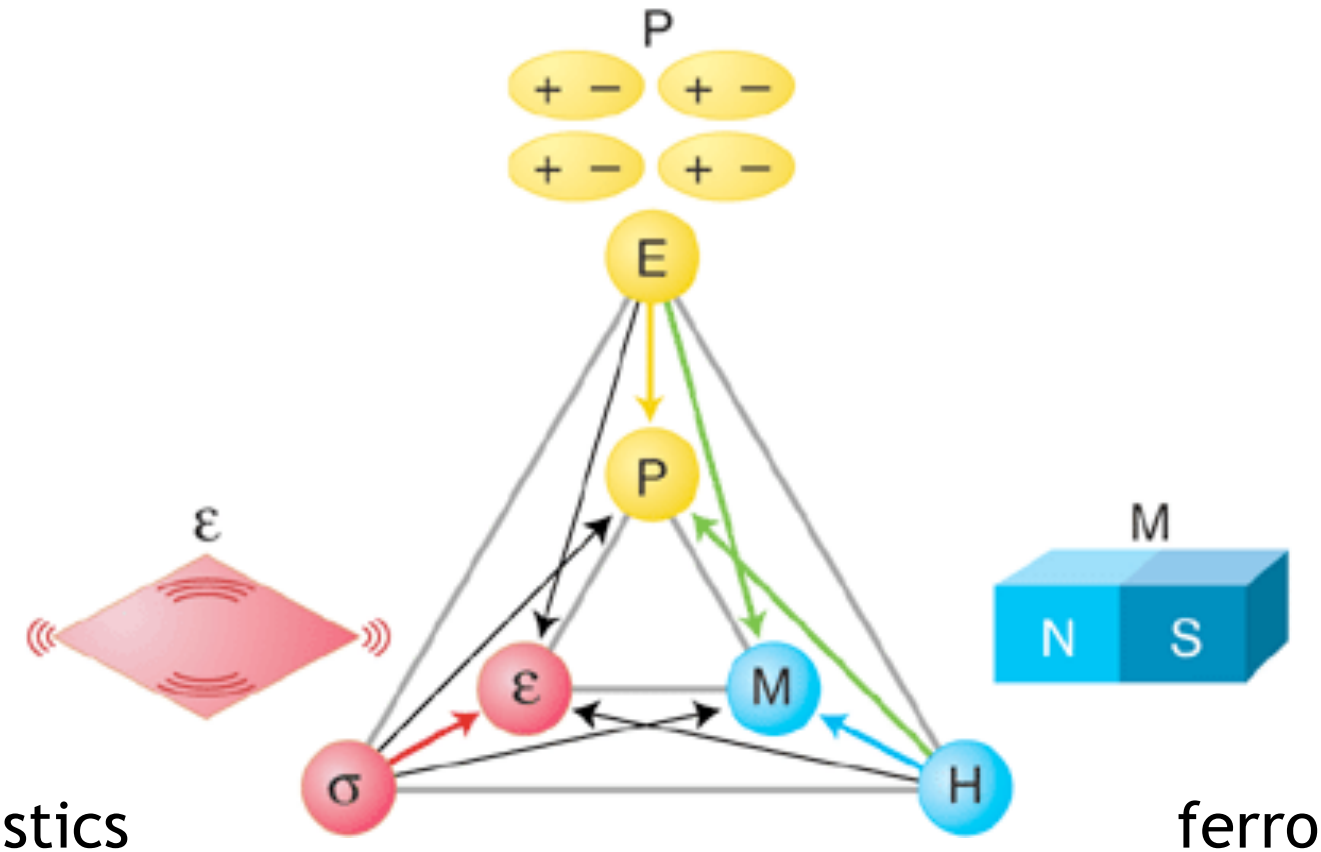
Whither (or Withers?) Multiferroics

ferroelectrics



ferroelastics

ferromagnets

The renaissance of magnetoelectric multiferroics, N. A. Spaldin and M. Fiebig, Science **15**, 5733 (2005)

MATERIALS
UC Santa Barbara

Goals

UCSB

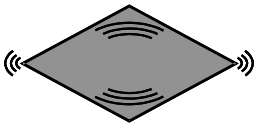
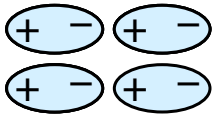
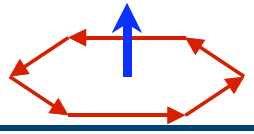
Why it's hard to combine ferroelectricity and magnetism

Why it's hard to calculate properties of multiferroics accurately

A zoology of known multiferroic types

Two examples of first-principles design of new multiferroics with specific functionalities

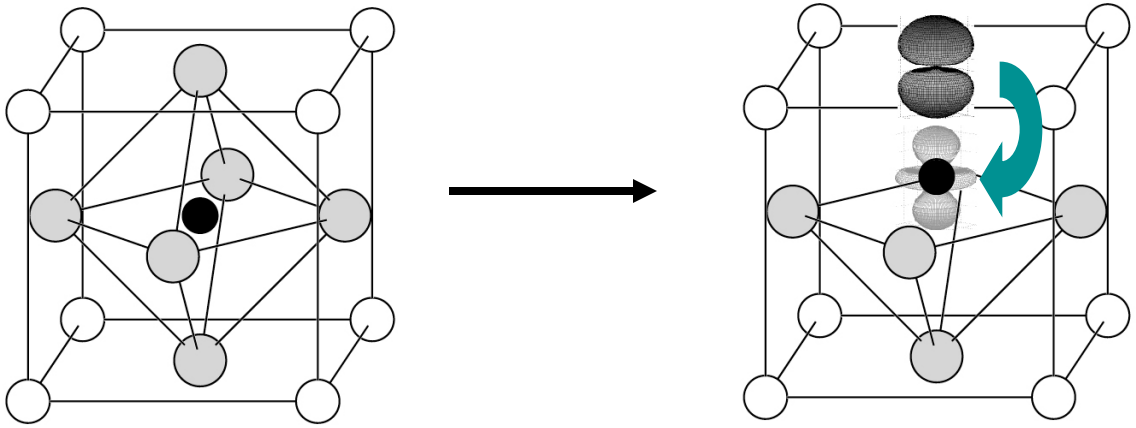
First open question:
Should the set of primary ferroics be expanded?

Time \ Space	invariant	change
invariant	ferroelastic 	ferroelectric 
change	ferromagnetic 	ferrotoroidic? 

The toroidal moment in condensed matter and its relationship to the magnetoelectric effect, N.A. Spaldin, M. Fiebig and M. Mostovoy, J. Phys. Condens. Matter 20, 434203 (2008).

Why is hard to make / find multiferroics?

Conventional ferroelectricity: Off-centering of cations from center of "cage" of oxygen anions



Empirical observation: Off-centering only occurs for "d^0" cations

WHY?

Off-centering increases Coulomb repulsion between electron clouds (energetically unfavorable) and increases it most for occupied *d* orbitals

Covalent bond formation between oxygen *p* electrons (filled) and cation *d* orbitals (energetically favorable) is most favorable for empty *d* orbitals

N.A. Hill, *Why are there so few magnetic ferroelectrics?* J. Phys. Chem. B **104**, 6694-6709 (2000)

Perturbation theory

Expand Hamiltonian as function of atomic distortion (normal coordinate), Q:

$$H = H^{(0)} + H^{(1)}Q + \frac{1}{2}H^{(2)}Q^2$$

where

$$H^{(1)}Q = (\delta H/\delta Q)_0 Q$$
$$H^{(2)}Q^2 = (\delta^2 H/\delta Q^2)_0 Q^2$$

then

$$E(Q) = E(0) + <0|(\delta H/\delta Q)_0|0> Q + \frac{1}{2}\left(<0|(\delta^2 H/\delta Q^2)_0|0> - 2\Sigma'_n \frac{|<0|(\delta H/\delta Q)_0|n>|^2}{E_n - E(0)}\right) Q^2 + \ldots$$

1st-order JT
Non-zero for orbitally degenerate states

always positive (moving nuclei with fixed electrons);
want this to be small

always negative (relaxation of electron distribution);
want this to be large
1) need a non-zero matrix element;
2) need En close to E(0)

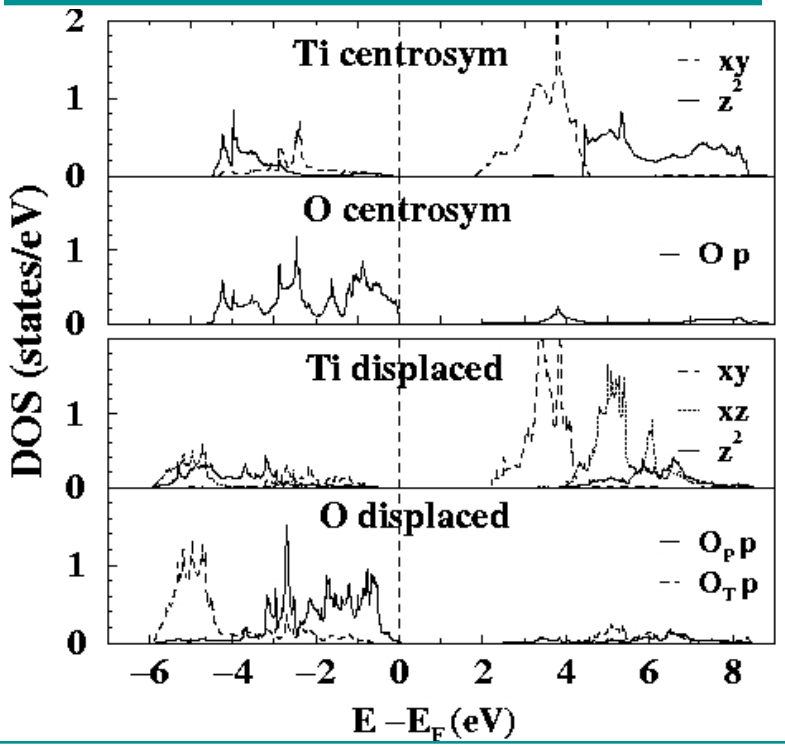
Second-order Jahn-Teller effect

Hand-waving single-particle picture

$$+\frac{1}{2}\left(<0|(\delta^2 H/\delta Q^2)_0|0> -2\Sigma'_n \frac{|<0|(\delta H/\delta Q)_0|n>|^2}{E_n - E(0)}\right) Q^2 \,.$$

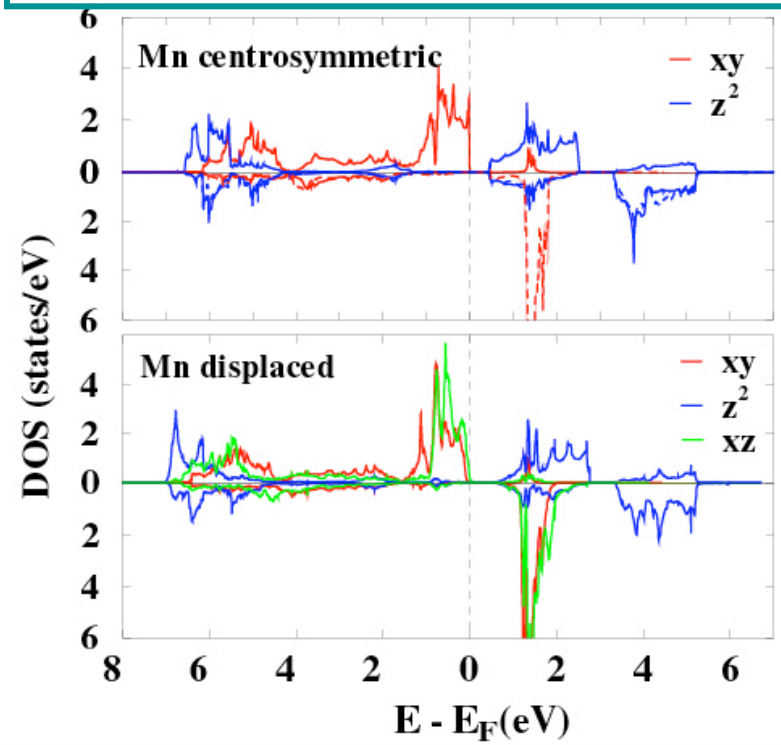
$BaTiO_3$ (d^0)

Repulsive term small
Energy-lowering term non-zero



$CaMnO_3$ (d^3)

Repulsive term large
Energy-lowering term 0 by symmetry

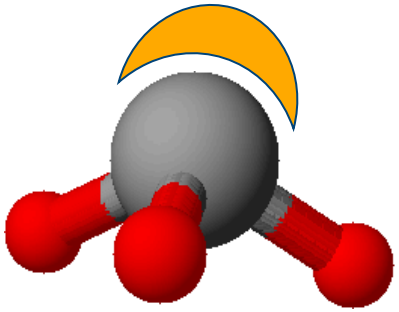


A. Filippetti and N.A. Hill, *Coexistence of magnetism and ferroelectricity in perovskites*, PRB **65**, 195120 2002

A zoology of known multiferroic mechanisms

Lone pair active

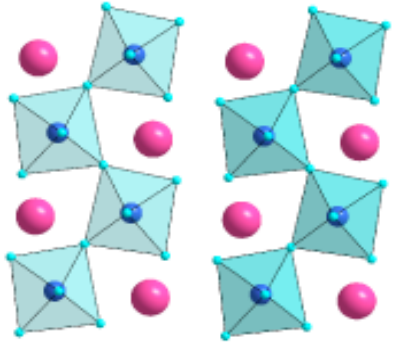
e.g. $BiMnO_3$, $BiFeO_3$



Geometric ferroelectricity

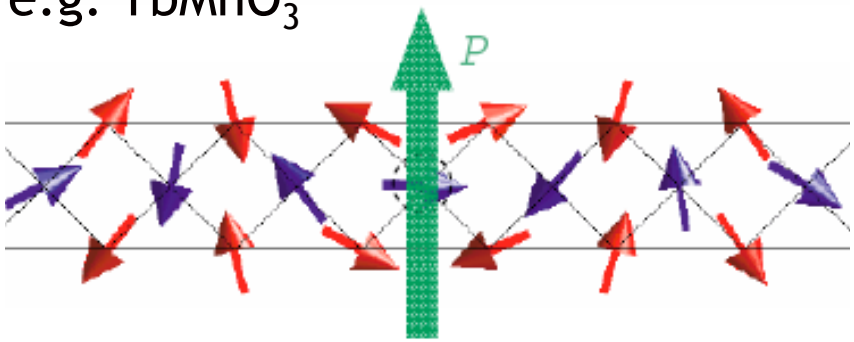
e.g. $BaNiF_4$

C. Ederer and N.A. Spaldin, Electric-field switchable magnets: The case of $BaNiF_4$, PRB **74**, 020401(R) (2006)



Magnetically driven

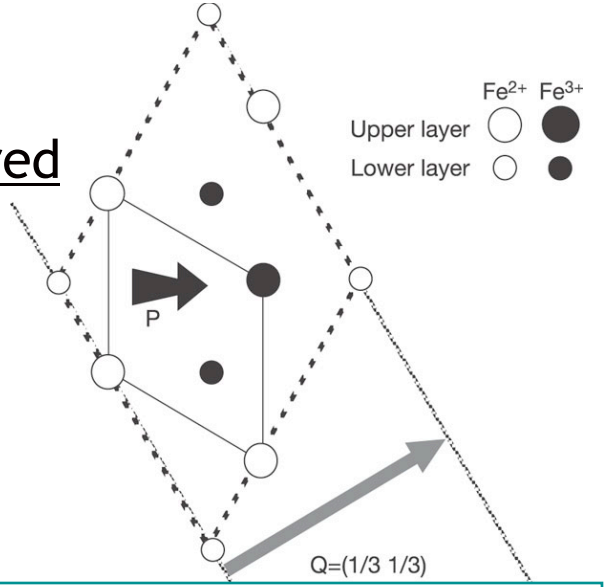
e.g. $TbMnO_3$



T. Kimura et al., *Magnetic control of ferroelectric polarization*, Nature **426**, 55 (2004)

Charge ordered

e.g. $LuFe_2O_4$



N. Ikeda et al., *Ferroelectricity from iron valence ordering in the charge-frustrated system $LuFe_2O_4$*, Nature 436, 1136 (2005)

MATERIALS
UC Santa Barbara

Why is it hard to calculate the properties of multiferroics?

UCSB

1) Need to get ferroelectric polarization right

   $BaTiO_3$: LDA, LDA lattice constant: tiny polarization

   LDA, experimental lattice constant: P=about right

   GGA, GGA lattice constant: P=excessively large

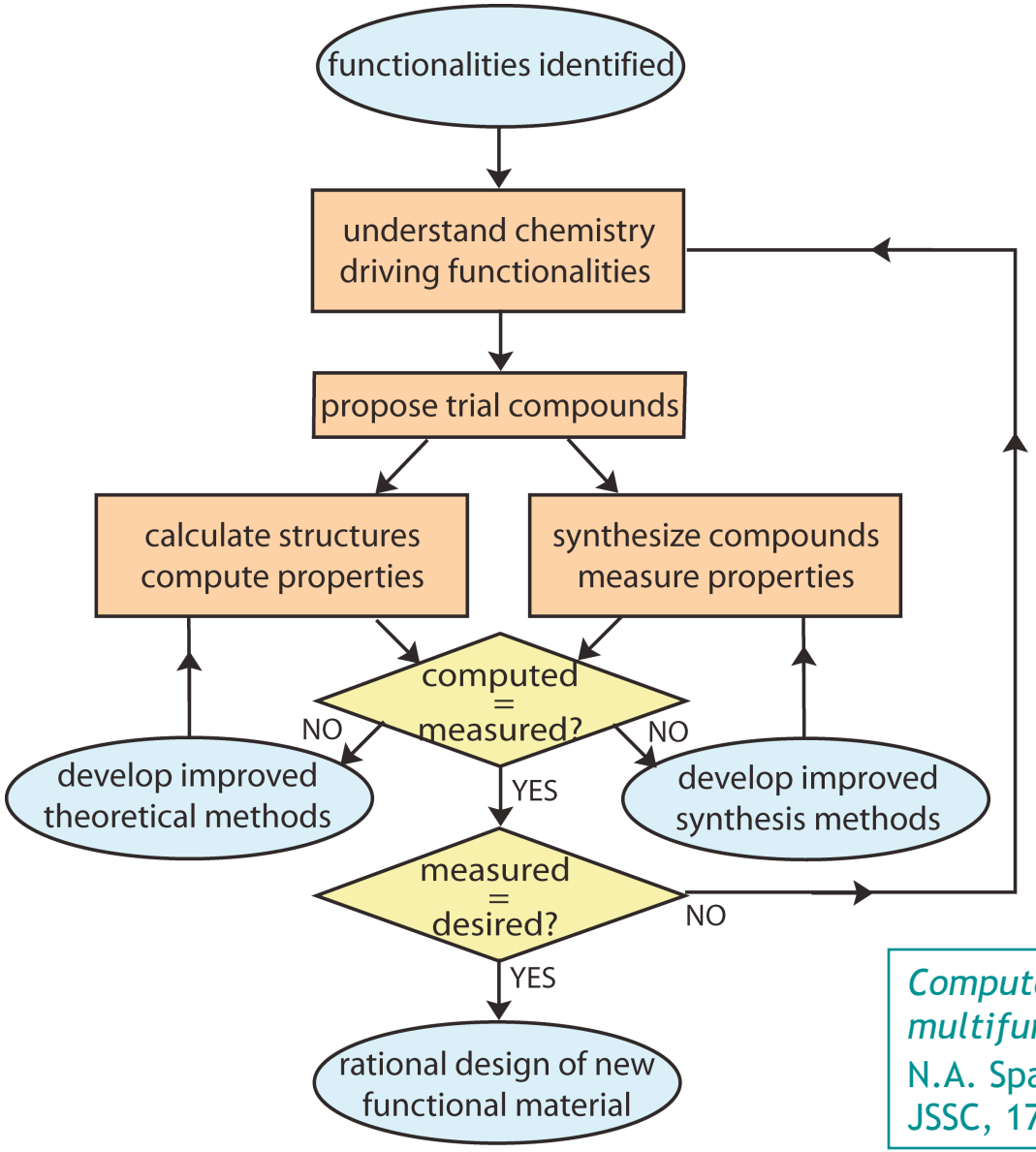
   (volume effect)

2) Magnetic insulators -- need to describe strong correlations while retaining correct “band” physics

3) Often magnetic anisotropies are important -- very small energy differences

4) Sometimes interested in applied electric or magnetic fields or optical properties

Materials by Design



Computational design of multifunctional materials, N.A. Spaldin and W.E. Pickett, JSSC, 176, 615 (2003)

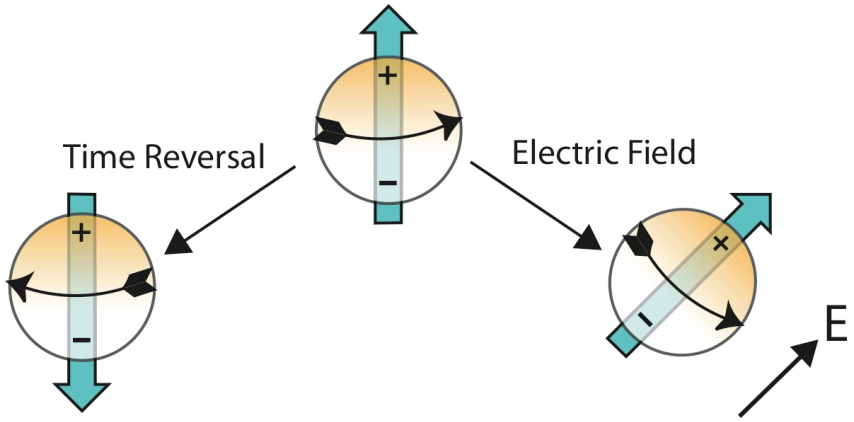
Multiferroics and the origin of the universe

Testing various extensions to the Standard Model by measuring the electron dipole moment

Existence of a non-zero EDM is a signature of violation time-reversal symmetry (and therefore CP-violation via CPT theorem)

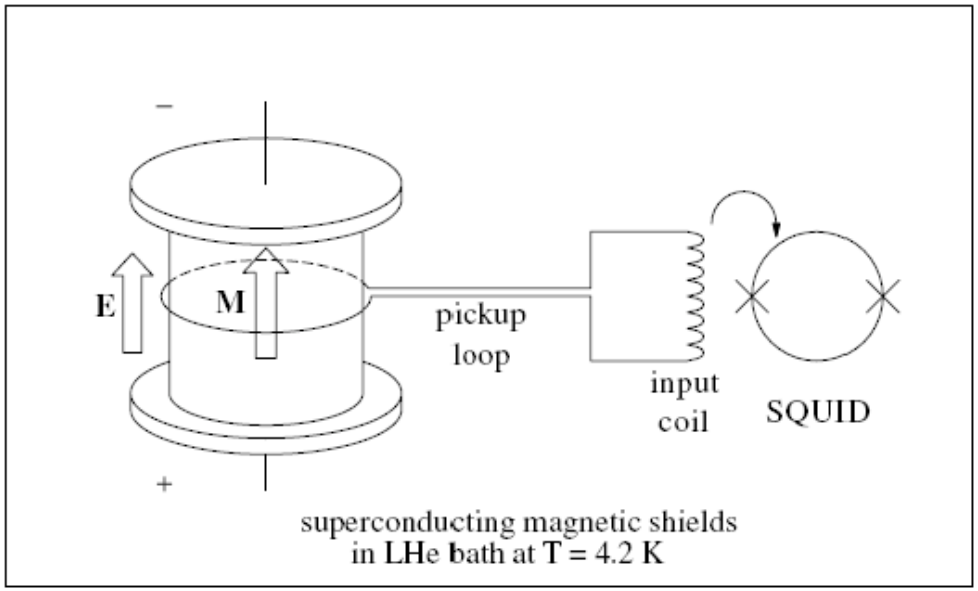
Current experimental upper limit is 1.6×10^{-27} e cm

Standard model predicts 10^{-42} e cm; extensions (Supersymmetry, Grand Unification, Multi Higgs) predict distinct values around 10^{-29} e cm



Proposed magnetoelectric switching experiment to measure electron electric dipole moment

Lamoreaux, Sushkov et al.



achievable EDM limit,

$$d_e = \frac{\mu_s}{\mu - 1}\frac{\delta B}{E_{eff}},$$

Material property requirements:

Ferroelectric, switchable at a few K, large polarization

Magnetic, but not ordered at a few K

Bulk (around 1 cm) sample

A low temperature multiferroic!

$EuTiO_3$ – $BaTiO_3$

$EuTiO_3$	$BaTiO_3$
Magnetic, T_N = 7K	Not magnetic
Not ferroelectric	Good ferroelectric
Small lattice constant	Large lattice constant

Guess for the phase diagram:

$EuTiO_3$ $(Eu,Ba)TiO_3$ $BaTiO_3$

$EuTiO_3$ – $BaTiO_3$

$EuTiO_3$	$BaTiO_3$
Magnetic, T_N = 7K	Not magnetic
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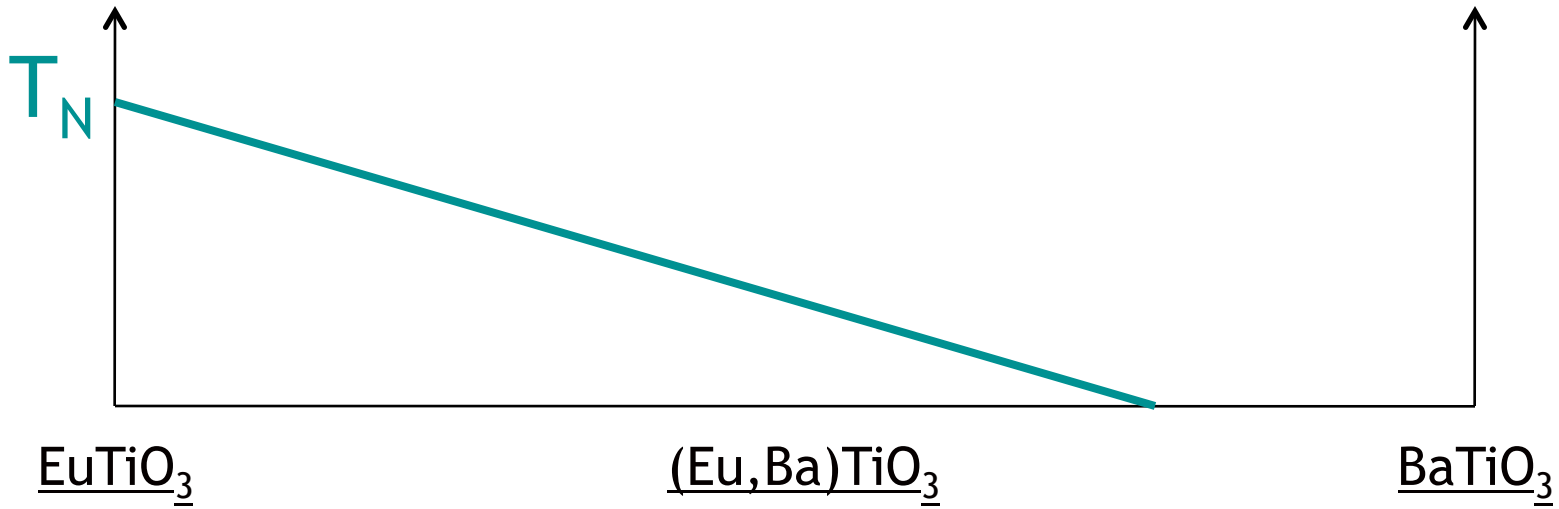

$EuTiO_3$ – $BaTiO_3$

$EuTiO_3$	$BaTiO_3$
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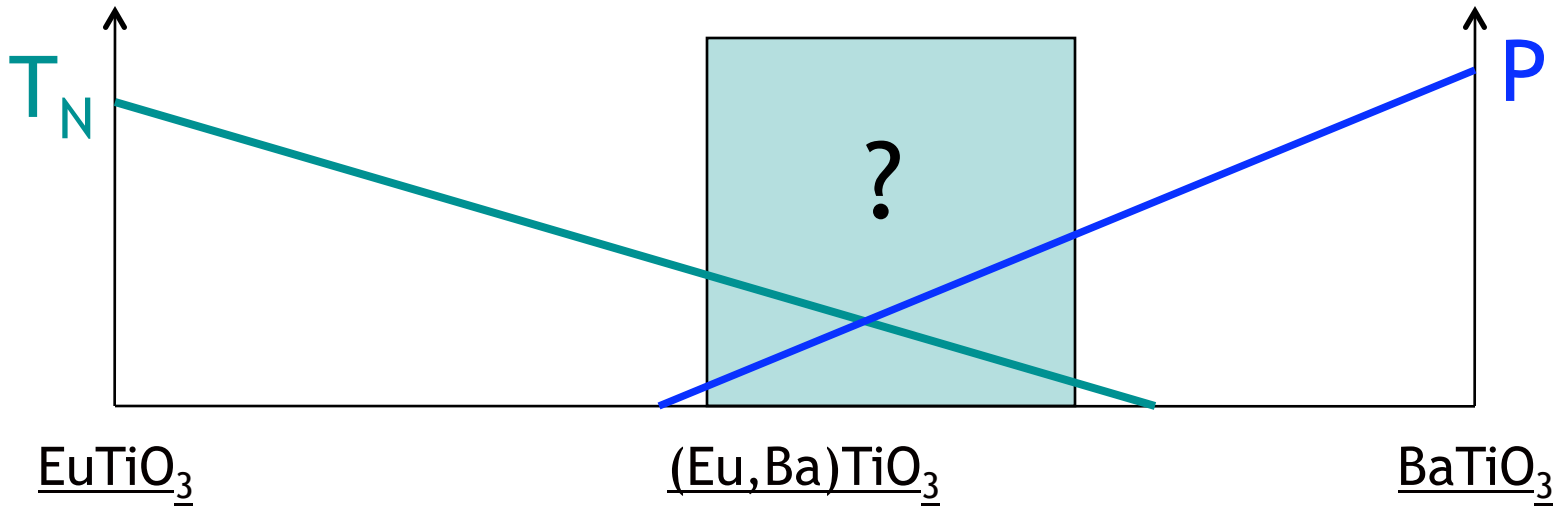


Proposed material: $(Eu,Ba)TiO_3$

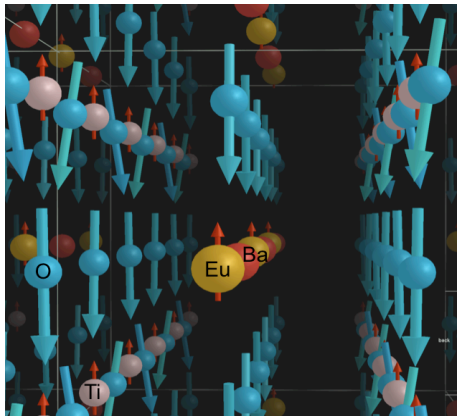
DFT Calculations (Kostja Rushchanskii and Marjana Lezaic, Julich):

P $(Eu_{0.5}Ba_{0.5})TiO_3$ = 25μC/cm²

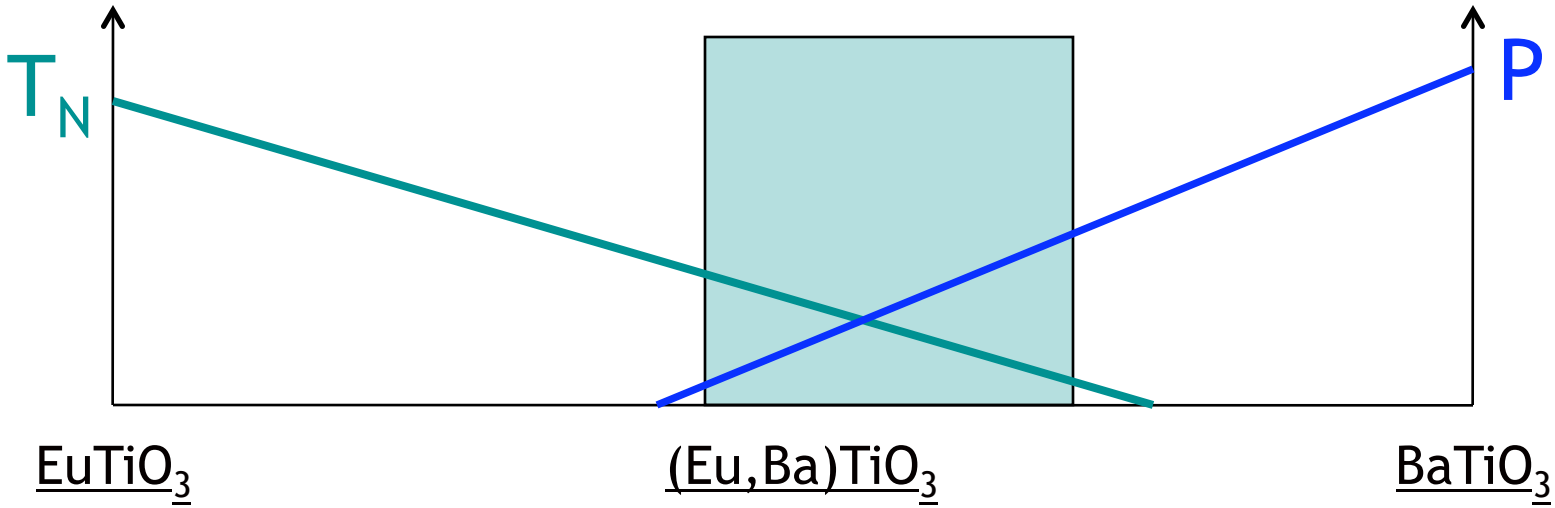
P ⟶ 0 at 3.5 GPa

Large Eu displacements (small size)

Magnetic interactions strongly suppressed



DESIRED BEHAVIOR WITHIN DFT!

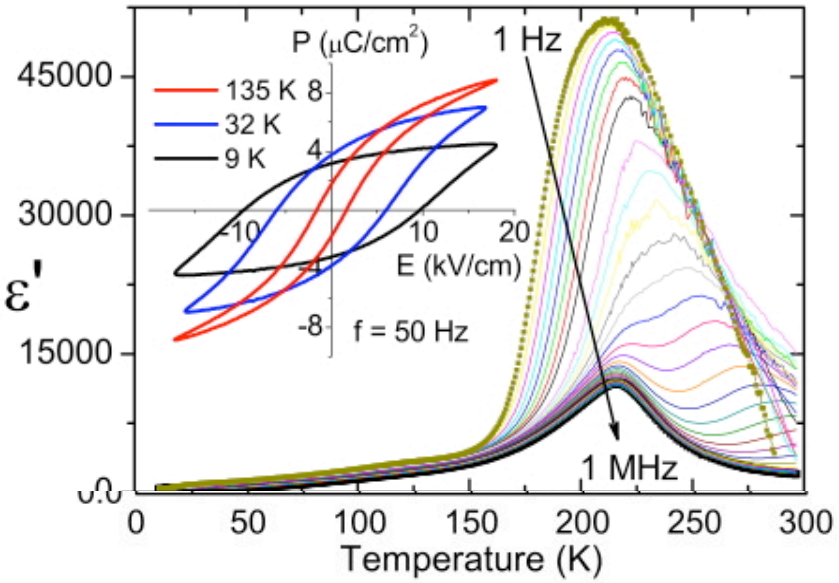


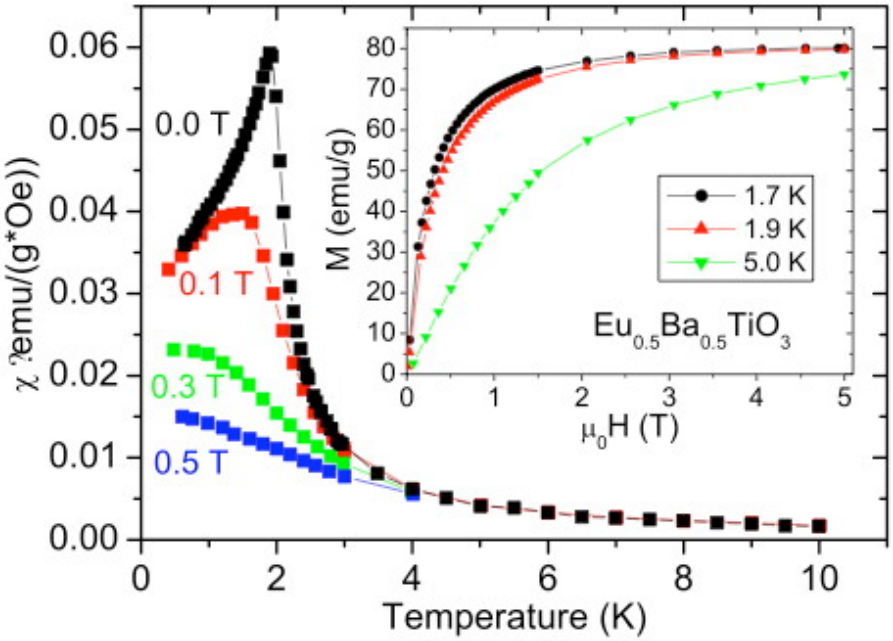
Proposed material: $(Eu,Ba)TiO_3$

Synthesis and Characterization (Stanislav Kamba, Praha, and Yale group)

95% dense ceramics

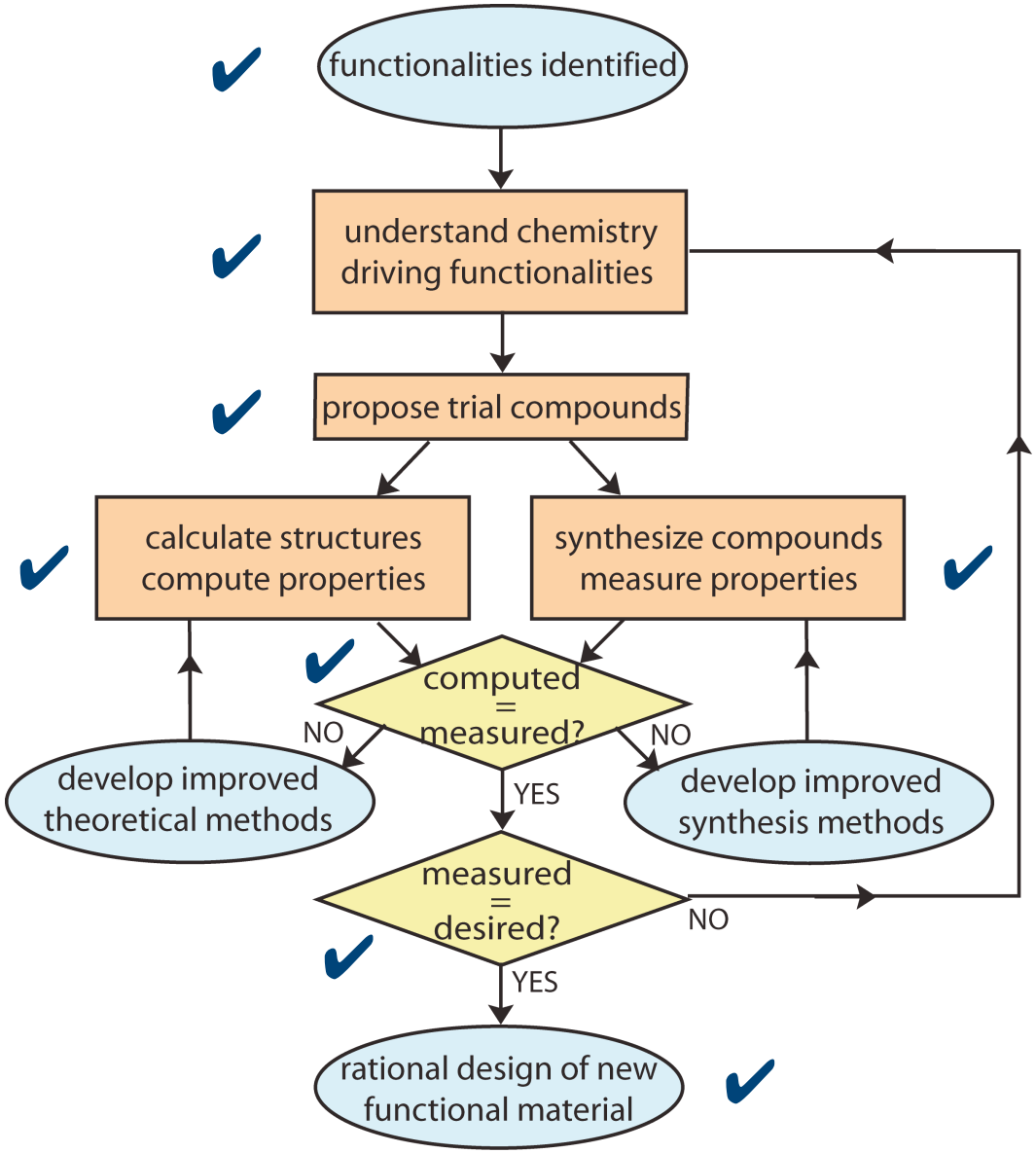
Ferroelectric, Tc around 240K; magnetic T_N around 1.6K





K. Rushchanskii et al., *First-principles design and subsequent synthesis of a material to search for the permanent electric dipole moment of the electron*, in preparation

Materials by Design



From my program manager:
"I am very simple minded. Do you mean to say that you designed a material that was made and had properties you predicted?"

Multiferroics; Whither, Wither or Whiter?

Predicted material with giant magnetoelectric response:

A. Smith, H. Mizoguchi, K. Delaney, N. A. Spaldin, A. Sleight and M. A. Subramanian, *Mn^{3+} in Trigonal Bipyramidal Coordination: a New Blue Chromophore*, JACS **131**, 17084 (2009)

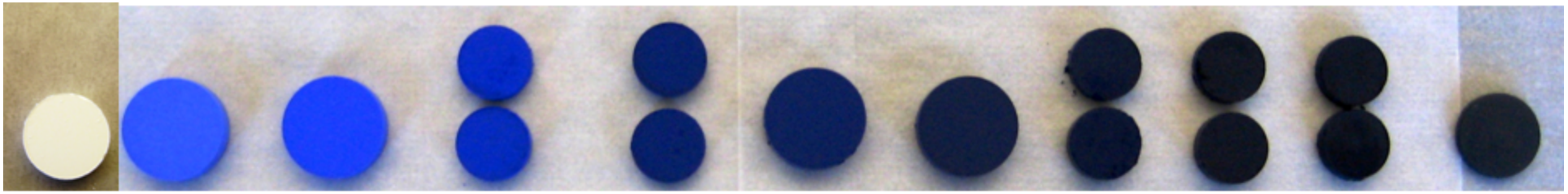
Chemical & Engineering News **87**, 8 (2009)

"We were not looking for a blue pigment", confesses Oregon State University professor **Mas A. Subramanian**, who led the research effort. "In fact, we were actually looking for a multiferroic material and toward that goal were doping $YInO_3$ with Mn to make $YIn_{1-x}Mn_xO_3$". Although Subramanian's group expected to pull black or gray material from their furnace, they were surprised to see a bright blue powder instead. "I had never seen anything like this in all my years working with metal oxides", he recalls.

Because $YInO_3$ is white and $YMnO_3$ is black, Subramanian wondered what made the new compound blue. In collaboration with University of California, Santa Barbara's **Nicola A. Spaldin**, his group determined that the color comes from the unusual trigonal bipyramidal coordination of Mn^{3+}. This gives rise to energy levels in manganese's *d* orbitals that result in an intense absorption in the red/ green region of the visible spectrum.

Multiferroics; Whither, Wither or Whiter?

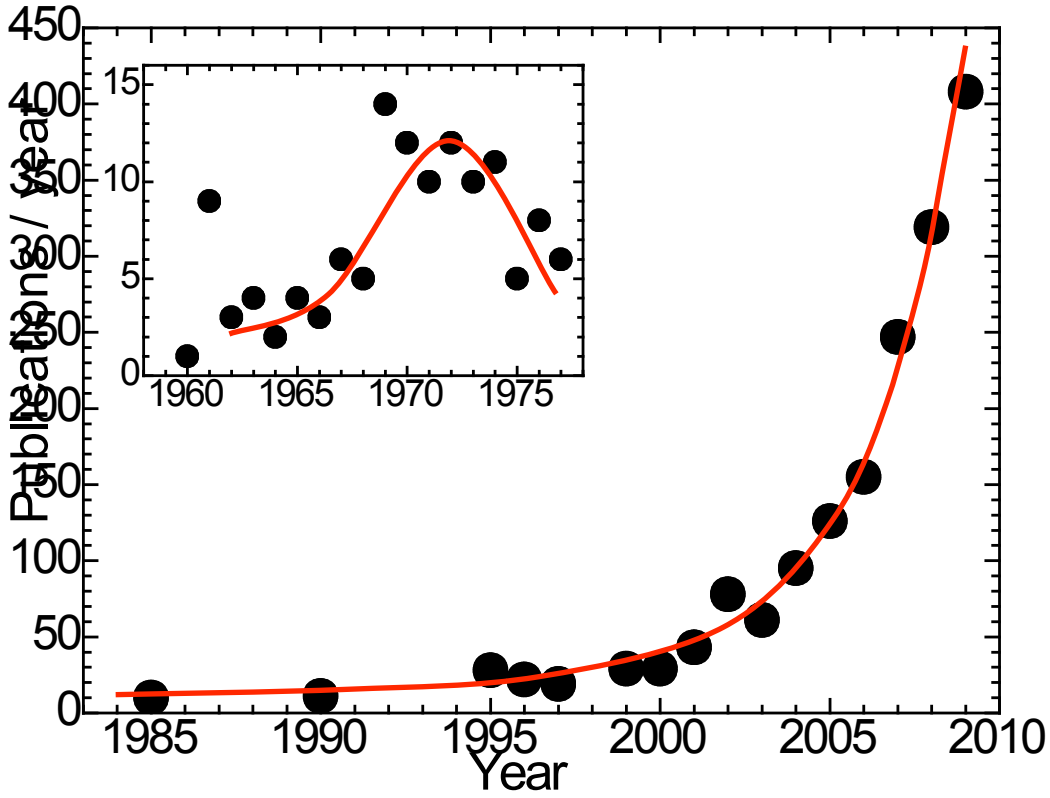
$YIn_{1-x}Mn_xO_3$



Can we explain evolution of optical properties even posthumously?

Need an excited state technique that correctly describes strong correlation…

Whither, Wither or Whiter?



Science
AAAS Magazine

Current Issue

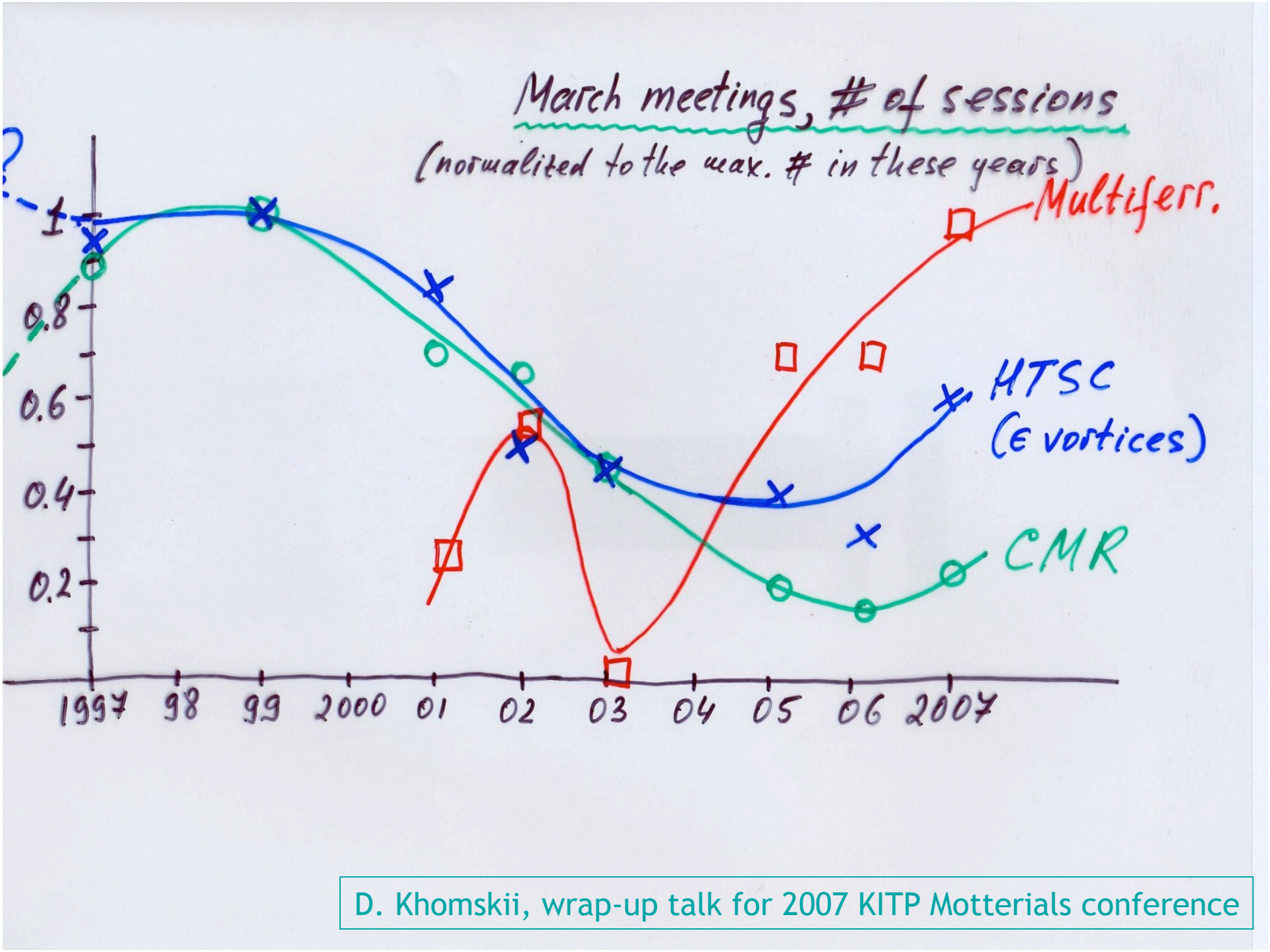
Home > *Science* Magazine > 21 Decem

Science 21 December 2007:
Vol. 318. no. 5858, pp. 1848 – 1849
DOI: 10.1126/science.318.5858.1848

NEWS

BREAKTHROUGH OF THE YEAR:
Areas to Watch

Multiferroics. Relatives of ceramic oxide superconductors, the compounds called multiferroics form a group in which single materials display multiple electronic, magnetic, and structural behaviors. Physicists recently used electric fields to manipulate magnetic domains in a multiferroic. Now, they are racing to better control this switching and shape the materials into novel computer chip devices. Success could pave the way for chips that combine the logic functions normally handled by semiconductors with the memory functions now carried out by magnetic materials.



D. Khomskii, wrap-up talk for 2007 KITP Motterials conference