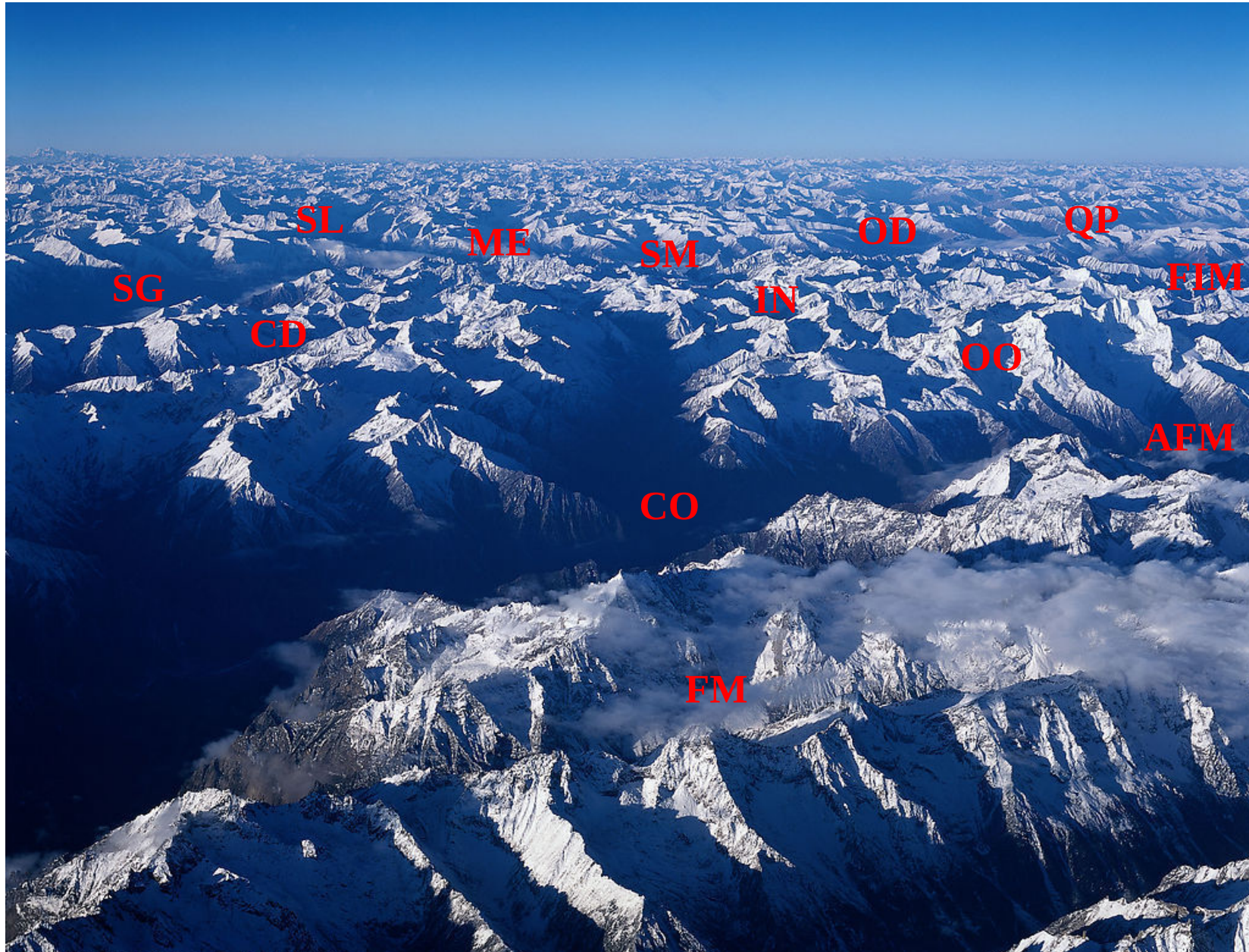
Insulators: $U > W$

Stable ground state

Kotliar, Phys. Today 2004 & GC, private comm.



What we learn from chemists: **multifold** landscape in energy





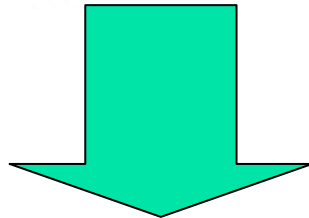
What we learn from chemists: delicate balance





What we learn from chemists: effects & properties

- ✓ **Always exhibit physical complexity and tunability**
- ✓ **Hard materials act like soft matter**
- ✓ **On the edge of multi-fold competitions**
- ✓ **Tend to show giant responses and dynamics in response to small perturbations**



Four classes of typical and emergent materials

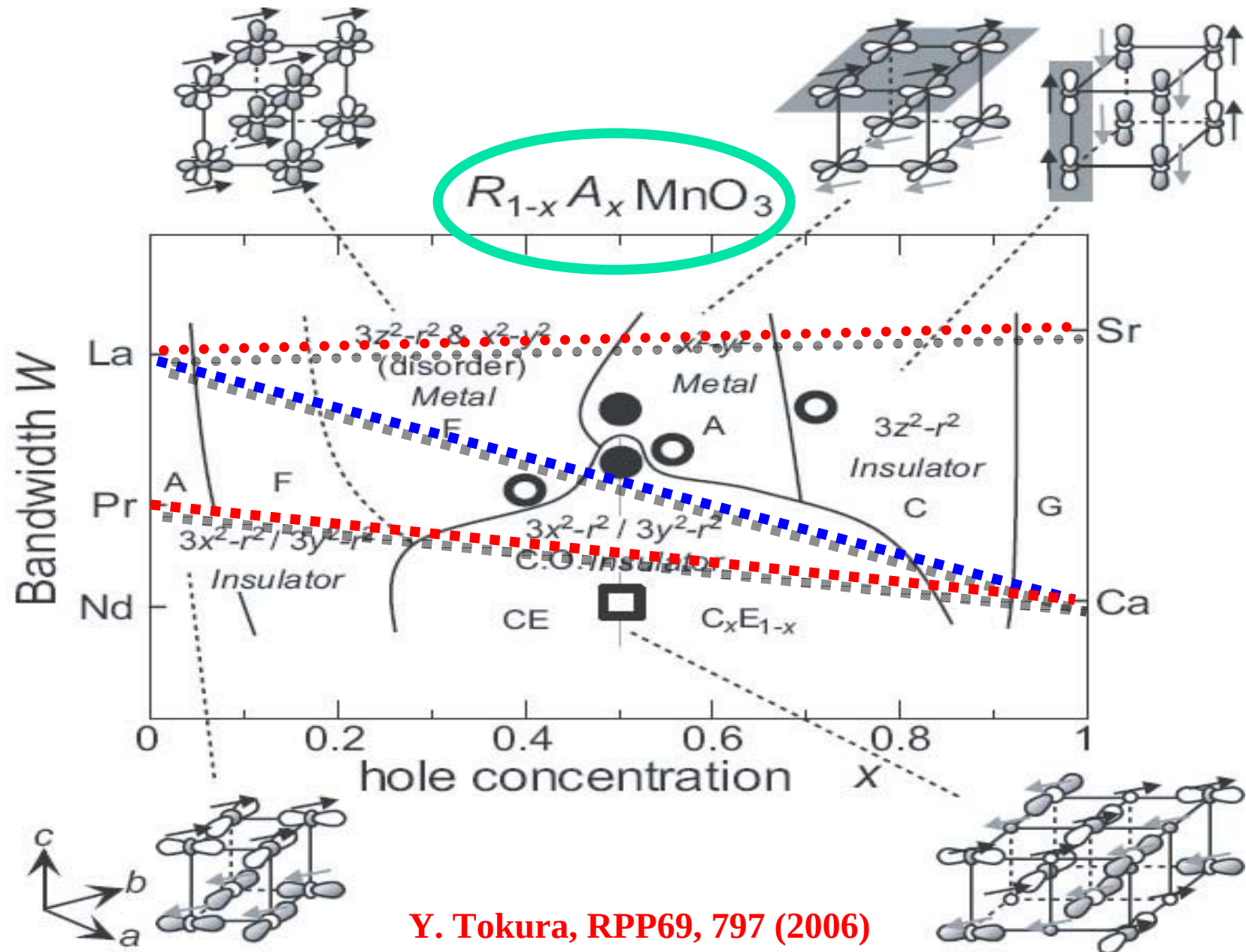


CMR manganites





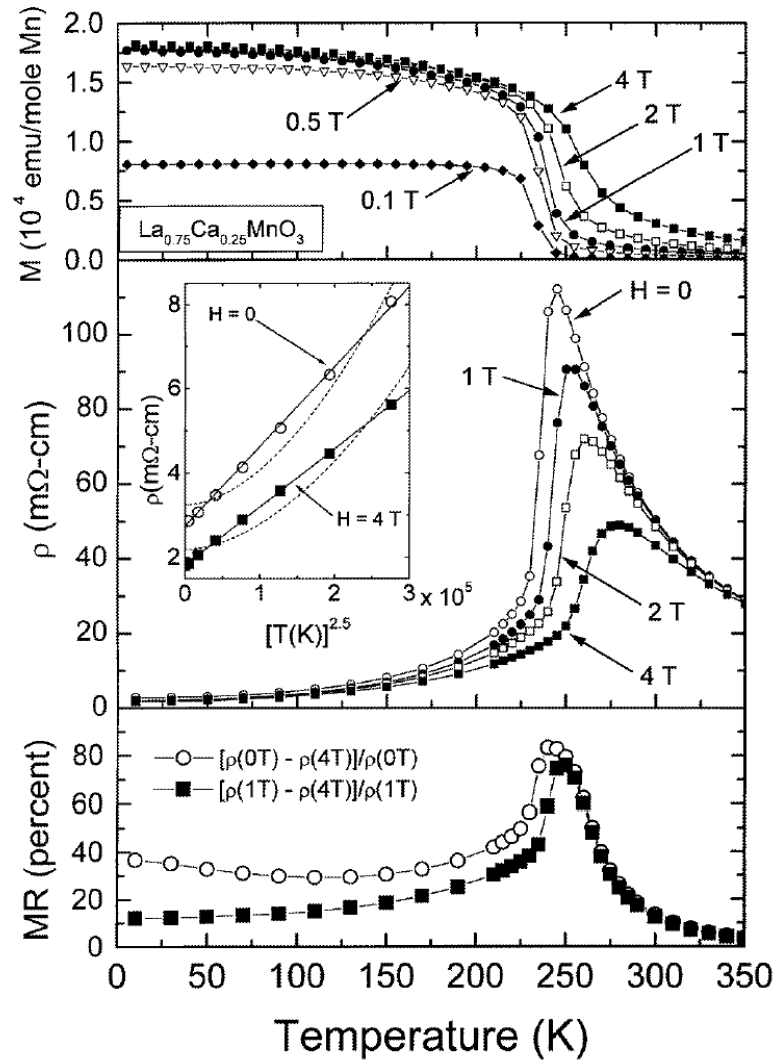
CMR manganites: structure, charges, & orders



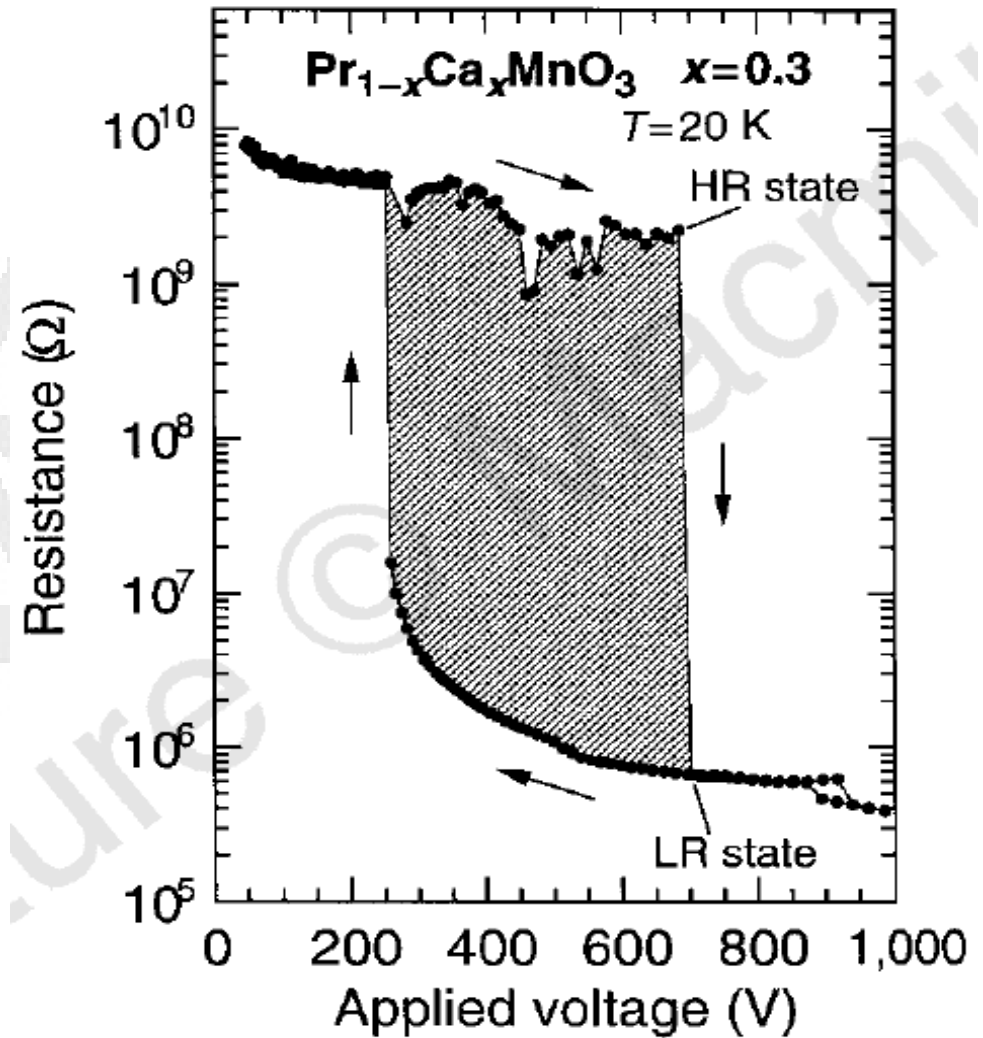
Y. Tokura, RPP69, 797 (2006)



CMR manganites: transport behaviors



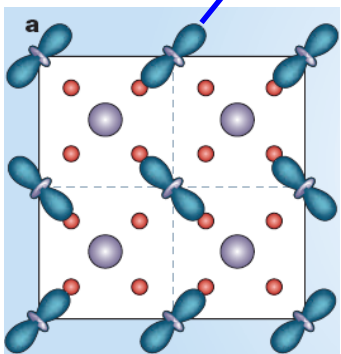
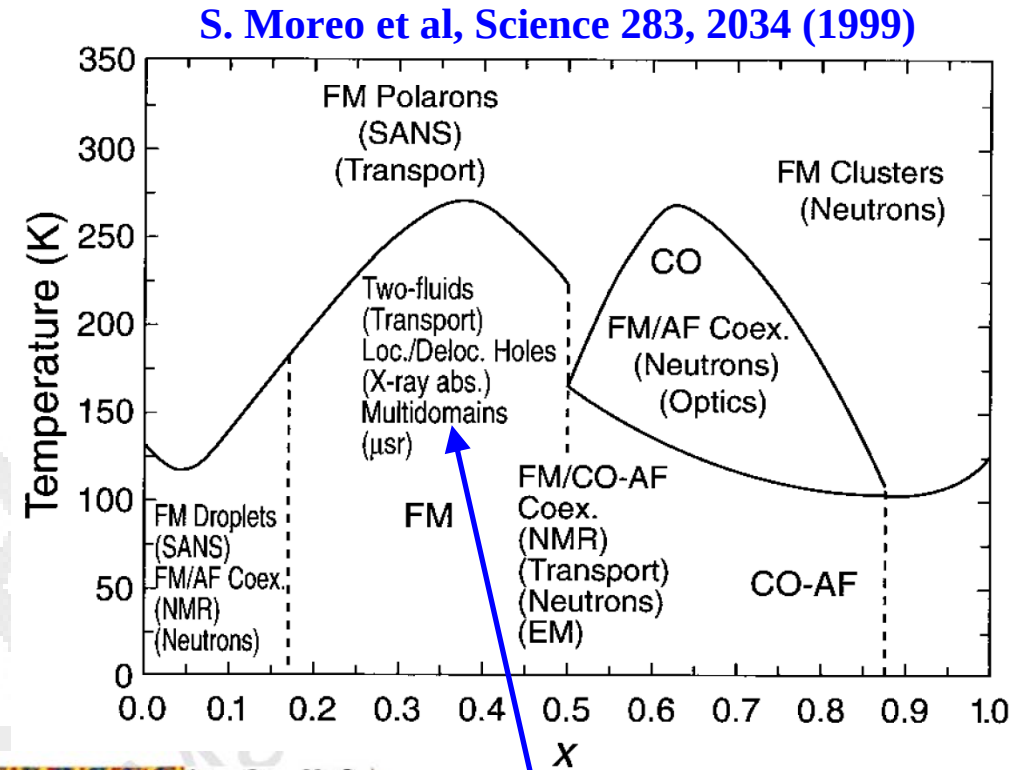
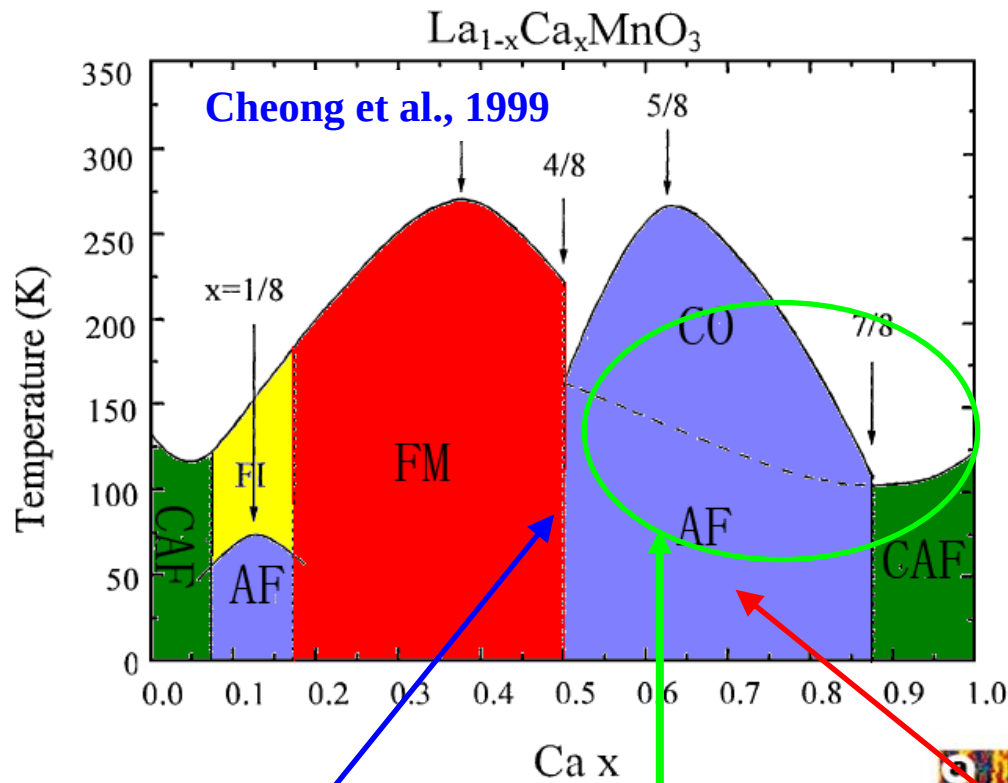
Y. Tokura et al, JPSJ 63, 3931 (1994)



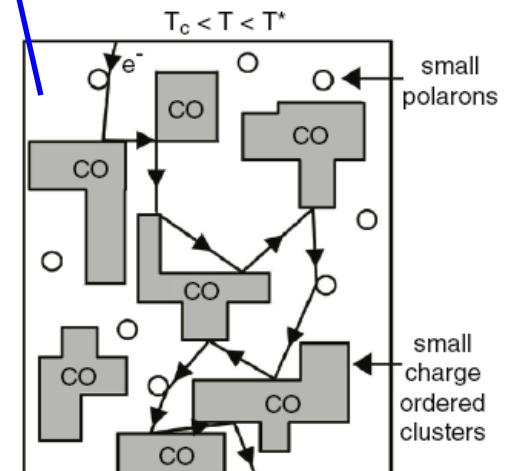
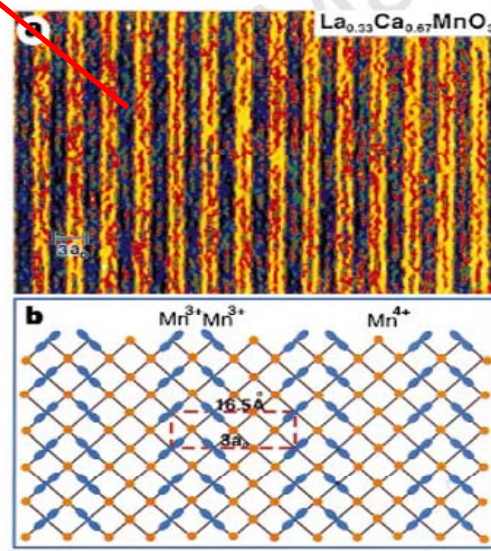
A. Asamitsu et al. Nature 388, 50(1997)



CMR manganites: phase diagram



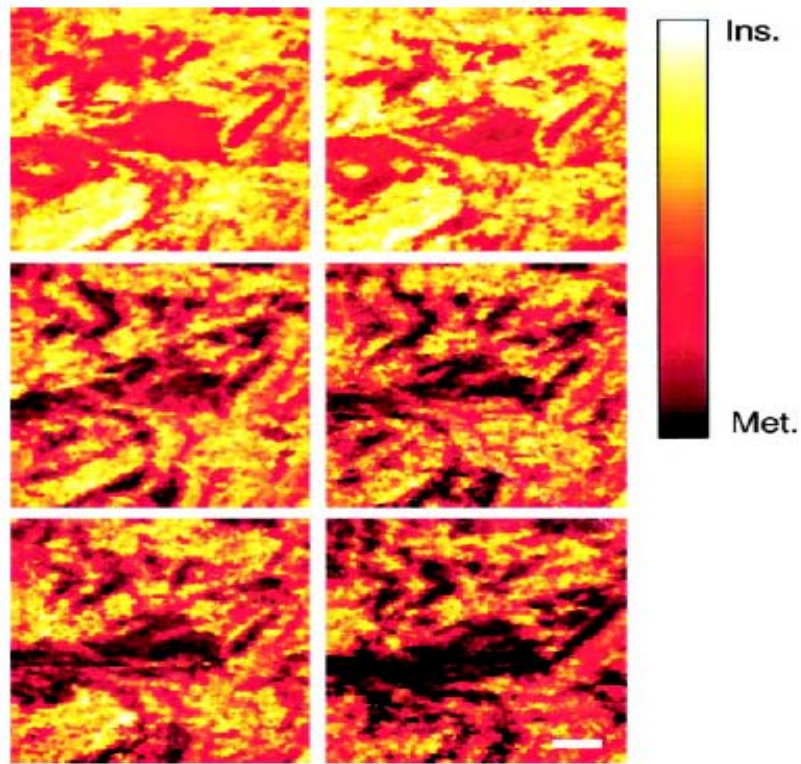
Synthesis issues





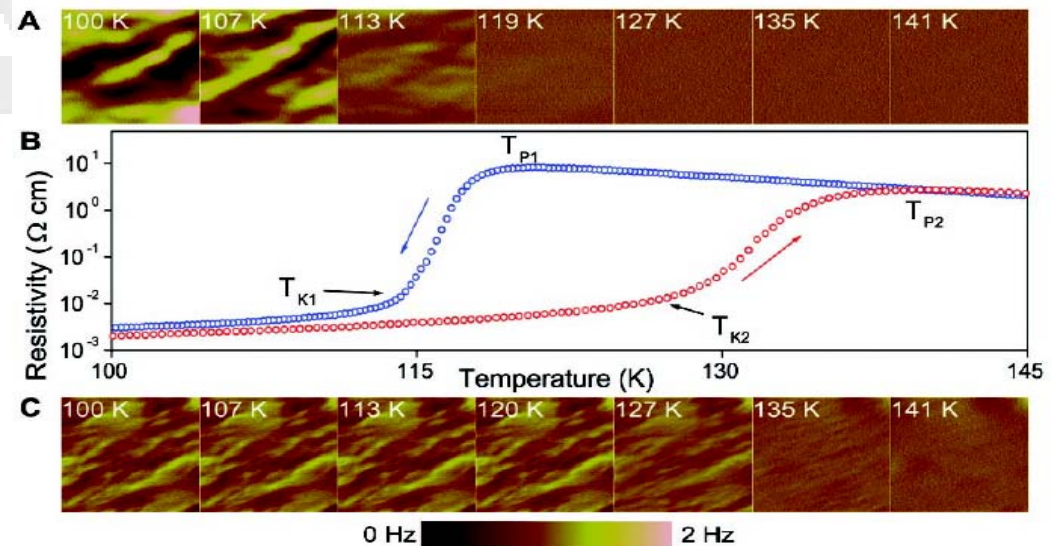
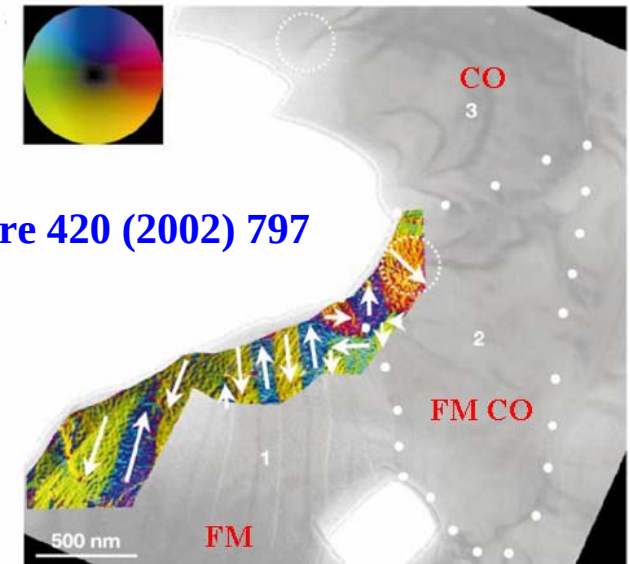
CMR manganites: electronic phase separation

Quantum metal-insulator transitions (MIT) and electronic phase separation



M. Fäth et al., *Science* 285(1999) 1540

J. C. Loudon et al. *Nature* 420 (2002) 797

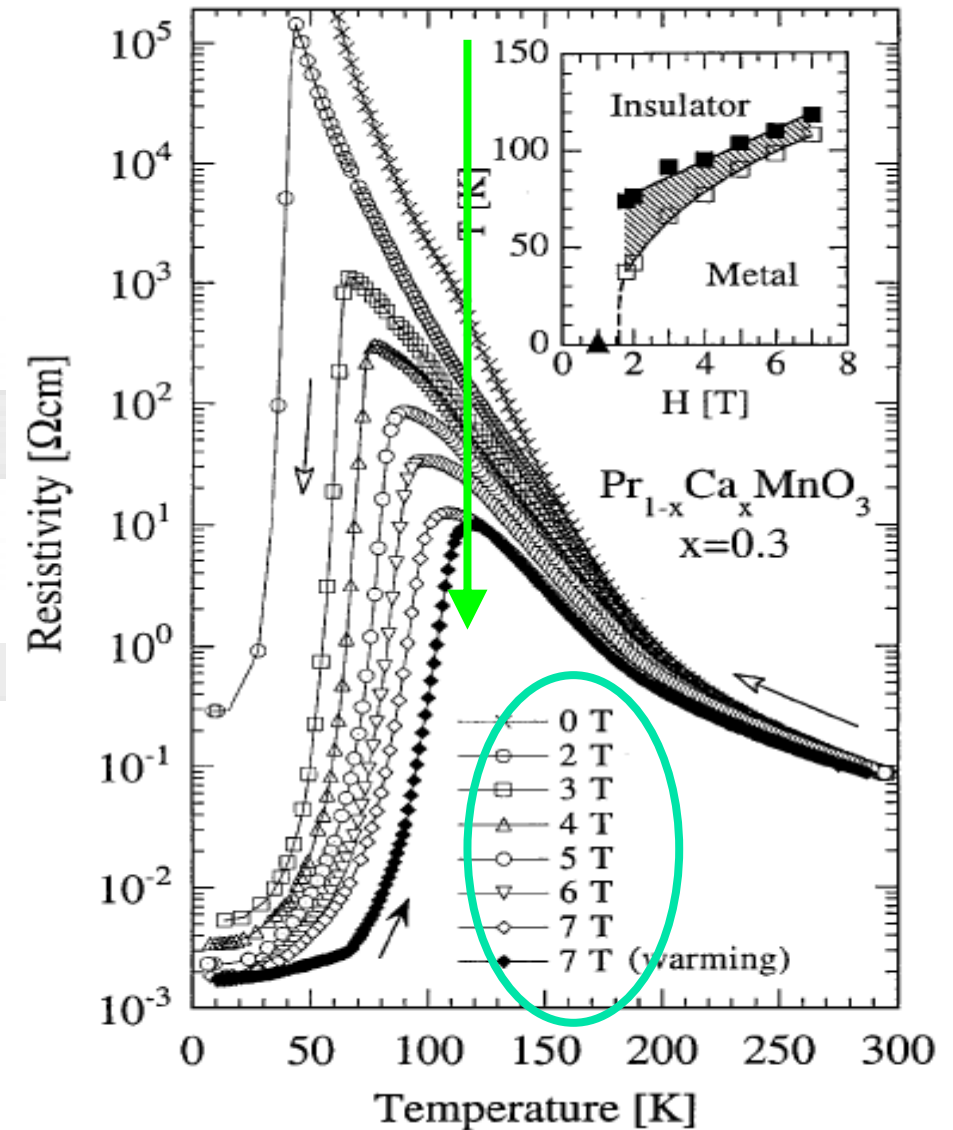


J. Burgy et al, *PRL* 87, 277202 (2001)



CMR manganites: focused issues

1. Low MR response to low magnetic field
2. Low temperature for applications
3. Synthesis of electron-type manganites

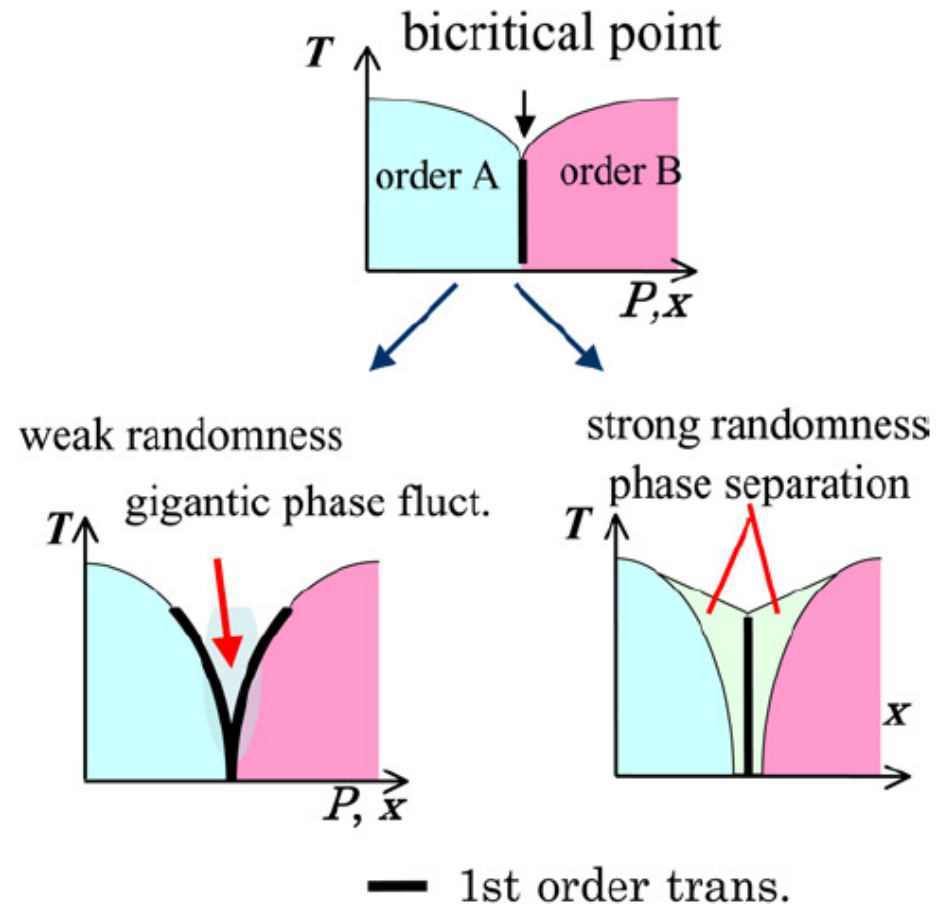
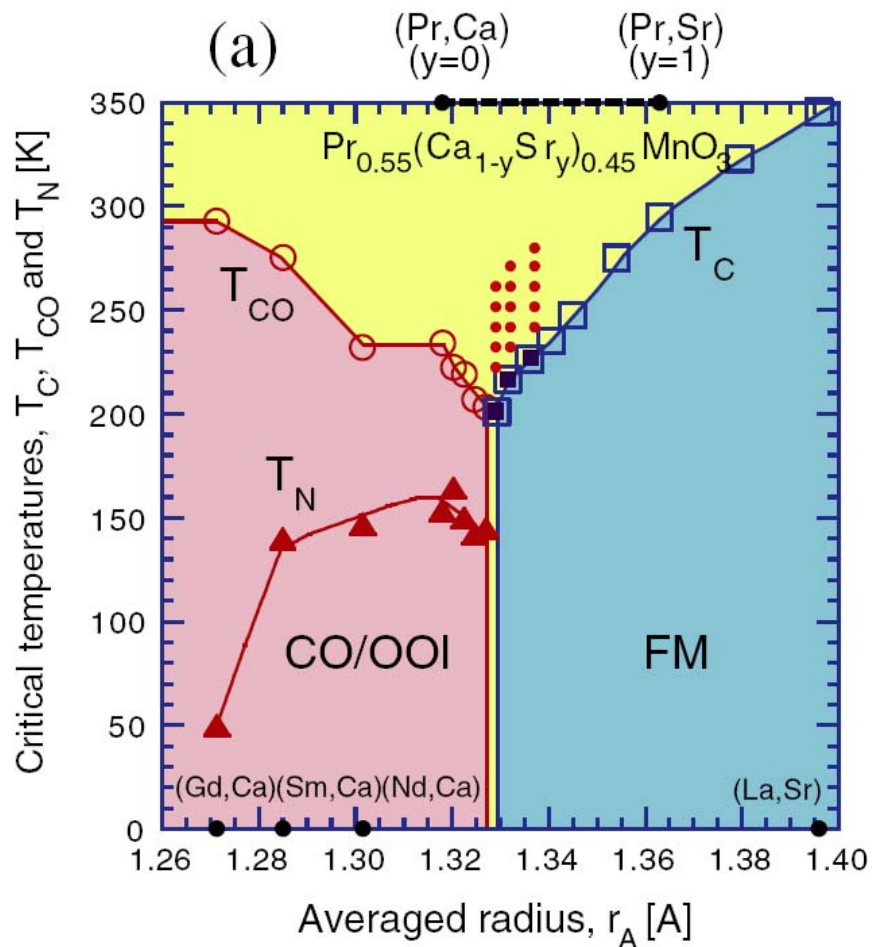


Tomioka and Tokura (1999)



CMR manganites: effects of disorder

Ground state competition at bi-critical points

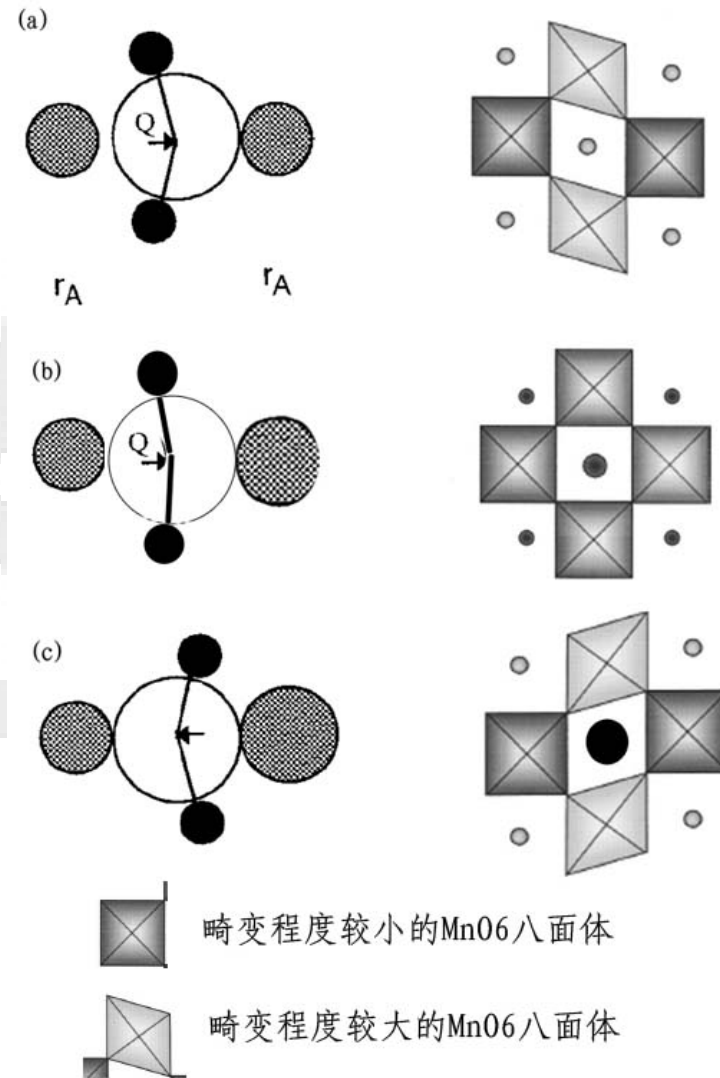
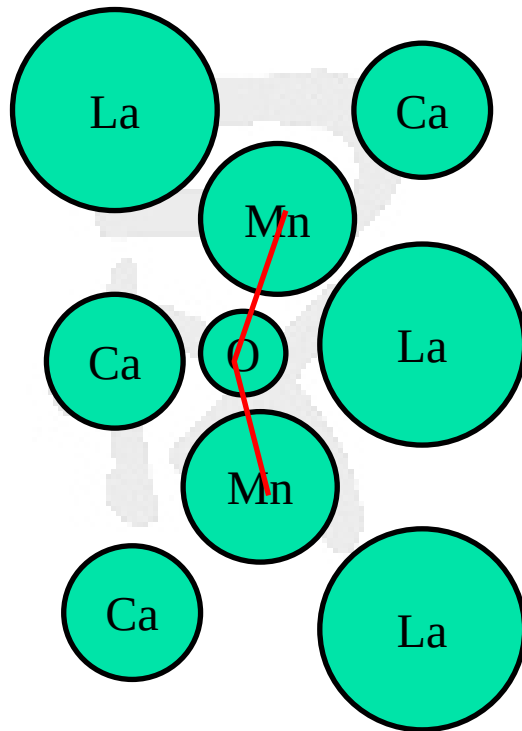


S. Murakami et al, PRL 90, 197201 (2003)

Y. Tokura, Rep. Prog. Phys. 69, 797 (2006)



CMR manganites: effects of disorder

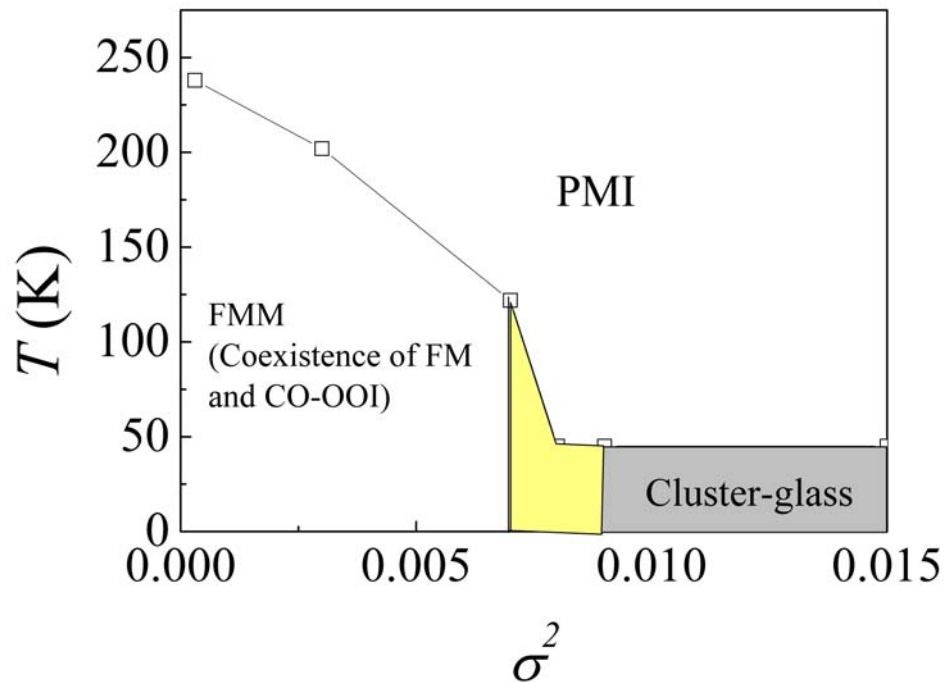


$$\sigma^2 = \sum_i x_i r_i^2 - \langle r_A \rangle^2$$



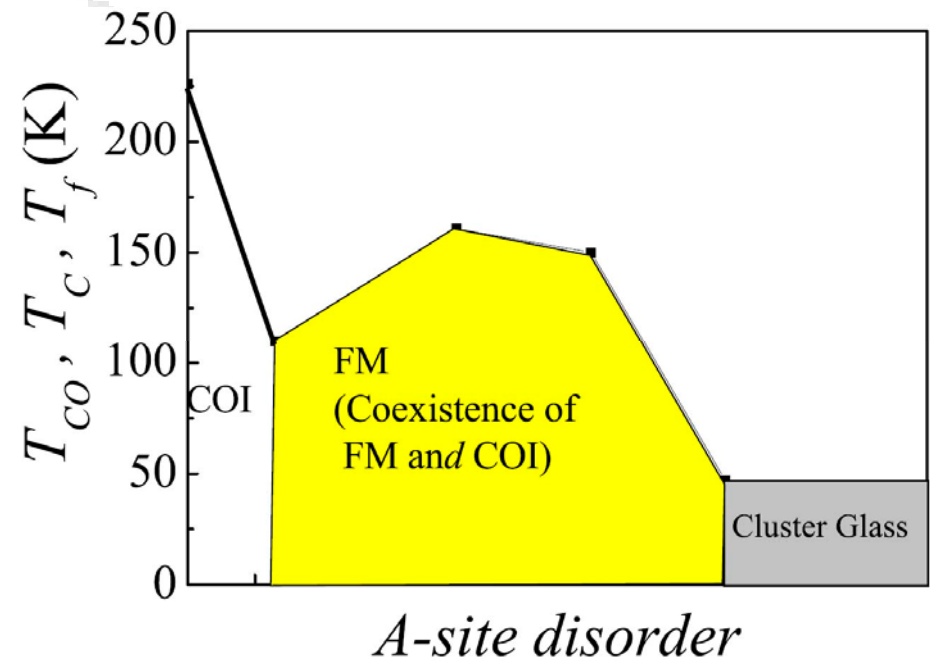
CMR manganites: effects of disorder

$\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$: $\langle r_A \rangle = 0.120\text{nm}$



**Disorder $\Rightarrow$ EPS but lower T
and lower MR**

$\text{Pr}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$: $\langle r_A \rangle = 0.118\text{nm}$

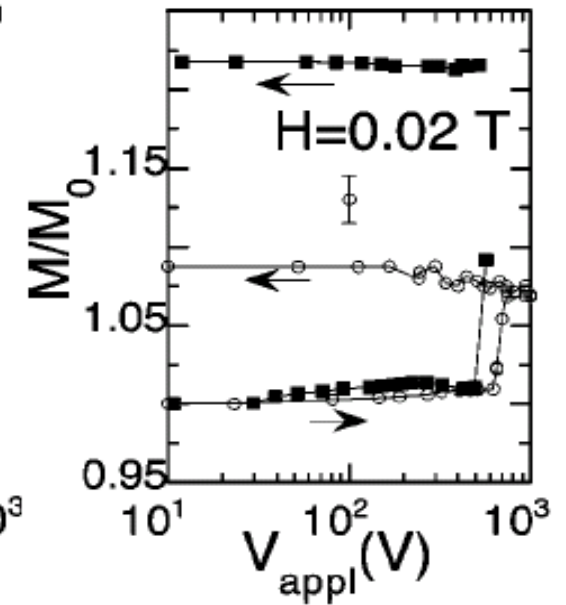
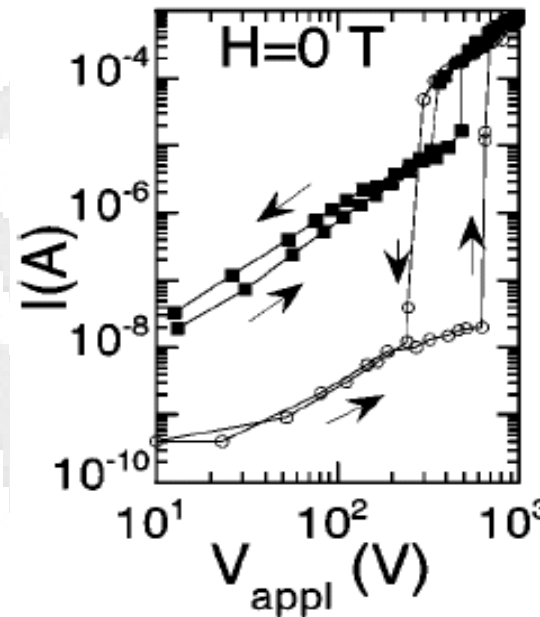
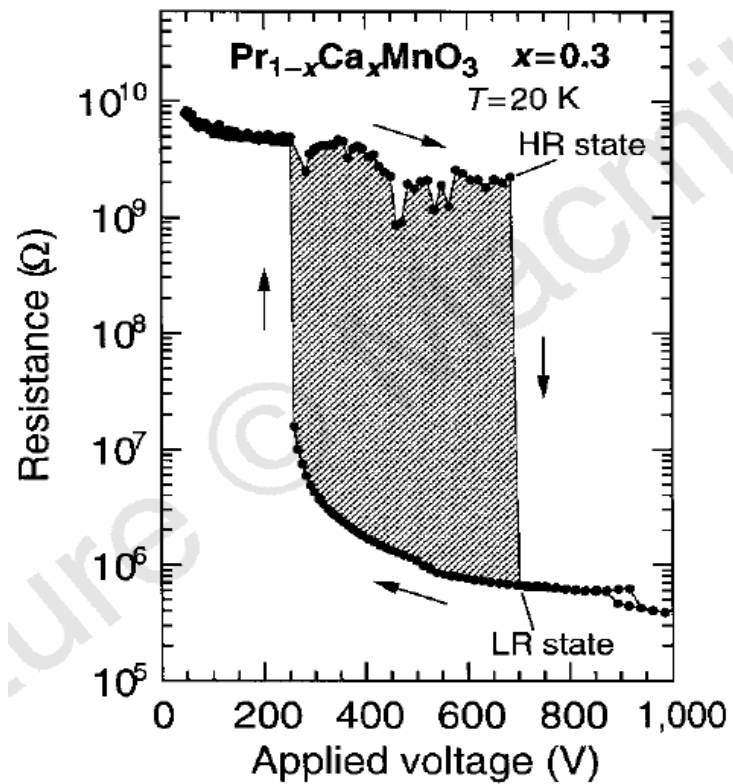


**Disorder $\Rightarrow$ EPS but higher T
and larger MR**



CMR manganites: electroresistance

Electroresistance in manganites



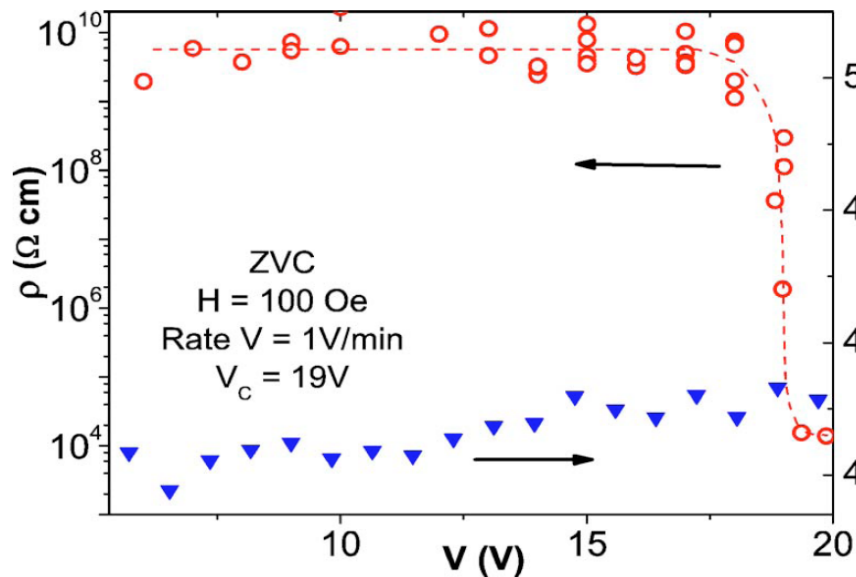
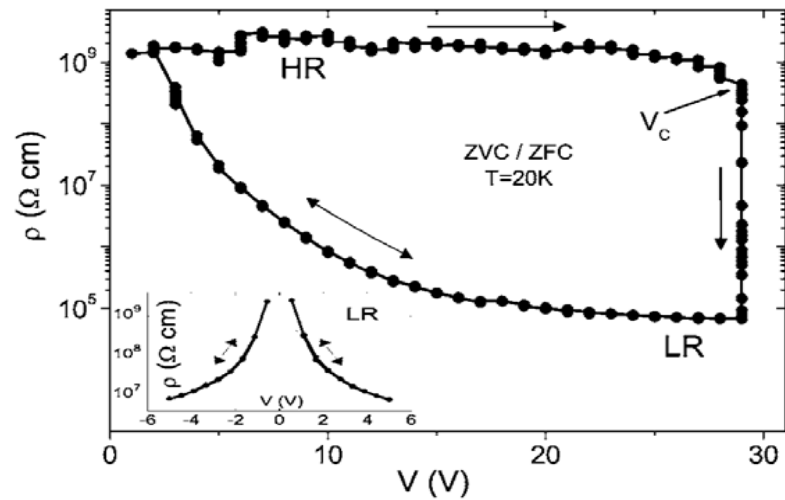
A. Asamitsu et al. Nature 388, 50 (1997)

J. Stankiewicz et al. PRB 61, 11236 (2000)

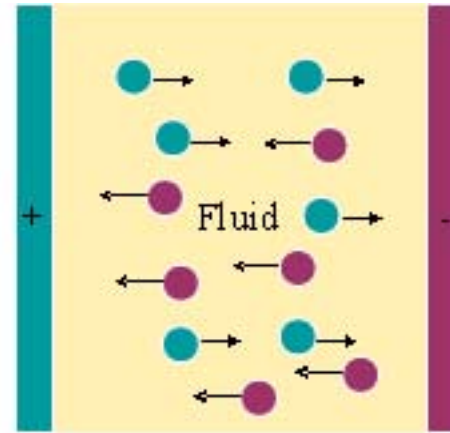


CMR manganites: electroresistance

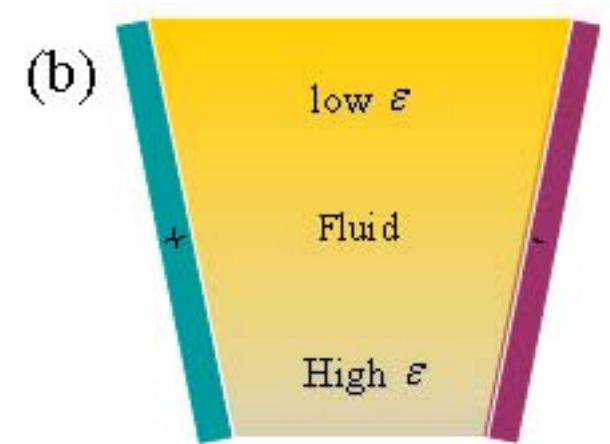
$\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ ($y \sim 0.4$)



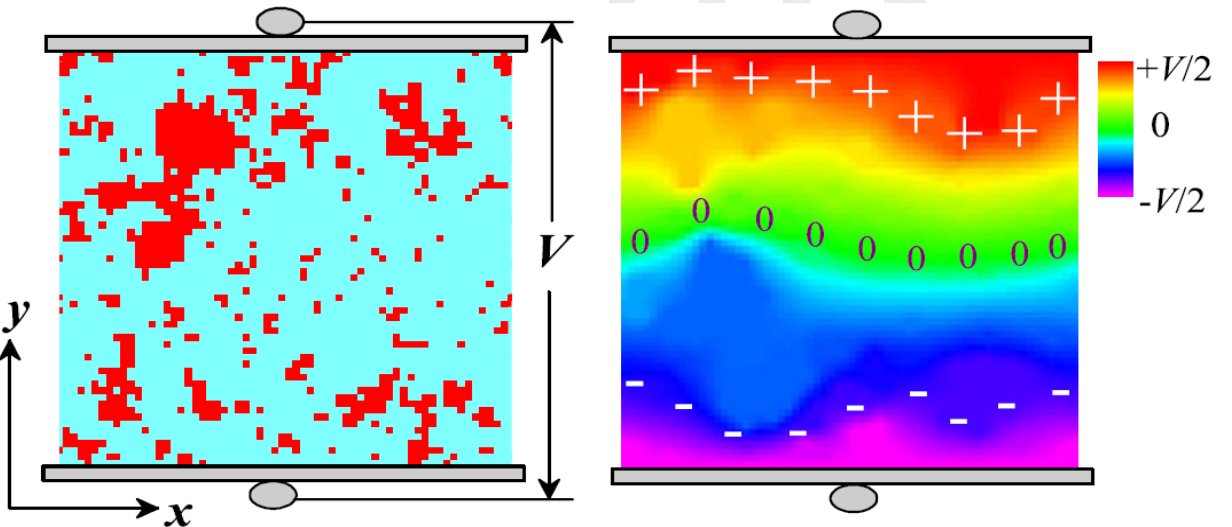
Dielectrophoresis mechanism



electrophoresis



dielectrophoresis

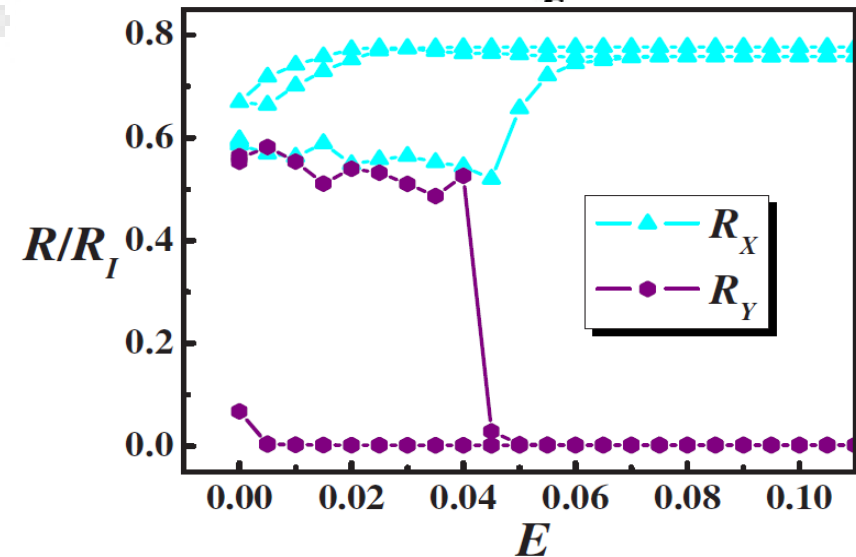
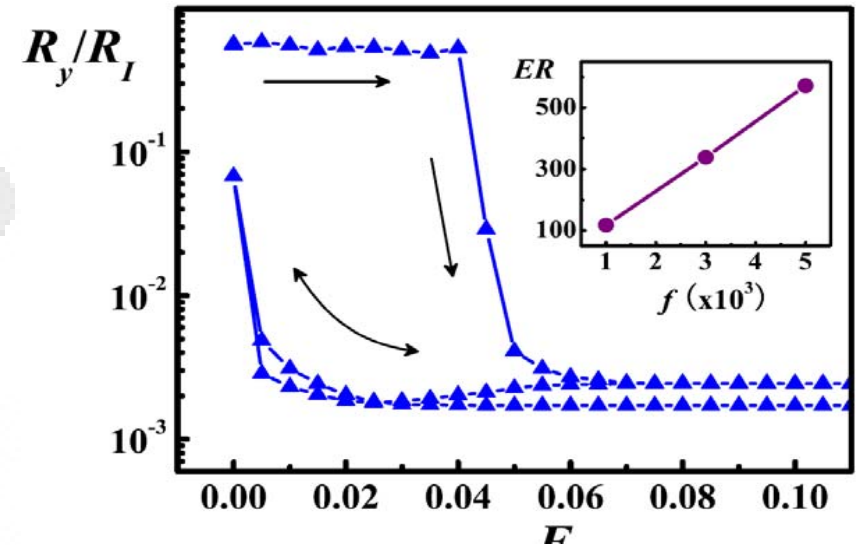
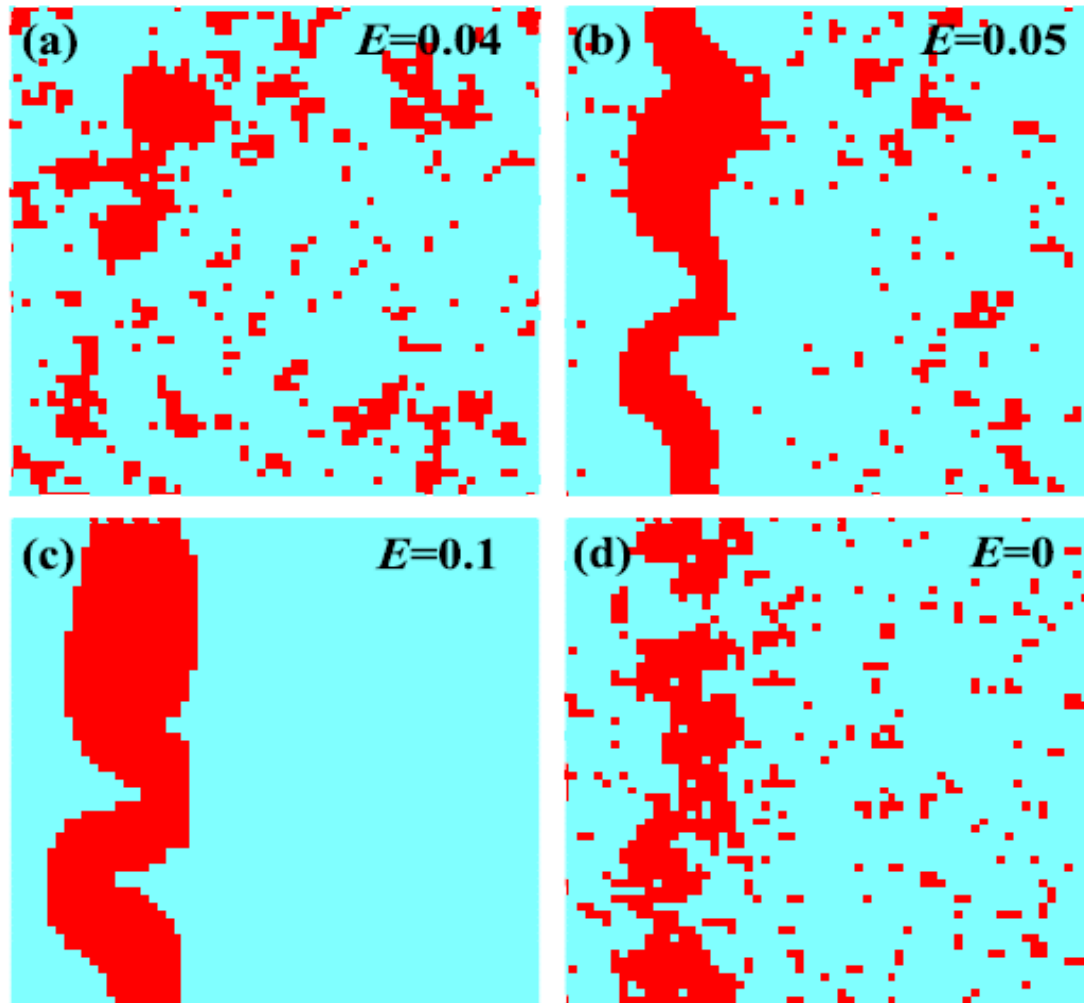


G. Garbarino *et al.* PRB 74, 100401(R) (2006)



CMR manganites: electroresistance

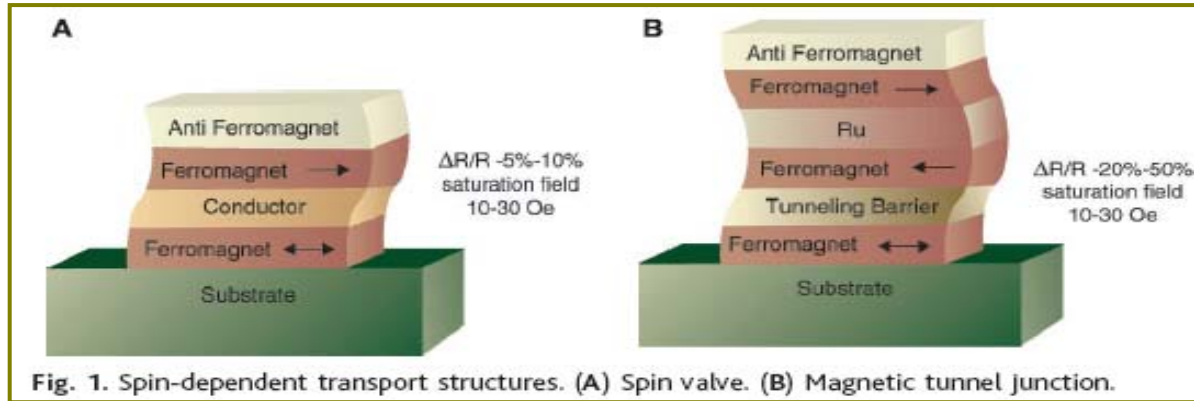
Dielectrophoresis scenario consistent with experiments



S. Dong et al. PRB 76, 32409 (2007)



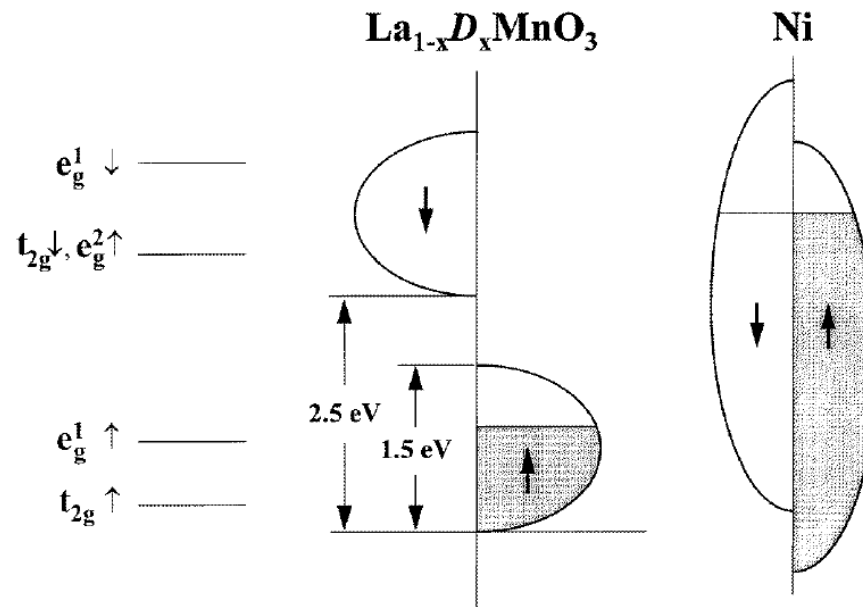
CMR manganites: spintronics & RRAM



$$MR = \frac{\rho_0 - \rho_H}{\rho_H} = \frac{(1 - \tilde{\gamma}) P^2 M^2}{1 + \tilde{\gamma}}$$

$$P = \frac{N_{\uparrow}(\mu) - N_{\uparrow}(\mu)}{N_{\downarrow}(\mu) - N_{\downarrow}(\mu)}$$

$$= \frac{\sqrt[3]{1 + m(T)} - \sqrt[3]{1 - m(T)}}{\sqrt[3]{1 + m(T)} + \sqrt[3]{1 - m(T)}}$$

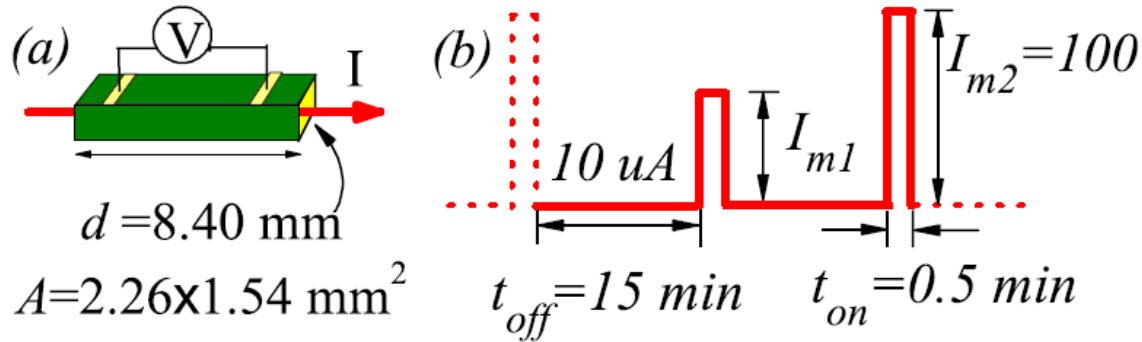


- High spin-polarized ratio
- Low T and high H

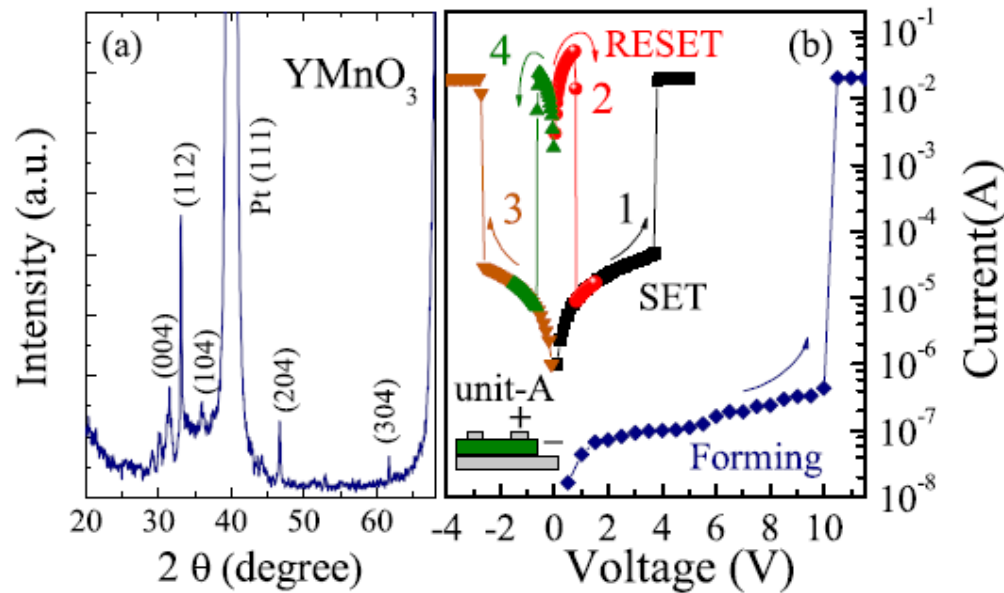


CMR manganites: spintronics & RRAM

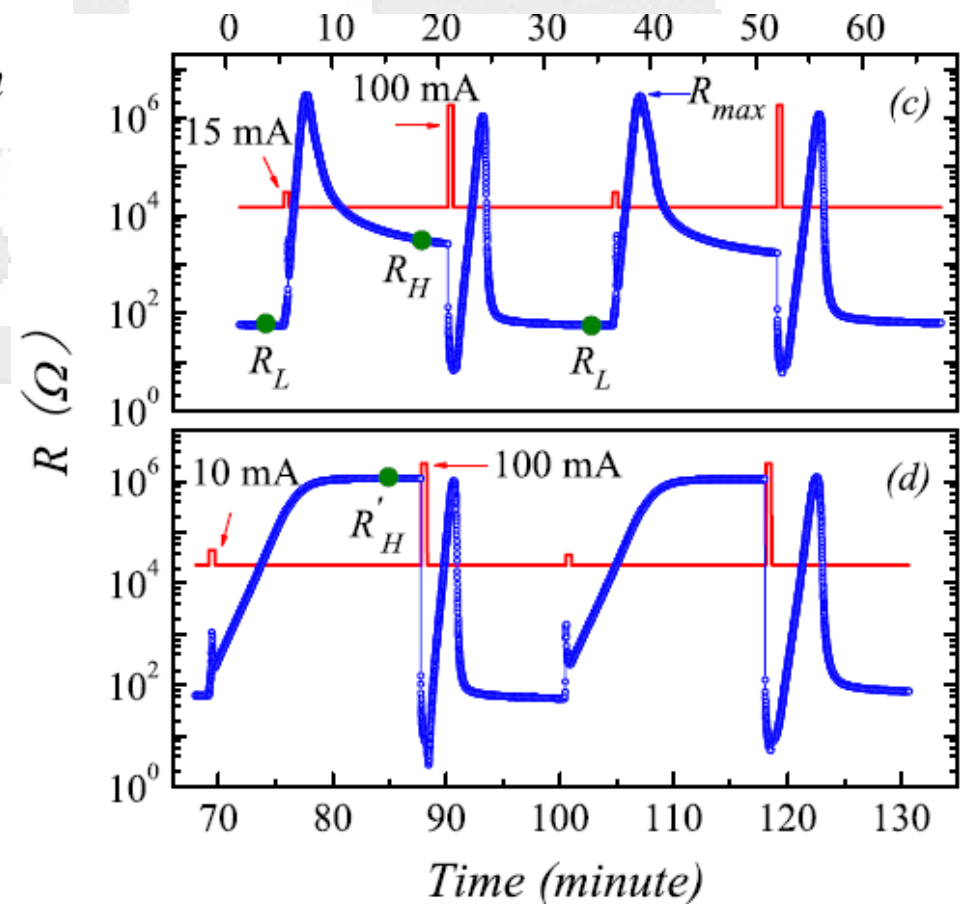
Application of dielectrophoresis to resistance RAMS



Z. Yan et al. APL 95, 143502 (2009)

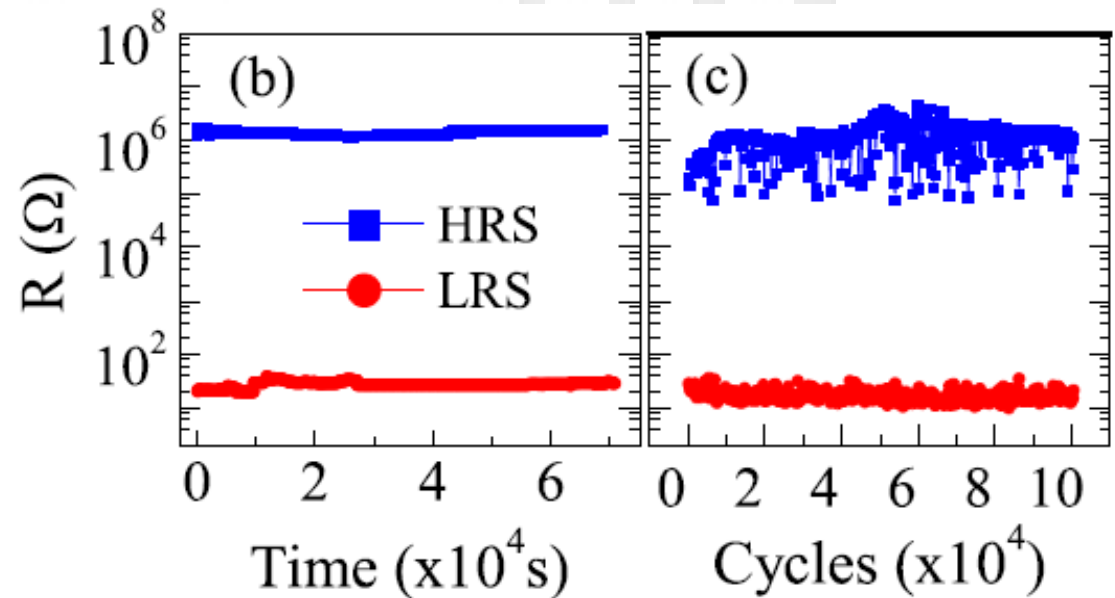
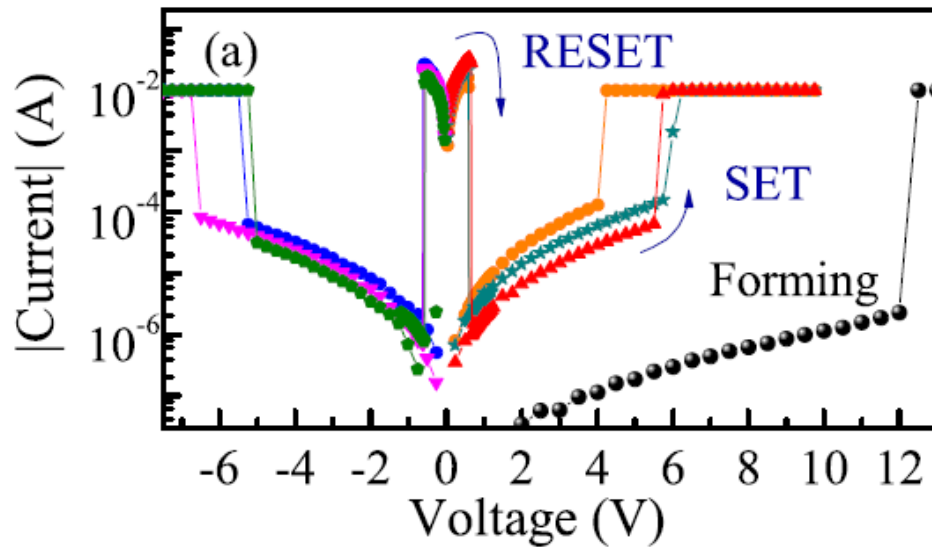
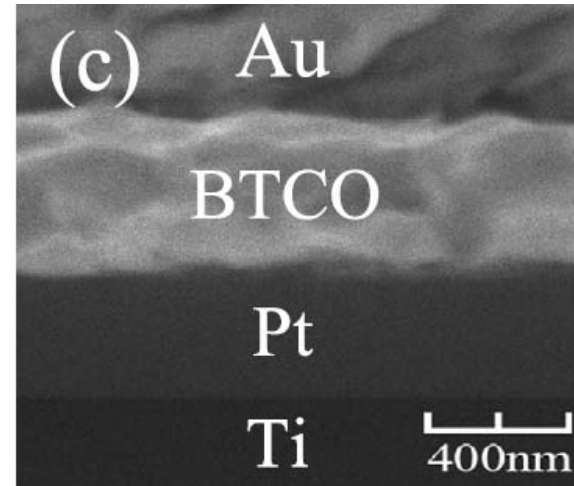
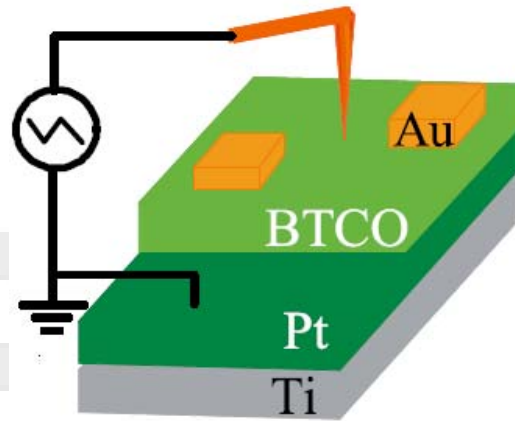


Z. Yan et al. APL 96, 012103 (2010)





CMR manganites: spintronics & RRAM





4d/5d multifunctional oxides

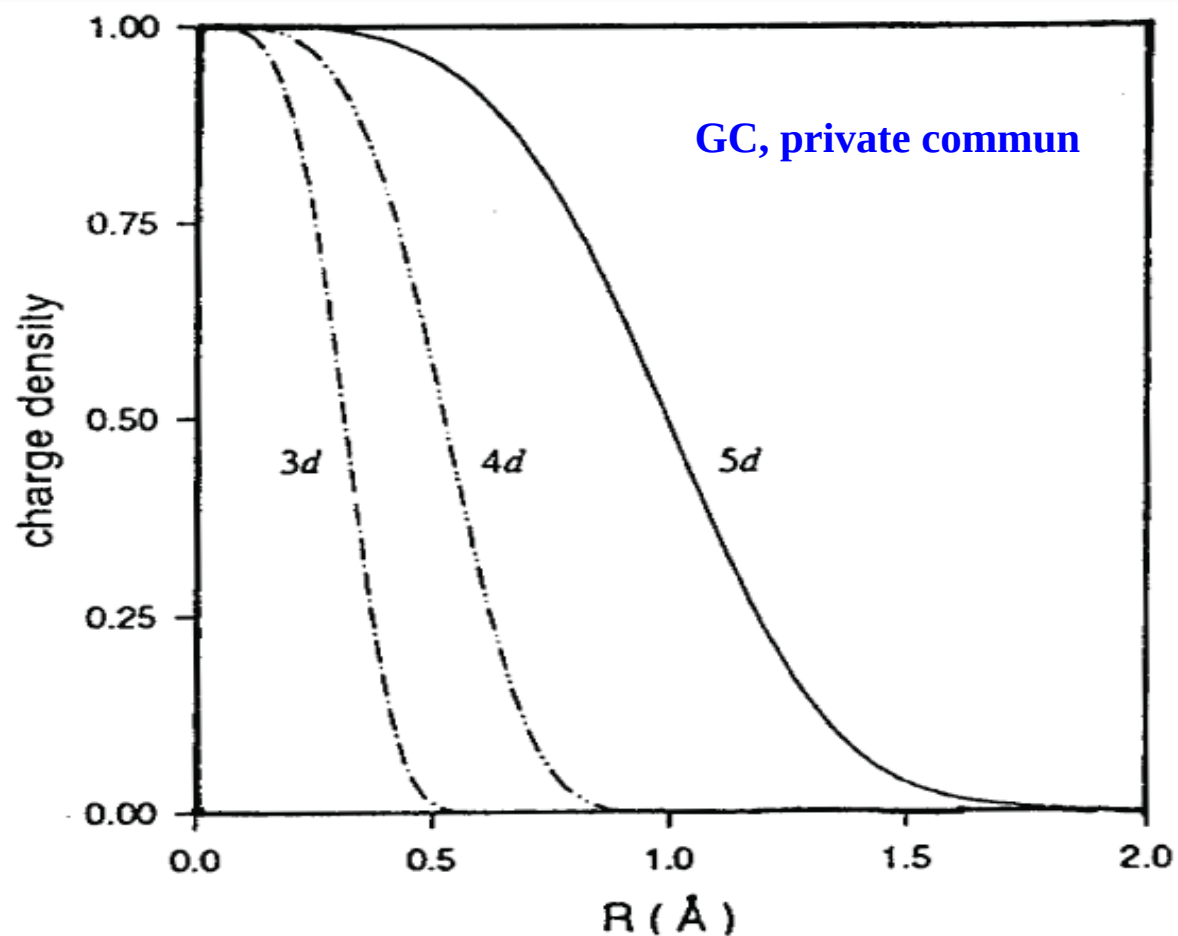


T=Ru, Ir, Rh etc



4d/5d oxides: extended charge density

Extended d-electron Orbitals



Charge Density as a Function of Spatial Extent



4d/5d oxides: Ruddlesden-Popper series

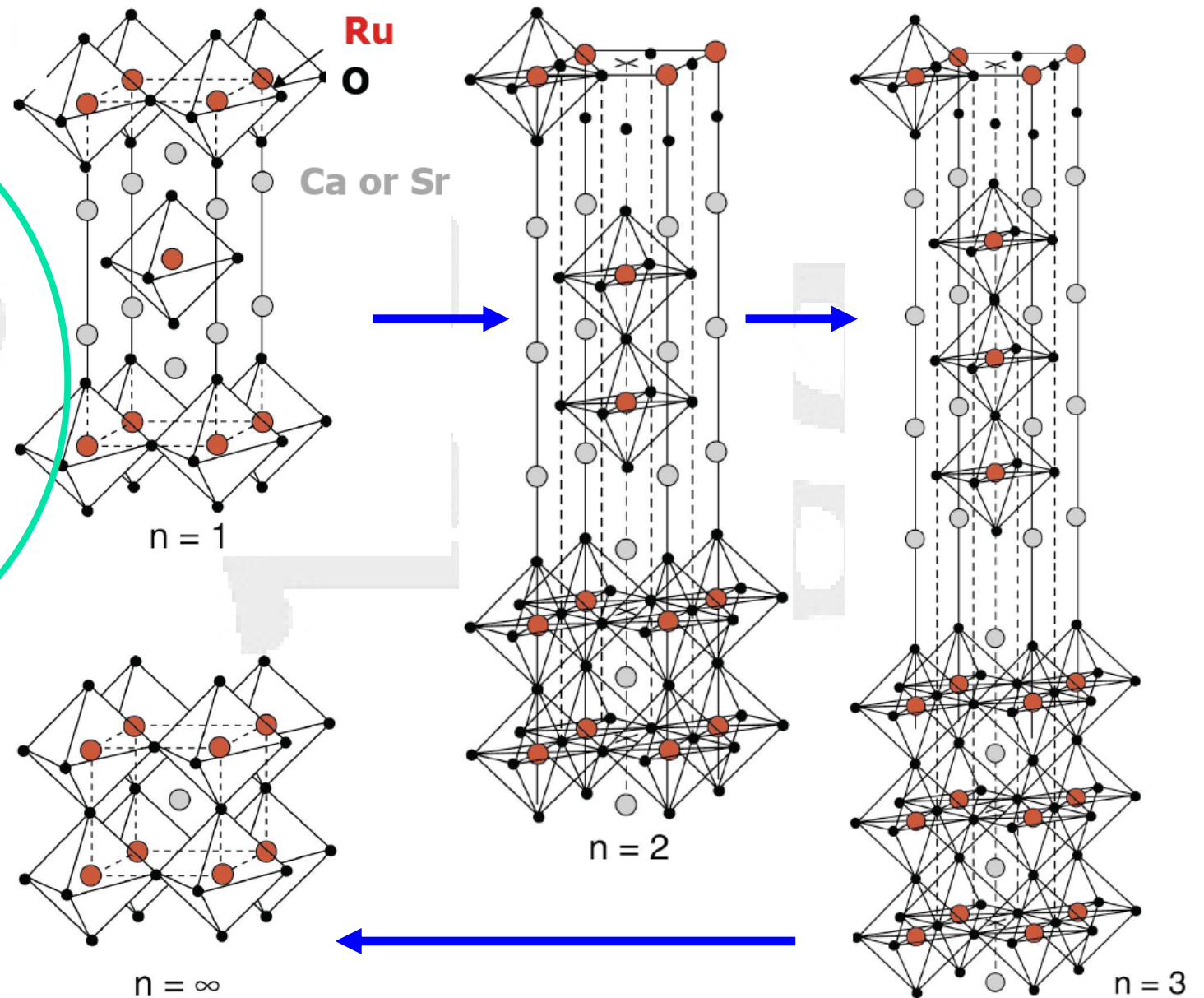
Ruddlesden-Popper
oxide series:



$n=1, 2, 3, \infty$

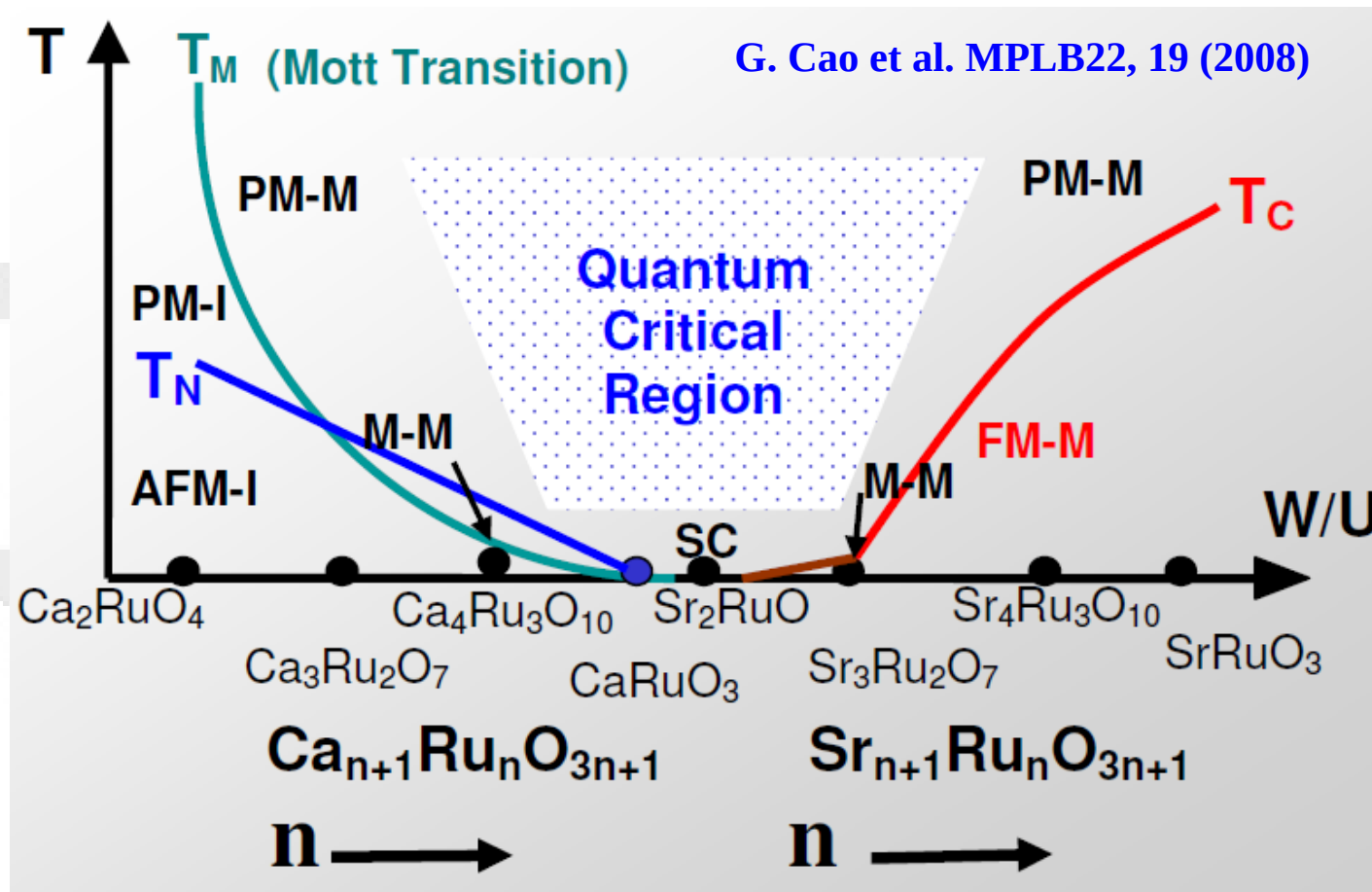
$\text{T}=\text{Ru}, \text{Ir}, \text{Rh}$ etc

Tough to synthesize





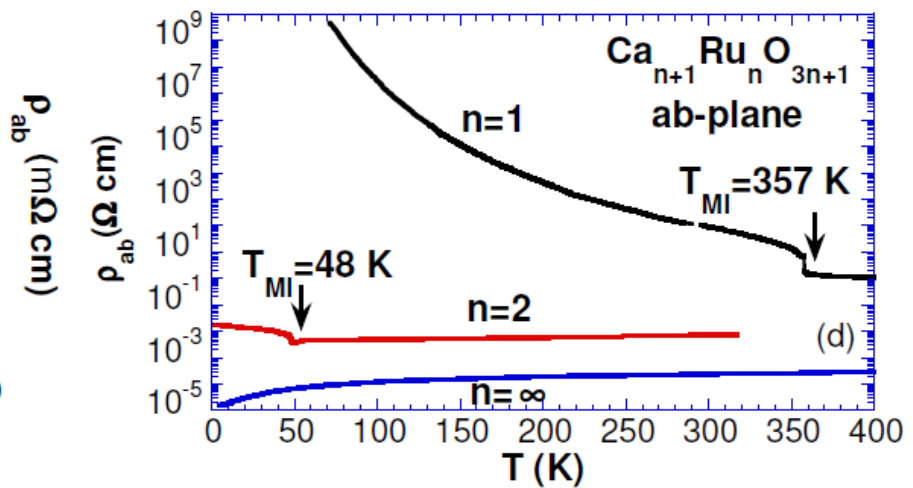
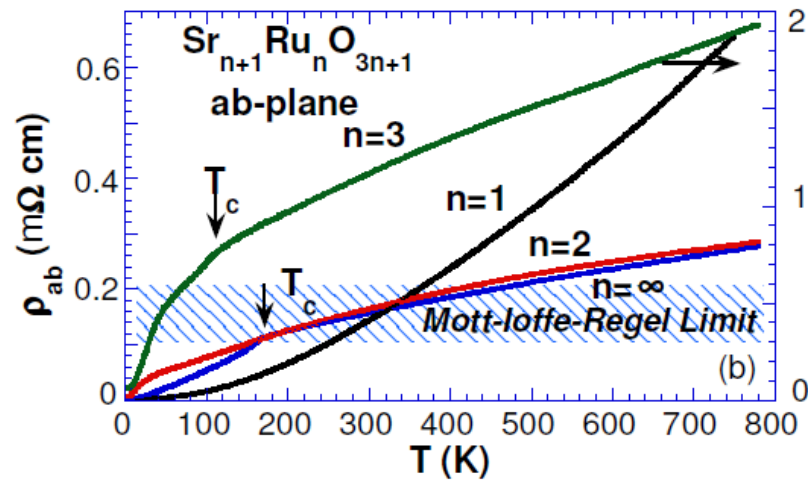
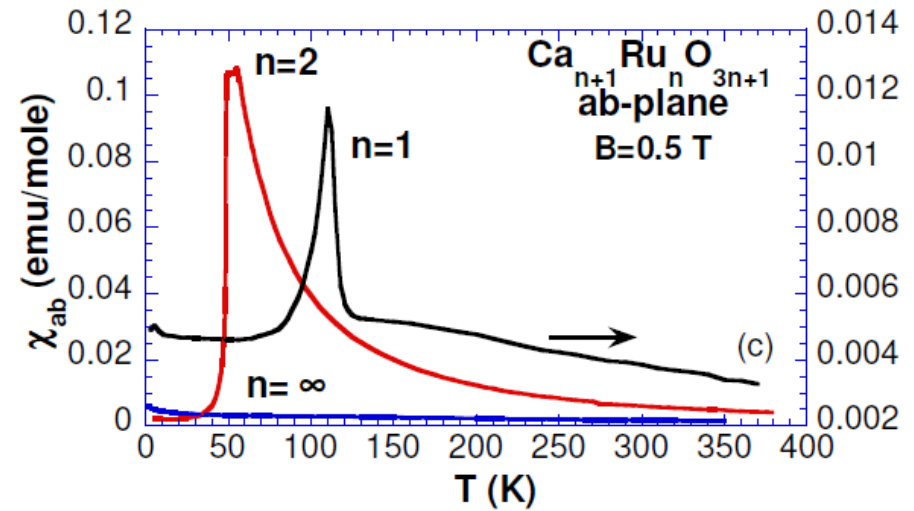
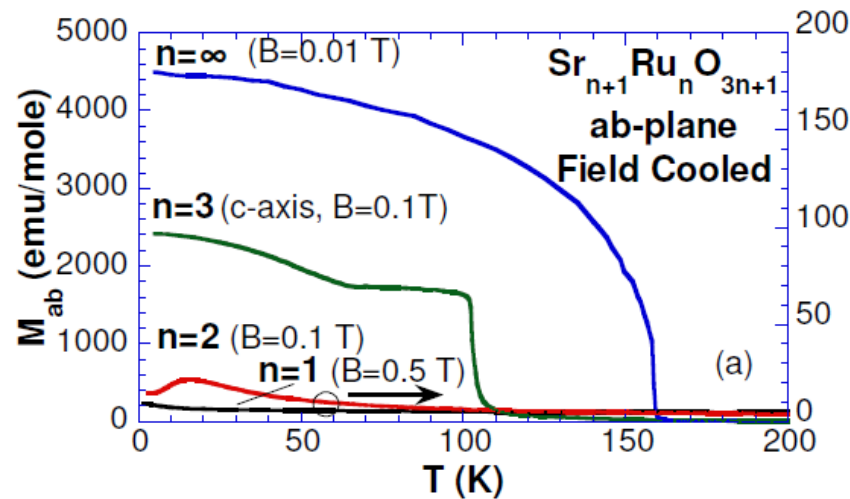
4d/5d oxides: T=Ru as an example from GC, MPLB (2008)



- Simplified phase diagram for $(\text{Ca,Sr})_{n+1}\text{Ru}_n\text{O}_{3n+1}$
- Rich phases competing to each other, depending on n



4d/5d oxides: T=Ru as an example



Very different behaviors between Sr- & Ca-based systems



4d/5d oxides: phenomena & possible physics in $n=2$

- ✓ **Crystal fields**
- ✓ **Hund's rule interactions**
- ✓ **p-d electron hybridization**
- ✓ **Electron-lattice coupling**
- ✓ **Spin-orbital coupling (~ 0.4 eV (5d), 0.1 eV (4d), 0.02 eV (3d))**

A set of balances between different degrees of freedom

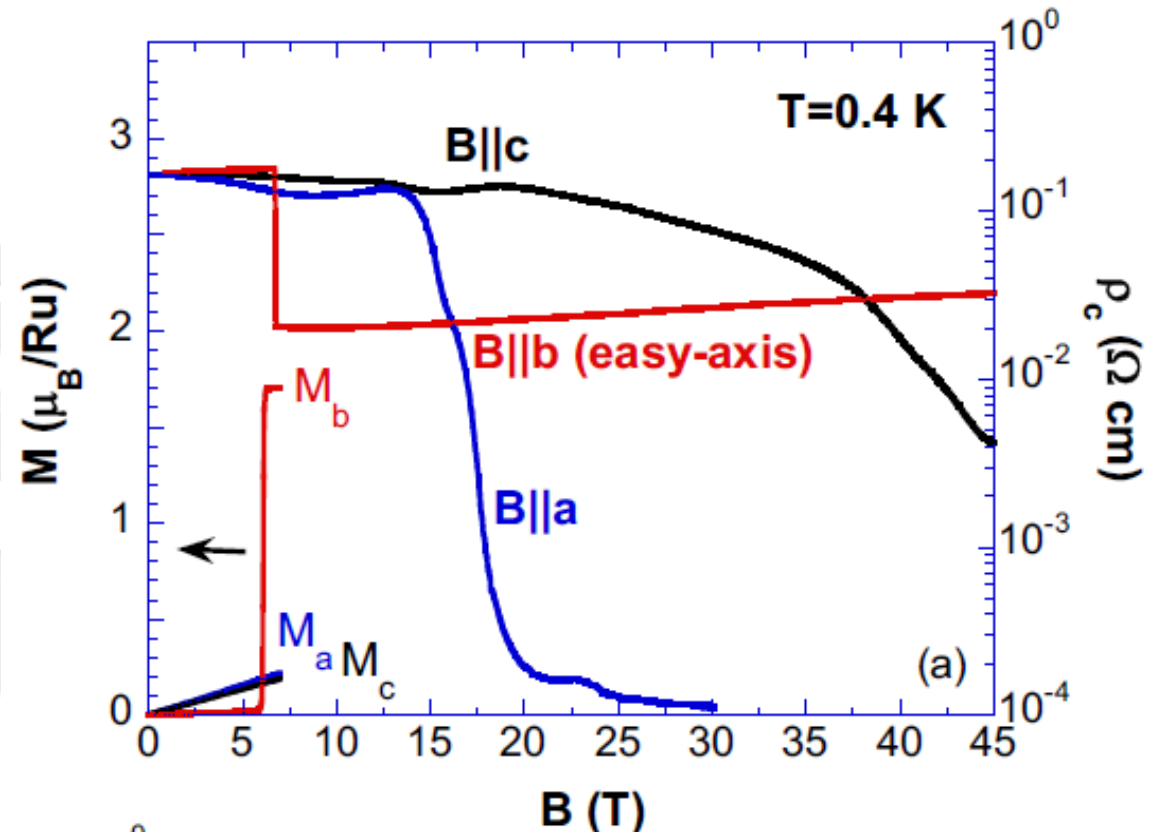
A wide range of novel physical phenomena surprisingly in one material

- | | |
|---|---|
| ✓ Highly anisotropic behaviors | ✓ Colossal magnetoresistance |
| ✓ Mott-like transition | ✓ Bulk spin-valve effect |
| ✓ Antiferromagnetic metallic state | ✓ Quantum oscillations & H-oscillation |
| ✓ Metamagnetism | ✓ Nonlinear conduction |



4d/5d oxides: phenomena & possible physics in n=2

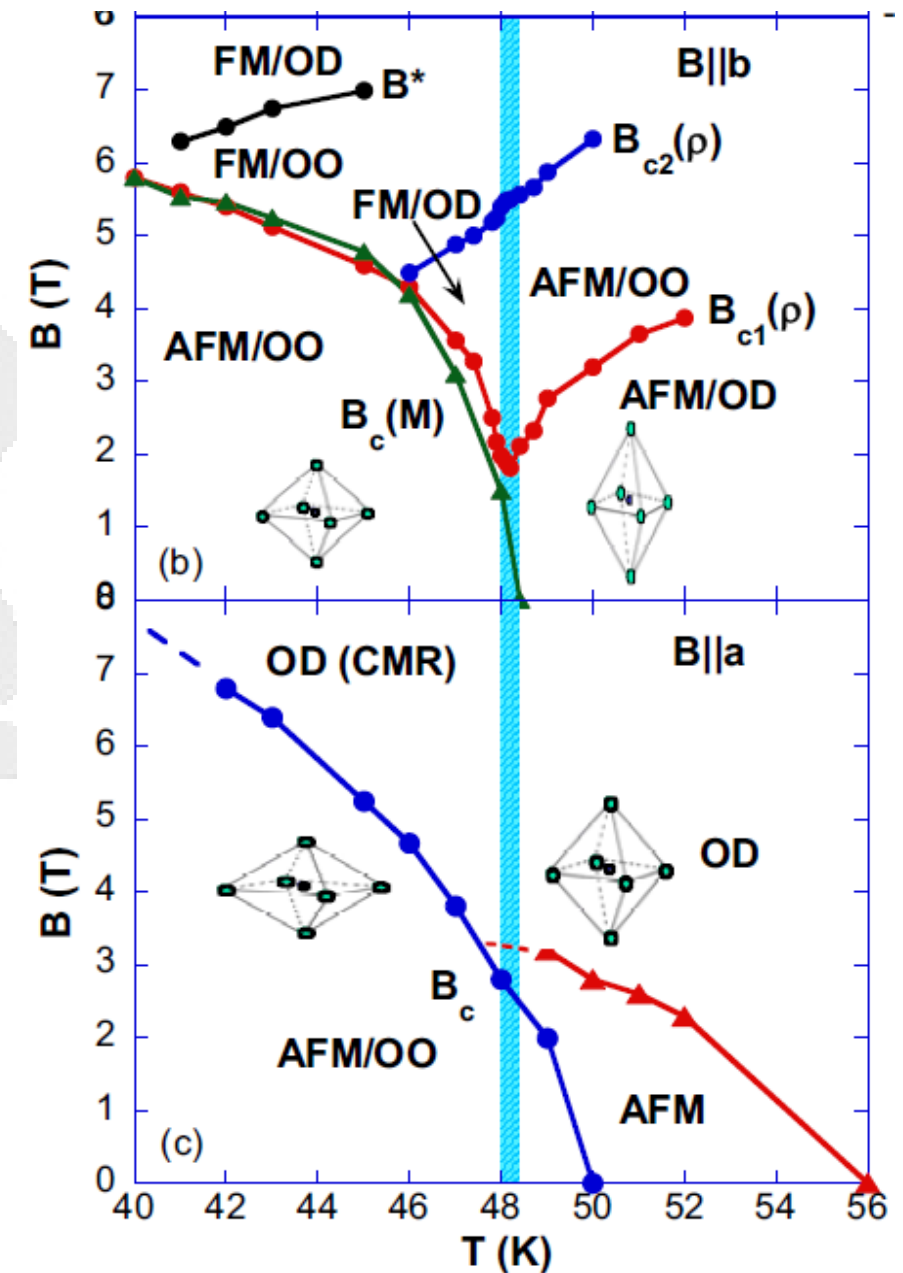
- ✓ b -axis is the easy axis
- ✓ For $B//b$, ρ_c drops at M-switching due to the spin-polarized transition. Then ρ_c increases due to the spin-orbit ordering
- ✓ For $B//a$, a rapid drop at $B \sim 15$ T
- ✓ For $B//c$, the Shubnikov-de Haas (SdH) oscillations
- ✓ The fully spin-polarized state may not be the most favored state for conduction.





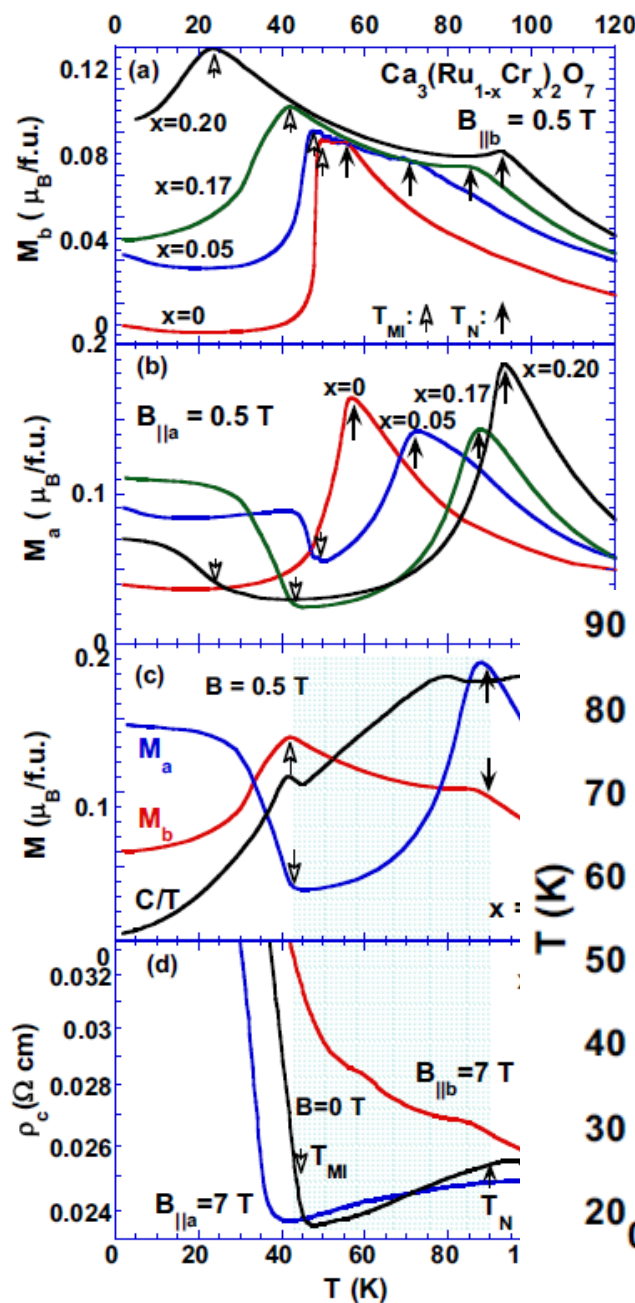
4d/5d oxides: phenomena & possible physics in n=2

- ✓ Very soft orbital order (OO) and spin order (SO)
- ✓ Delicate inter-coupling between these orders allow very different ground states and transport behaviors
- ✓ Effect of orbital ordering here seems extremely remarkable





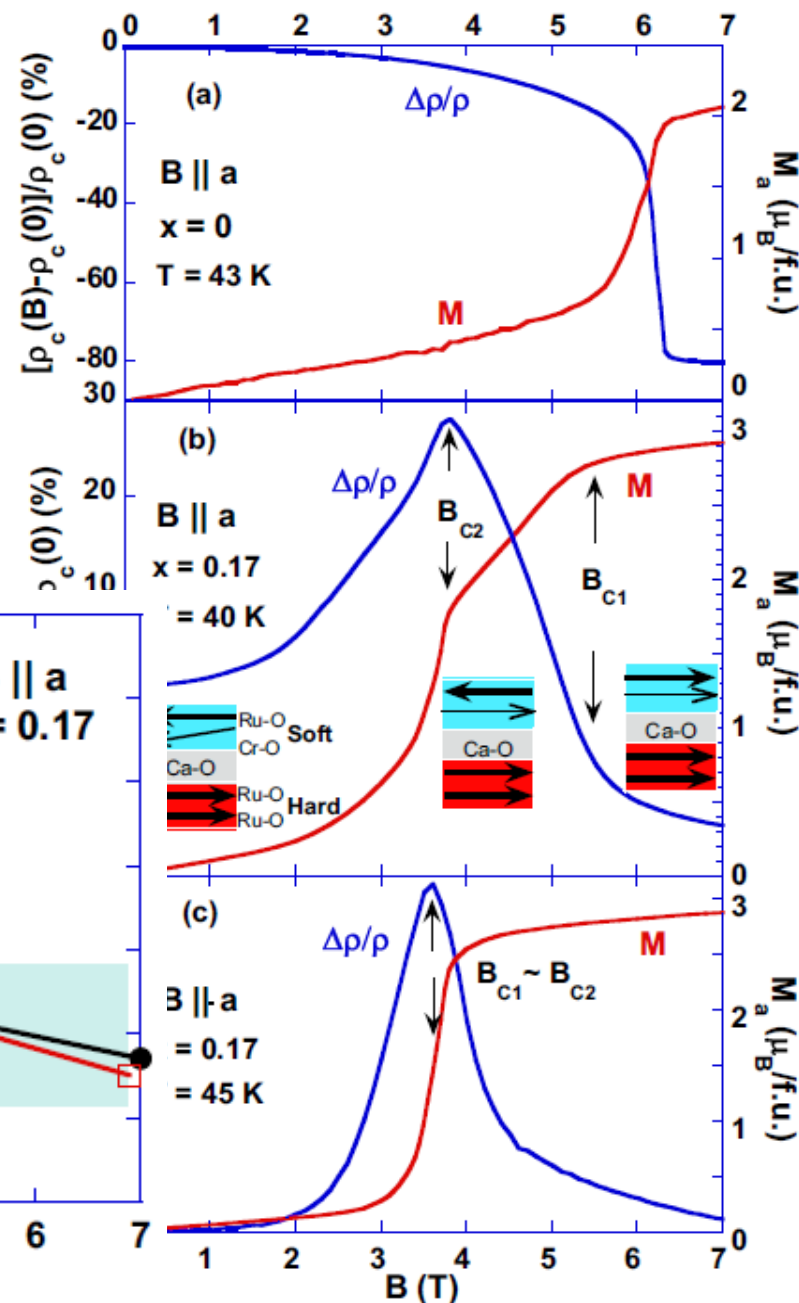
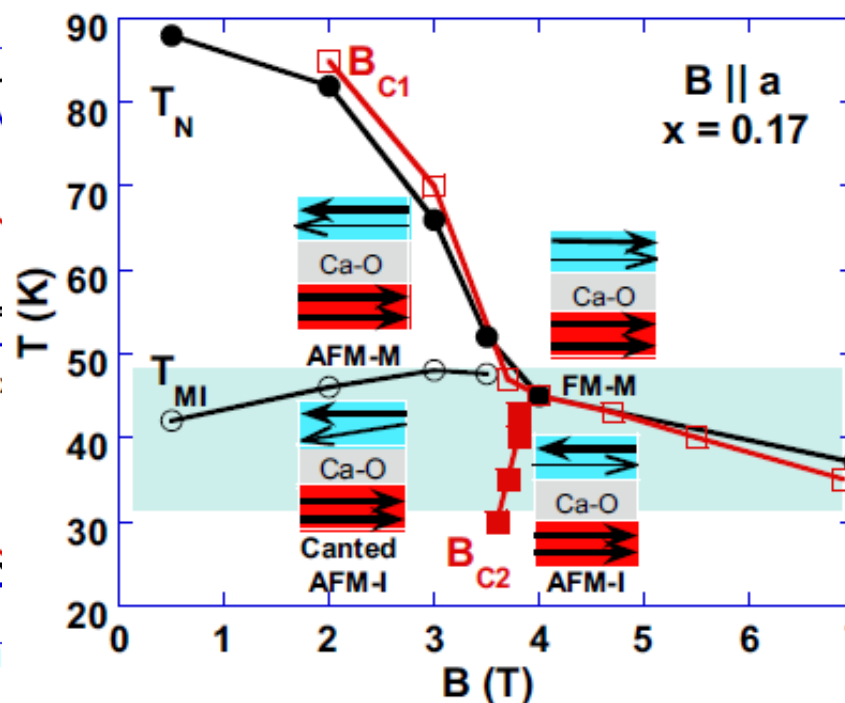
4d/5d oxides: phenomena & possible physics in n=2



✓ Cr-doping induces the extends the AFM-M state

✓ Cr-doping allows the spin cant at low B

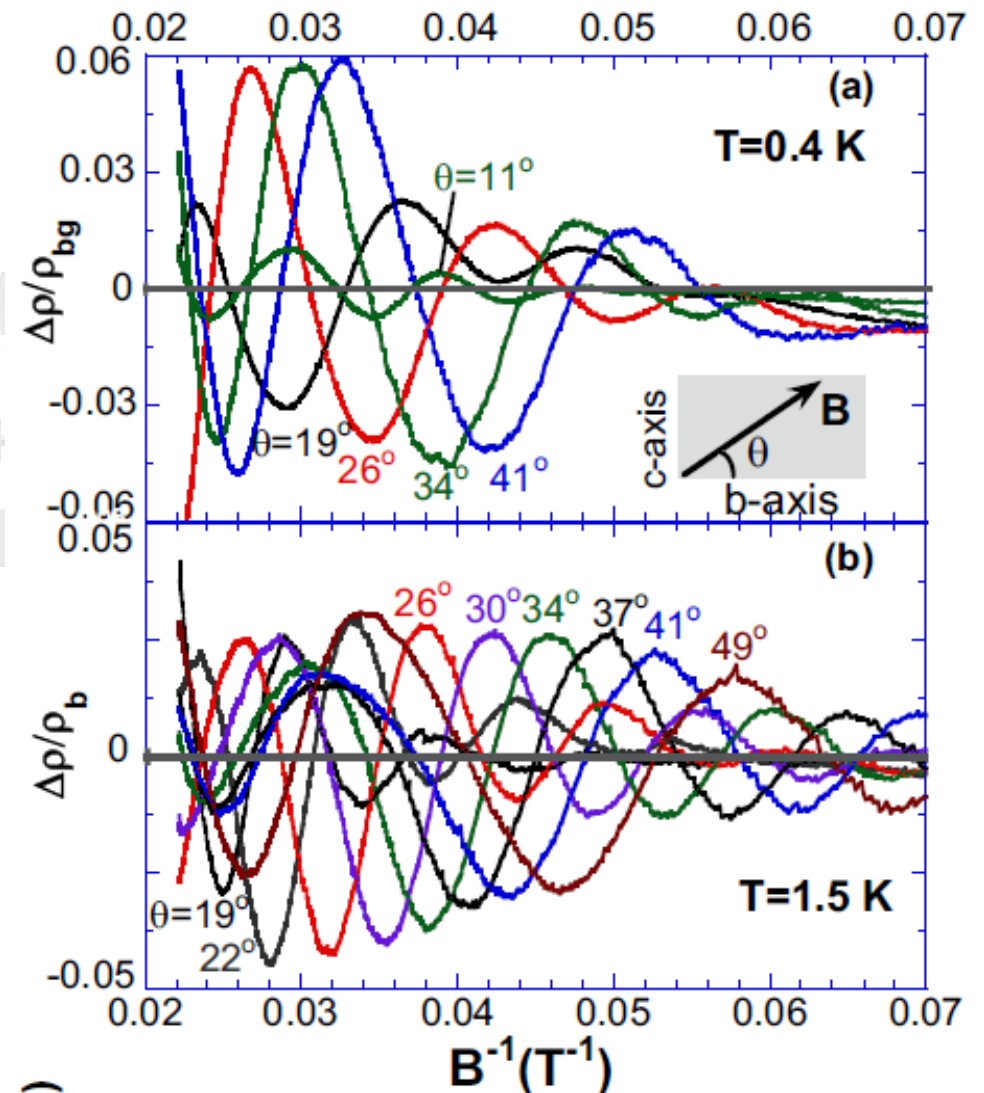
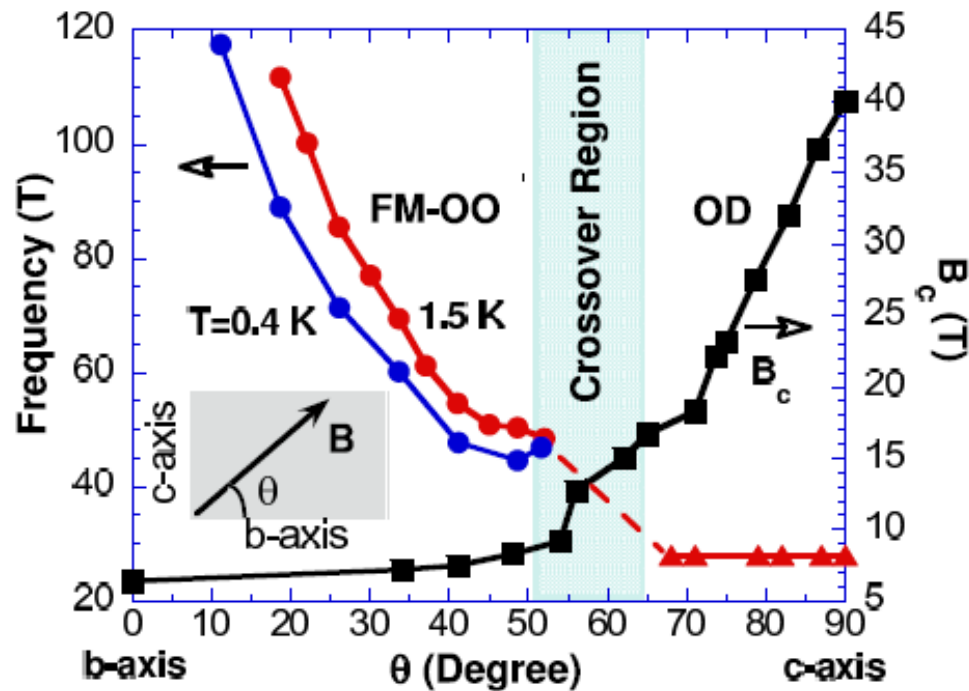
✓ Bulk spin valve effect





4d/5d oxides: phenomena & possible physics in n=2

- ✓ Quantum oscillation (SdH effect)
- ✓ Fine Landau level in response to external magnetic field



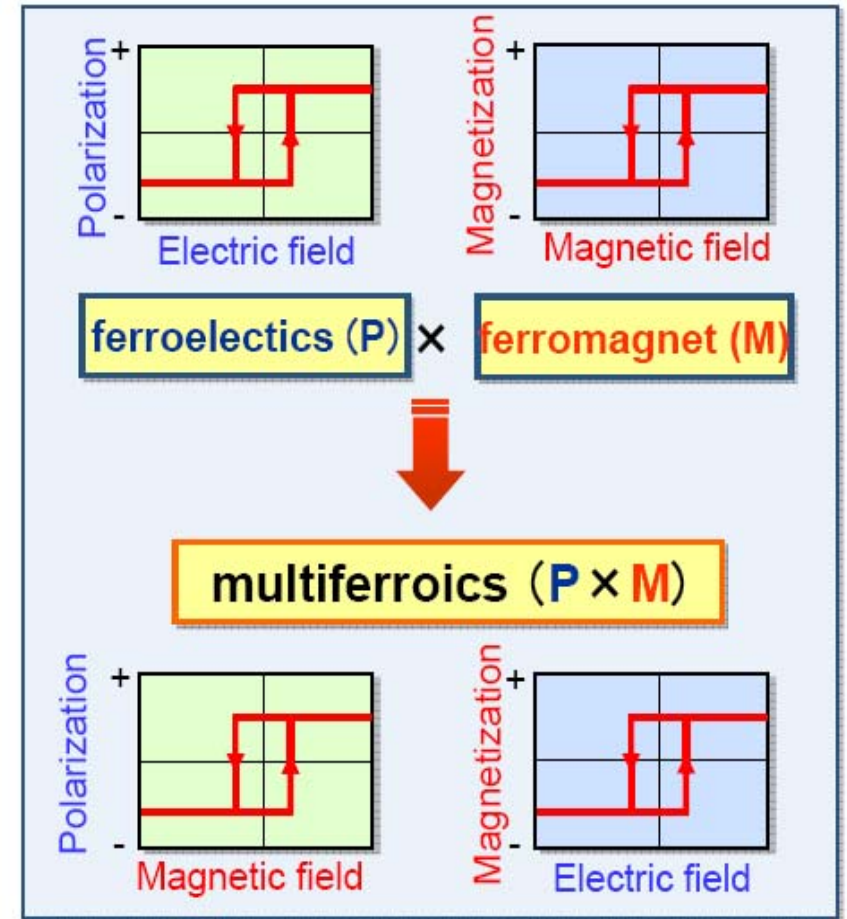
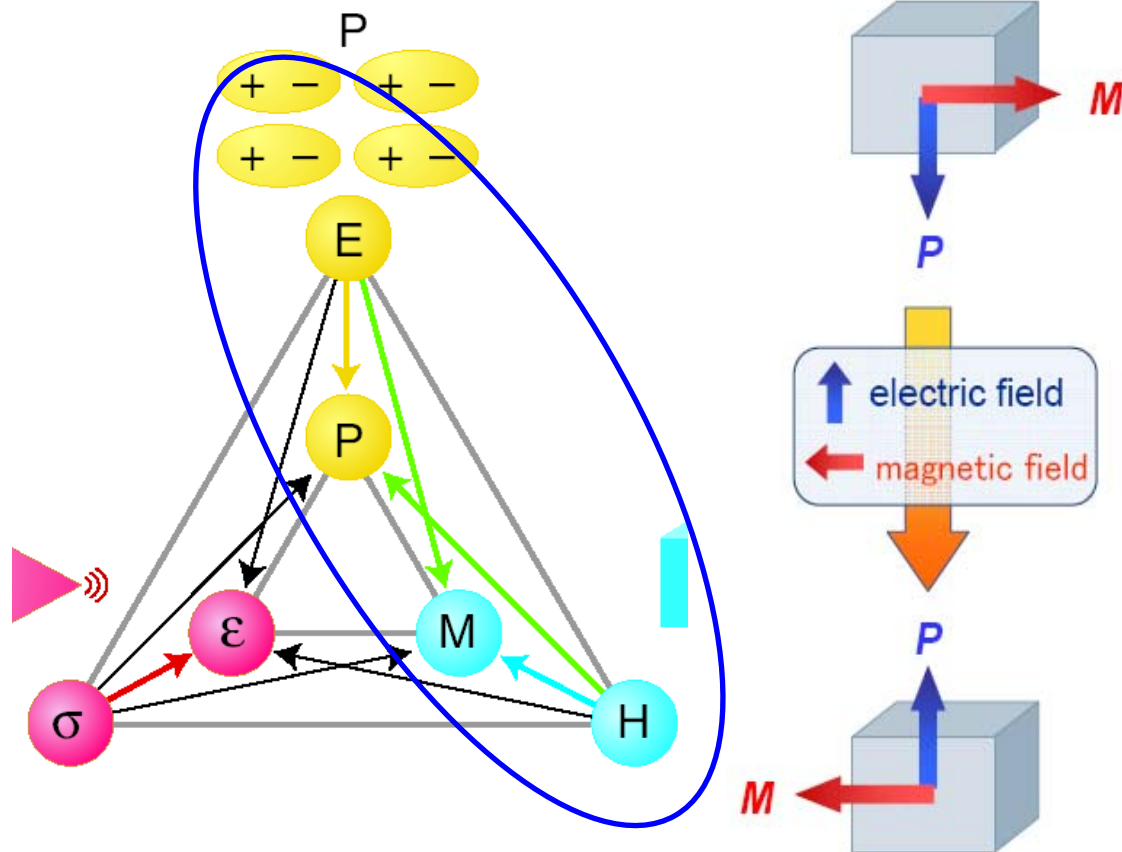


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Multiferroic oxides



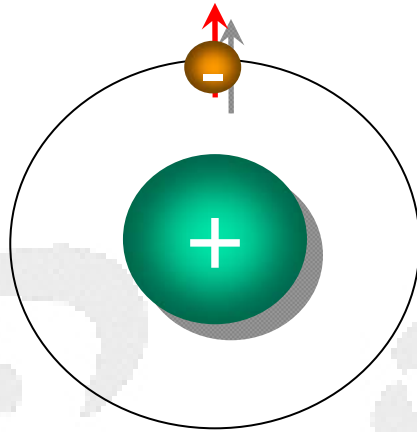
Multiferroics: motivation





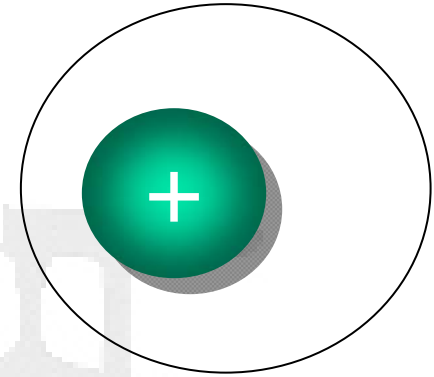
Multiferroics: spin/polarization exclusion

Magnetism



Partially filled d shells break
Time reversal symmetry

Ferroelectricity



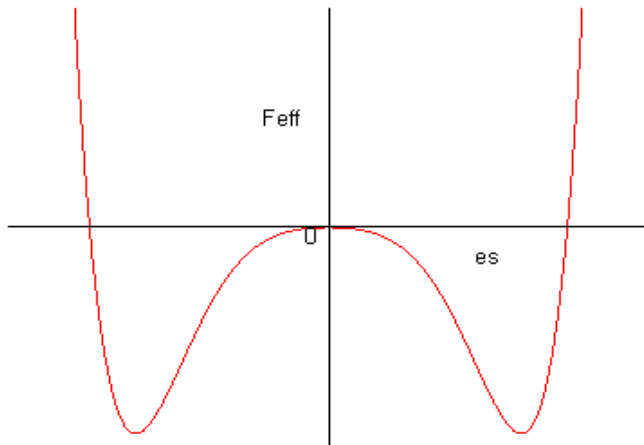
Empty d shells break
Space reversal symmetry

N. A. Hill, Why are there so few magnetic ferroelectrics? J. Phys. Chem. B 104: 6694 (2000).



Multiferroics: new symmetry argument

Mostovoy, PRL 96, 067601 (06)



If spin order is spatially inhomogeneous, symmetry allows for the 3rd-order coupling $P\partial M$ and then P may appear.

$$\Phi_{em}(\mathbf{P}, \mathbf{M}) =$$

$$\gamma \mathbf{P} \cdot [\mathbf{M}(\nabla \cdot \mathbf{M}) - (\mathbf{M} \cdot \nabla) \mathbf{M} + \dots].$$

$$\Phi = \Phi_{em} + \mathbf{P}^2 / 2\pi\epsilon$$

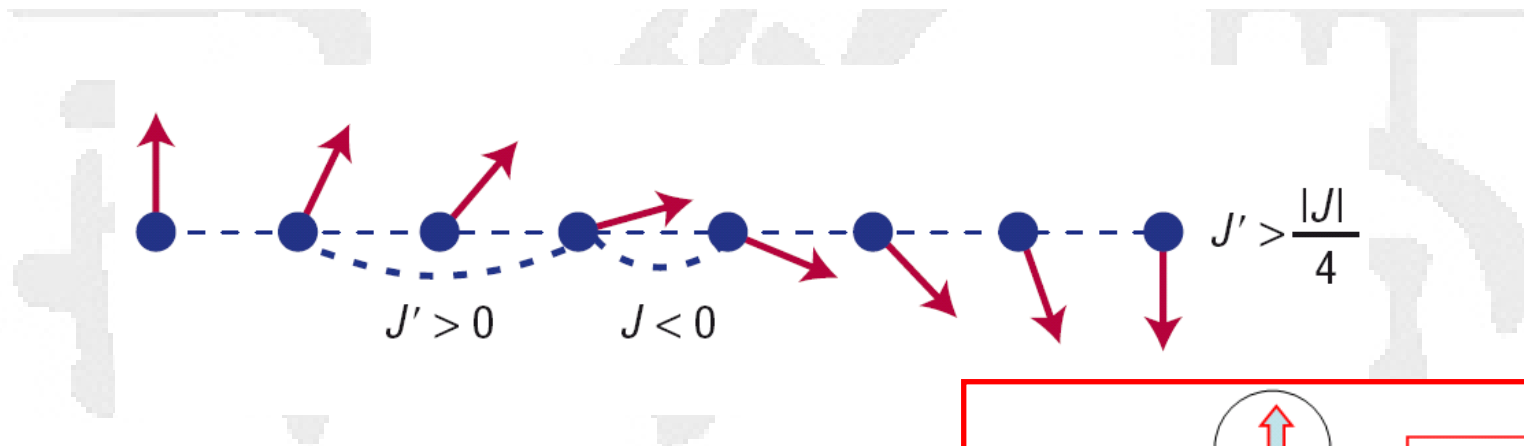


$$\mathbf{P} \propto [(\mathbf{M} \cdot \partial) \mathbf{M} - \mathbf{M}(\partial \cdot \mathbf{M})].$$

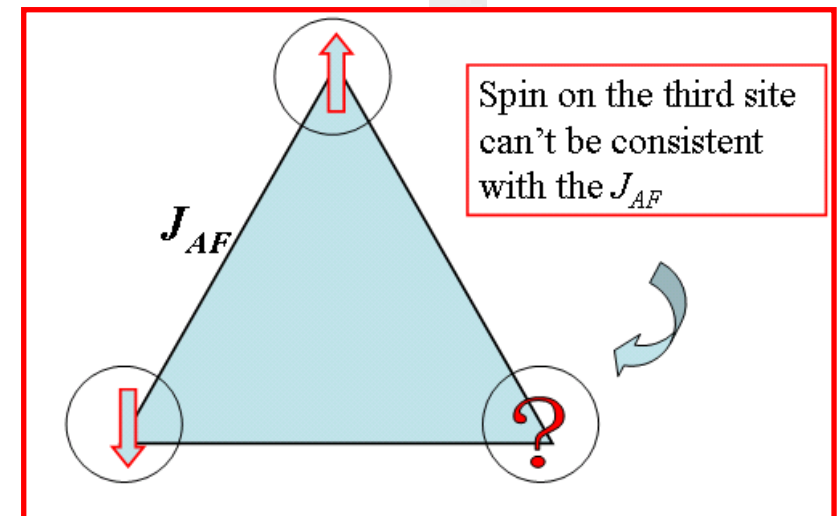


Multiferroics: frustration induced spiral spin order

- 1D chain magnet with the competition between NN FM coupling (J) and NNN AFM coupling (J') favors FSO if $|J'/J| > 1/4$. (JPCM 7, 8605 (1995))



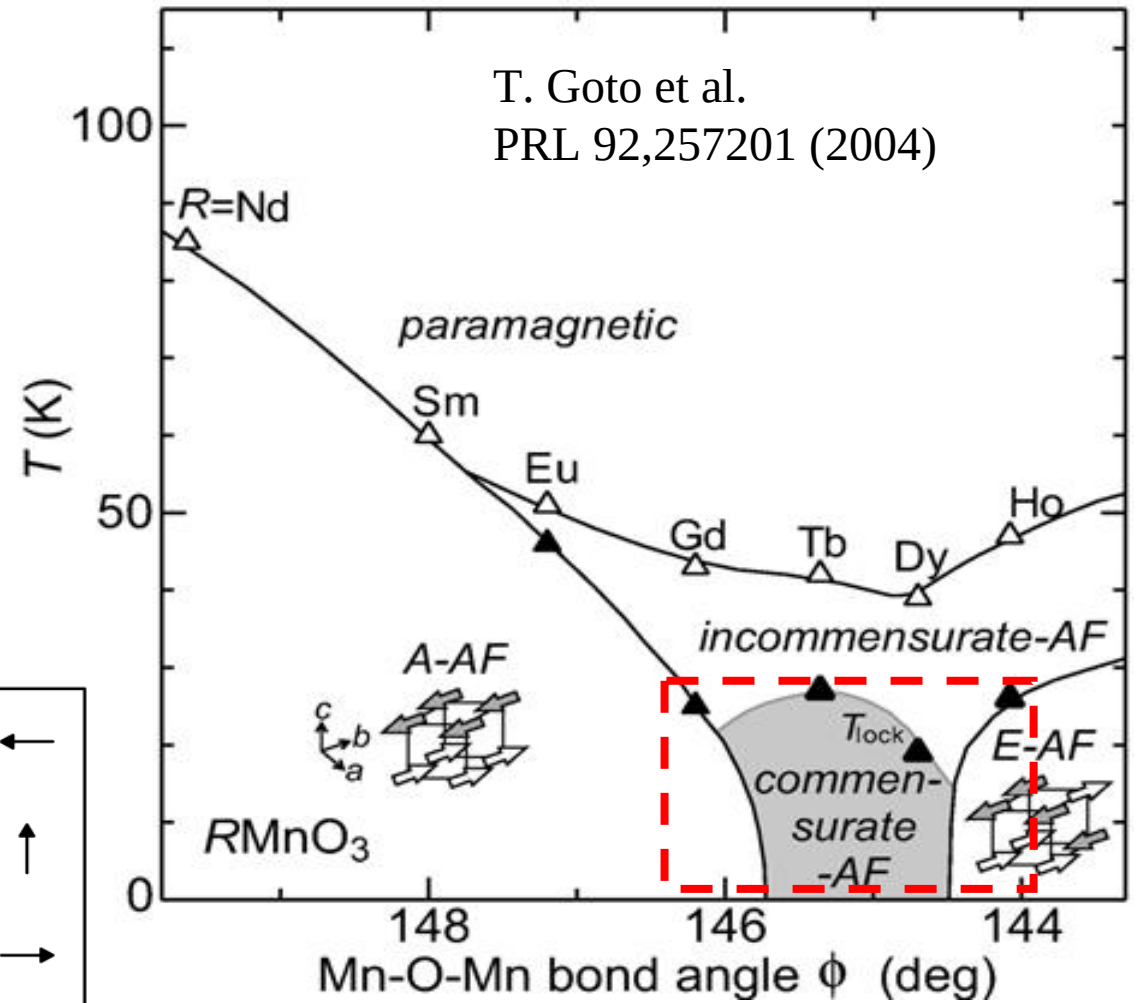
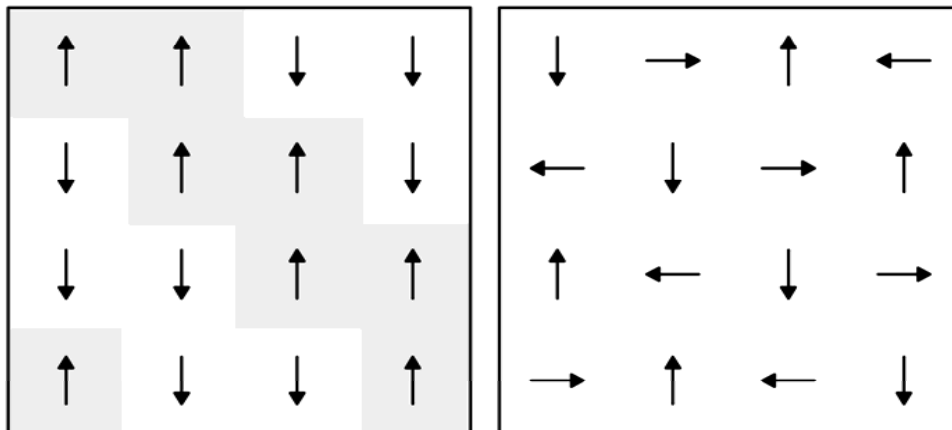
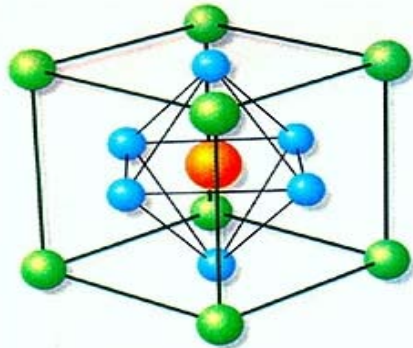
- AFM triangular-lattice favors FSO.





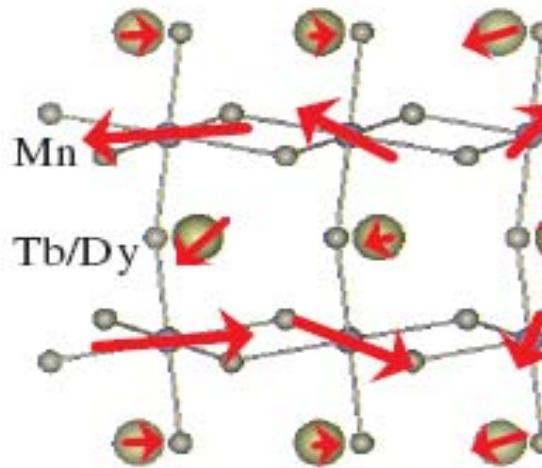
Multiferroics: frustration induced spiral spin order

$RMnO_3$ phases

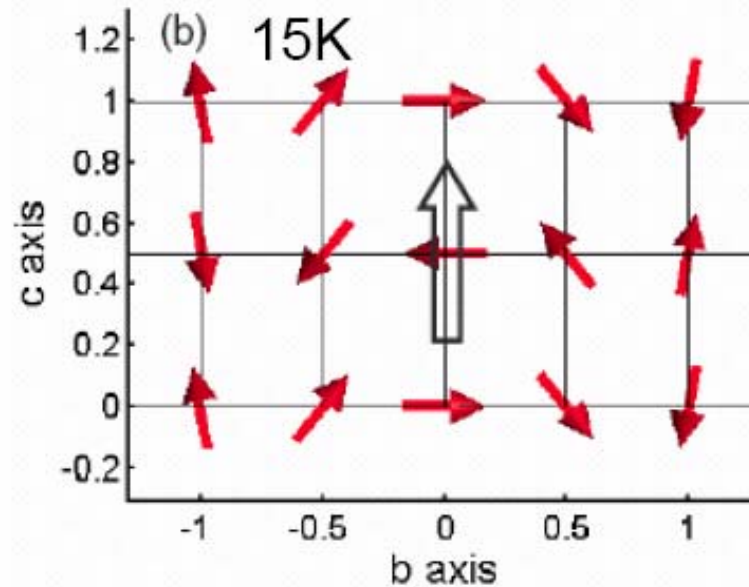
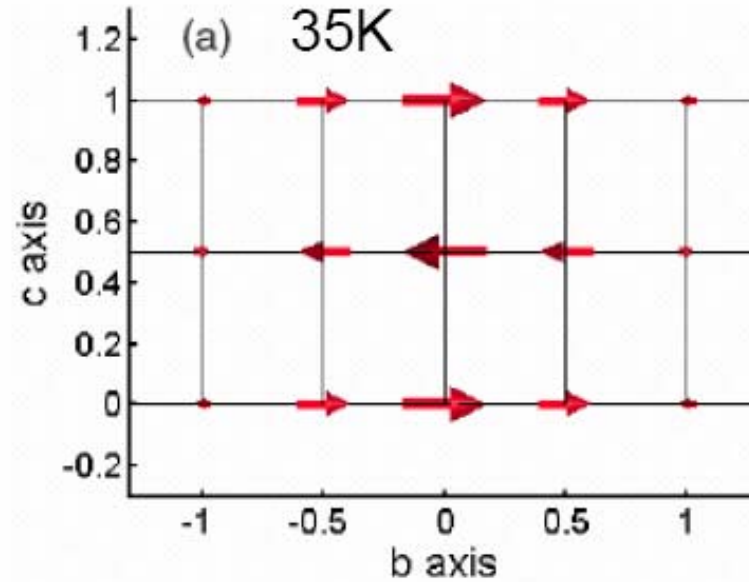




Multiferroics: take TbMnO_3 as an example



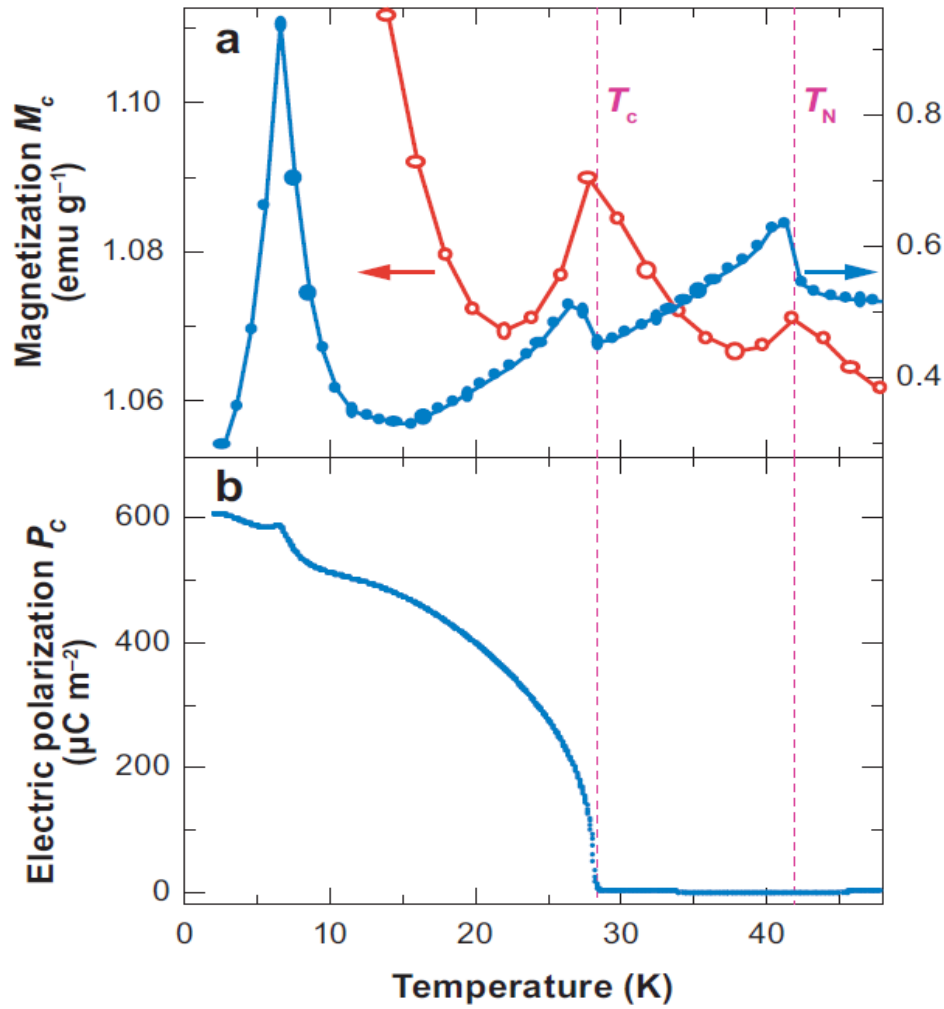
TbMnO_3



T. Arima et al.
PRL 96, 097202(2006)



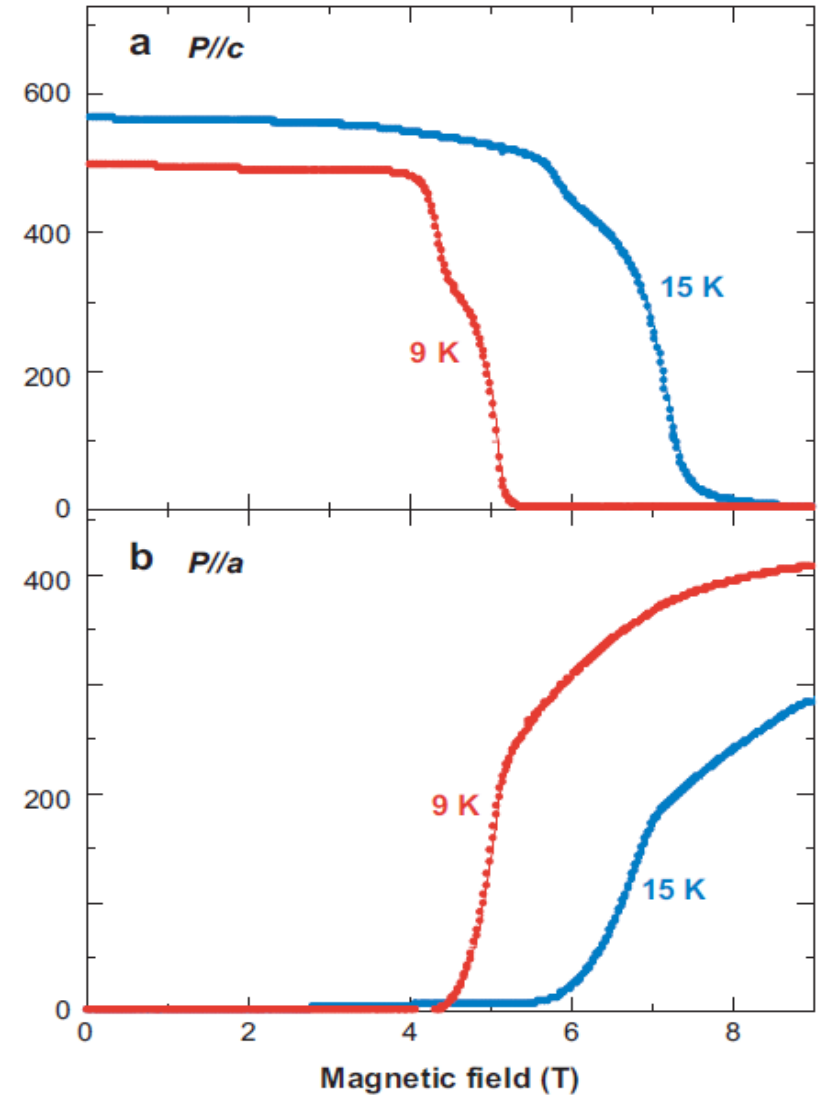
Multiferroics: take TbMnO_3 as an example



Specific heat/temperature
(J mol⁻¹ K⁻²)

Polarization P_c ($\mu\text{C m}^{-2}$)

Polarization P_a ($\mu\text{C m}^{-2}$)

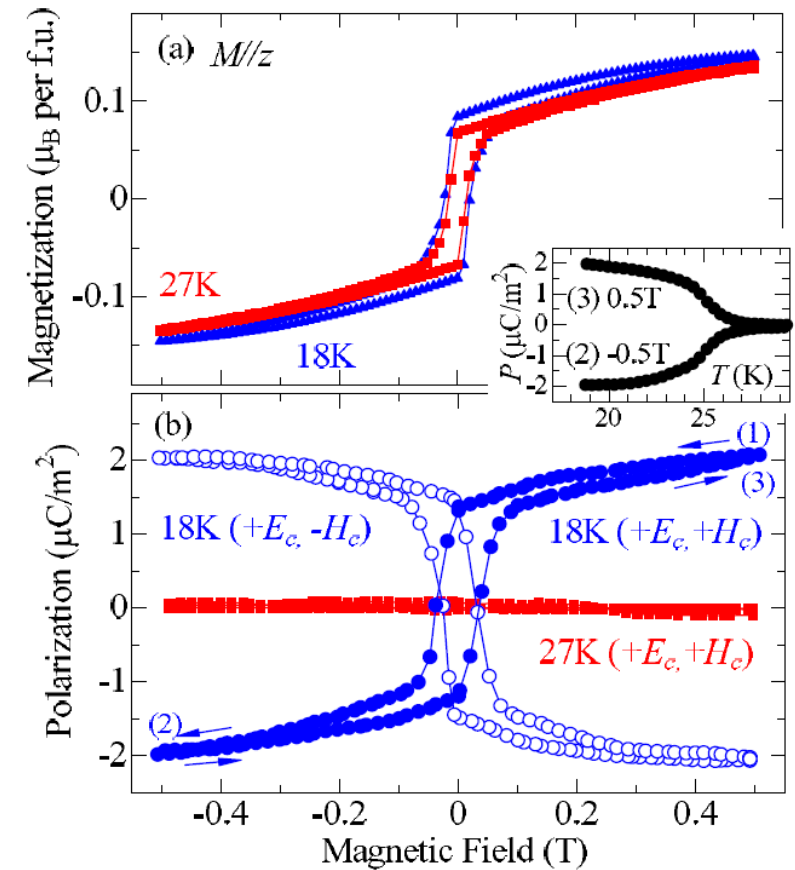
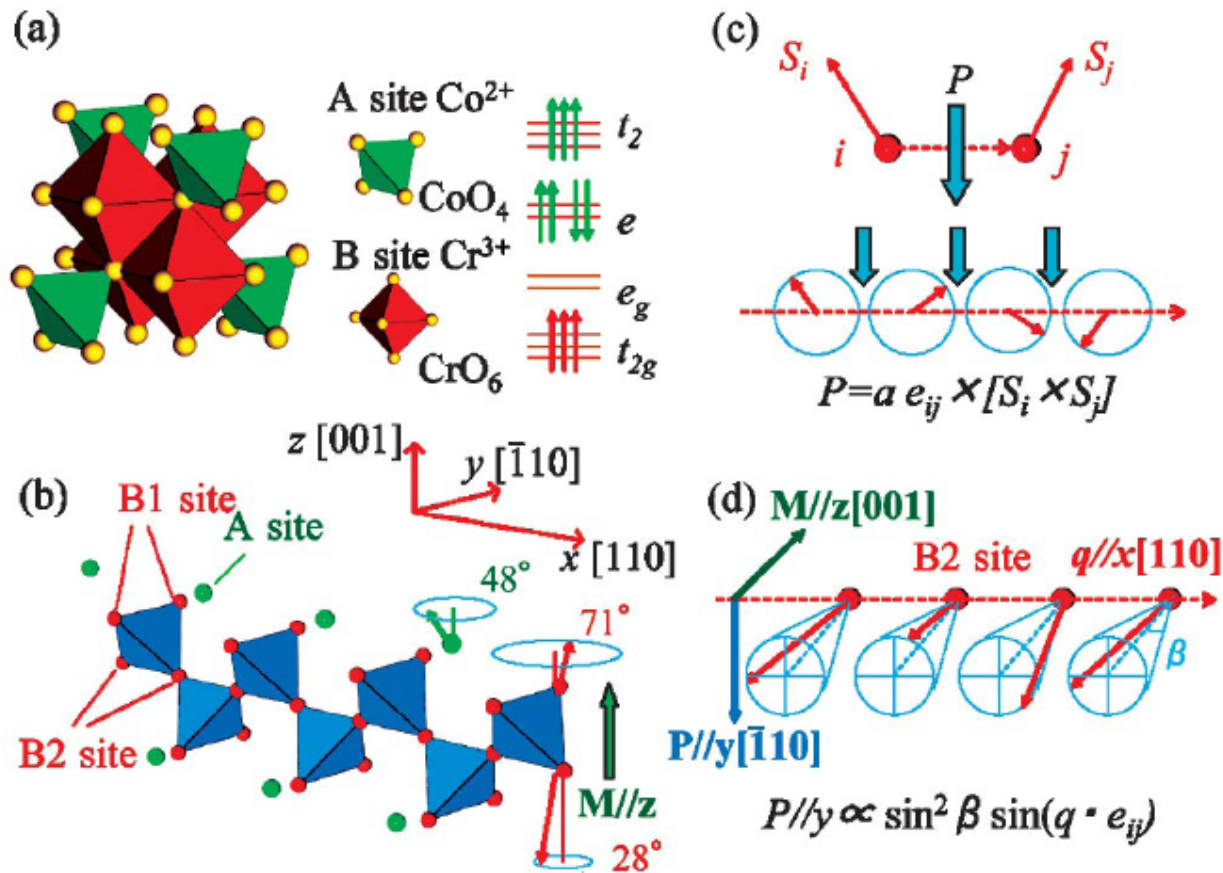


Kimura, Annu. Rev. Mater. Res.37, 387 (2007)



Multiferroics: take CoCr_2O_4 as an example

■ CoCr_2O_4 system with conical spin order:

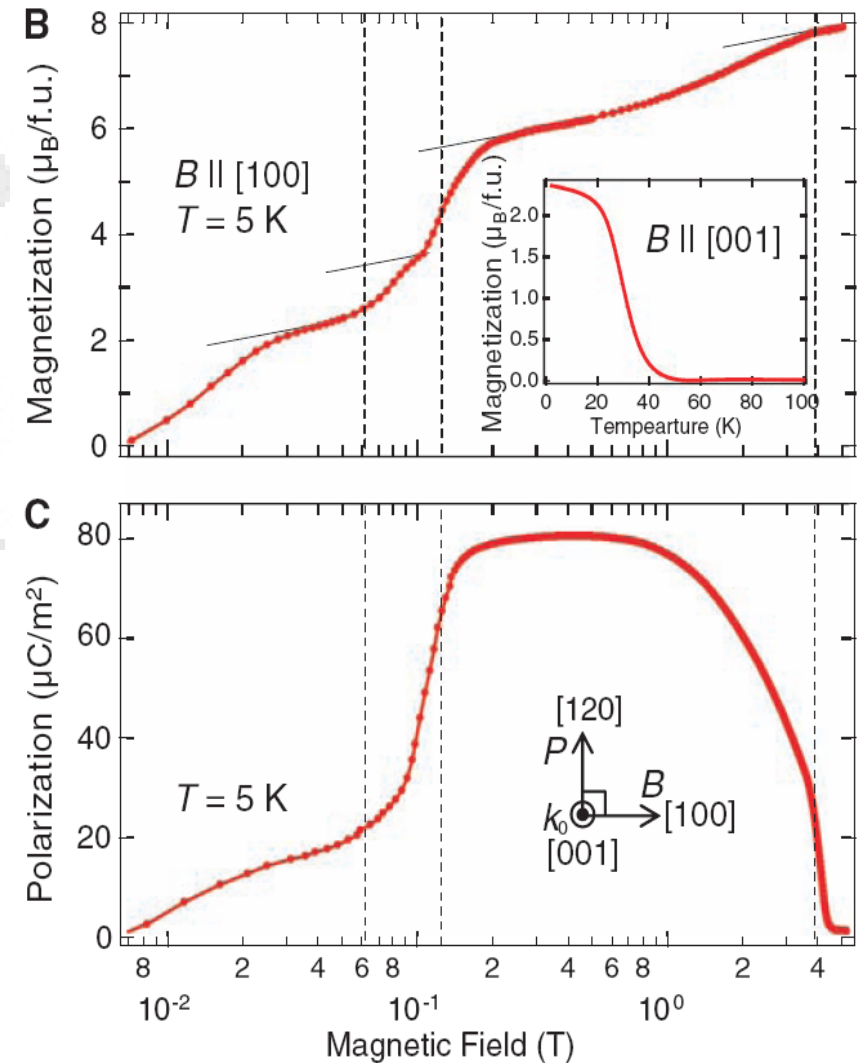
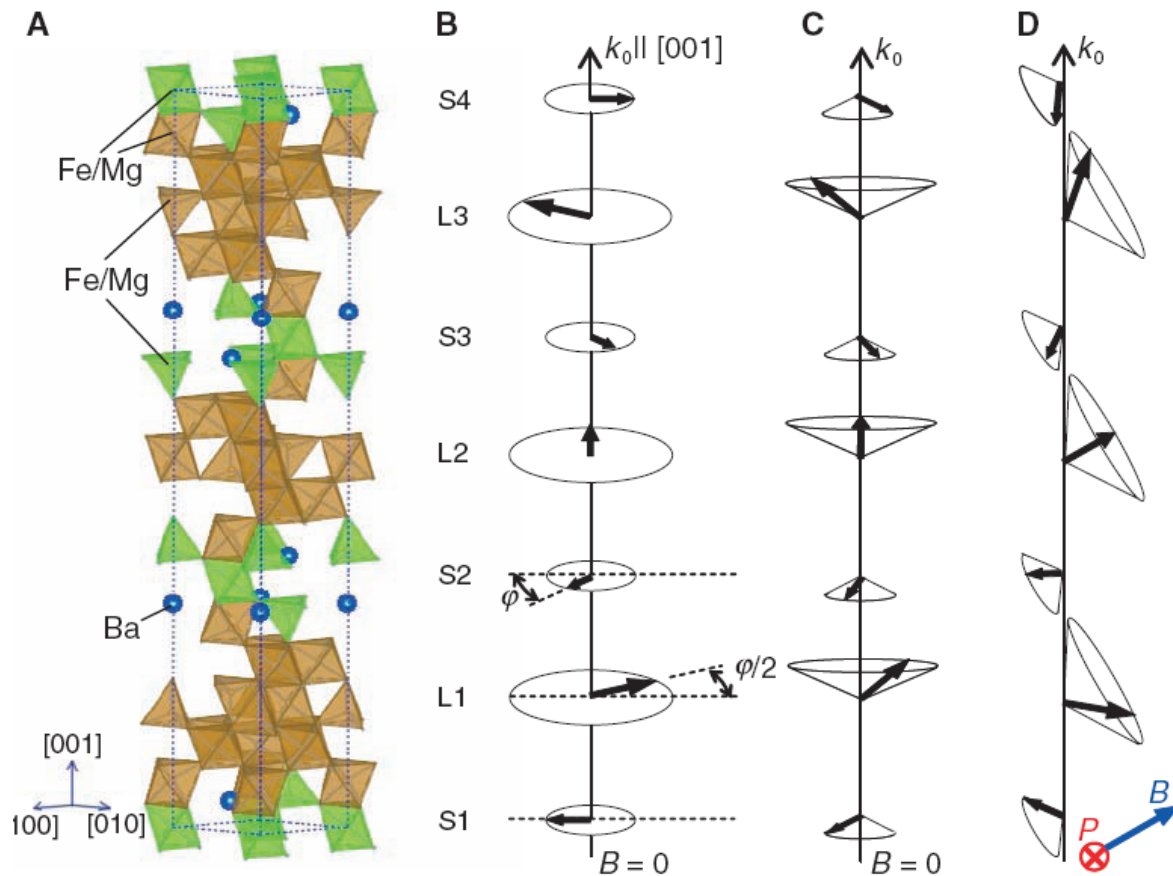


Yamasaki et al, PRL 96, 207204 (06)



Multiferroics: take $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ as an example

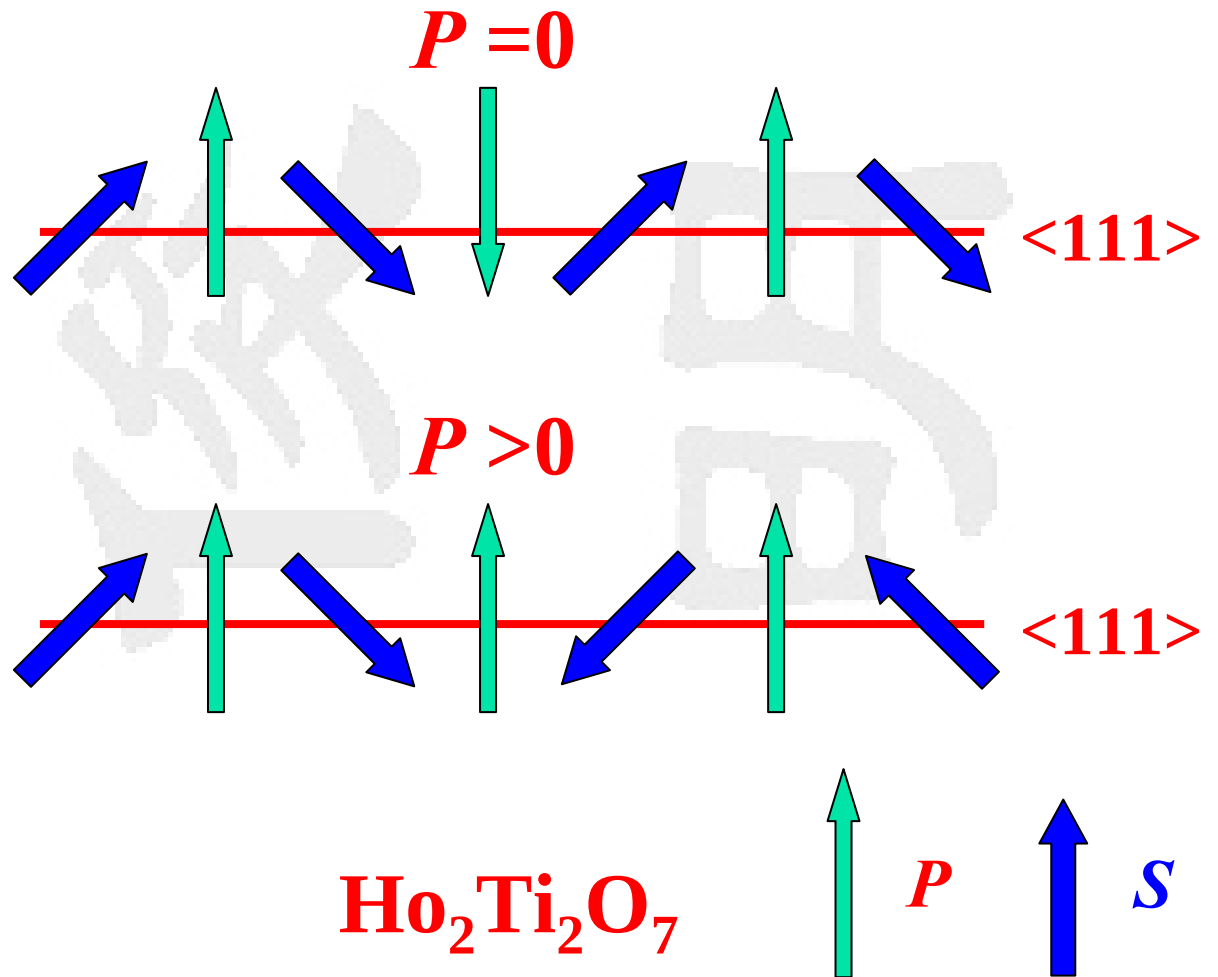
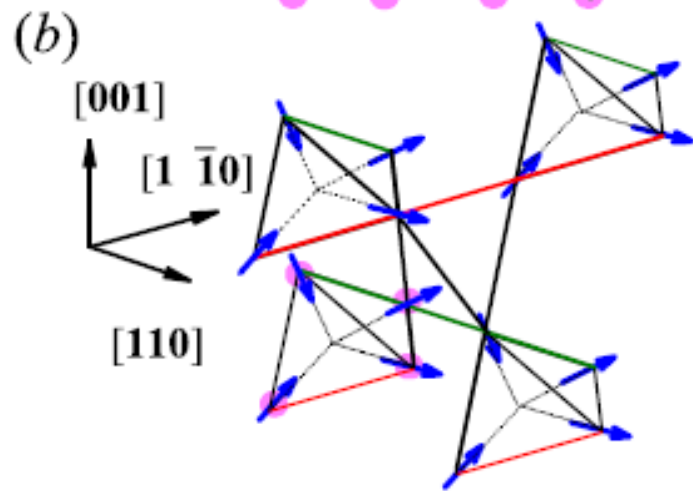
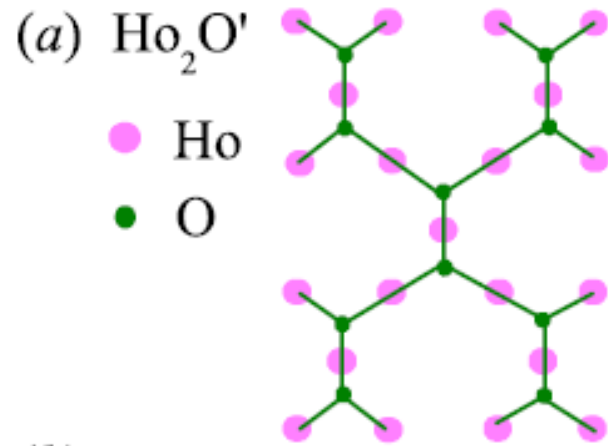
■ $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ helimagnet:



Ishiwata et al, Science 319, 1643 (08)

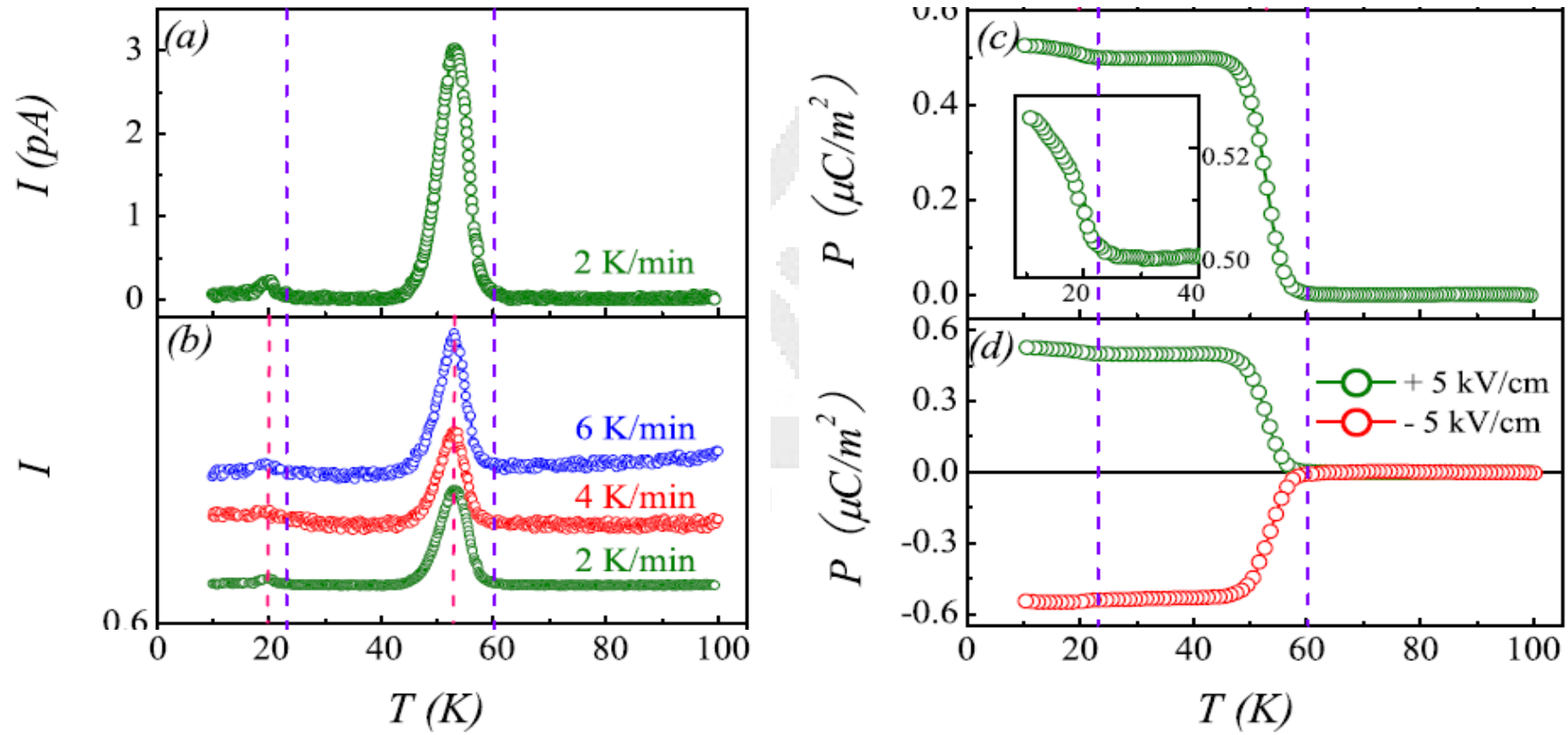


Multiferroics: take spin ice as an example



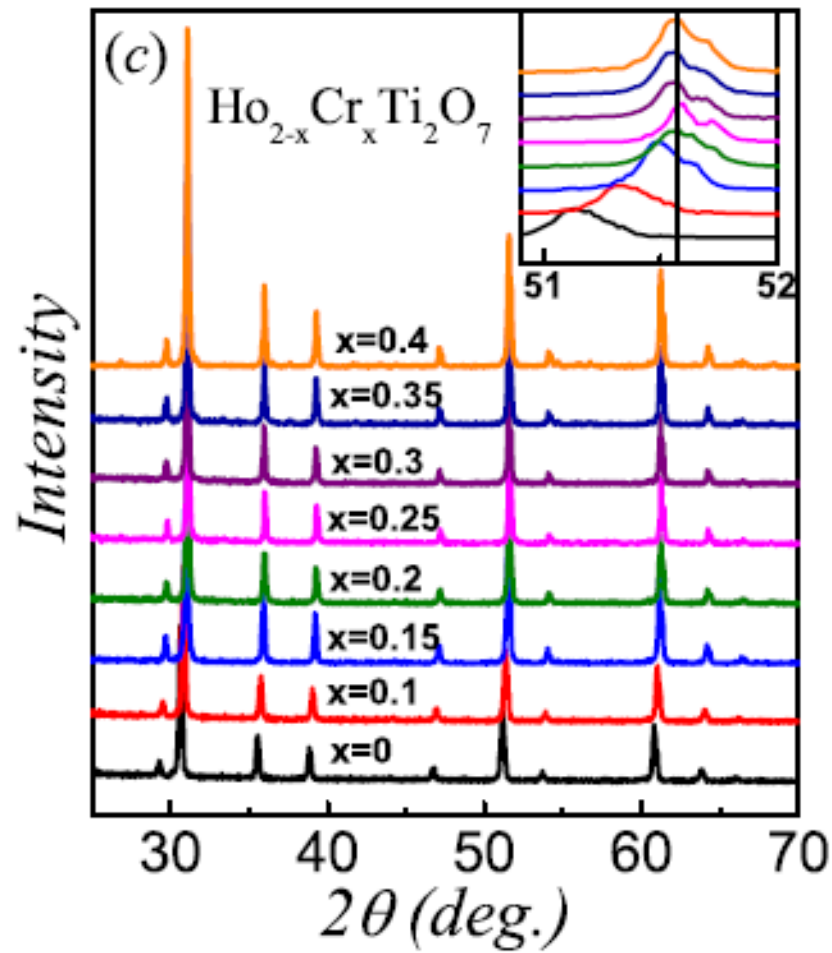


Multiferroics: take spin ice as an example



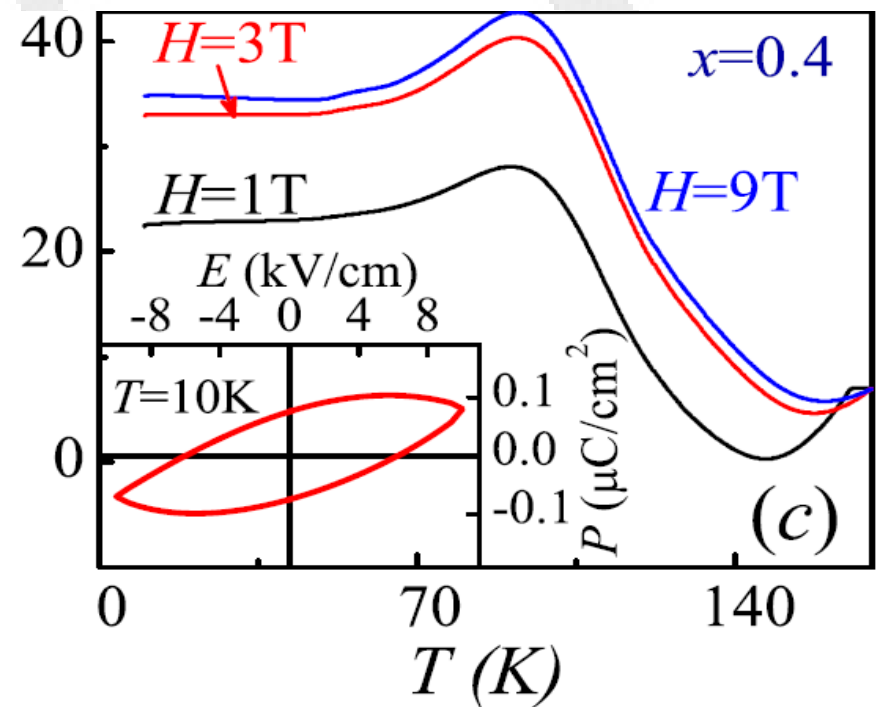
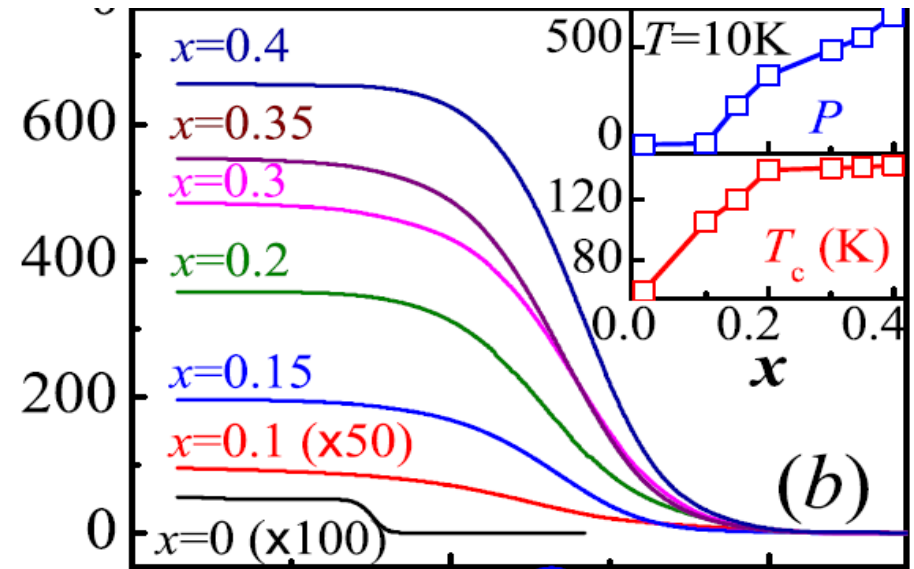


Multiferroics: take spin ice as an example



P ($\mu\text{C}/\text{m}^2$)

ΔP ($\mu\text{C}/\text{m}^2$)

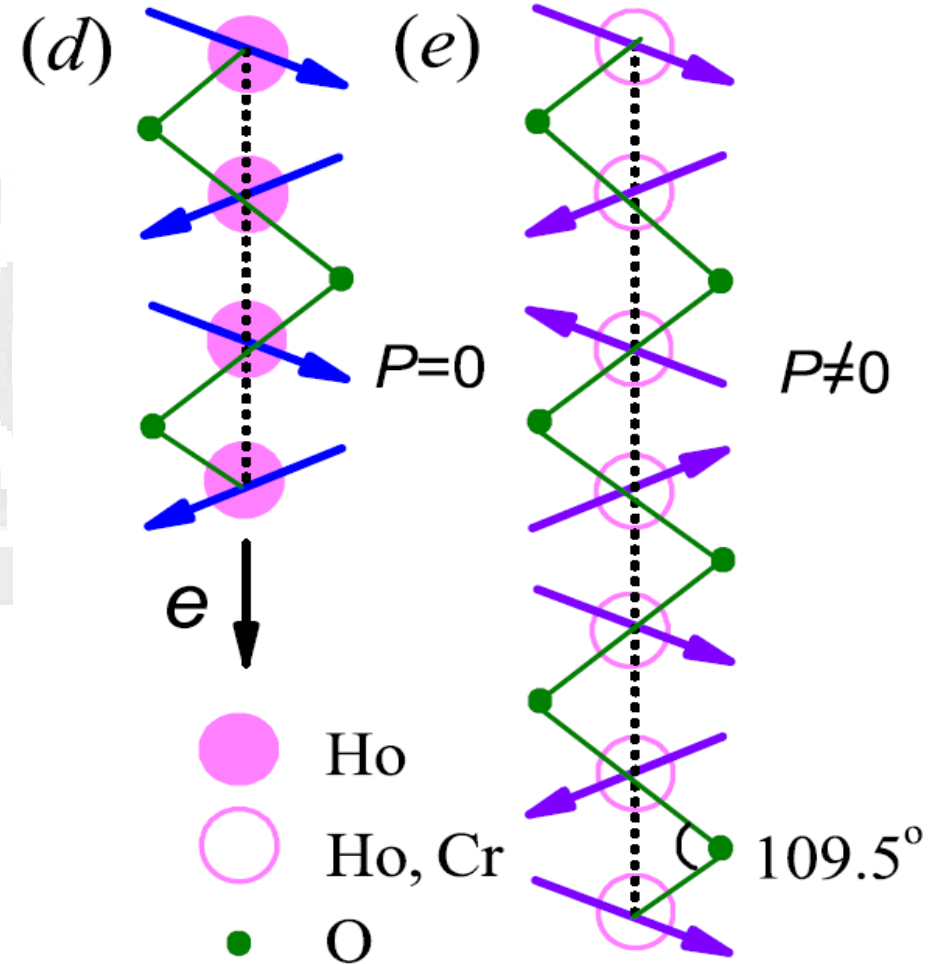




Multiferroics: take spin ice as an example

$\rightarrow S_{\text{Ho}}$
 $\rightarrow S_{\text{Ho}}, S_{\text{Cr}}$

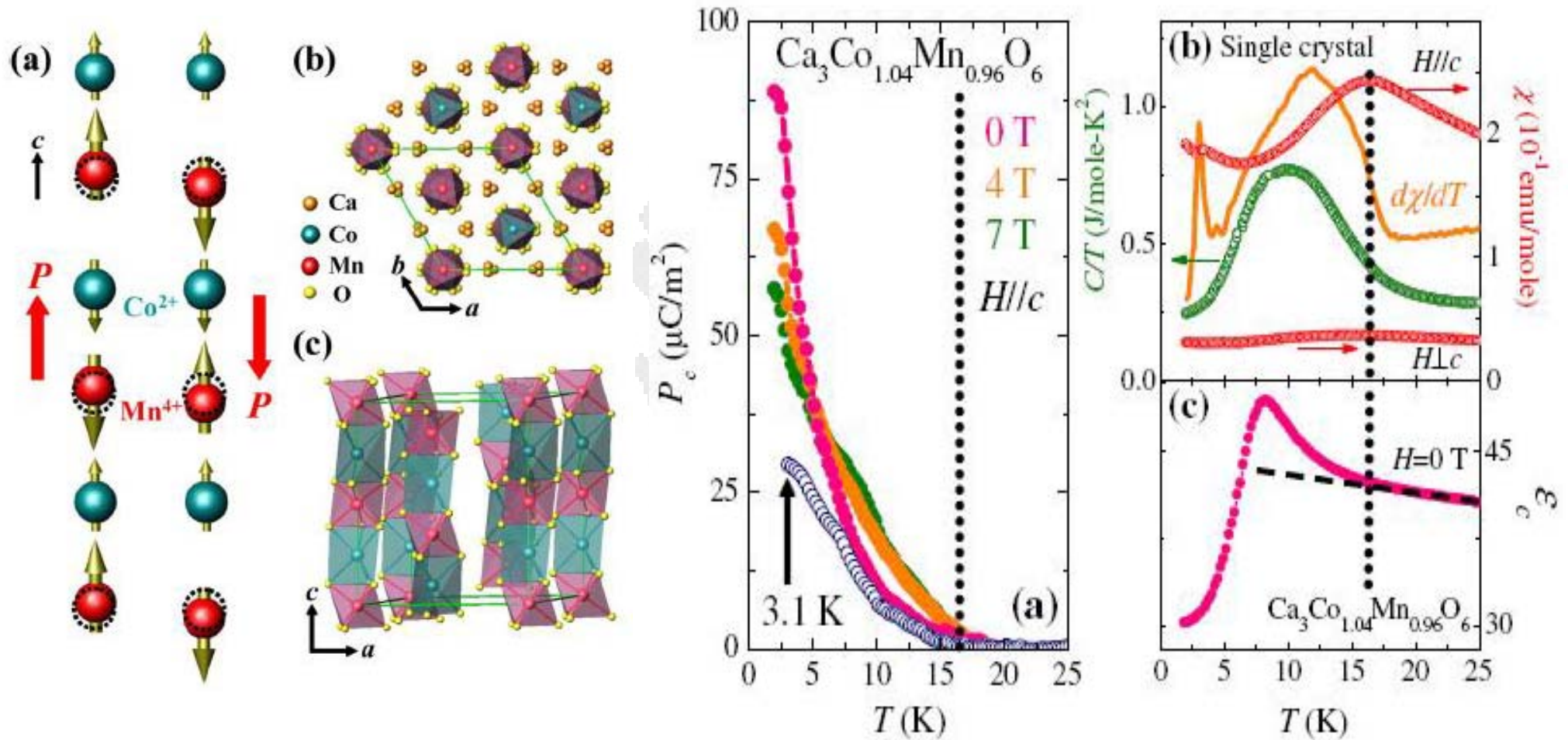
$$P = \eta e_{ij} \times (S_i \times S_j)$$





Multiferroics: charge-order induces polarization

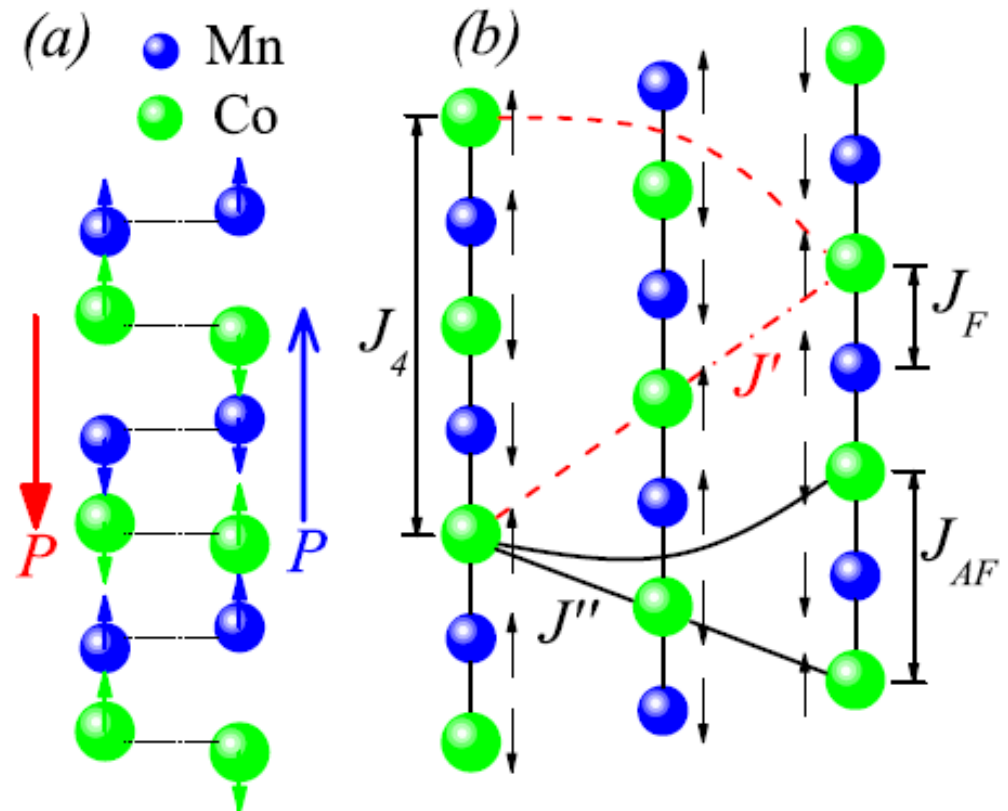
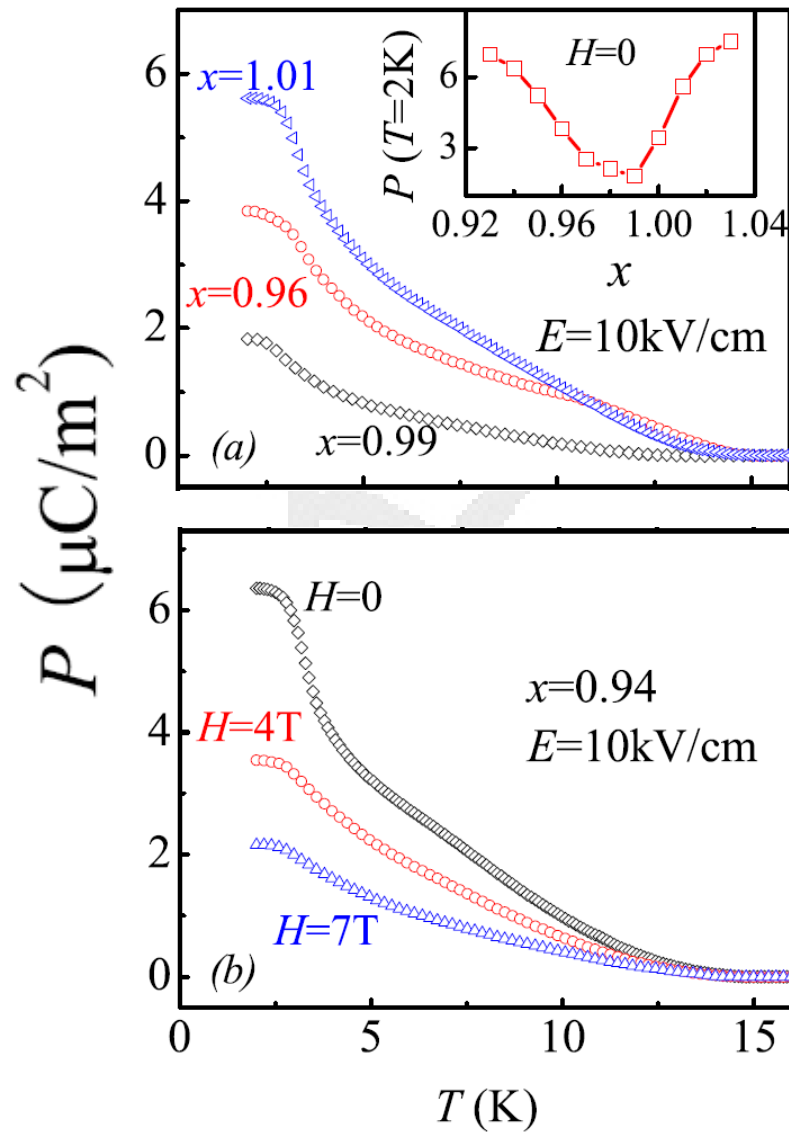
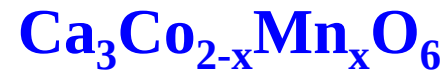
$\text{Ca}_3\text{CoMnO}_6$



PRL 100, 047601 (2008).



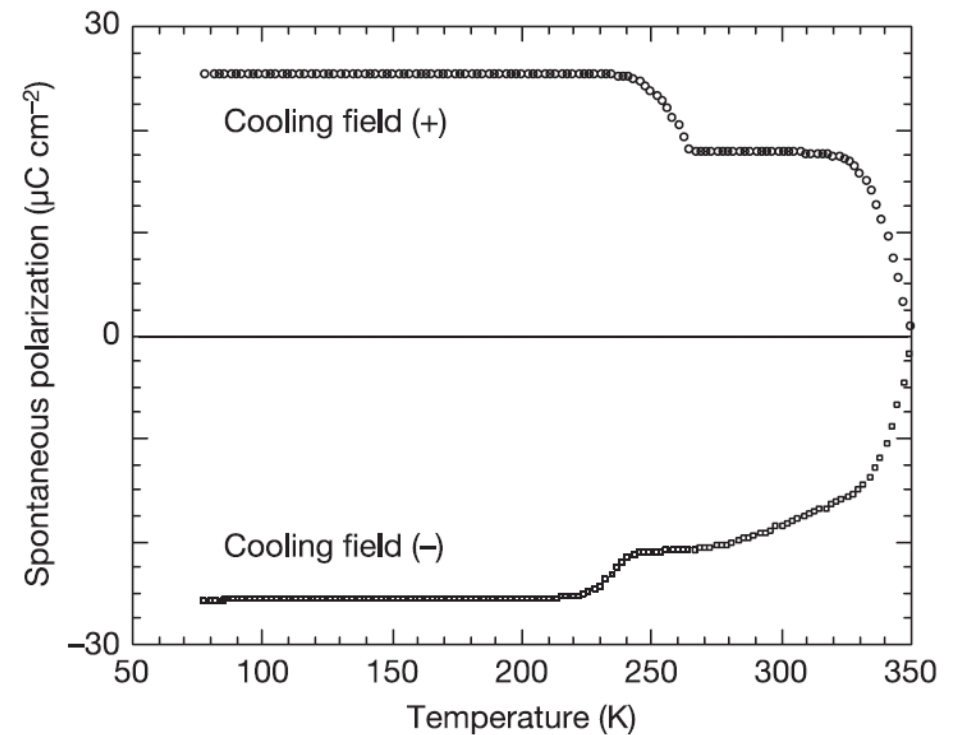
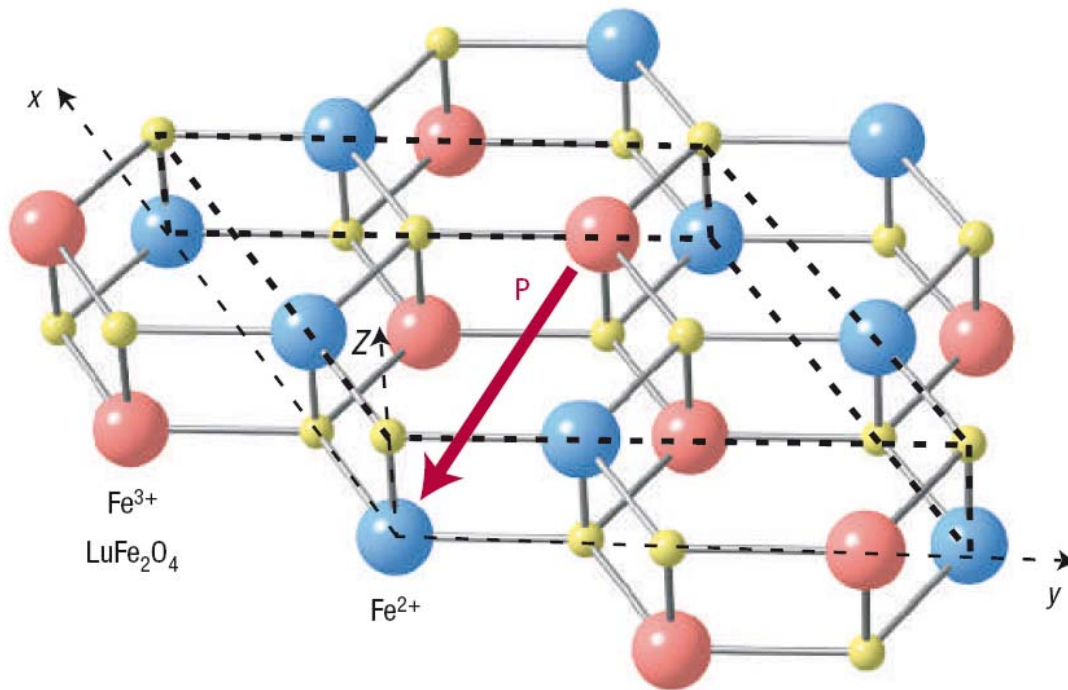
Multiferroics: charge-order induces polarization





Multiferroics: charge-order induces polarization

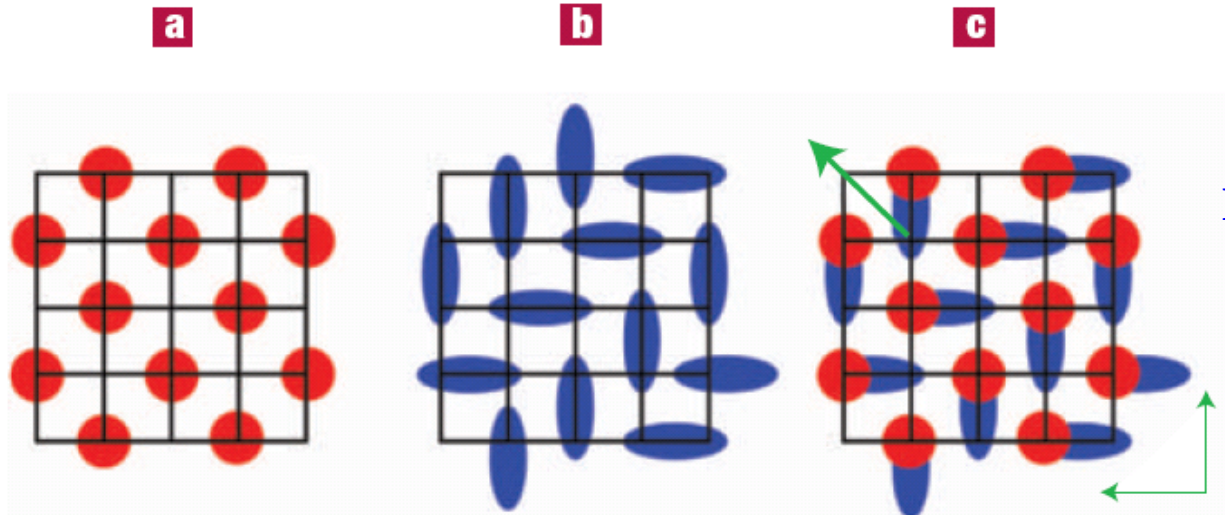
LuFe_2O_4 – charge order below $\sim 350\text{K}$ creates alternating layers with $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of 2/1 and 1/2, inducing net polarization.



Ikeda et al, Nature 436, 1136 (05)

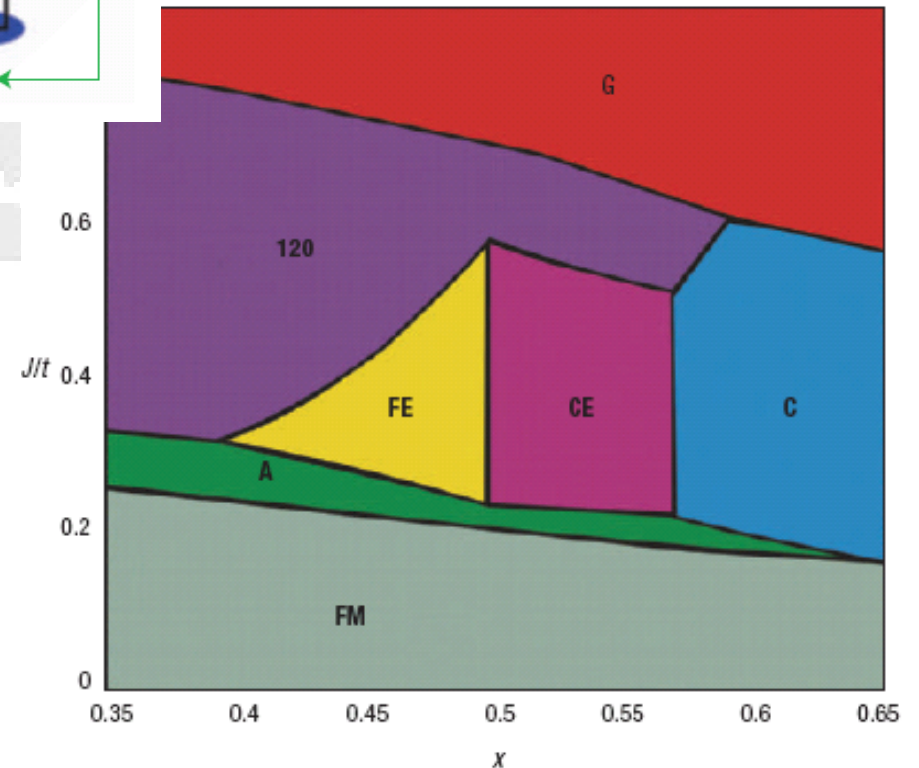


Multiferroics: charge-order induces polarization



Efremov et al, Nature Mat. 3, 853 (04)

- $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ – possible polarization due to the site-center (a) and bond-center (b) charge order.

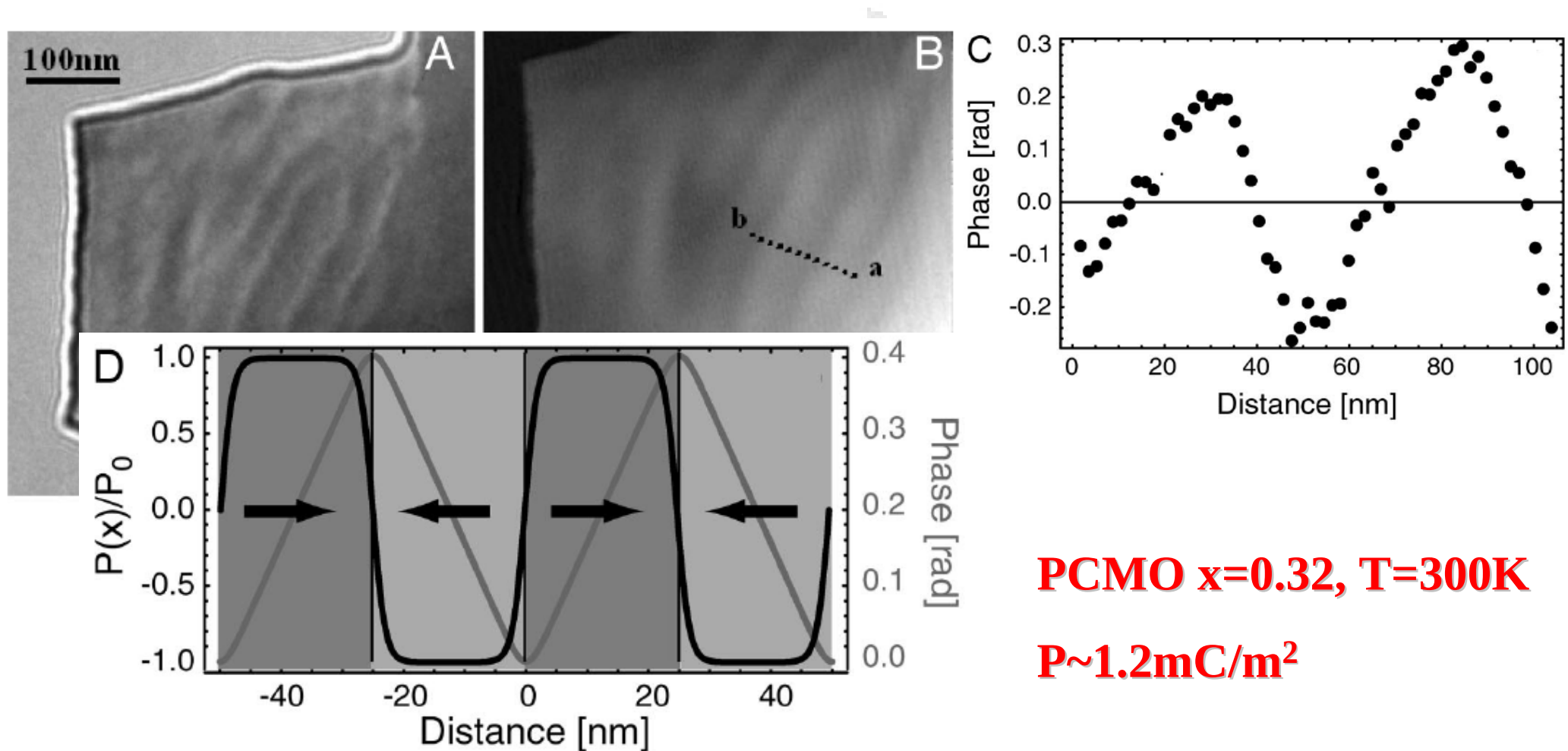




Multiferroics: charge-order induces polarization

- $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ – Indirect evidence for local ferroelectric domains by HRTEM+electron optics.

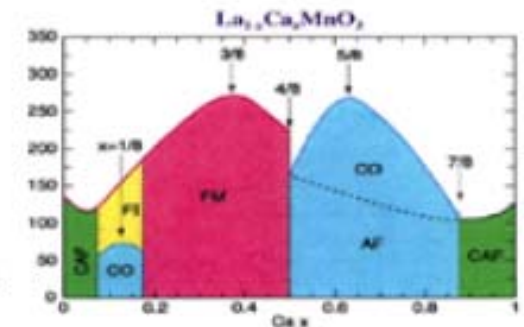
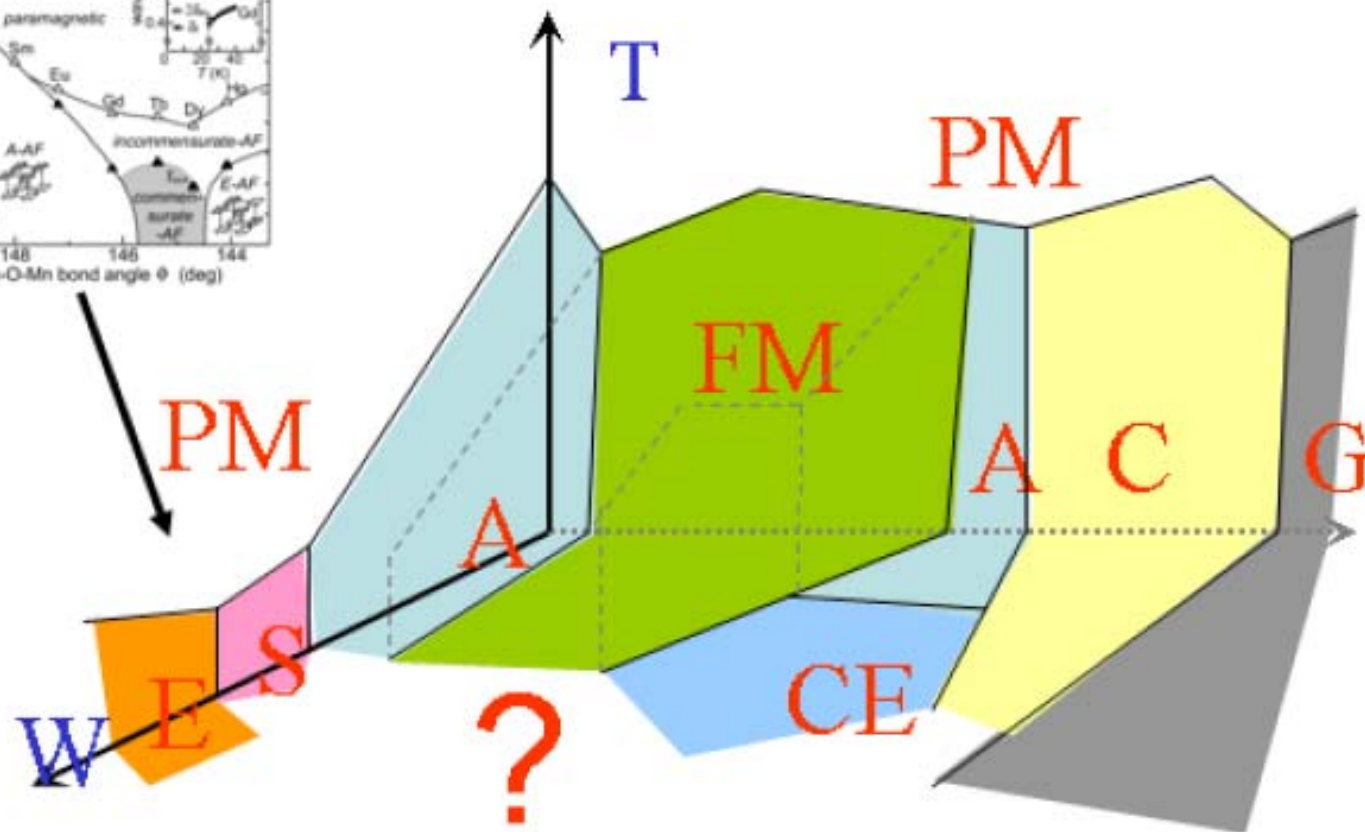
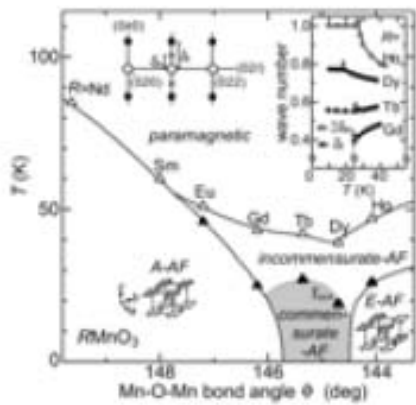
Jooss et al, PNAS 104-13597 (07)





Multiferroics: charge-order & orbital order

- Unknown region in X-W-T phase diagram



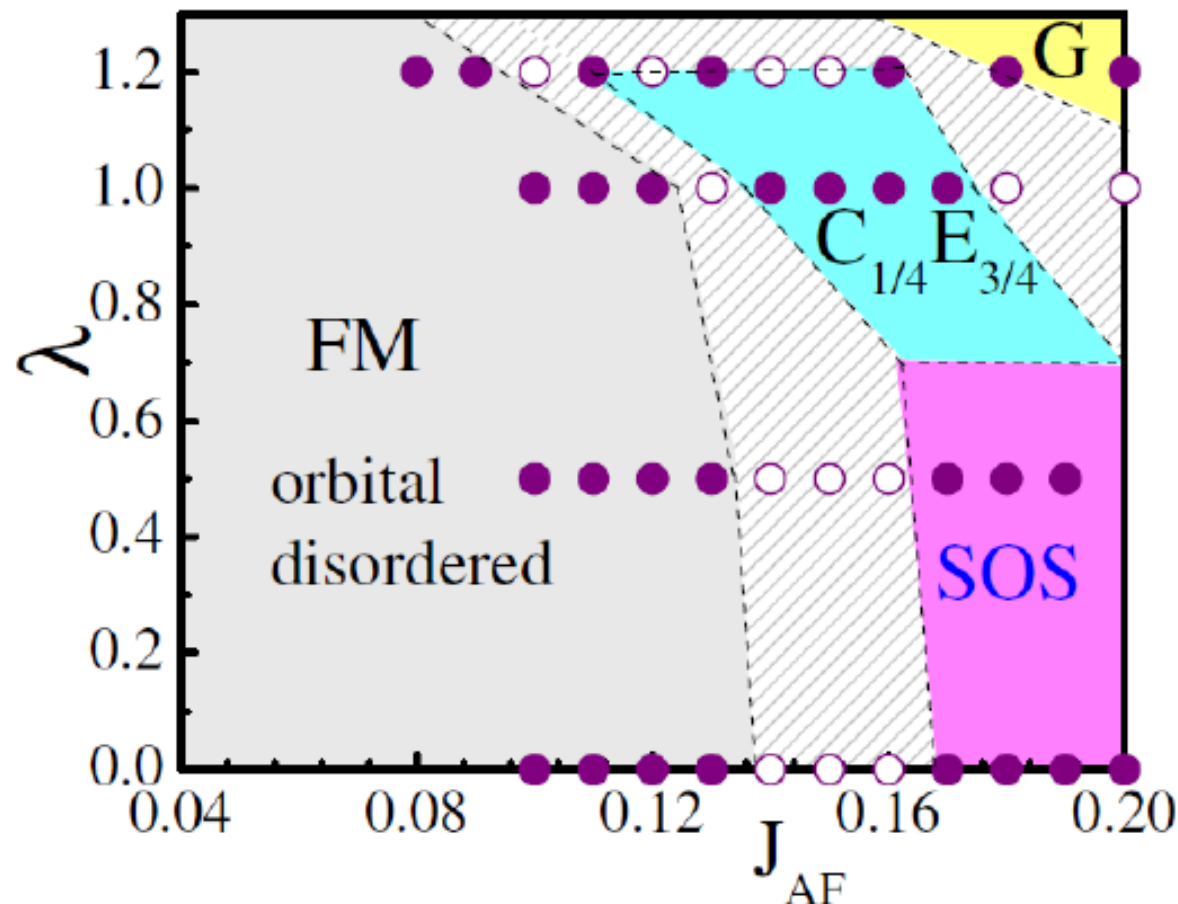
X





Multiferroics: charge-order & orbital order

- For doped manganites: $R_{1-x}A_x\text{MnO}_3$, $x=1/4$.
- DE+NN-SE+JT, without DMI and NNN-SE



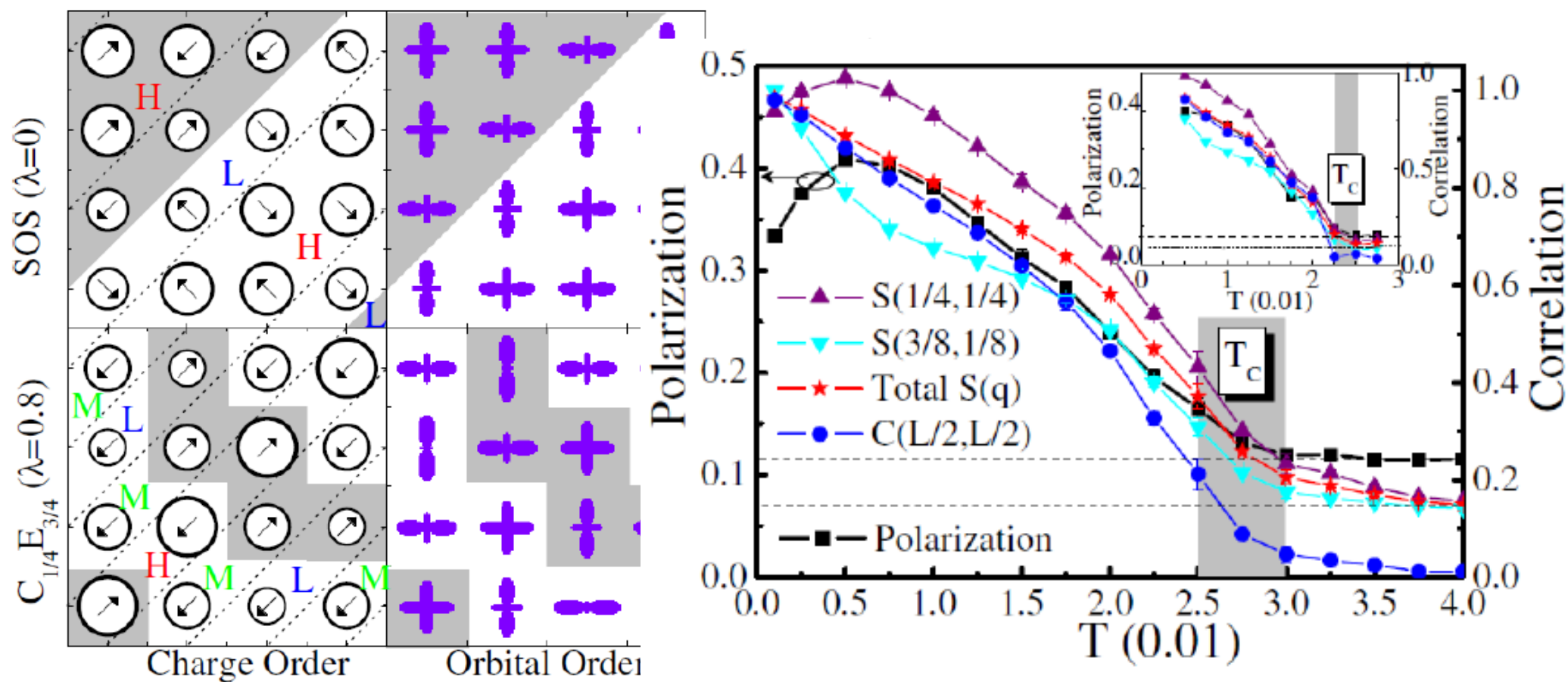
- ✓ New phase: spin-orthogonal stripe (SOS) phase.
- ✓ Large J_{AF} & small JT (λ).
- ✓ C_xE_{1-x} phase: x C-AFM+(1-x)E-AFM.

Dong et al. PRL



Multiferroics: charge-order & orbital order

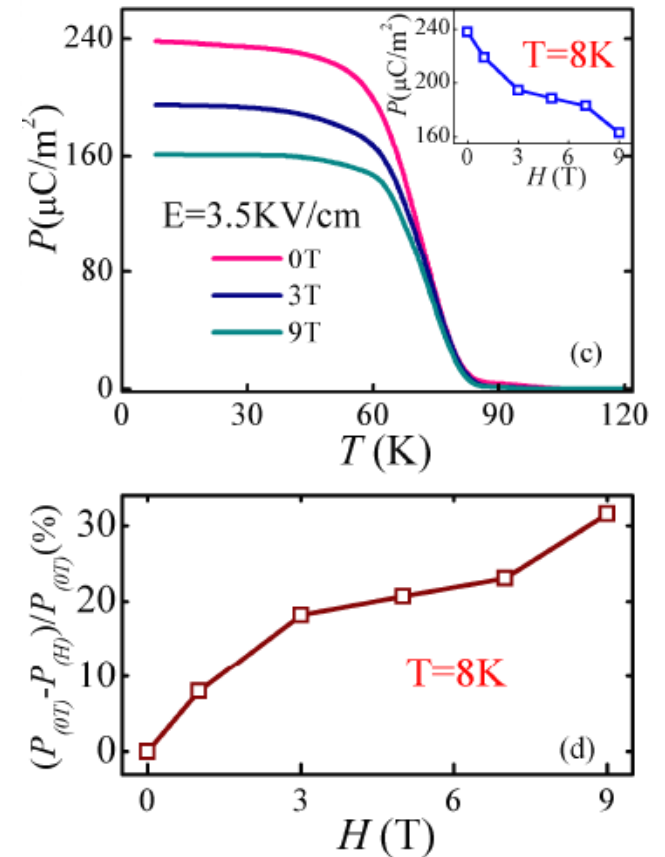
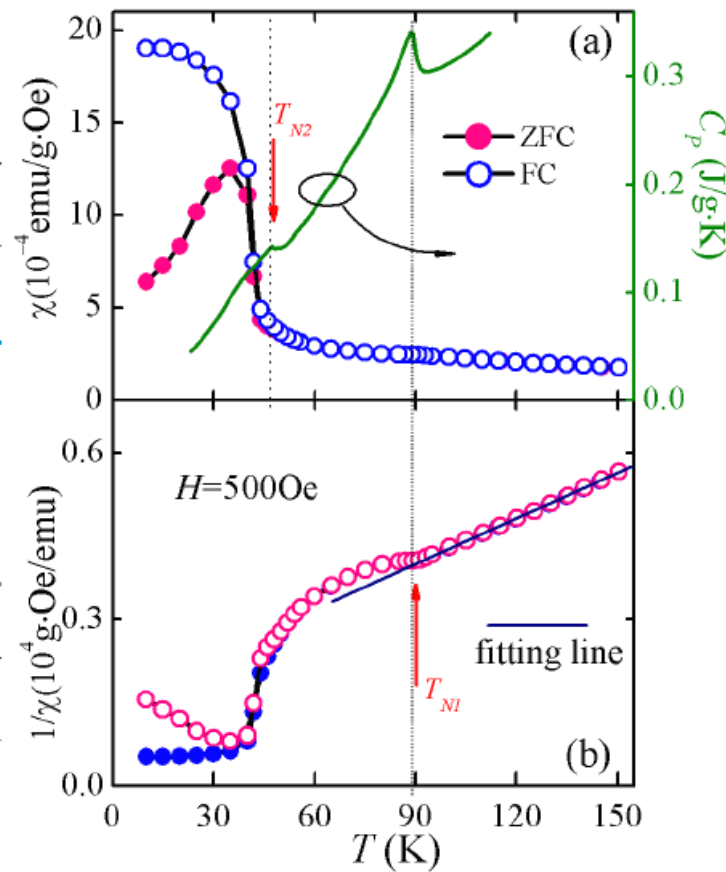
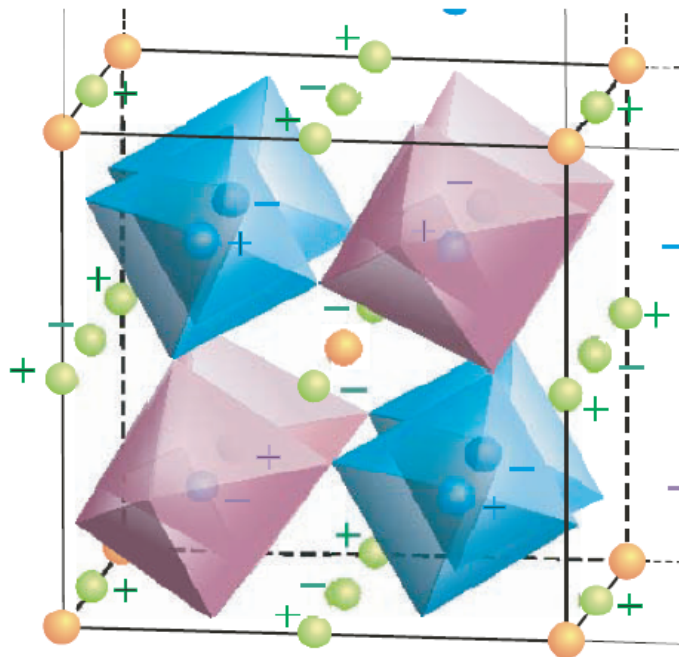
Charge order, orbital order, & ferroelectricity





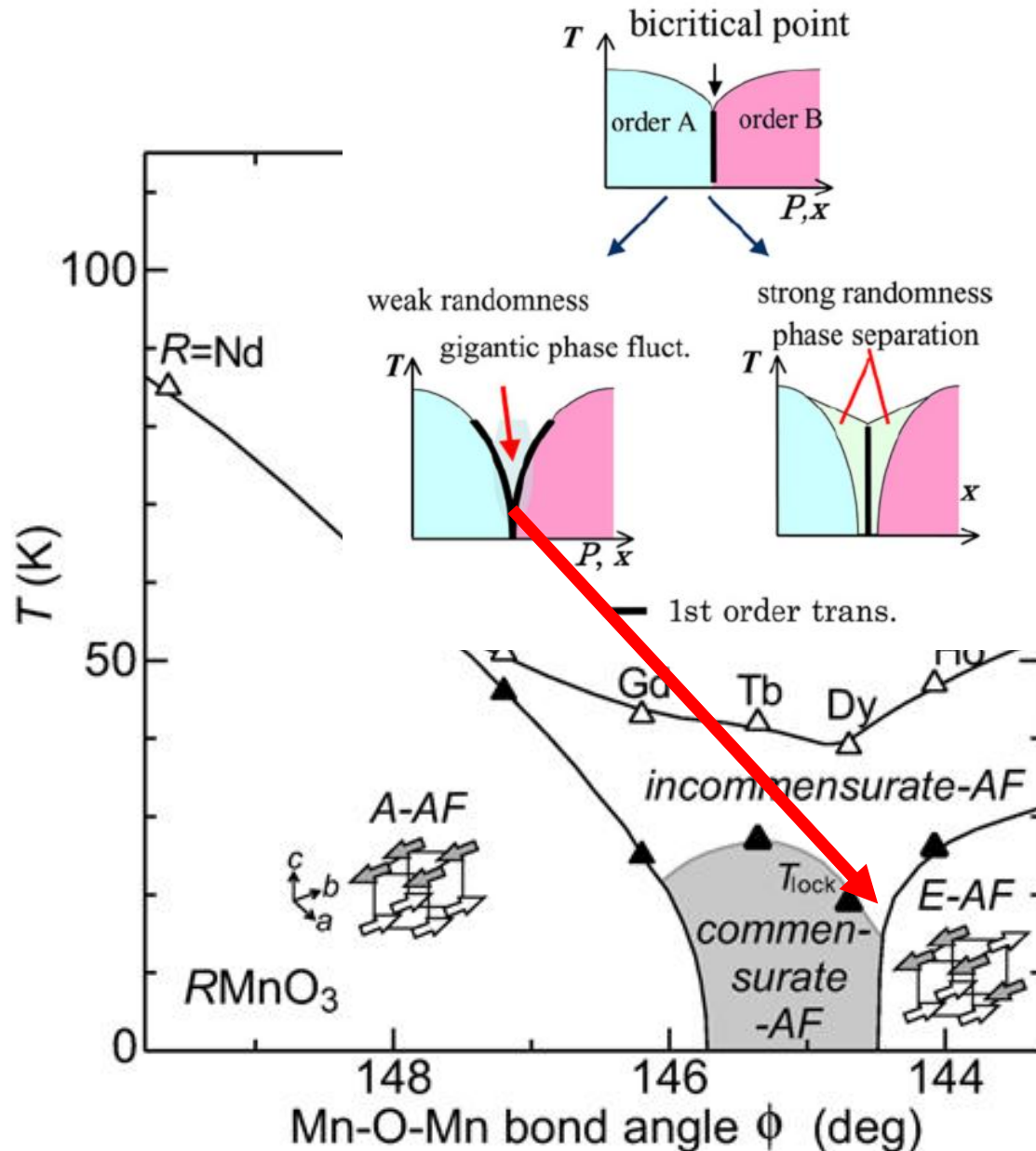
Multiferroics: charge-order & orbital order

- Large J_{AF} (narrow bandwidth) and small JT distortion
- quadruple $(AA'_3)B_4O_{12}$ family, e.g. $(A^{2+}B_3^{3+})(B_3^{3+}B_4^{4+})O_{12}$.
- B-O-B angle less than 140° and the JT Q_2 mode can be weak.

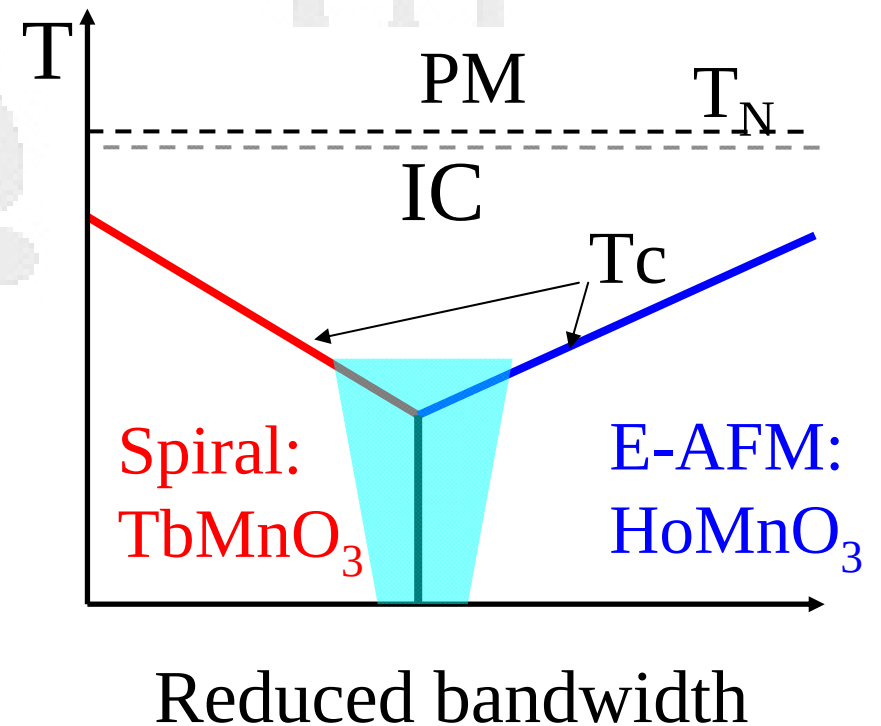




Multiferroics: possible electronic phase separation

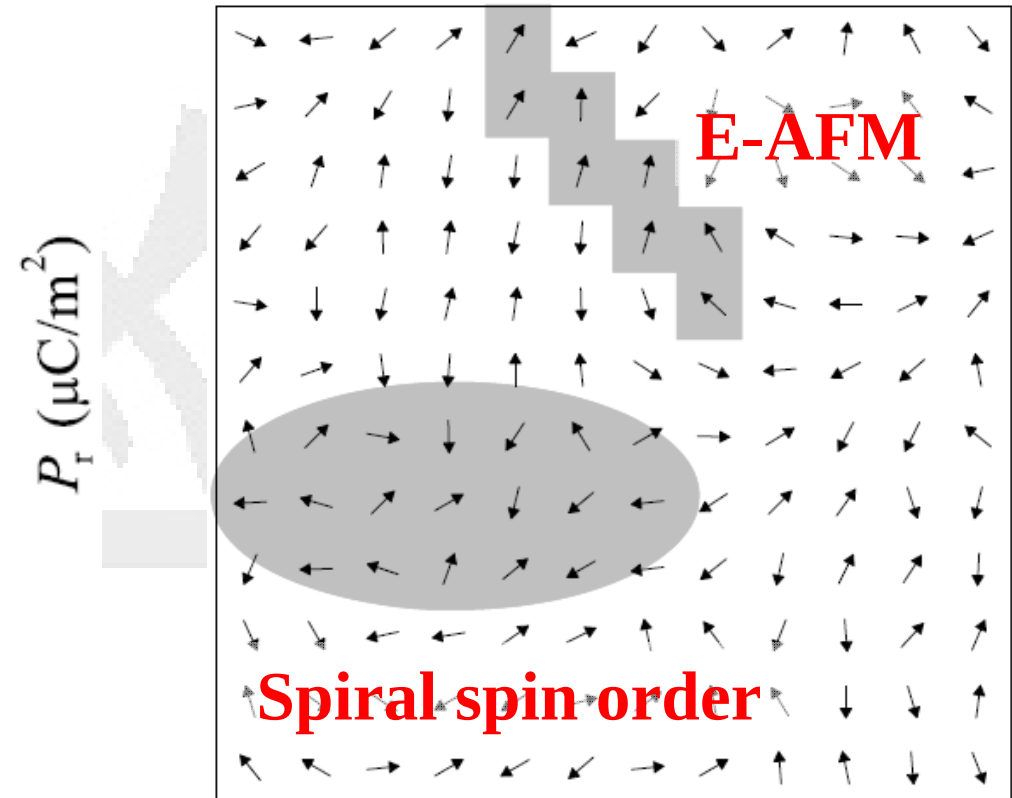
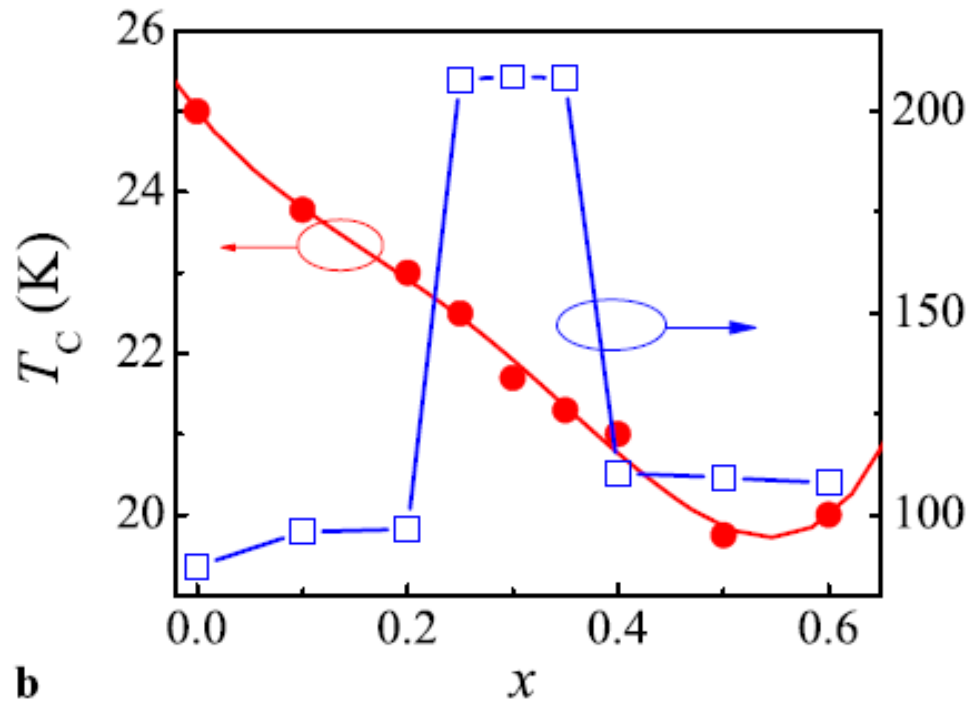


Bicritical point of dual multiferroic phases?
Phase separation by disorder?





Multiferroics: possible electronic phase separation





回顧與展望

Perspectives & challenges



Thank you for your attentions!!!

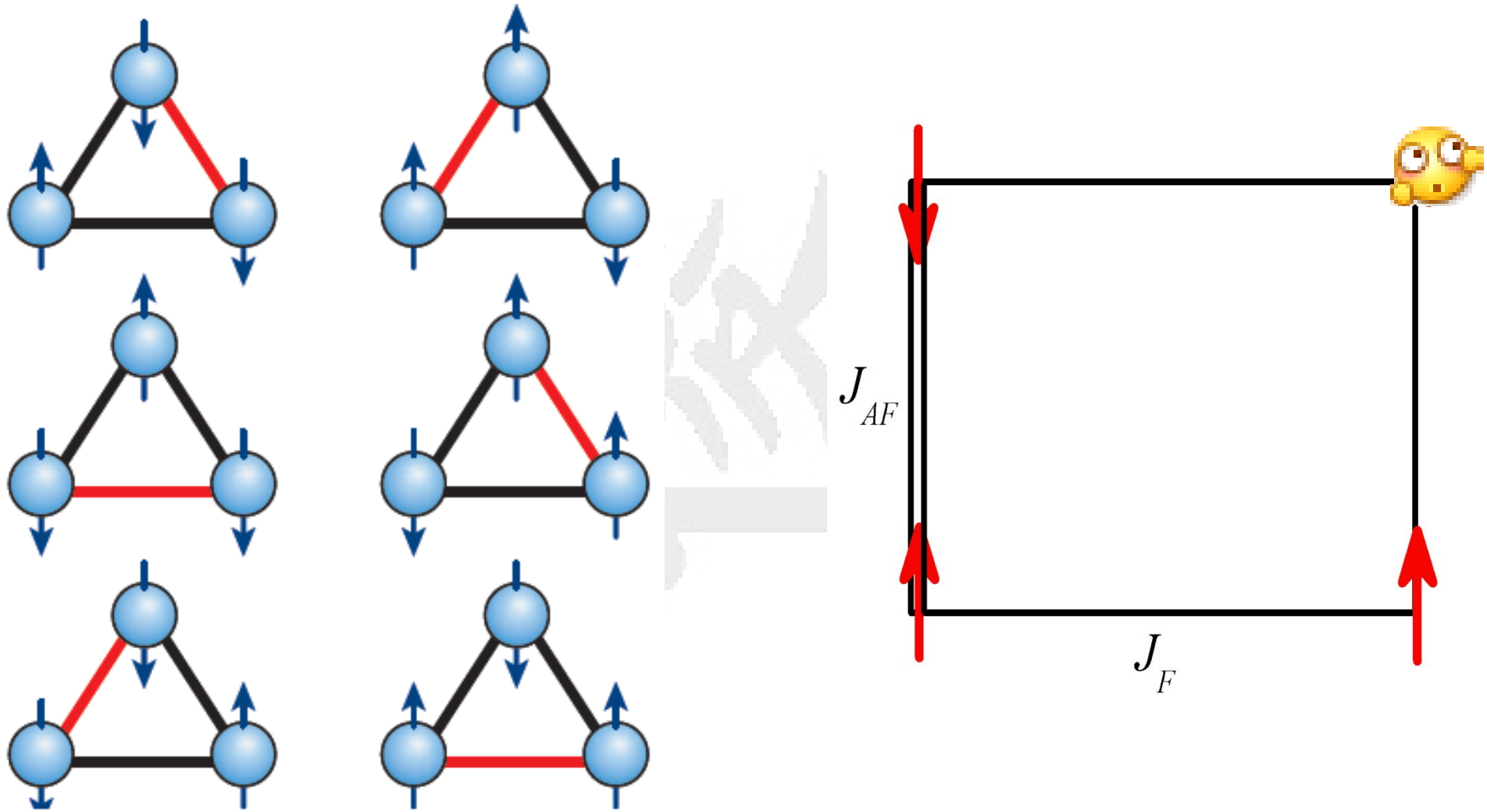
- ✓ A variety of materials to be explored
 - ✓ A comprehensive understanding of the strongly correlated properties
 - ✓ Rich physics but soft electronic & magnetic structure/property
 - ✓ Enhancement of these effects up to room temperature: physically accessible?
-



Spin liquid and spin ice

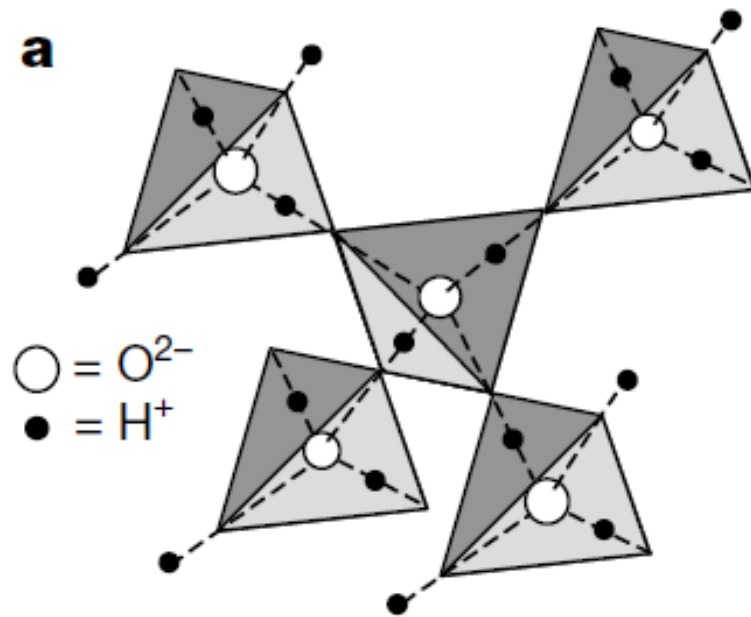


Spin liquid & spin ice: spin frustration

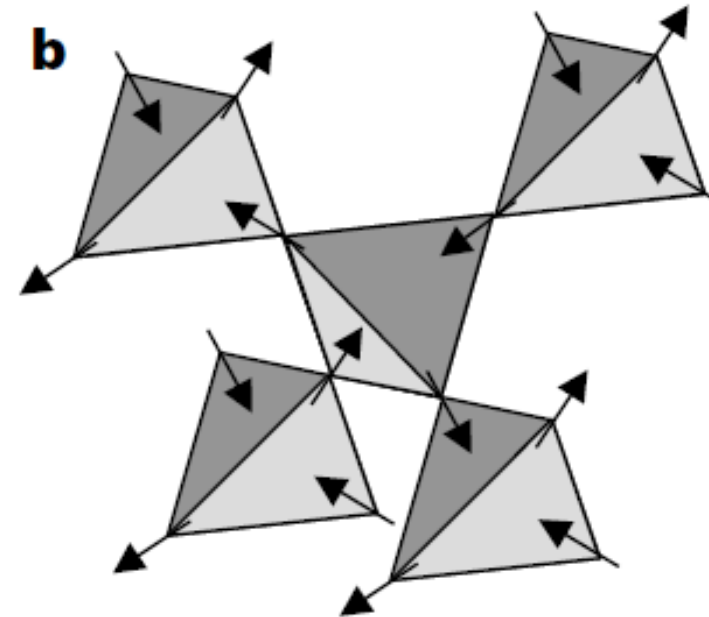




Spin liquid & spin ice: spin ice



Water ice

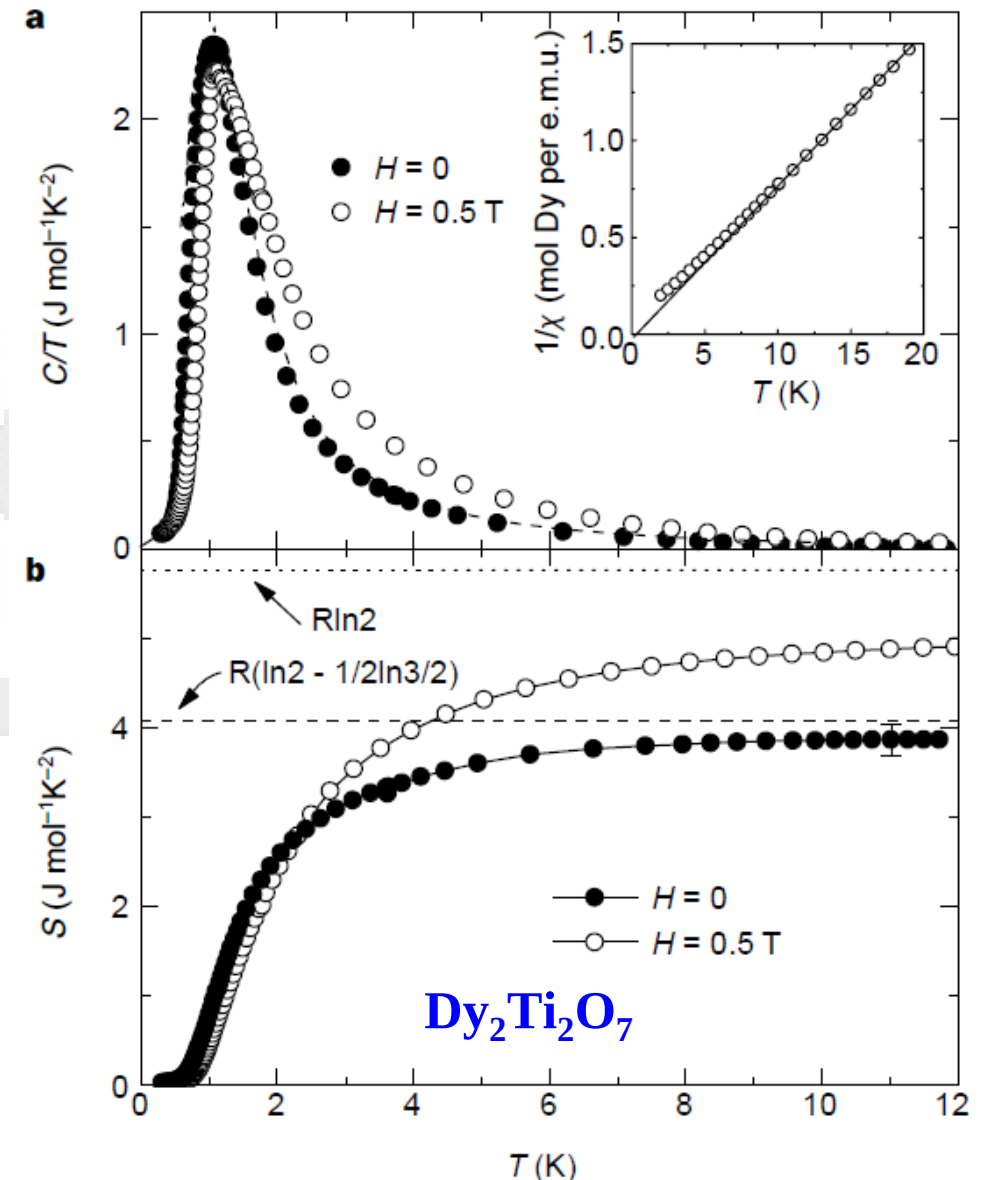


Spin ice



Spin liquid & spin ice: zero-point entropy

- ✓ Highly frustrated configurations
- ✓ A variety of energy equivalent states with remarkable zero-point entropy
- ✓ Classical spin ice frozen into disorder state at $T \Rightarrow 0$
- ✓ Quantum spin ice with strong quantum fluctuations at $T=0$
- ✓ Magnetic monopole and anti-monopole

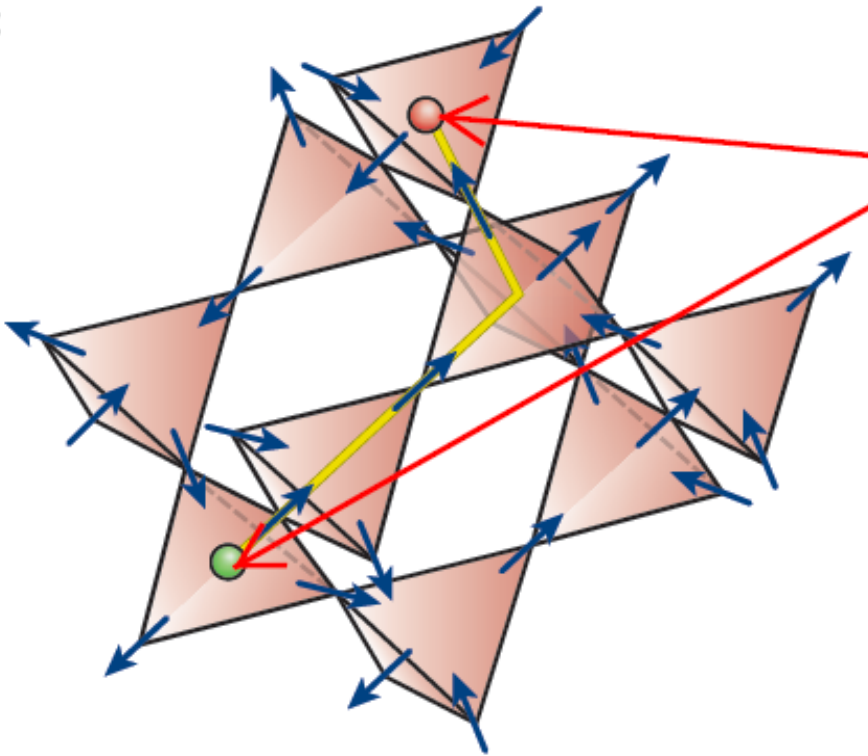


A. P. Ramirez *et al*, Nature 399, 333 (1999)

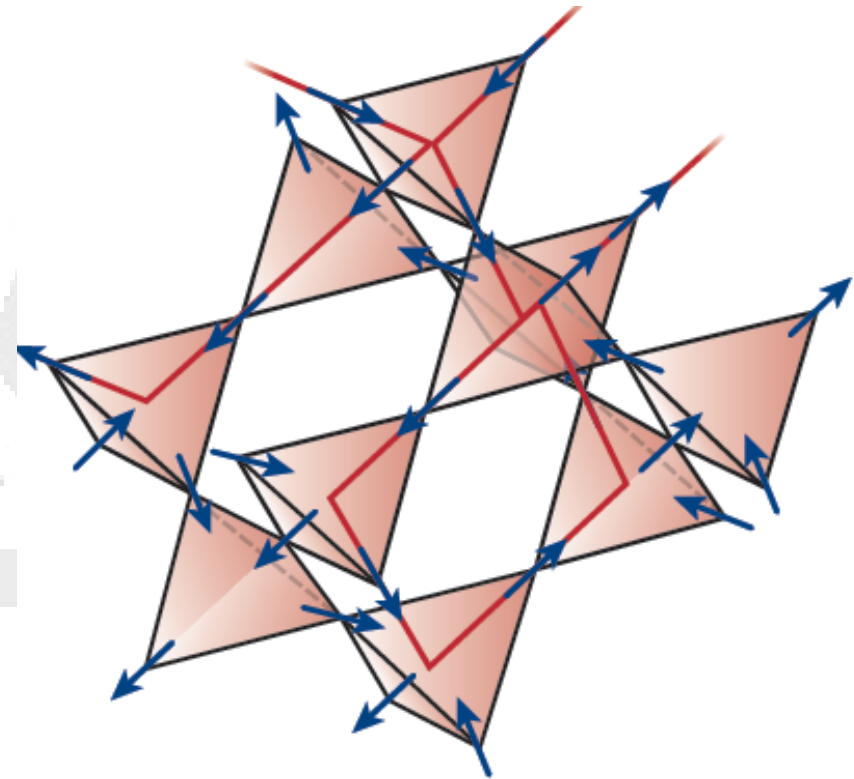


Spin liquid & spin ice: magnetic monopole & antimonopole

A topological defect without breaking the lattice symmetry



Magnetic monopole & anti-monopole (pair)

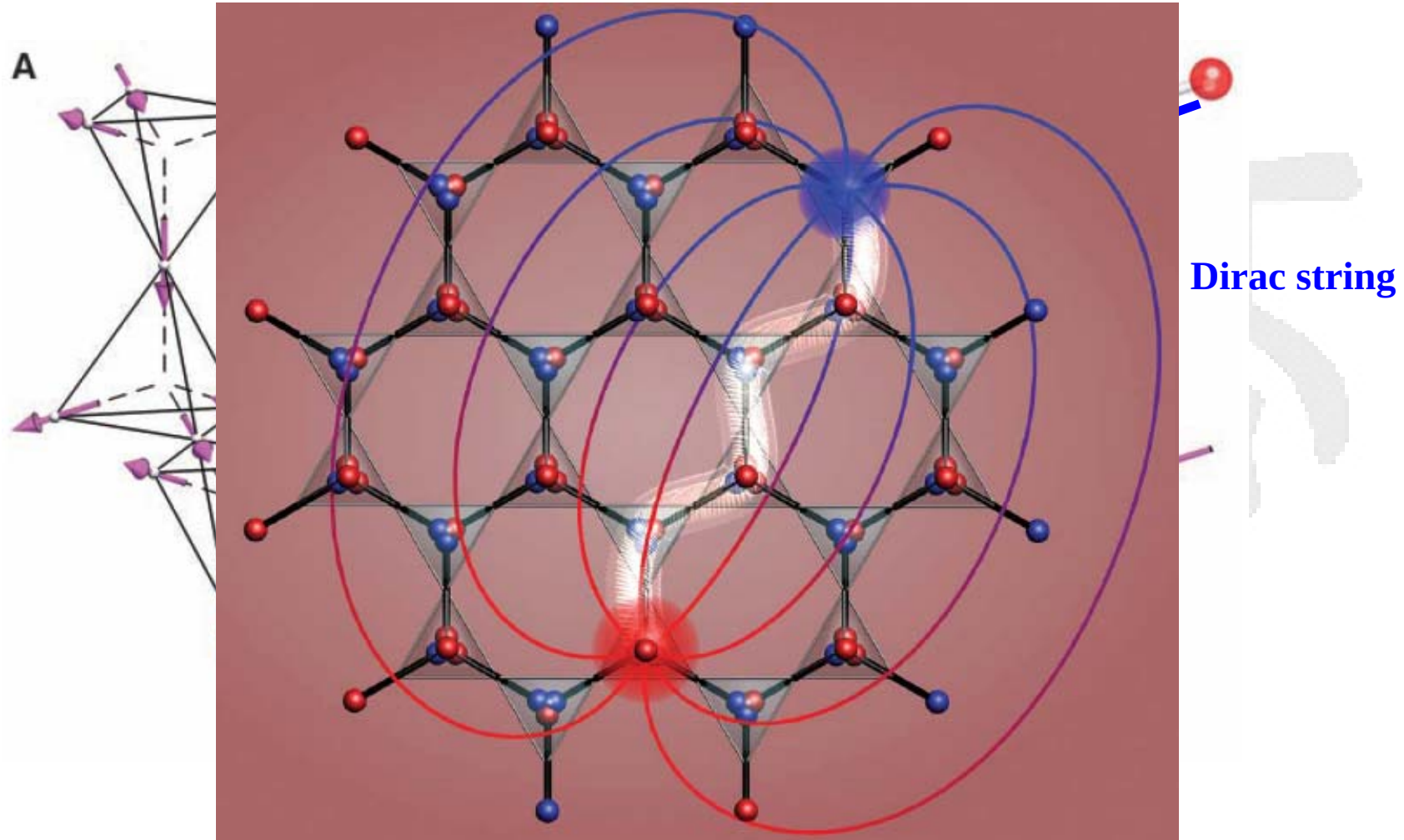


Magnetic flux loop & chirality



Spin liquid & spin ice: Dirac string

A pair of monopoles apart from each other by a trail flipped spins



C. Castelnovo *et al*, Nature 451, 42 (2008)

T. Fennel *et al*, Science 326, 415 (2009)



Spin liquid & spin ice: magnetic monopole & antimonopole

A simple Hamiltonian to spin systems with localized electrons:

$$H = -\frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Classical or quantum
spin interaction

$$H_{\text{cf}} = -D \sum_i (\mathbf{S}_i \cdot \hat{\mathbf{n}}_i)^2$$

Crystal field effect, inducing
Magnetocrystalline anisotropy

$$H_{\text{Hubbard}} = -\sum_{ij, \alpha} t_{ij} c_{i\alpha}^\dagger c_{j\alpha} + U \sum_i n_i (n_i - 1)$$

For non-localized electrons, consult
to Hubbard model & Mott transition