

New Directions for Multiferroic Materials

Mattias' Rules

Cheong's Rules

Musfeldt's Modification to Cheong's Rules

Goal: 300 K Multiferroic in 10 Years?

New Mechanisms and Materials

Make the Materials that We Already Have
Work Better!

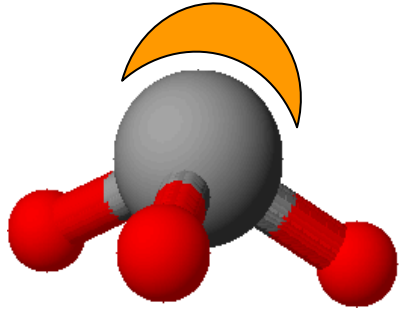


Chavannes, The Dream

Classification of known types of multiferroics

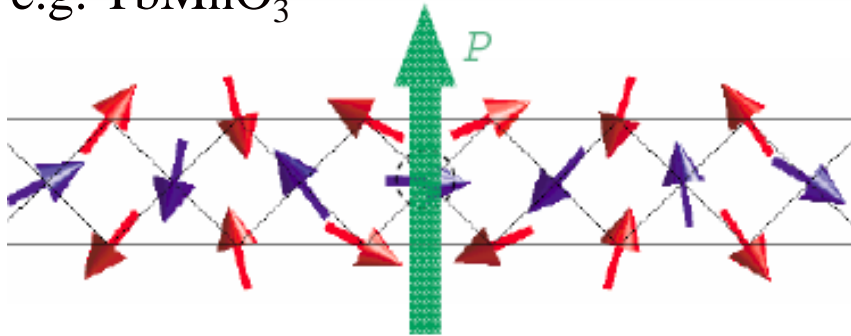
Lone pair active

e.g. BiMnO_3 , BiFeO_3



Magnetically driven

e.g. TbMnO_3

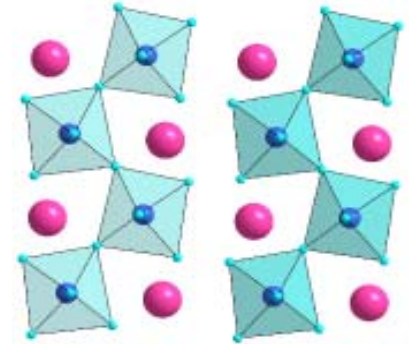


T. Kimura et al., *Magnetic control of ferroelectric polarization*, Nature **426**, 55 (2004)

Geometric ferroelectricity

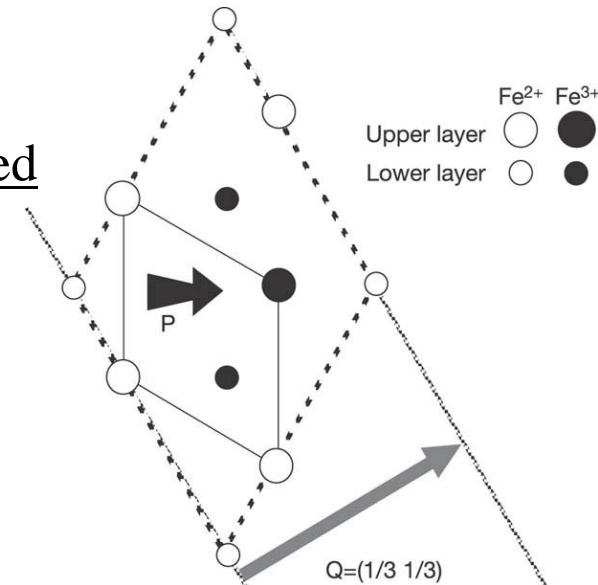
e.g. BaNiF_4

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



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)

Moving Away From Oxides is Scary...

- Organic-Inorganic Hybrids
- Organic Materials
- Molecular Magnets
- Nanoscale Materials

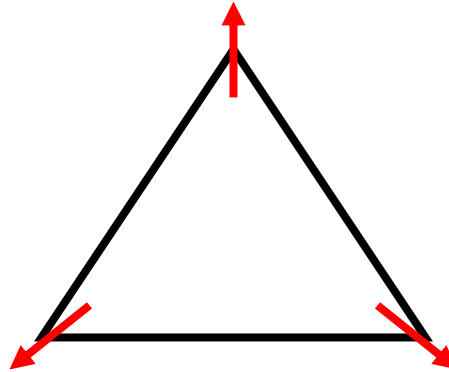
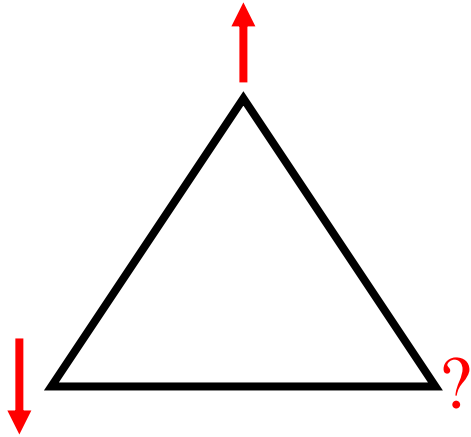
My Plan: Survey interesting materials systems and present possible ways forward.

No learning objectives what-so-ever, except to perhaps convince you that non-oxide materials also have interesting opportunities!

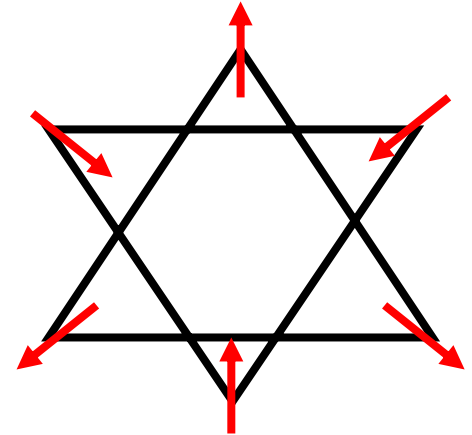


Goya: Satan devouring his Son

Starting at the Beginning



Triangular System



Kagome System



Creation of Adam, Michelangelo

Close-Up View: Carbon

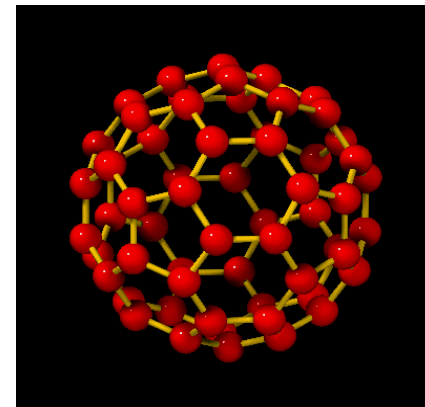
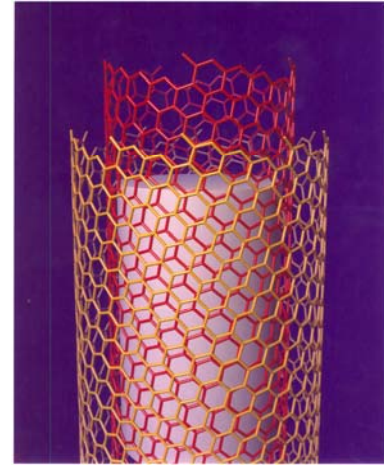
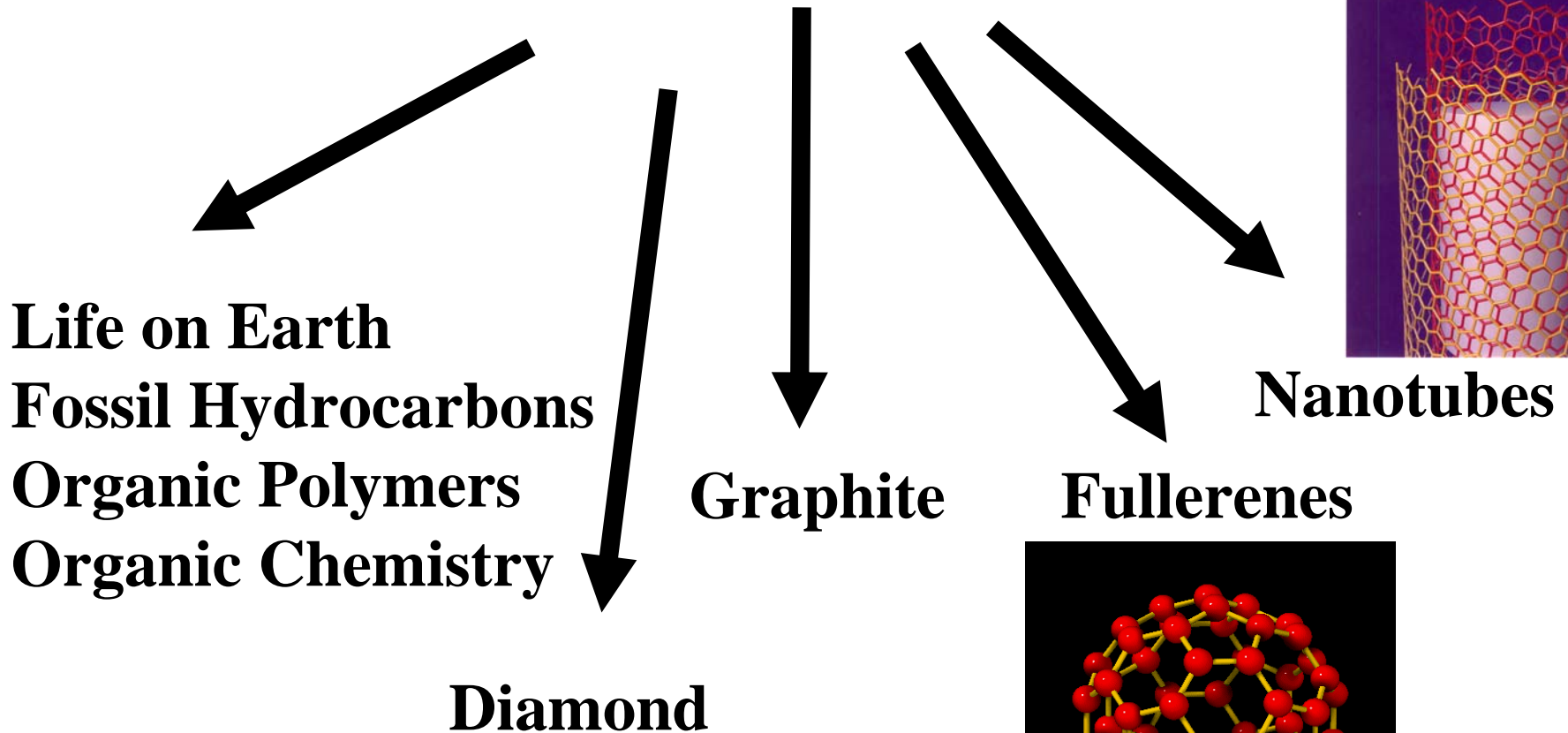
The image shows a close-up of the periodic table for the element Carbon (C). The element's cell is highlighted in light blue. The cell contains the following information:

- Group:** IVB (indicated by a dashed arrow from the label 'Group' to the 'IVB' header)
- Atomic Number:** 6 (indicated by a dashed arrow from the label 'Atomic Number' to the number '6')
- Symbol:** C (indicated by a dashed arrow from the label 'Symbol' to the letter 'C')
- Element Name:** Carbon (indicated by a dashed arrow from the label 'Element Name' to the word 'Carbon')
- Molecular Weight:** 12.0107 (indicated by a dashed arrow from the label 'Molecular Weight' to the number '12.0107')

Additional information visible in the cell includes the electron configuration $1s^2 2s^2 2p^2$ and the value 11.2603. The cell is part of a larger grid with other elements visible, such as 14 and 1 in the row below, and 7 in the column to the right.

	IVB	
12	6 C Carbon 12.0107 $1s^2 2s^2 2p^2$ 11.2603	7
12	14 $3P_0$	1

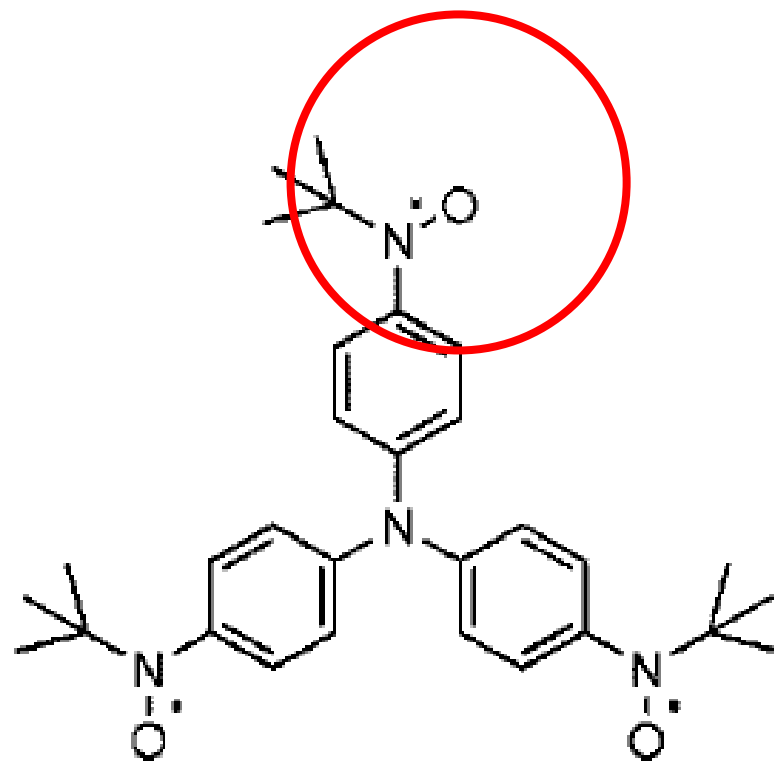
Carbon is Special



Chemical and physical properties are different!

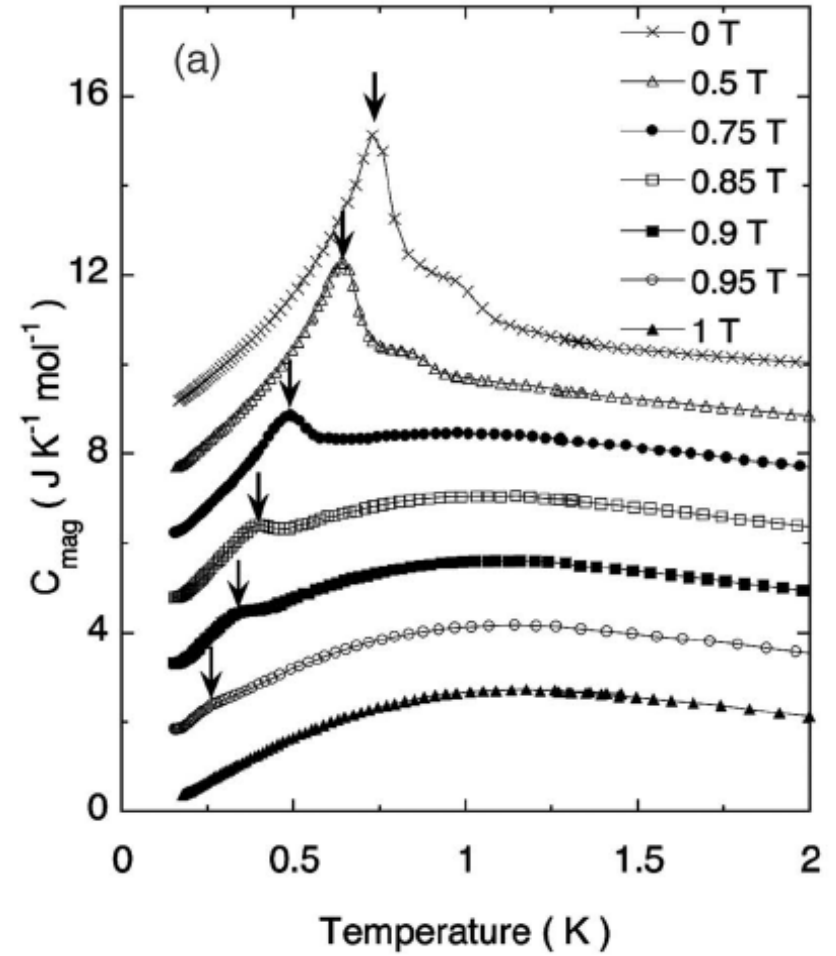
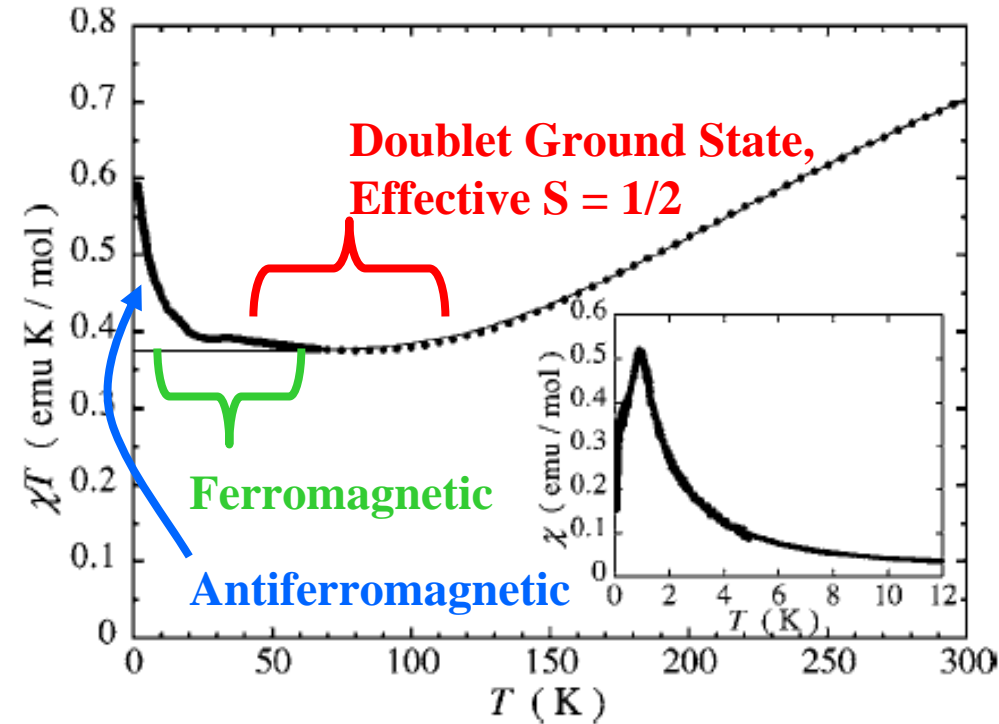
Organic Radical Materials

- Triangular antiferromagnetic spin unit
- “Tri-radical” building block molecule: N,N,N-Tris[p-(N-oxyl-tetra-butylamino)phenyl]amine
 - Also “mono” and “biradical” analogs
 - Boron replacement of N center
- Magnetic ordering in crystal
- $T_c = 0.74$ K



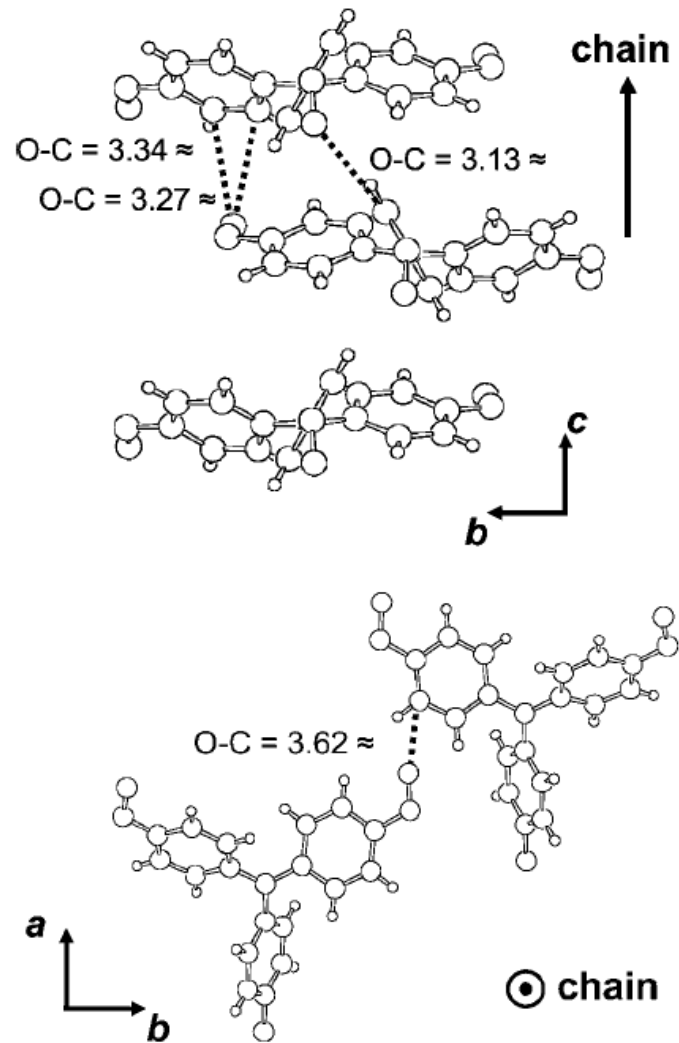
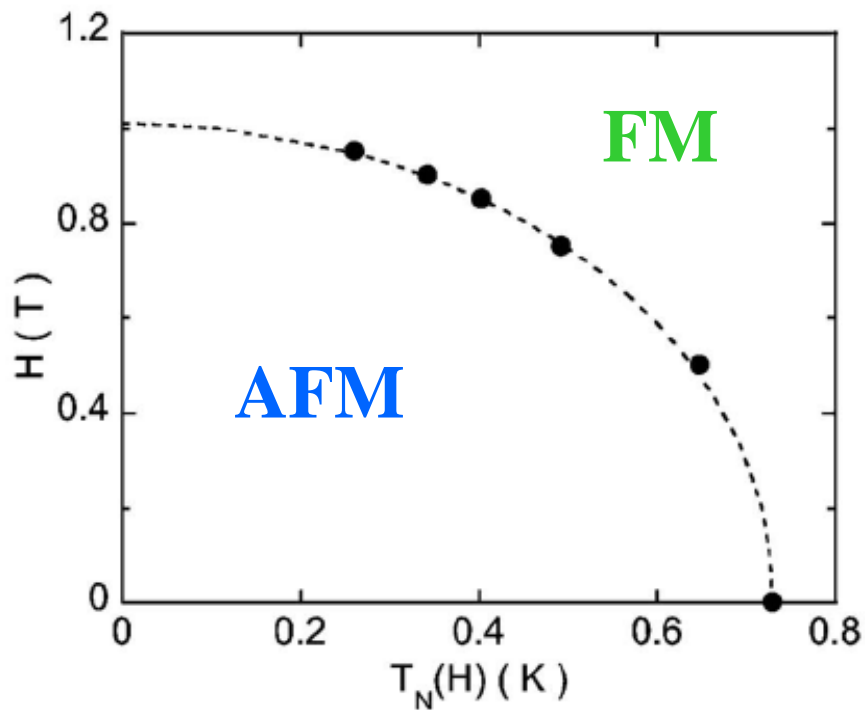
Takeda et al, PRB (2005)

Competing Magnetic States



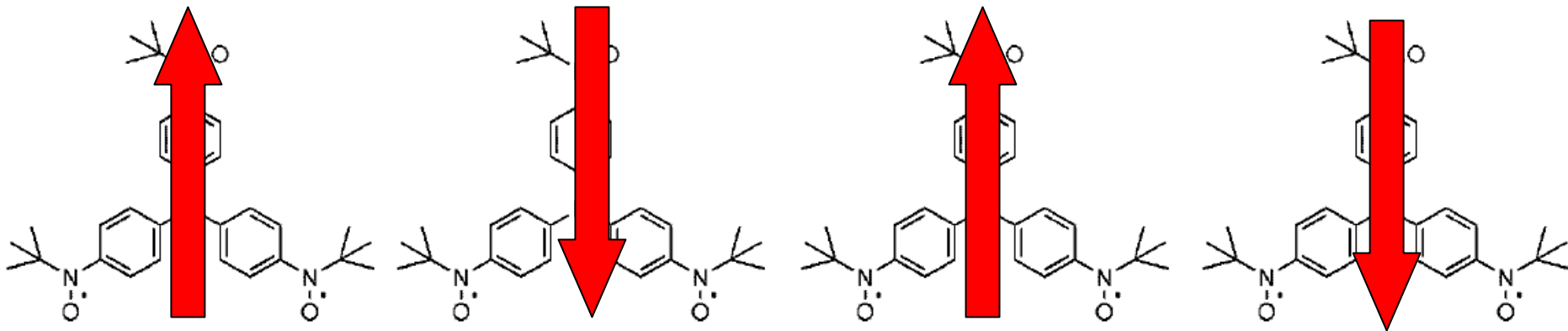
$$f = \left| \frac{\Theta}{T_c} \right| = \left| \frac{-600}{60} \right| \approx 10$$

Intermolecular Interactions Control Ordering Temperature



Rings are tilted, so intramolecular spin interactions are not symmetric

Intermolecular Interactions Control the Low Temperature Ground State



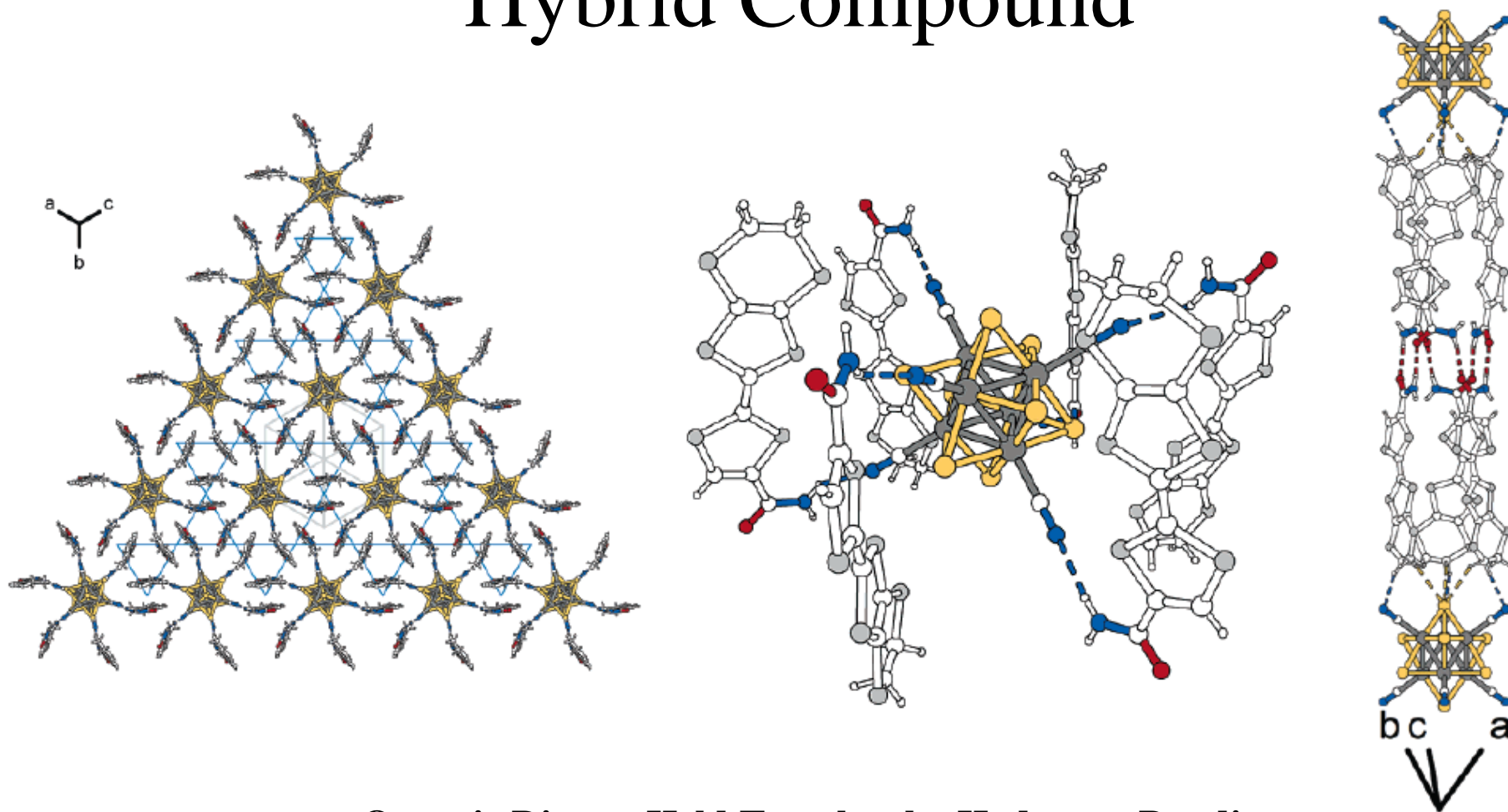
$$J_{\text{IM,F}} = 3 \text{ K}, J_{\text{IM,AF}} = -0.7 \text{ K}$$

TABLE I. Comparison of experiments of magnetic ordering temperature of the prototype genuine organic systems to theoretical values for the isotropic Heisenberg system. The parameters for 2,5,-DFPNN and DTDA are taken from Refs. 16 and 17, respectively.

	S	$2zJ/k_B$	T_c (theo.)	T_c (obs.)
β -phase p -NPNN	$1/2 \times 1$	3.6	0.60	0.61
Dupeyredioxyl	$1/2 \times 2$	3.6	1.7	1.48
Tris-NO	$1/2(\times 3)$	4.6	0.76	0.74
2,5,-DFPNN	$1/2 \times 1$	2.8	0.46	0.48
DTDA	$1/2 \times 1$	9.0	1.5	1.30

Other Organic FerroMagnets:

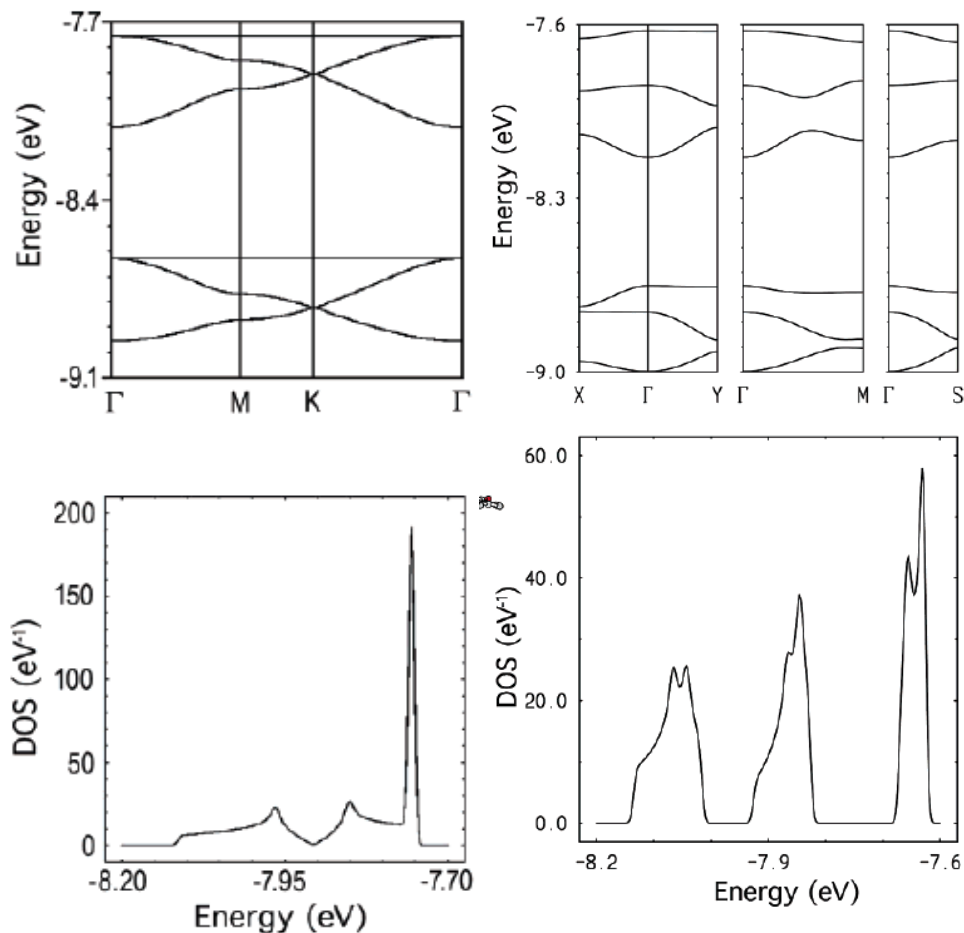
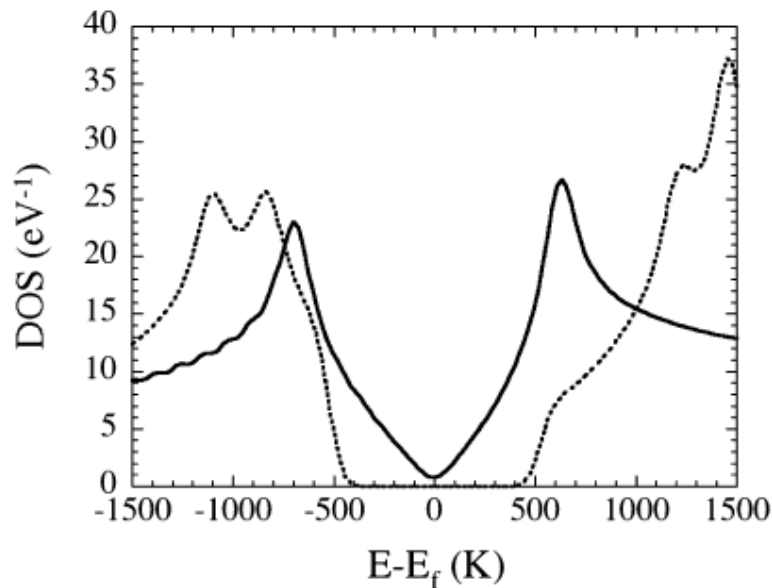
$(\text{EDT-TTF-CONH}_2)_6[\text{Re}_6\text{Se}_8(\text{CN})_6]$ is a Kagome-Type Organic-Inorganic Hybrid Compound



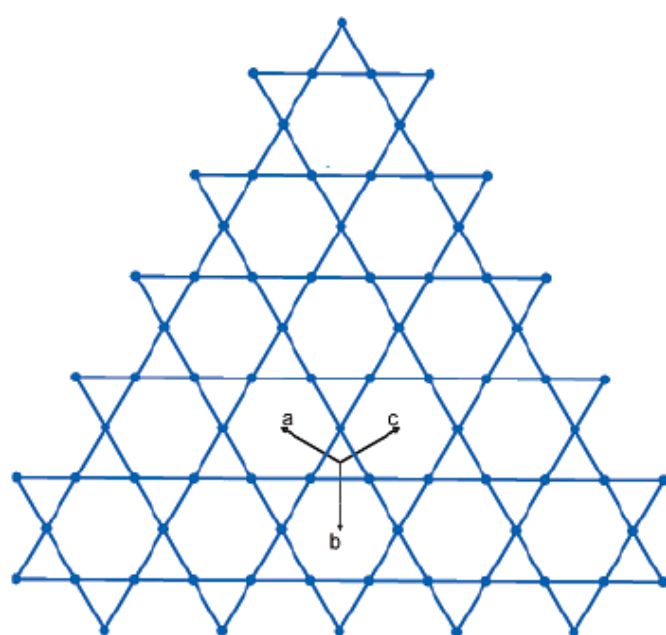
Organic Dimers Held Together by Hydrogen Bonding

Perfect Kagomes are Rare

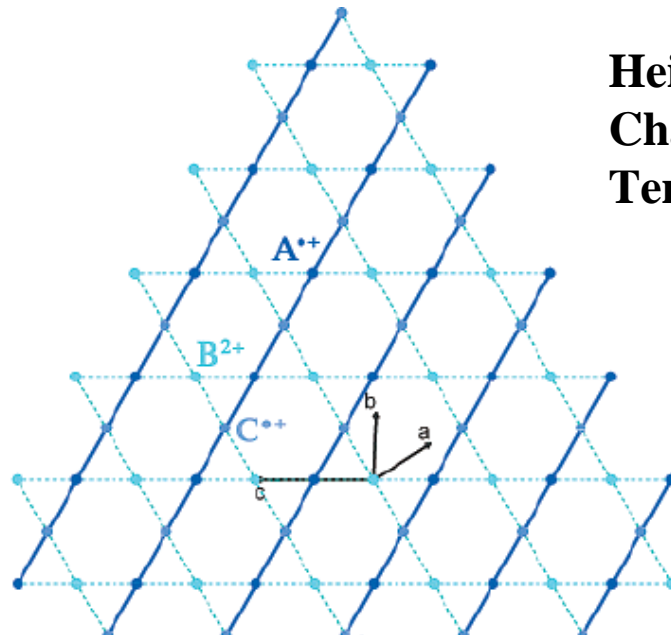
- Metallic at 300 K, with strong 2D character
- Electronic instability causes distortion and charge localization below 150 K.



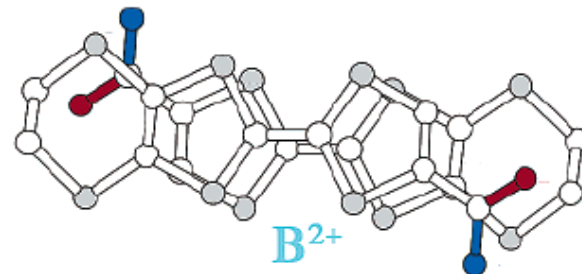
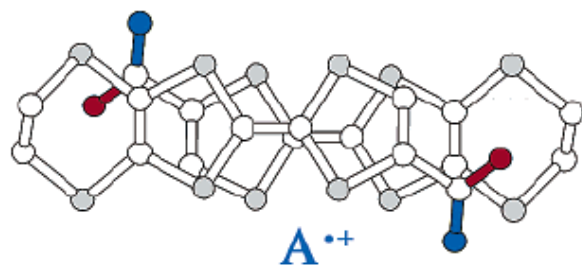
Symmetry of Kagome New is Broken at Low Temperature



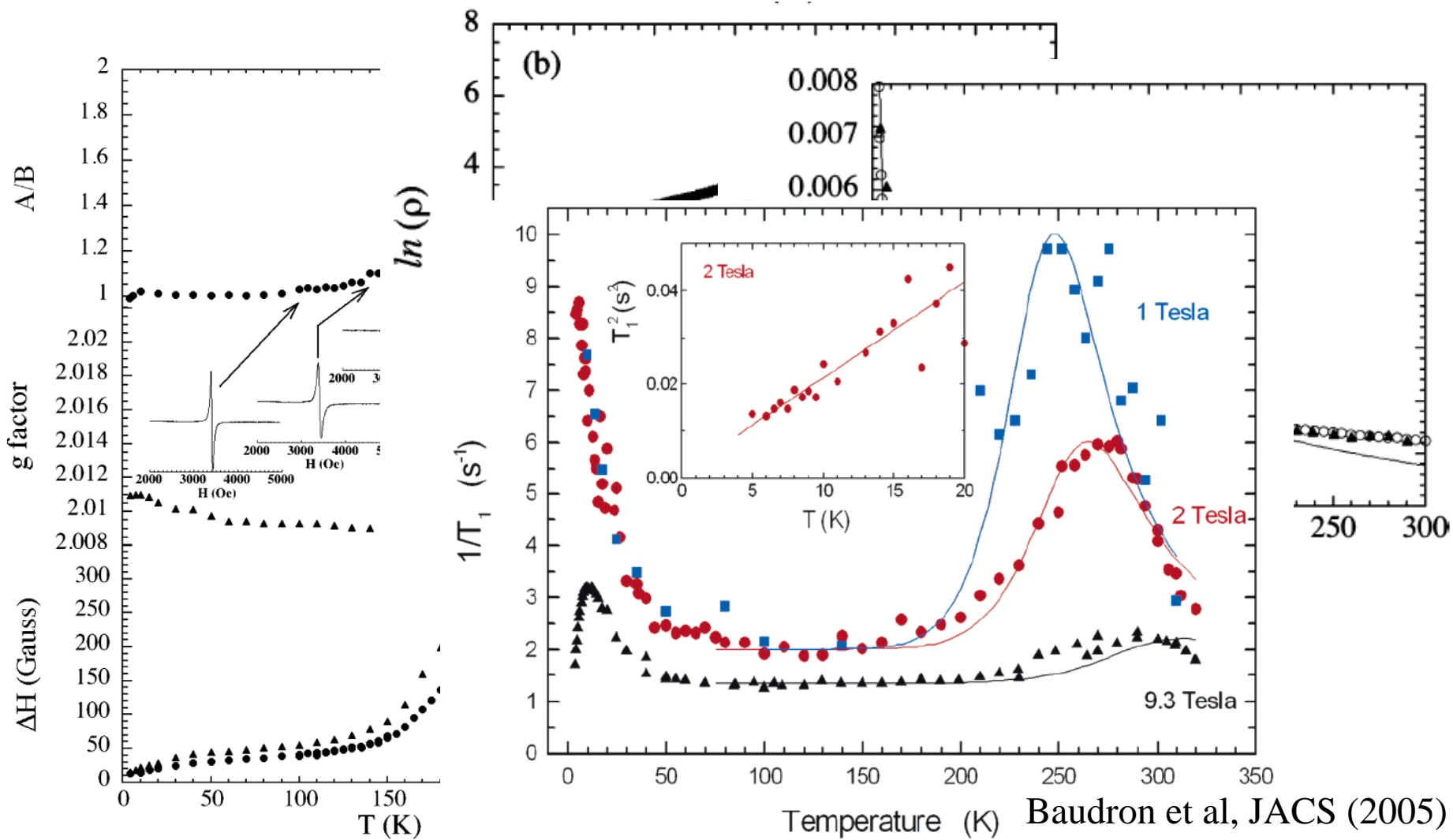
a)



Heisenberg
Chains at Low
Temperature



Frustration, Broken Symmetry, Charge Ordering, New Magnetic States: Hmmm....



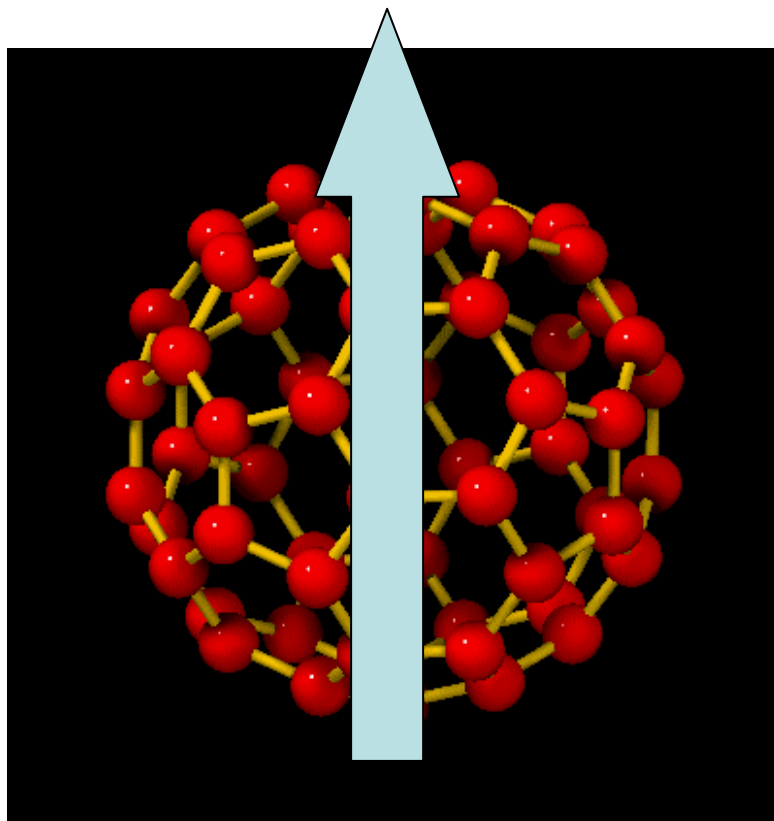
Low Symmetry is Beautiful in Hybrids



Portland Vase, Roman

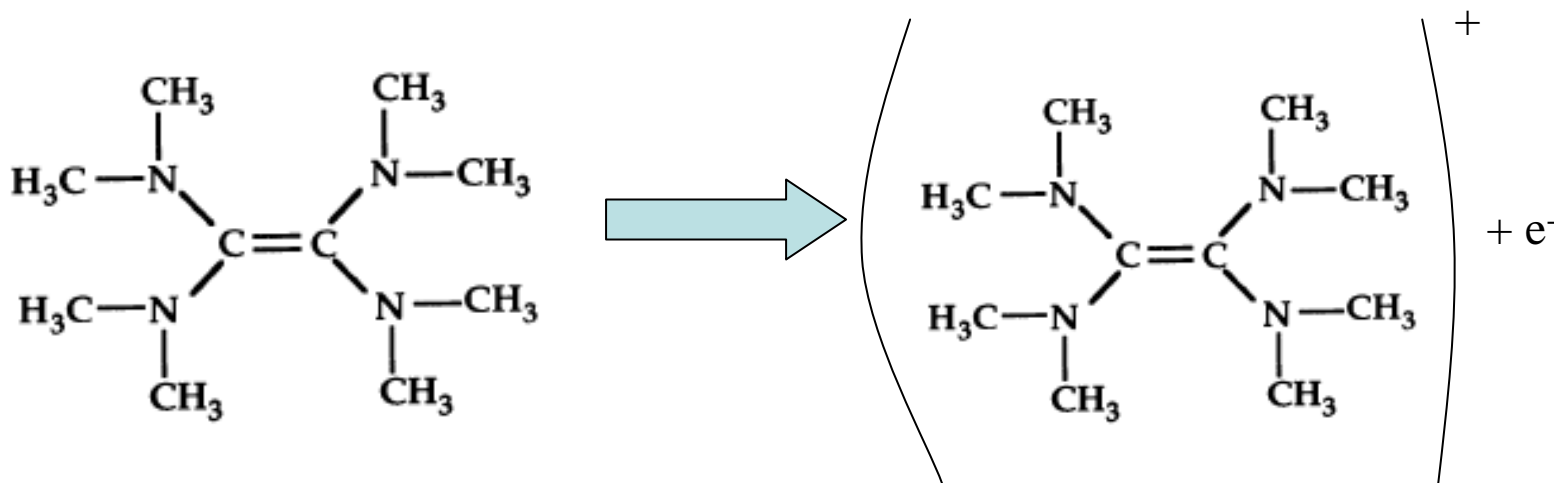
Let's Go Back to Organic Systems...

Main Challenge: Putting Charge and Spin onto C₆₀ Ball and Keeping the Spin-Containing Units Well-Isolated



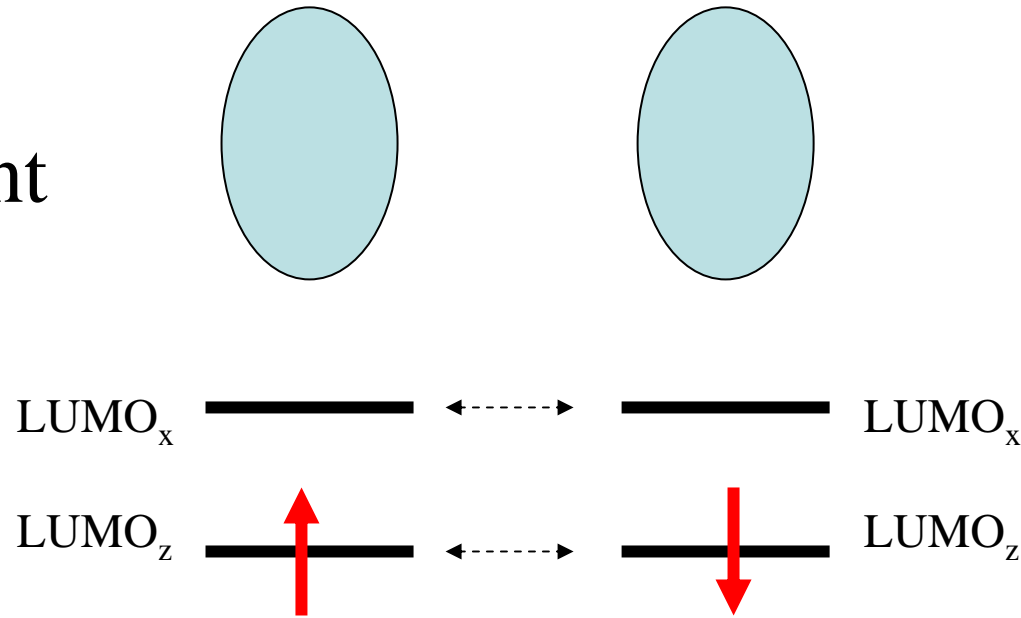
Many Chemical Modifications Possible to this Prototype System.

TDEA Molecule Donates One of its Electrons to the C_{60} Molecule, Producing a Charge-Transfer Complex

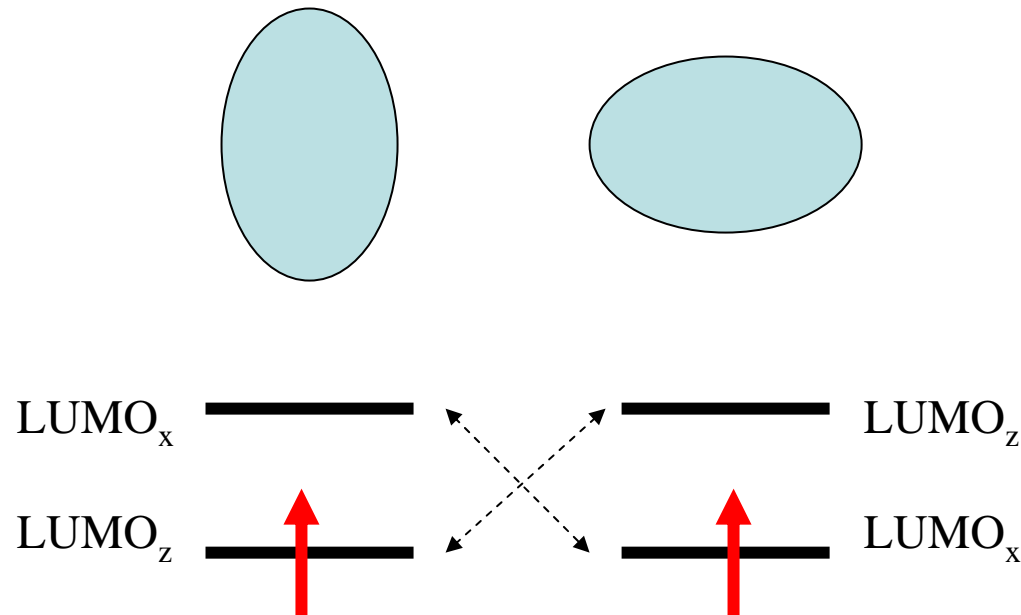


**Charge on the Fullerene Ball Causes a Jahn-Teller Distortion,
Which is Responsible for Formation of Spin Singlets**

- If the axes of the JT distortions of 2 adjacent C_{60}^- anions coincide, then coupling is antiferromagnetic

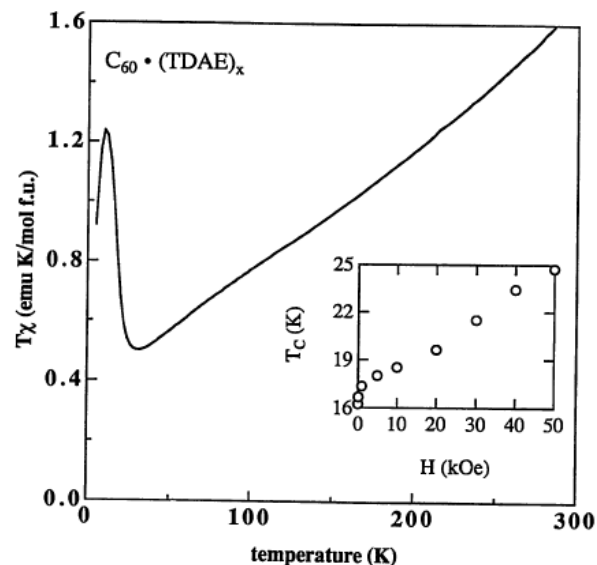
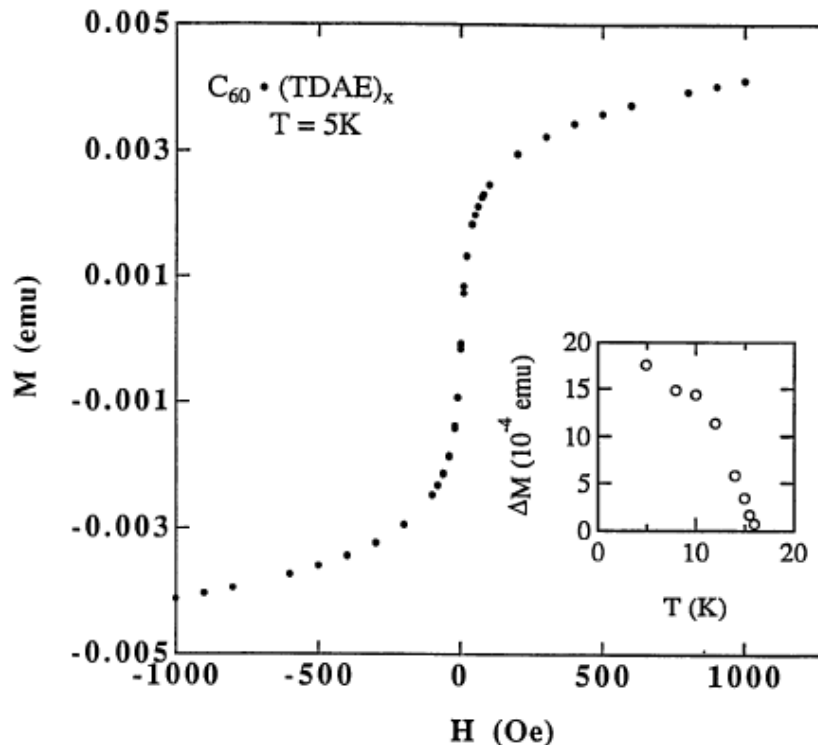
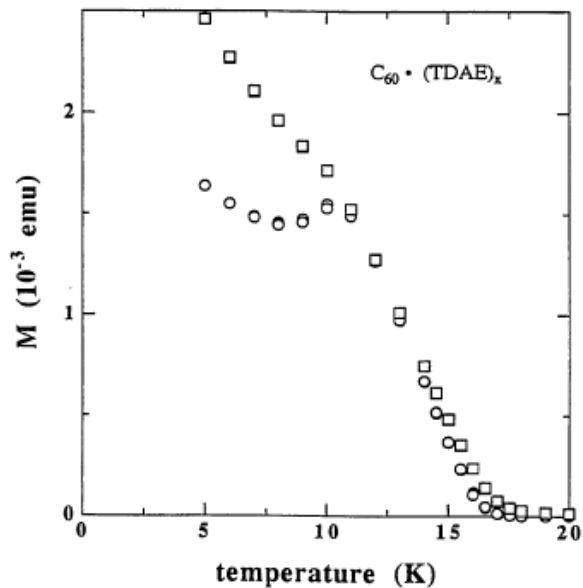


- If they are orthogonal, the coupling should be ferromagnetic.



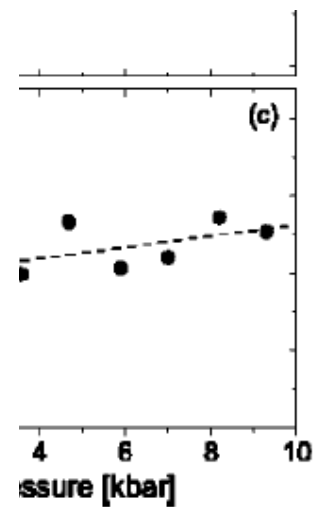
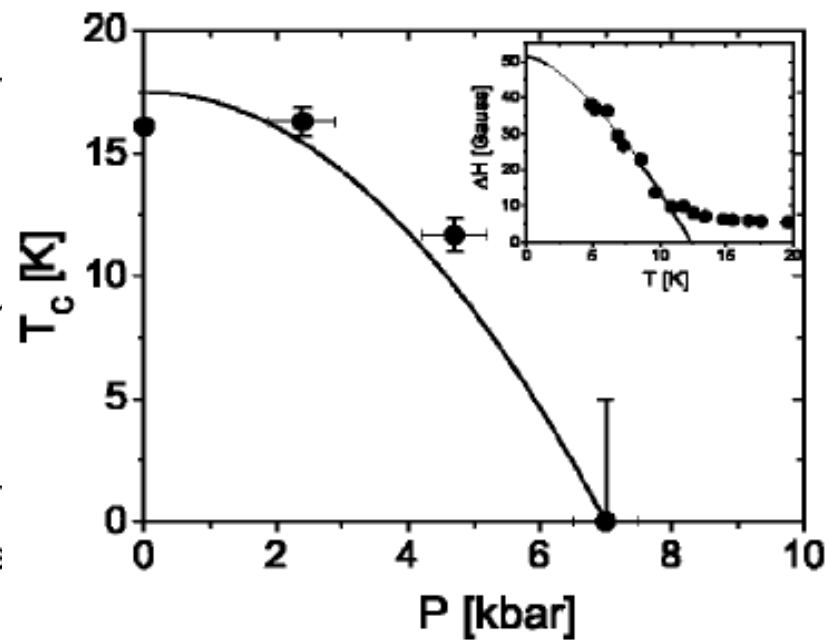
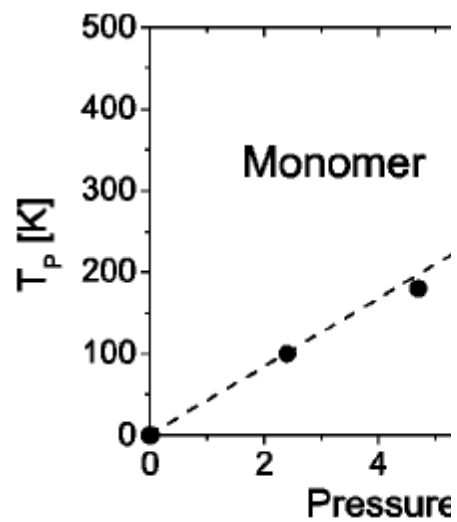
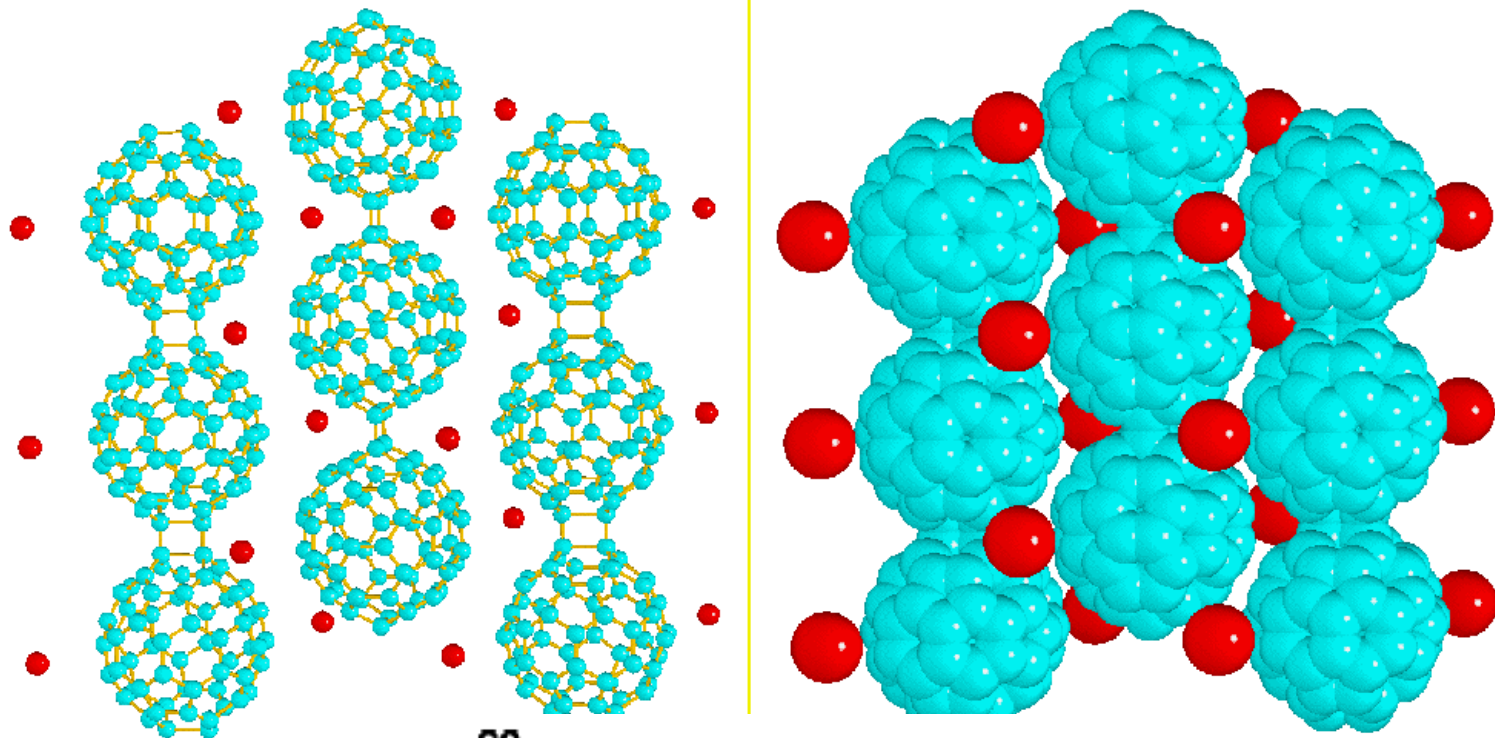
Crystal obviously has 3D FM Ordering.

TDEA-C₆₀: Metallic Organic FM at 16 K



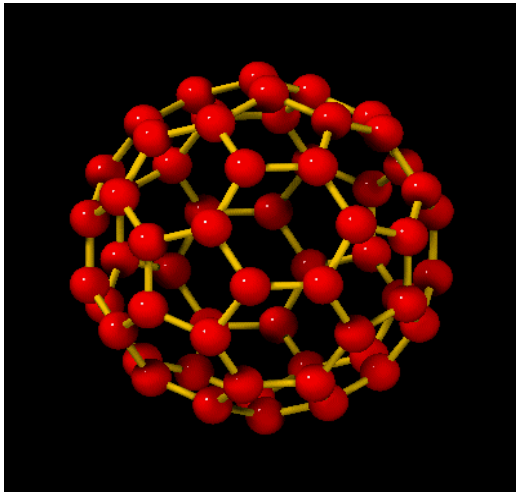
- Coercive field and remnant magnetization are zero
- Spontaneous magnetization very small, on order of $\sim 0.11 \mu_B / C_{60}$

ESR susceptibility [arb. units]



Garaj, PRB (2003)

Fullerenes are Very Elegant and Flexible Materials...

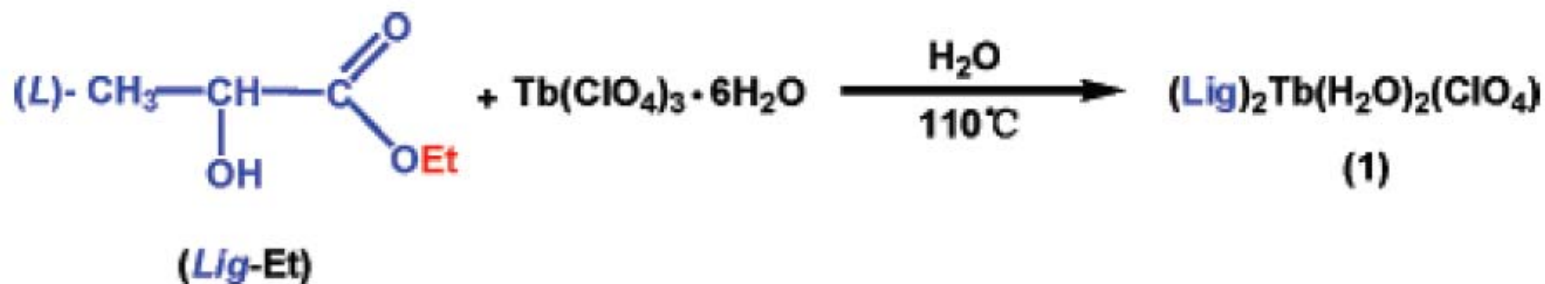


David, Michelangelo

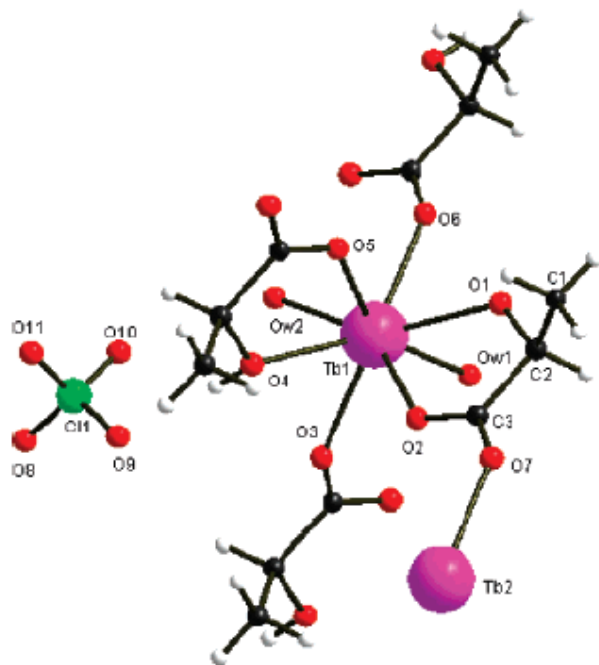
Possible Source for New Materials!

Discovery of a Multiferroic Homochiral Metal-Organic Framework

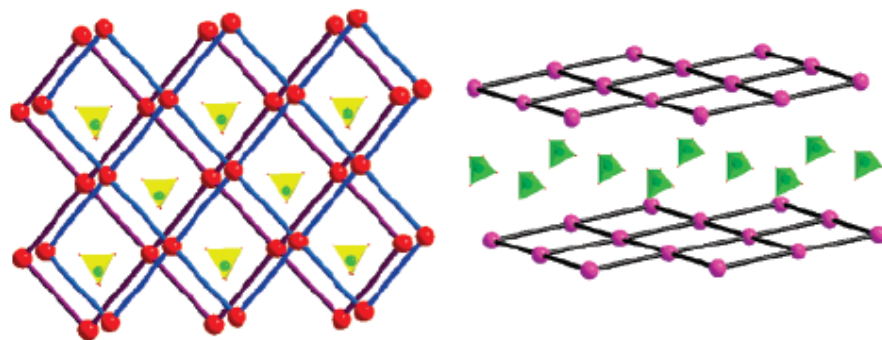
- Chiral Centers to Give Ferroelectricity, Provide Polarizability, Control Oxidation State
- Layered Perovskite-Like Structure with Transition Metal Centers May Give Rise to Magnetic Properties
- Hydrothermal Reaction



The Structure

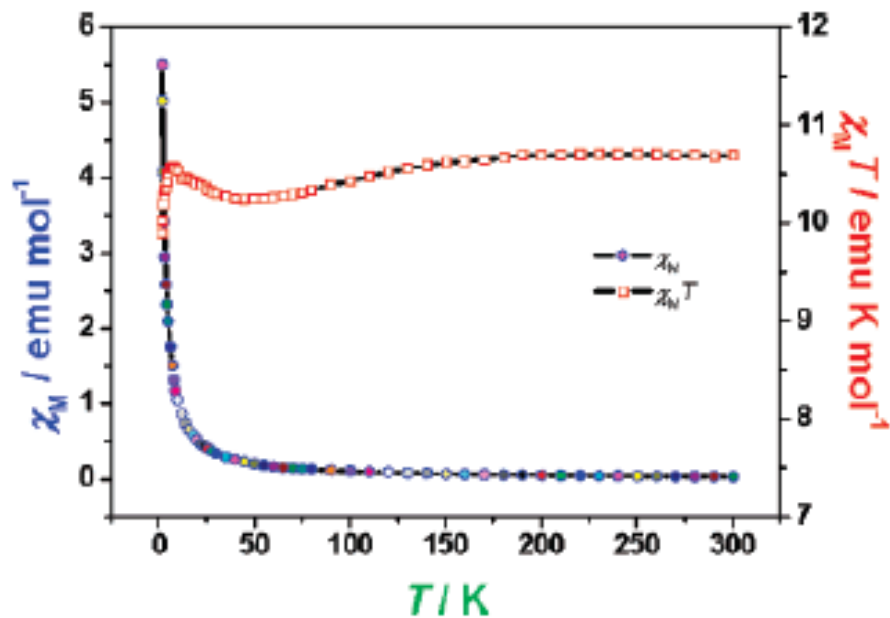


Local environment around Tb ion is distorted square antiprism involving 4 different lactate ions and 2 waters.

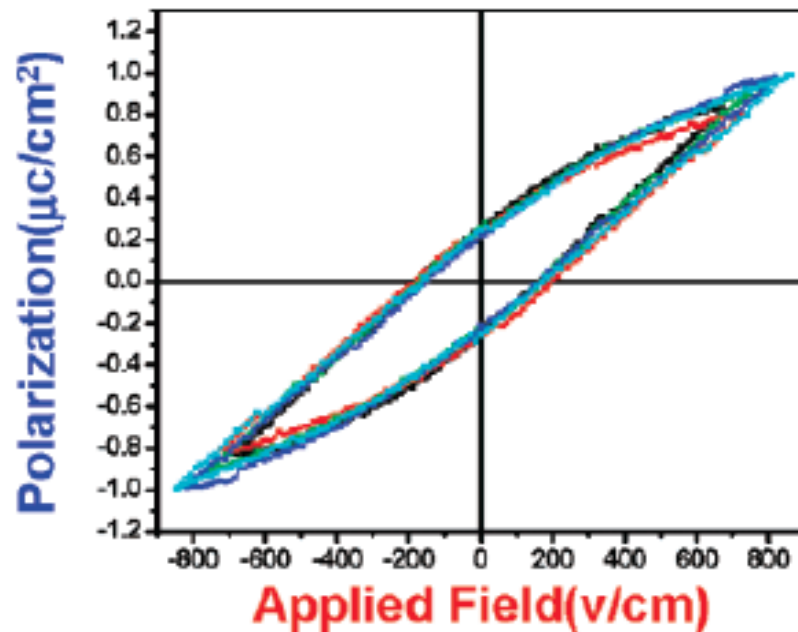


Crystallizes into chiral, polar (C₂) space group

Multiferroicity?



Low Temperature Ferromagnet

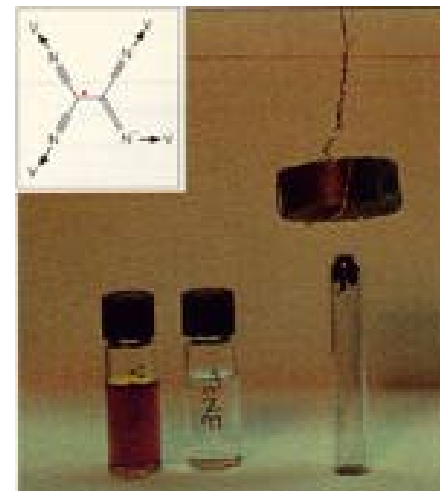
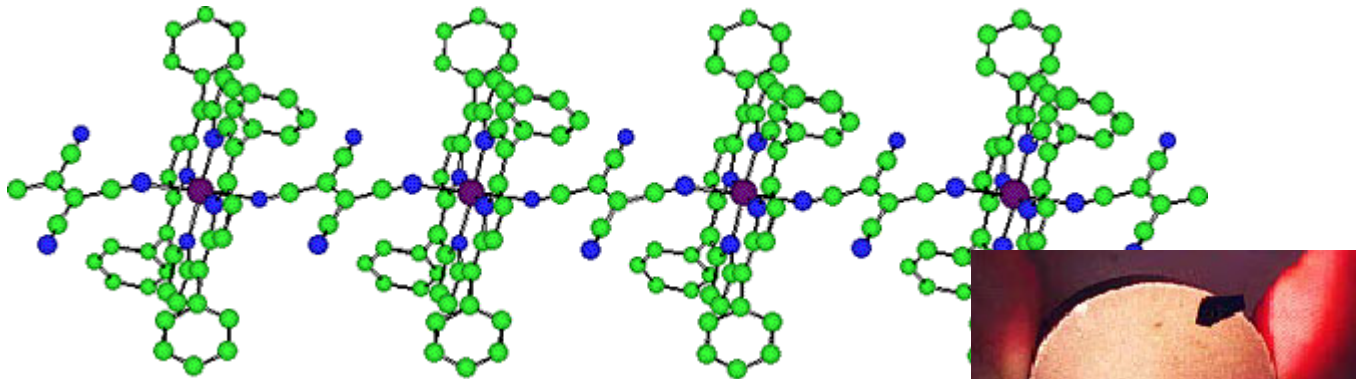


Low Temperature Ferroelectric

Remnant Polarization $\sim 0.25 \mu\text{C}/\text{cm}^2$
Coercive Field $\sim 0.2\text{V}/\text{cm}$

$V(\text{TCNE})_x(\text{solvent})_y$ & $Mn(\text{TCNE})_x(\text{solvent})_y$

- Small Organic Building Block Molecule: TCNE
- Linear Chain Structure, But Complicated Due to solvent Incorporation
- Mn Compound: $T_c \sim 75$ K
- V Compound: Magnetic at 300 K. ($T_c \sim 400$ K, above 350 K Decomposition Temperature)

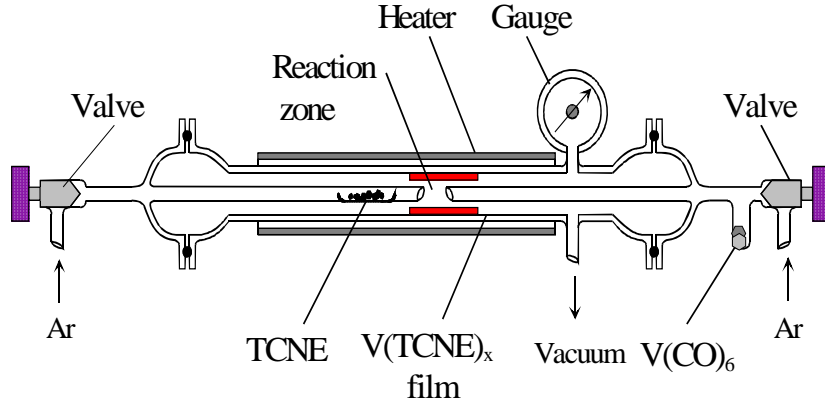


Manriquez et al, Science (1991).

Art Epstein's APS Tutorial, Joel Miller Web Site

The Reaction

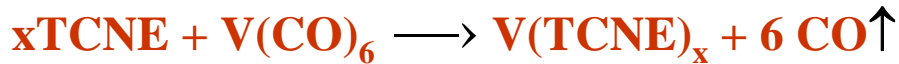
Low temperature (40 °C) chemical vapor deposition (CVD) setup



Electron transfer salt:

$S = 3/2$, donor: $[V]^{++}$

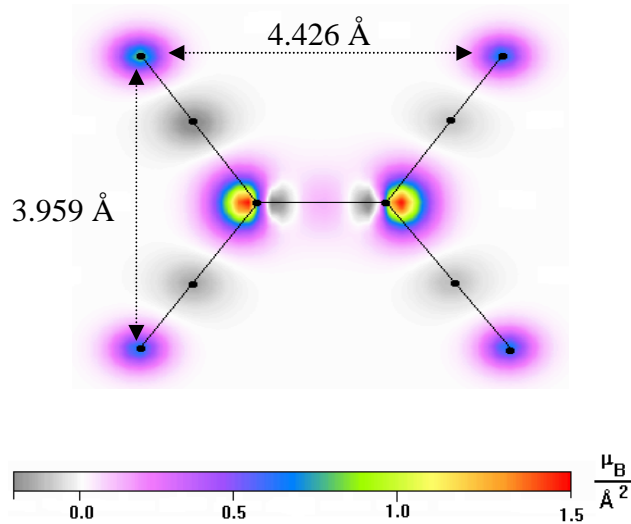
$S = 1/2$, acceptor: $[TCNE]^-$



The Spin States

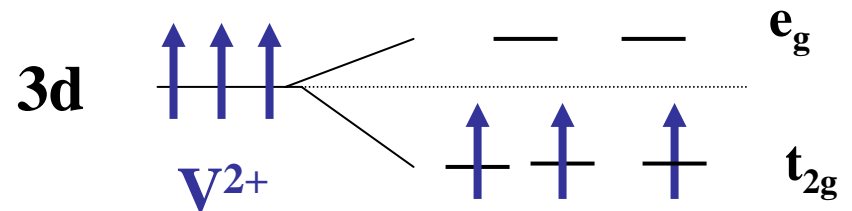
[TCNE]⁻ : S = 1/2

unpaired electron in p* state



Spin density distribution in [TCNE]⁻
J. Am. Chem. Soc. **116**,7243 (1994)

Octahedral coordination of
V with **N**s splits
3d-level of **V²⁺**
(EXAFS, ANL)

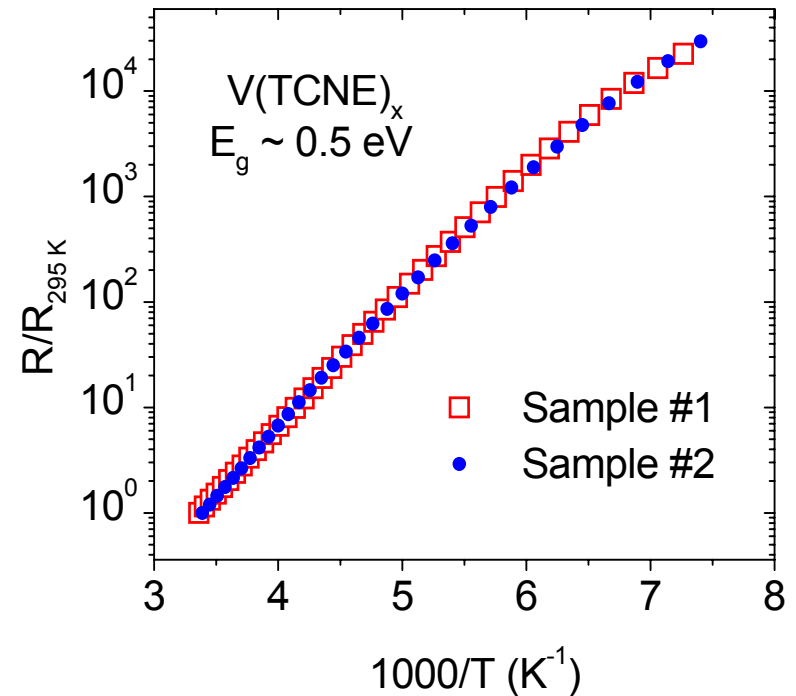
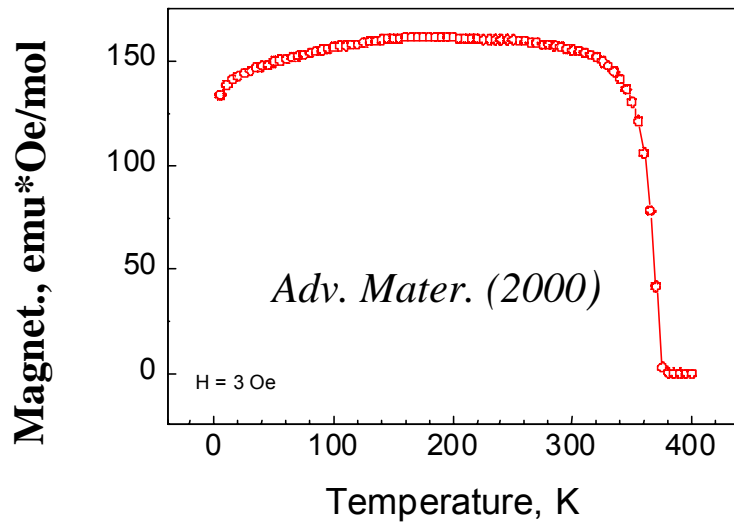


Large Hund's pairing energy
keeps all three spins parallel
providing high spin state

V²⁺ : S = 3/2

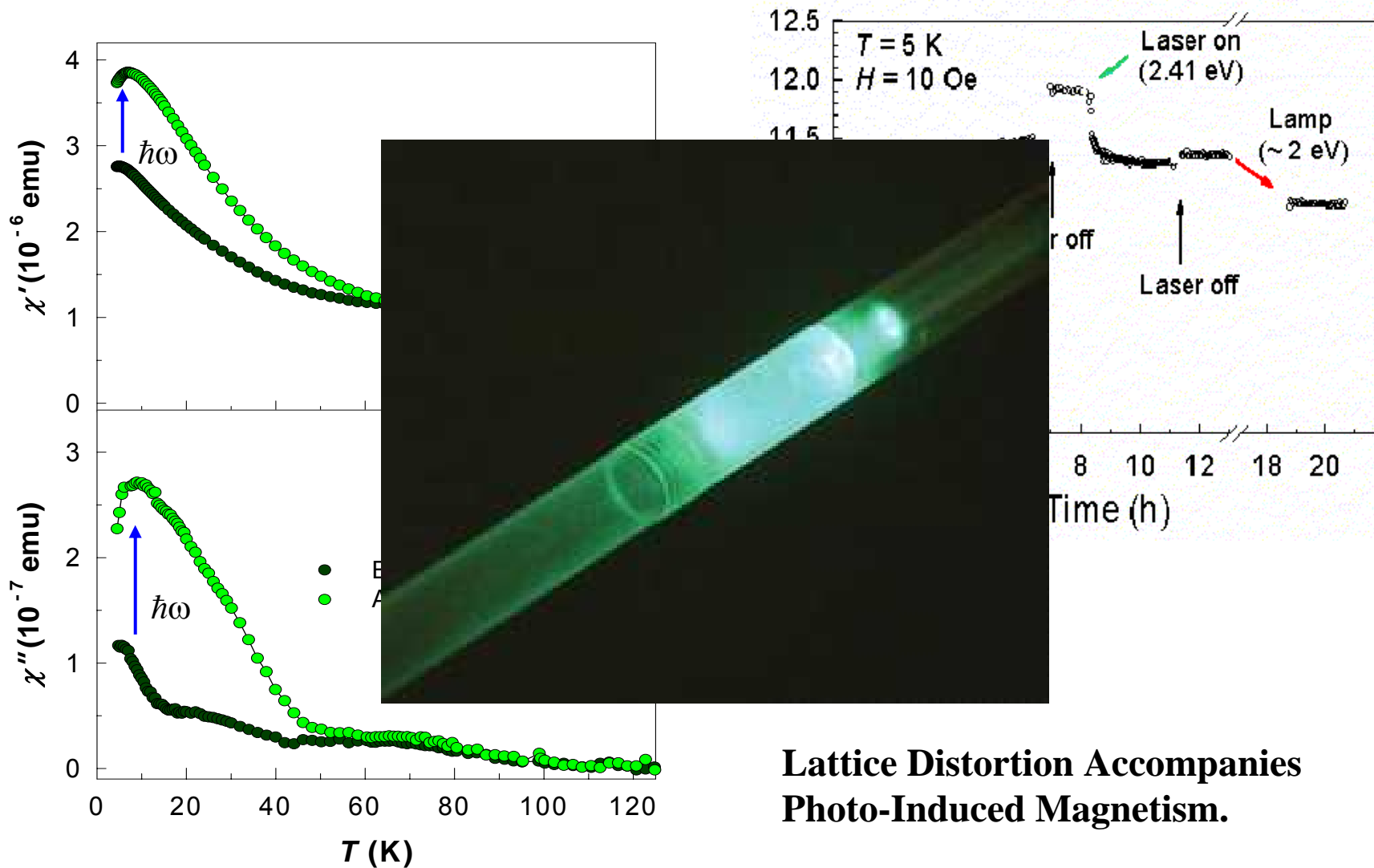
From Art Epstein's APS Tutorial

Magnetic Order and Conductivity



Magnetic Semiconductor! Can these Materials Support Magnetically-Induced FerroElectricity?

$\text{Mn}(\text{TCNE})_x(\text{solvent})_y$ is PhotoMagnetic



**Lattice Distortion Accompanies
Photo-Induced Magnetism.**

Pejaković *et al.*, PRL (2002)

Inorganic Molecular Magnets:

$$[\text{Mo}^{\text{V}}_{12}\text{O}_{30}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_4]\cdot 14 \text{H}_2\text{O}$$

PHYSICAL REVIEW B 77, 184410 (2008)

Single-ion and exchange anisotropy effects and multiferroic behavior in high-symmetry tetramer single-molecule magnets

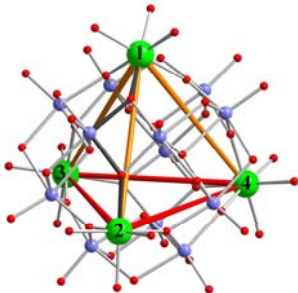
Richard A. Klemm^{1,*} and Dmitri V. Efremov^{2,†}

¹*Department of Physics, University of Central Florida, Orlando, Florida 32816, USA*

²*Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden, Germany*

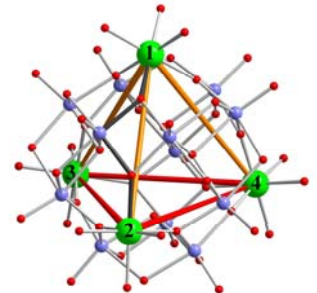
(Received 26 April 2007; revised manuscript received 29 February 2008; published 12 May 2008)

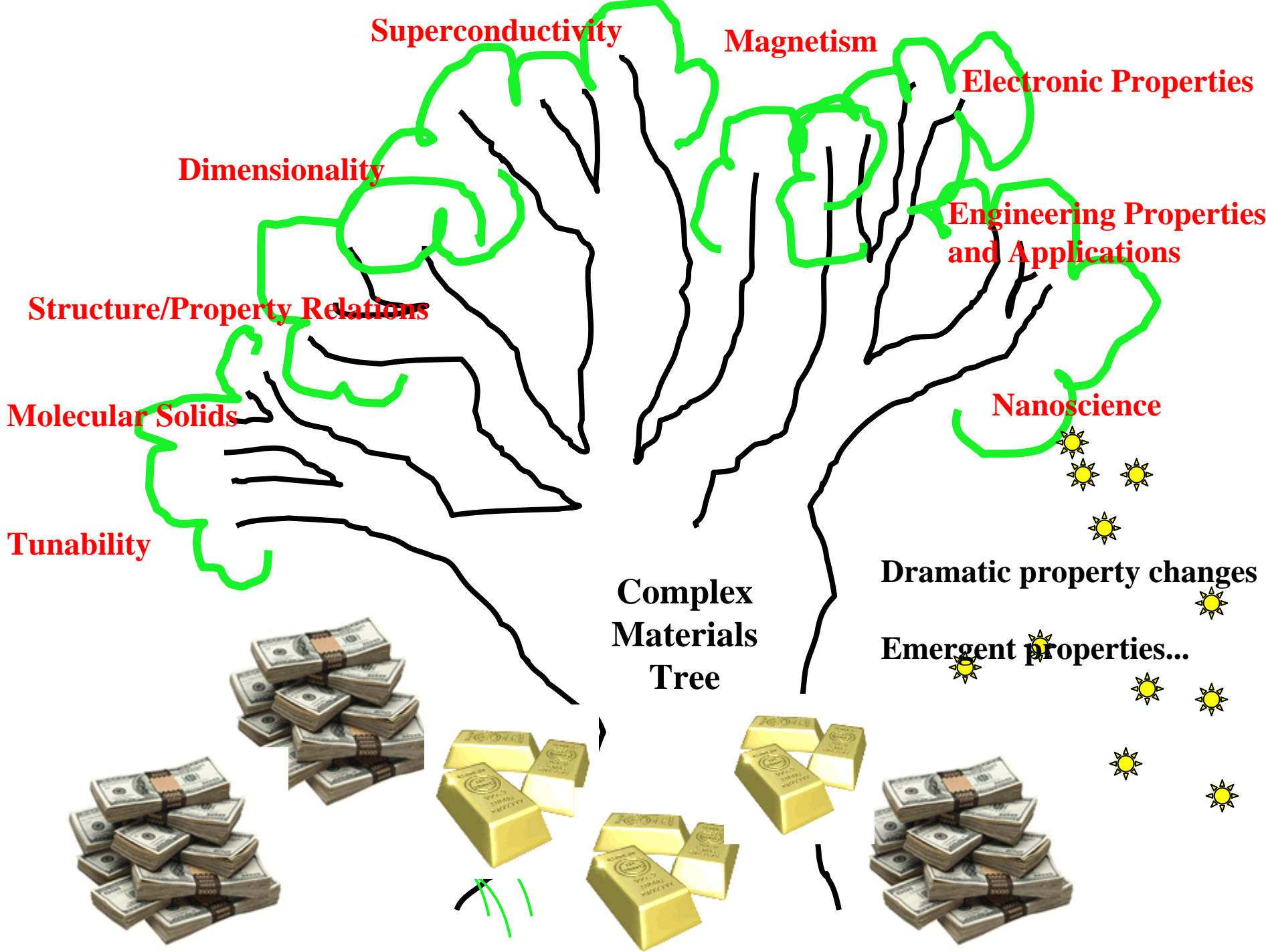
We study single-ion and exchange anisotropy effects in equal-spin s_1 tetramer single-molecule magnets exhibiting T_d , D_{4h} , D_{2d} , C_{4h} , C_{4v} , or S_4 ionic site point group symmetry. We first write the group-invariant quadratic single-ion and symmetric anisotropic exchange Hamiltonians in the appropriate local coordinates. We then rewrite these local Hamiltonians in the molecular or laboratory representation, along with the group-invariant Dzyaloshinskii-Moriya (DM) and isotropic Heisenberg, biquadratic, and three-center quartic Hamiltonians. Using our exact, compact forms for the single-ion spin matrix elements, we analytically evaluate the eigenstate energies to first order in the microscopic anisotropy interactions, corresponding to the strong exchange limit, and provide tables of simple formulas for the anisotropy energies of the lowest four eigenstate manifolds of ferromagnetic (FM) and antiferromagnetic (AFM) tetramers with arbitrary s_1 . For AFM tetramers, we illustrate the first-order level-crossing inductions for $s_1=1/2$, 1, and $3/2$, and obtain preliminary estimates of the microscopic parameters in a Ni_4 from fits to magnetization data, indicating the presence of strong symmetric anisotropic exchange interactions. Accurate analytic expressions for the thermodynamics, electron paramagnetic resonance absorption, and inelastic neutron scattering cross section are given, allowing for a determination of three of the microscopic anisotropy interactions from the second excited state manifold of FM tetramers. We also predict that tetramers with symmetries S_4 and D_{2d} should exhibit both DM interactions and multiferroic states, and we illustrate our predictions for $s_1=1/2$ and 1.



Multiple Magnetic States are Available!

Role of Electric Field = ?

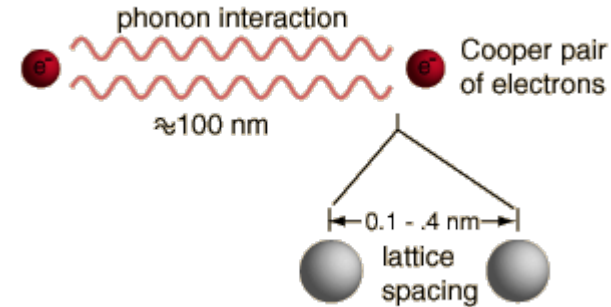




Nanoscale Effects in Bulk Superconductors and Nanoscale Superconductors



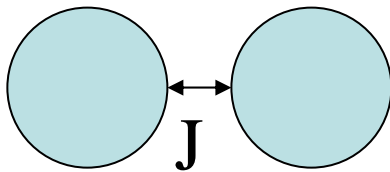
3D Bulk



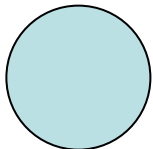
2D SC (nm layer thickness)



One-dimensional SC (thin wire)



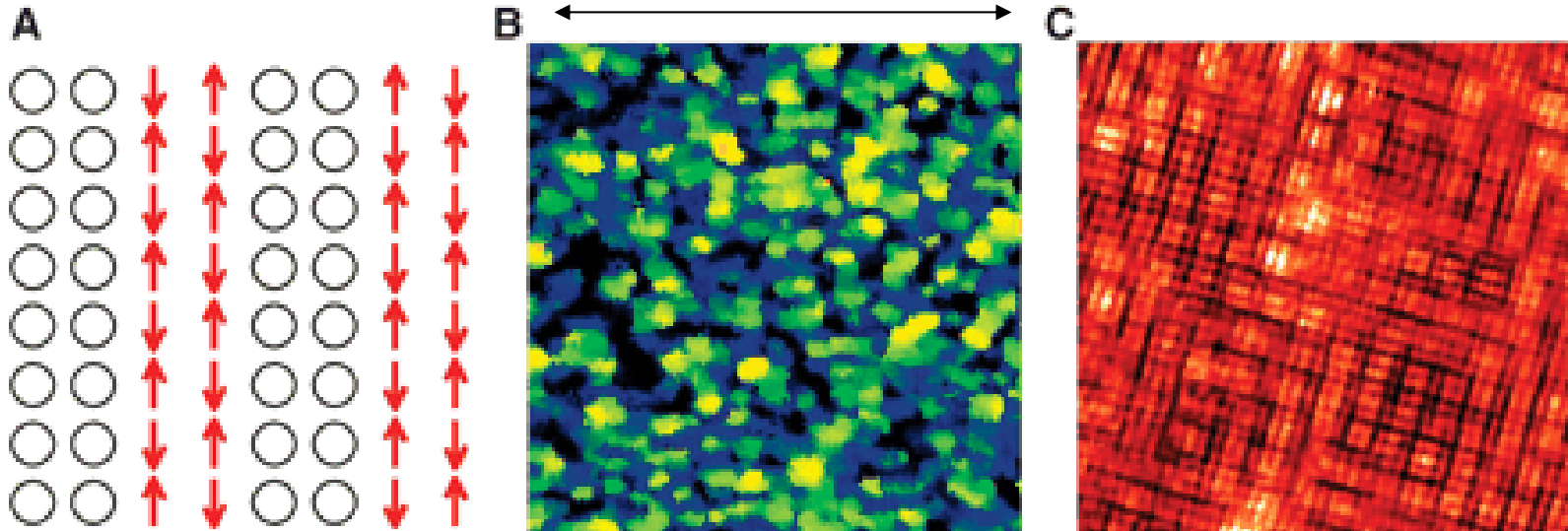
Two coupled zero-dimensional SC's



Zero-dimensional SC

Cuprates: Superconducting layers are inhomogeneous on the nanoscale!

560 nm



**schematically perfect stripes,
holes + spins**

**d-wave SC gap real-space
distribution via STM. Nano
inhomogeneities are observed.**

**Checkerboard charge-ordered
state in Na-doped cuprates**

Could be phase competition or
random O distribution.

Charge stripes set in first, and spin patterns arrange to accommodate the charge.

WOW!
Bulk materials are not really bulk!

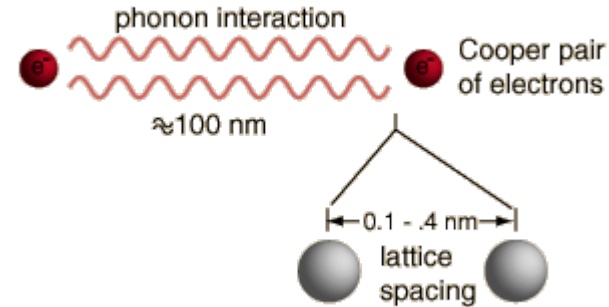
Examples: Micro- and Nano-scale Texture in $\text{Ca}_3\text{Co}_2\text{O}_6$ and BiFeO_3

Who knew???

Nanoscale Effects in Bulk Superconductors and Nanoscale Superconductors



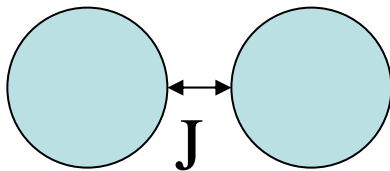
3D Bulk



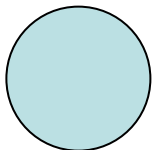
2D SC (nm layer thickness)



One-dimensional SC (thin wire)



Two coupled zero-dimensional SC's



Zero-dimensional SC

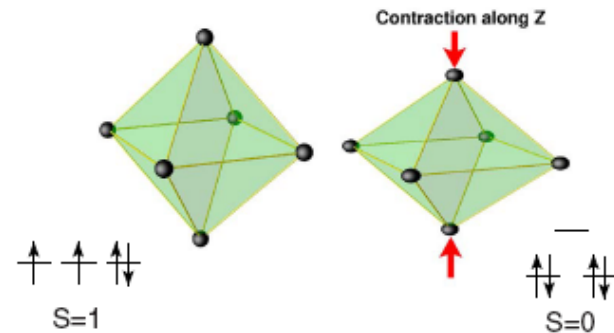
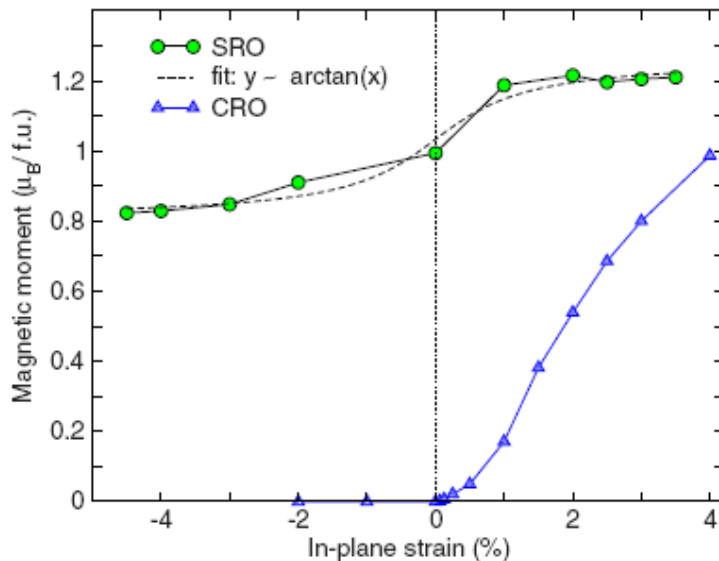
2D Confinement and Multiferroics



Film

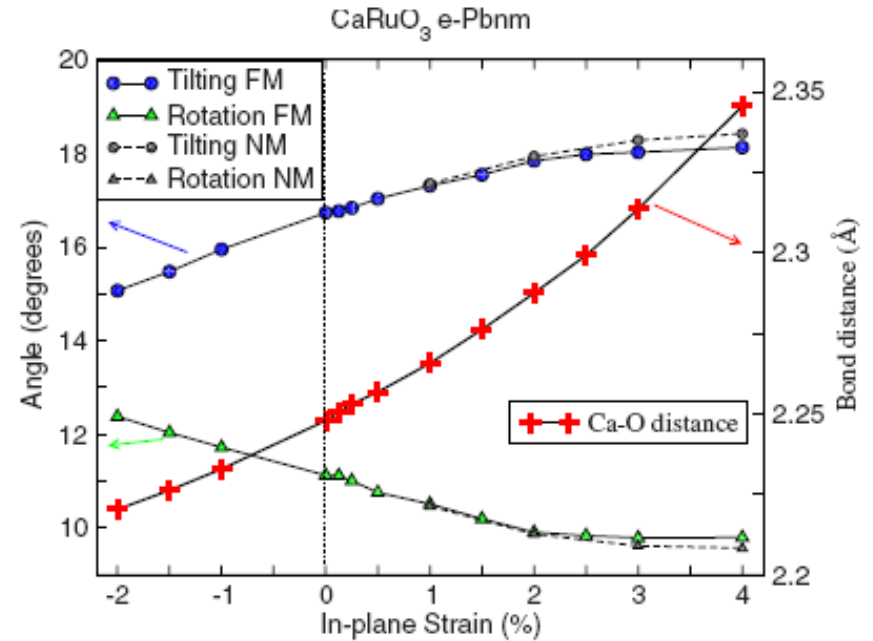
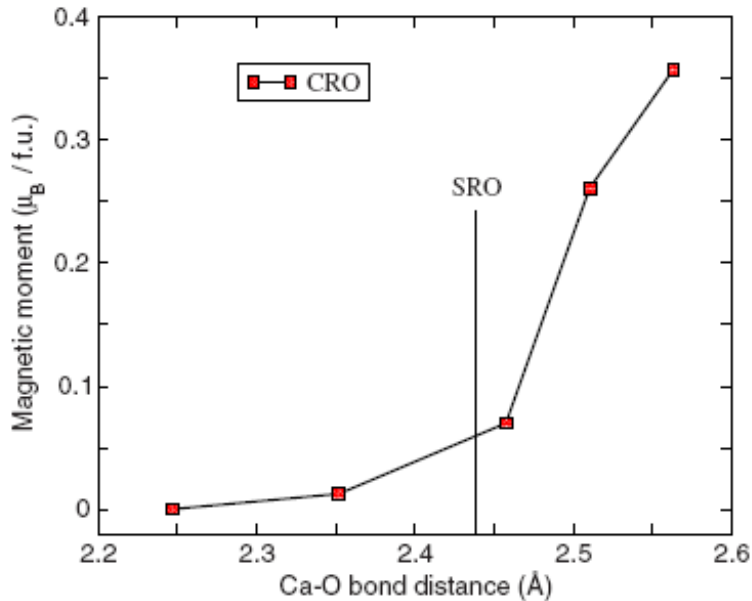
Substrate

Rare to find Perfect Lattice Match... Film is Under Compressive or Expansive Strain



Zayak, PRB (2008).

How Does This Work?



Magnetic Properties Depend on Distance but Also on Angle

$$J \sim \frac{t^2}{U} + \text{Goodenough-Kanamori Rules}$$

Can We Get Strain WithOut a Substrate?

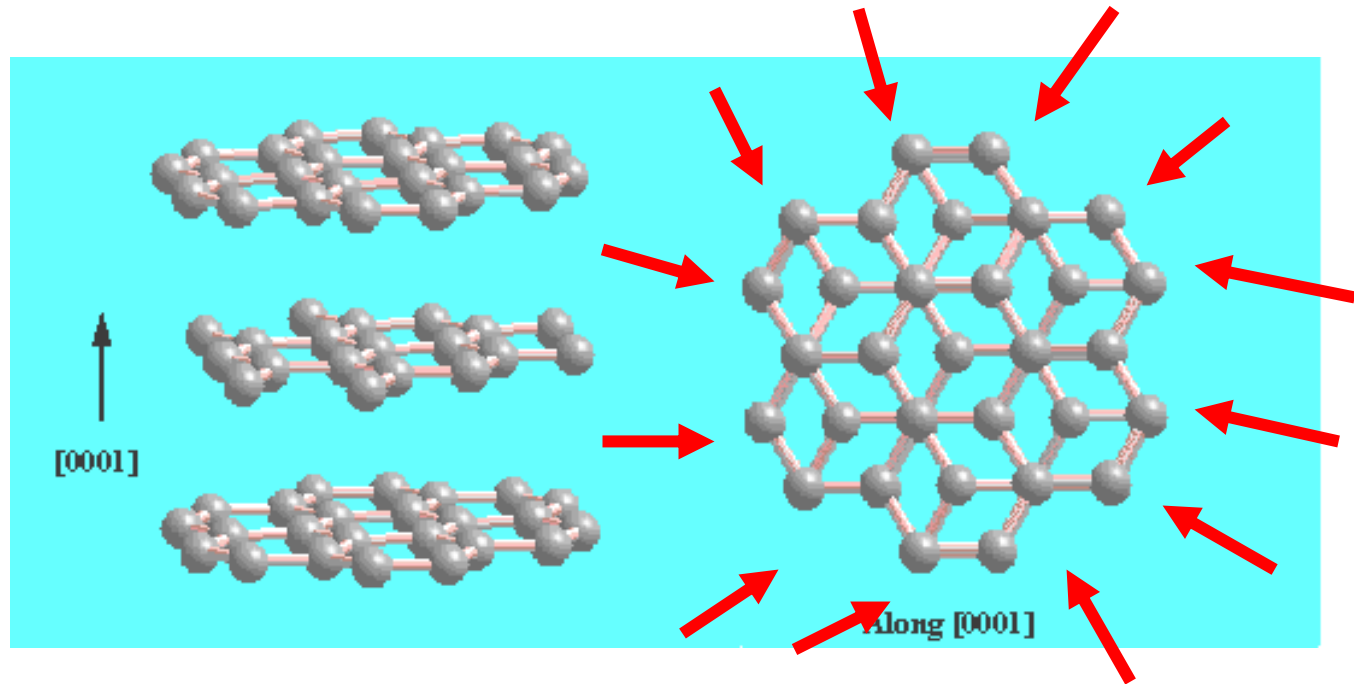
Yes!

Nanomaterials are very inhomogeneous



(The chocolate also gives rise to quantum effects.)

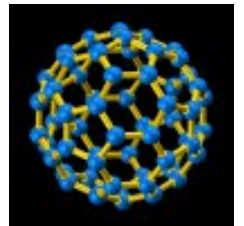
Edges and Surfaces Matter



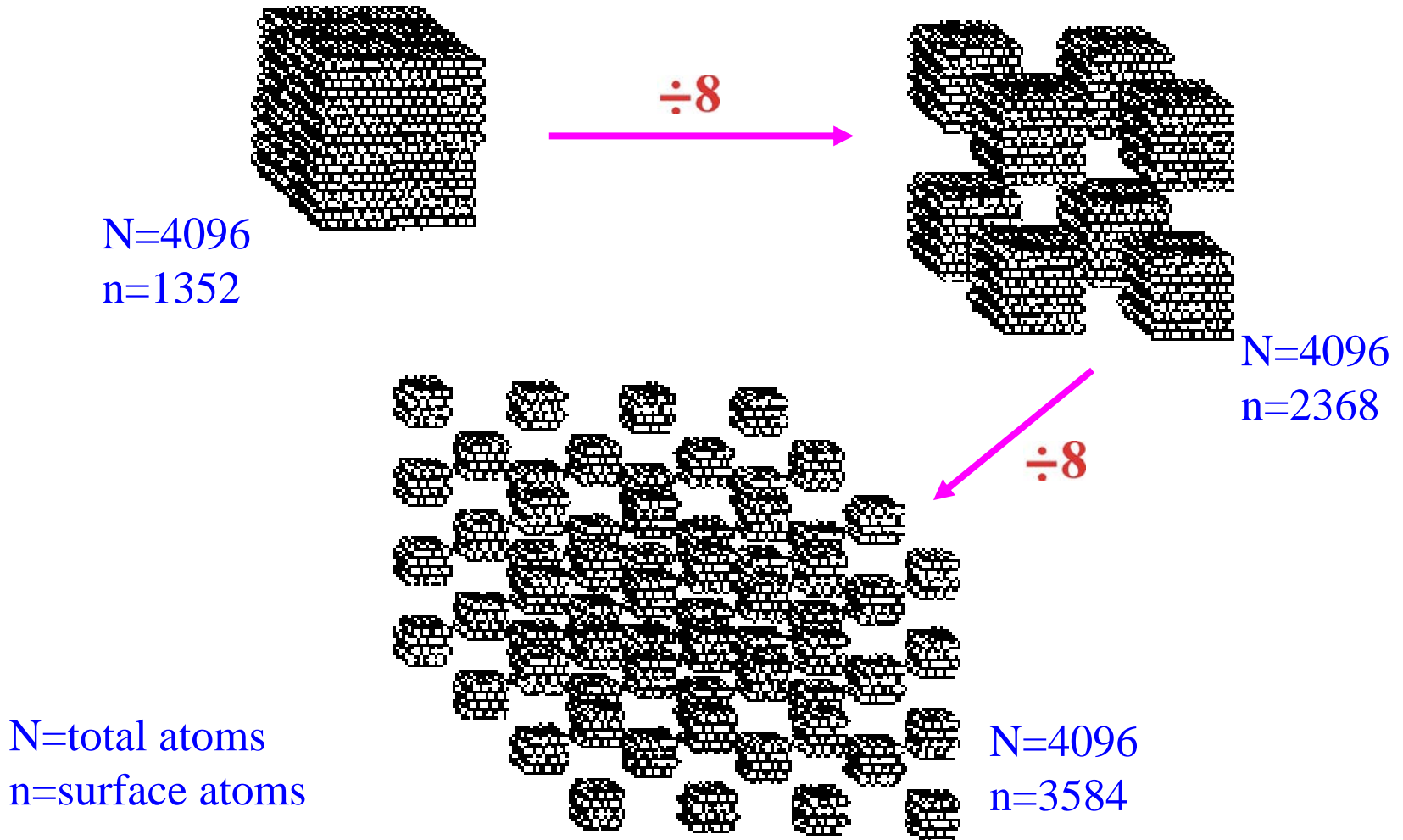
A tiny piece of graphite would have many atoms at the edge, which is unstable.

Such a material would be very reactive and not very stable. Solution???? Curve!

The ultimate shape of the nanoobject depends on both energetic and kinetic drivers.



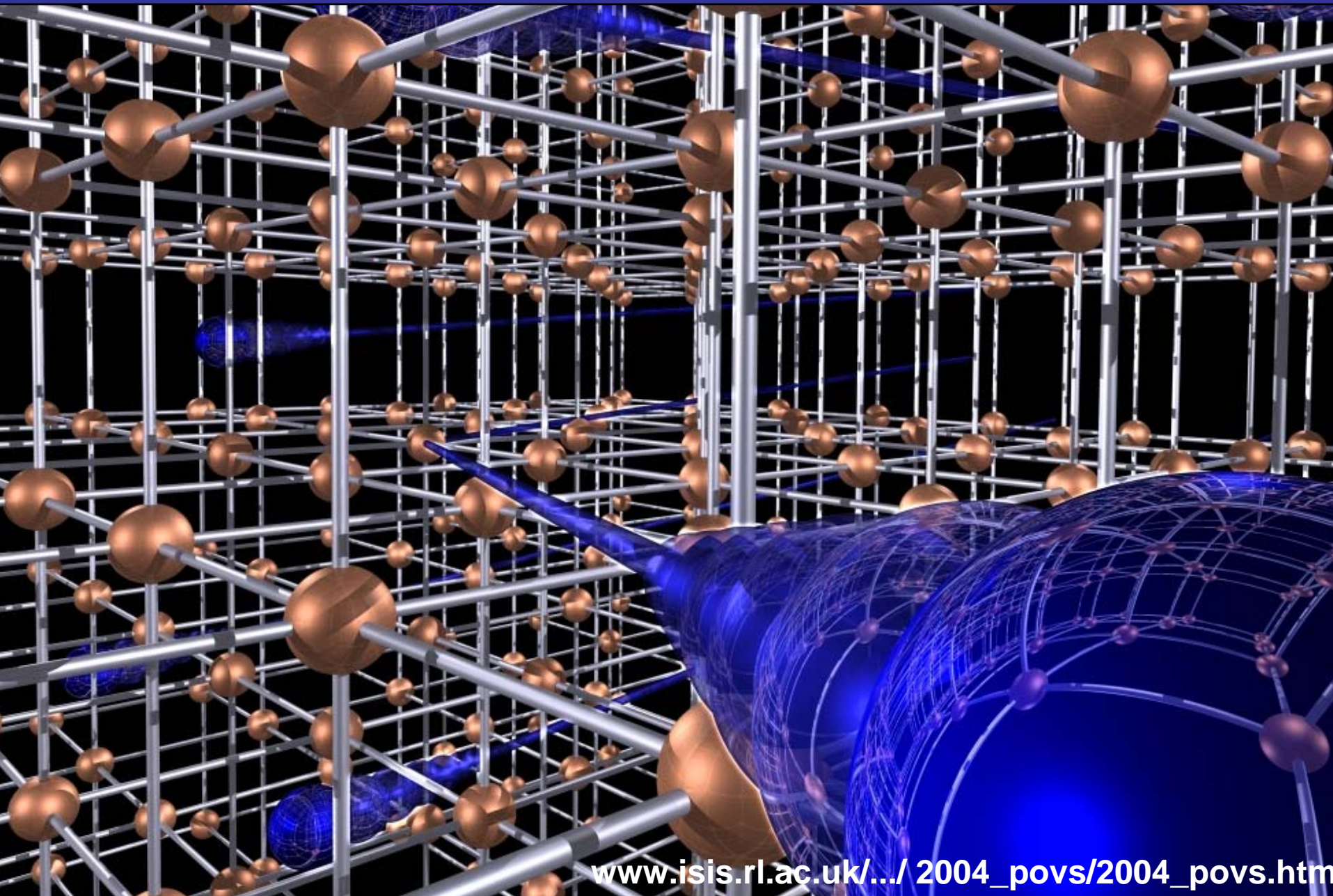
Nature of matter: increasing surface area per unit volume



Scheme adapted from G. Schmid in *Clusters and Colloids*, (VCH, Weinheim, 1994)

Surface atoms plays a crucial role in determining the physical and chemical properties of the material

Solid state perspective: all properties are determined by the lattice
(The surface is far away)



Is all that glitters gold?



What makes gold look golden?

- Electronic characteristics
- Impurities
- Size/shape effects

Bulk Gold

- **The standard electrodynamic models for a metal predict that free electrons slosh around in the solid.**
- **Yellow color due to absorption characteristics**
- **Addition of impurities changes the color and hardness**



24 carat



22 carat



18 carat



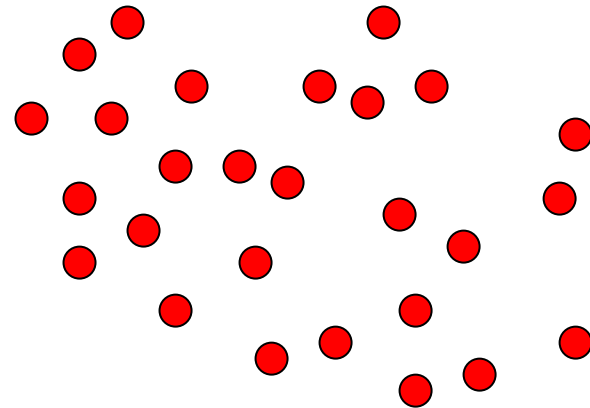
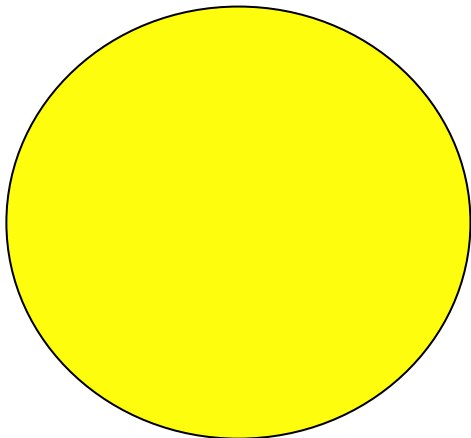
14 carat



Increasing Copper Content

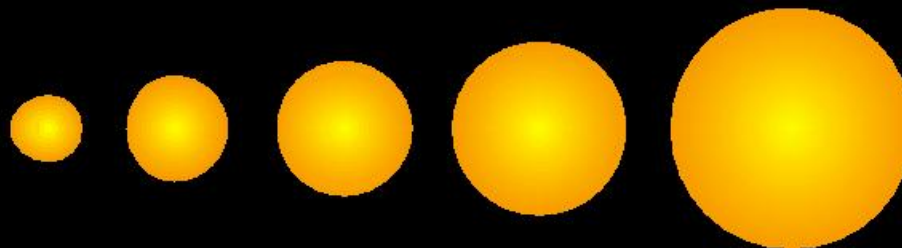
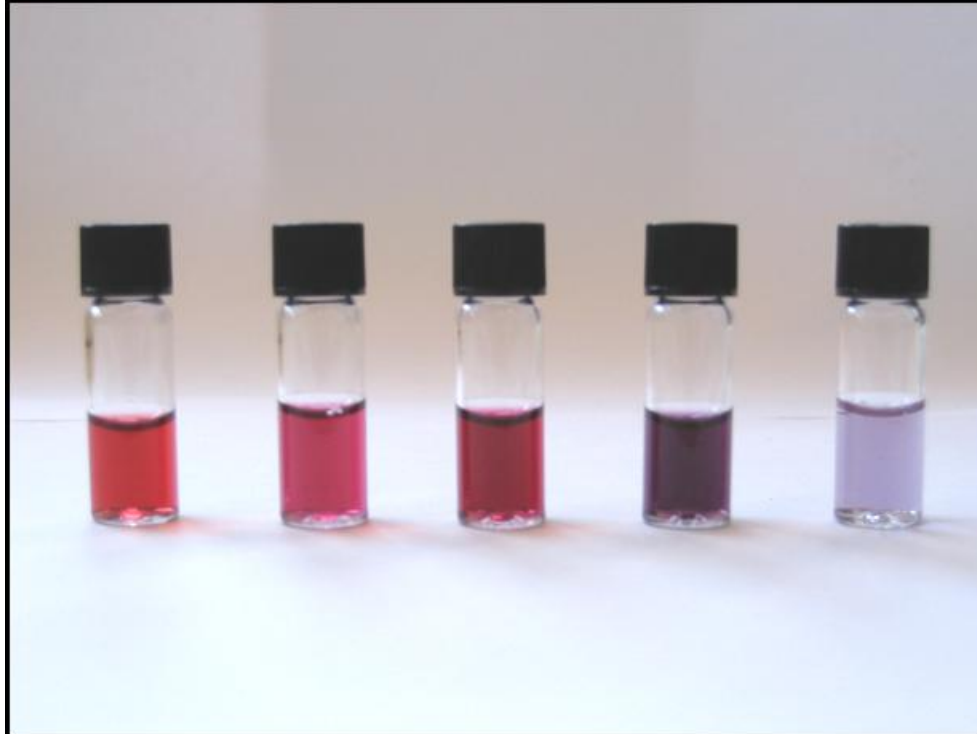
What color is nanogold?

- Not only are shapes and structures of nanomaterials different from their corresponding bulk, but properties are different as well.
- Bulk gold = Yellow; Nanogold = Red
- Size is the variable to tune color! Quantum confinement effect!

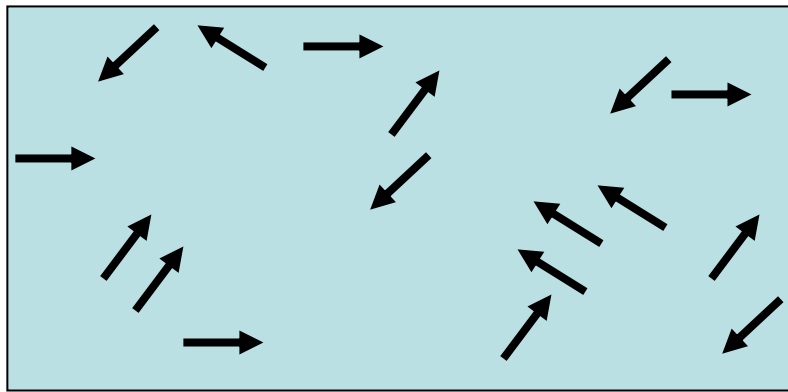


(actually, the nanoparticles tend to form clusters)

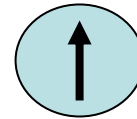
Particles absorb at different wavelengths depending on the size of particles



Local Strain & Curvature to Control and Change P, M, α ?



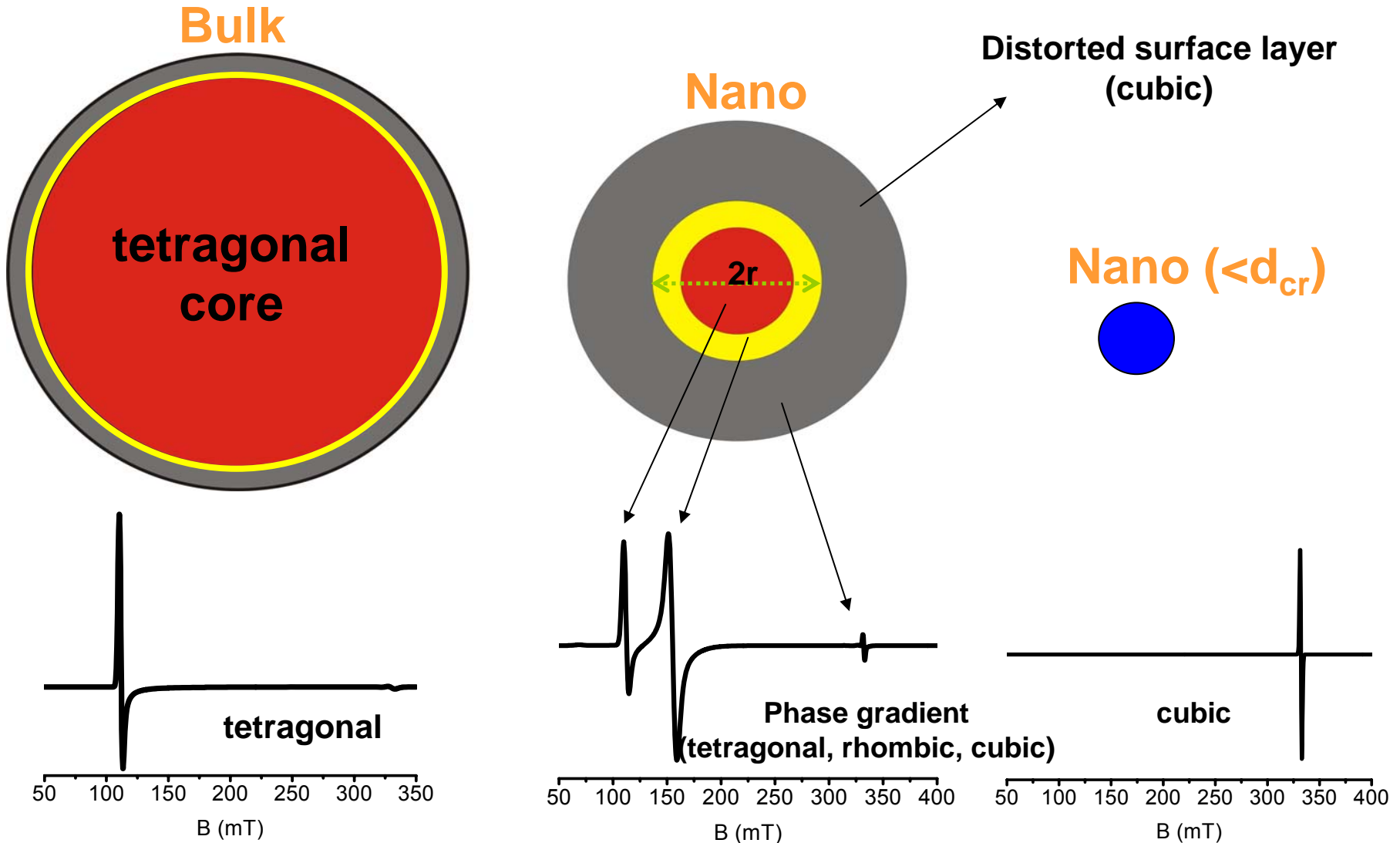
Bulk Magnetism



NanoMagnetism

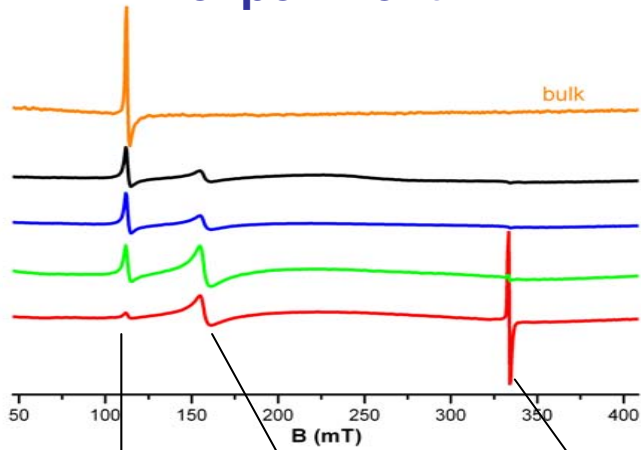
Use Length Scale to Control
Magnetic Domain, Optical
Properties, Polarization, Other
Things!

CORE-SHELL MODEL FOR A FERROELECTRIC NANOPARTICLE: $\text{PbTiO}_3:\text{Fe}^{3+}$

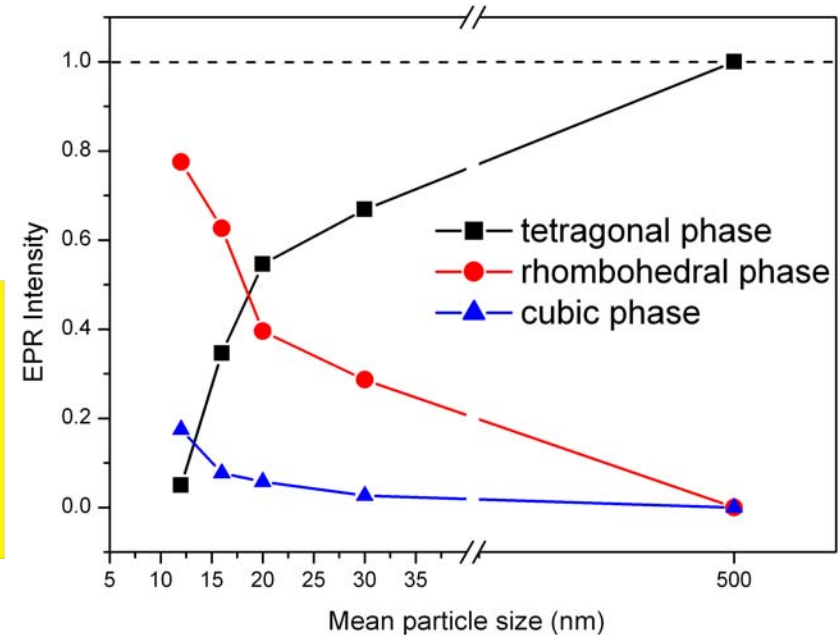
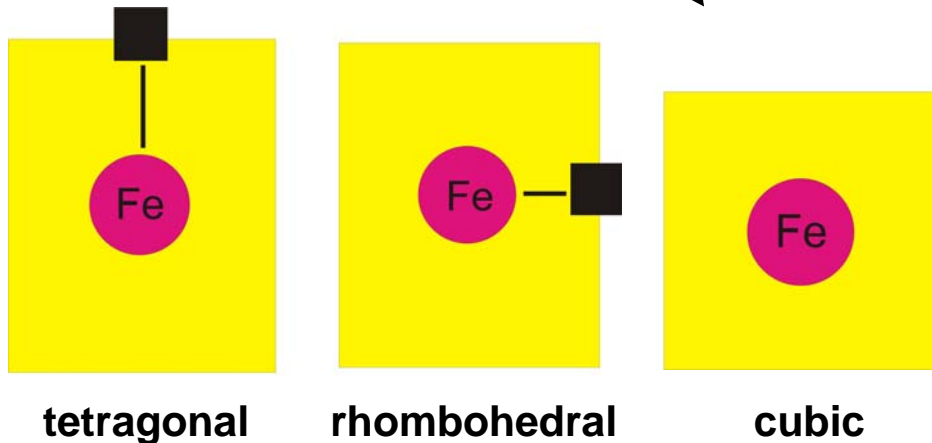
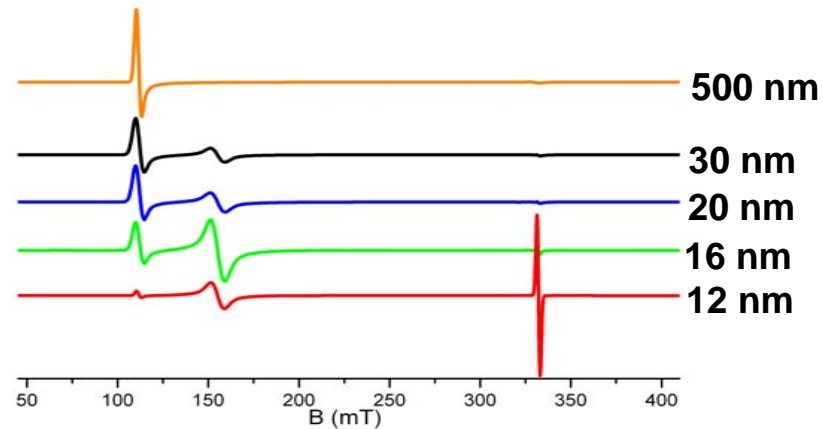


EPR is very sensitive to structural changes. At bulk material, we have only tetragonal core. At nano-sizes we have the mixing of all symetries due to lattice distortions. Finally below critical size we have only cubic particles left \rightarrow disaapearenc of ferroelectricity. This is called size driven phase transition

EPR experiment

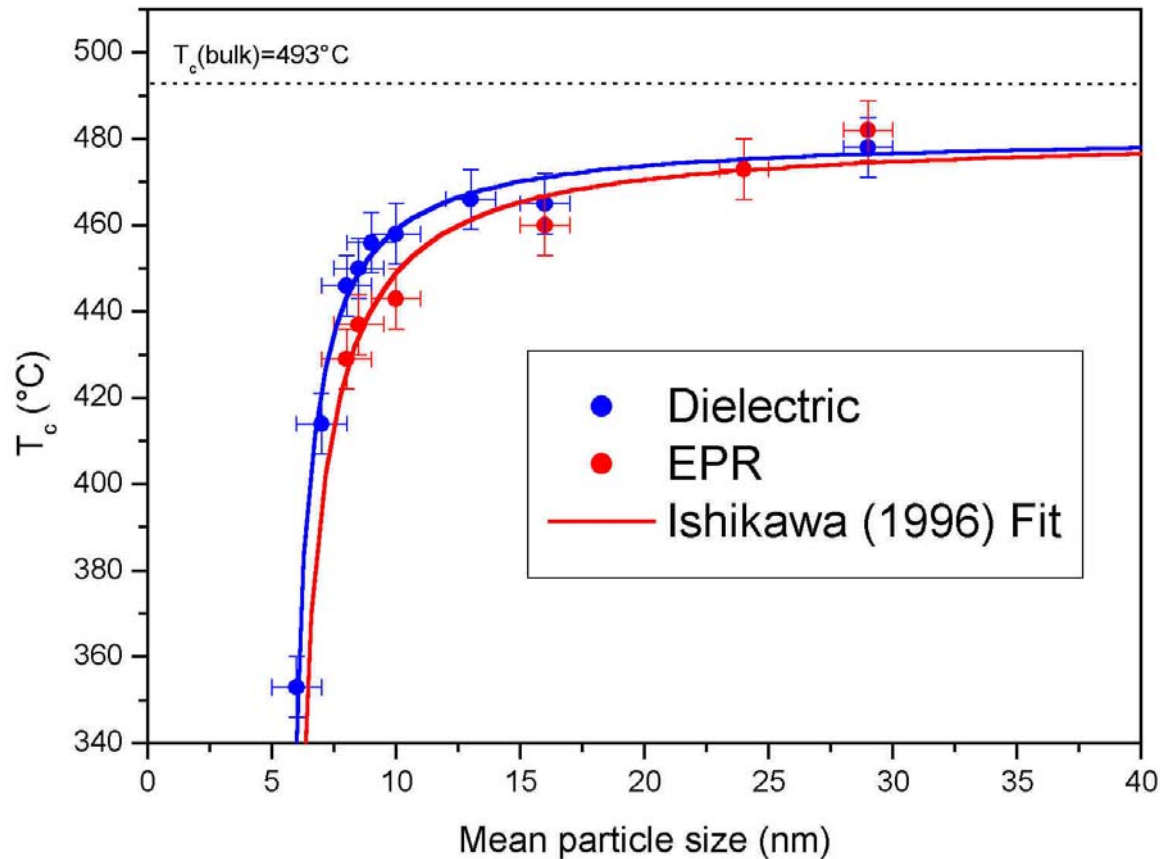


Simulation



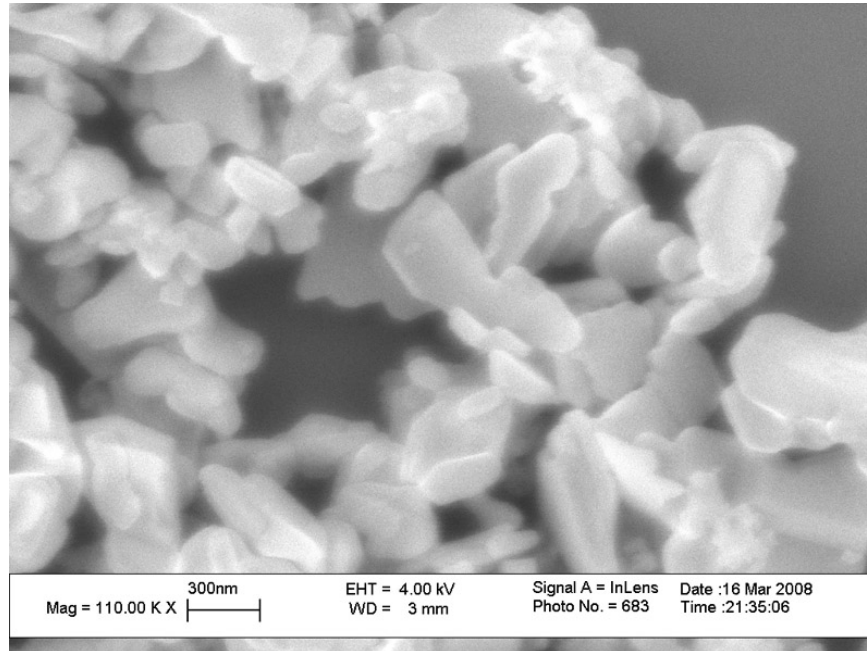
We can prove the core-shell model by EPR. From the EPR intensity we can determine the ratio of each symmetry in the material (see figure)

T_c reduction by reducing the size of PbTiO_3



EPR and dielectric spectroscopy give the same results.

What about nanoscale BiFeO_3 or RMnO_3 ?



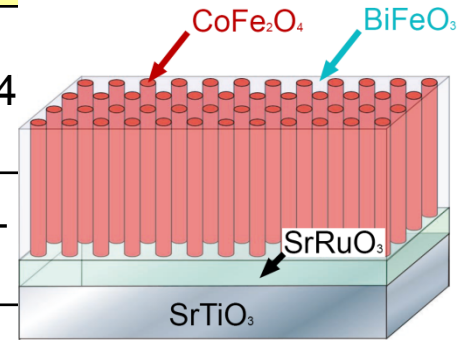
Sol-Gel Growth of BiFeO_3 Nanoparticles.

Modulate Properties with Size and Shape!

Unpublished Work, J. Cao and J. Wu.

Strain induced MES enhancement in the nanopillar BFO-CFO film

Sample	α (s/m) ($\times 10^{-12}$)	$\alpha^r_{(max)}$	Conditions
BiFeO ₃ single crystal	1	3×10^{-5}	(33) 10 K, 4
BiFeO ₃ thin film 250 nm	10	3×10^{-4}	(31) 8K, 1T
BiFeO ₃ -CoFe ₂ O ₄ nanopillar 300 nm	100	3×10^{-3}	(31) 200K, 0.5T
PZT-NiFe ₂ O ₄ nanoparticulate film 700nm	10	3×10^{-4}	(33) 300 K, 0.3 T
GaFeO ₃	30	8×10^{-4}	(23) 150K, 0.6 T
Cr ₂ O ₃	4	1×10^{-4}	(33) 250 K, crystal



Proof of the enhanced ME coupling in the nanopillar composite, possibly due to enhanced/controlled surface strain contact.

Many Opportunities with New Materials and Mechanisms!

Where to go first?



Imagio Mundi, Babylonian World Map, 6th Century

Searching for New Materials & Mechanisms: Do We Compete or Cooperate?

Model 1: Competition



Mayan Warfare

Model 2: Cooperation



Saqqara Tomb Art

Birth of Exciting New Field: Many Opportunities with New Materials



Birth of Venus, Botticelli

JLM thanks the National Science Foundation and the Department of Energy for research support.