Nanomagnetism

Ram Seshadri
Materials Department and Materials Research Laboratory
University of California, Santa Barbara CA 93106
seshadri@mrl.ucsb.edu   http://www.mrl.ucsb.edu/~seshadri

UC SANTA BARBARA engineering

Thanks:

Daniel Shoemaker

Katharine Page

Christina Schade

Dr. Ombretta Masala (Nanoco Technologies, Manchester)

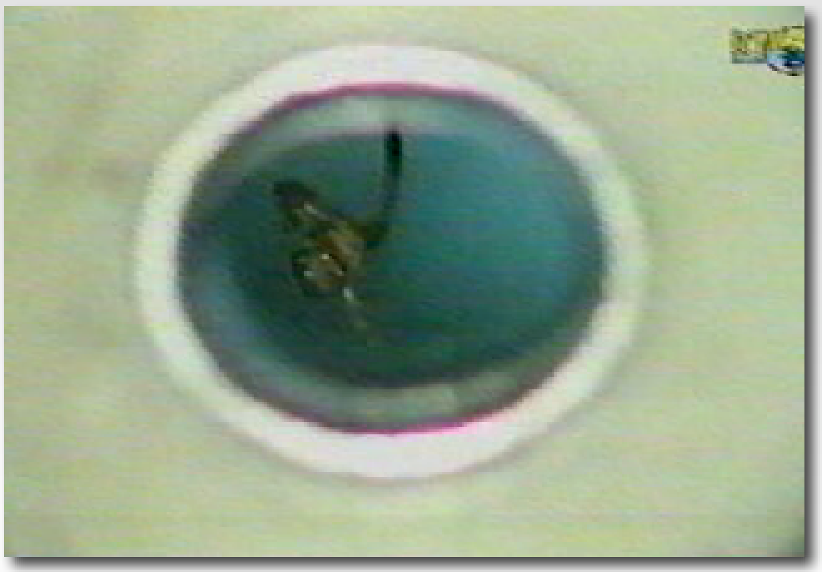
UC SANTA BARBARA engineering

Outline:

- Introduction to cooperative magnetism
- Size effects in magnetism
- Magnetic oxides
- Intermetallics
- Core/shell architectures
- Spontaneously formed magnetic composites

Cooperative Magnetism

Diamagnetism: Very weak effect possessed by *all bodies*. Characterized by materials repelling magnetic field lines.



Water is diamagnetic, and hence most living beings are as well.

Frogs (and humans) can be floated by very strong magnetic fields [work done at the European High Field Magnet Lab, Nijmegen, Netherlands]

Cooperative Magnetism

Paramagnetism: Associated with systems having unpaired electrons. Oxygen is a good example.

Electrons in atoms: ↑↑ paramagnetic

↑↓ diamagnetic

Paramagnetism is characterized by a weak attraction to a magnetic field. In the image, liquid oxygen is being held by an electromagnet.

Usually, dia- and paramagnetism are not cooperative.

Cooperative Magnetism

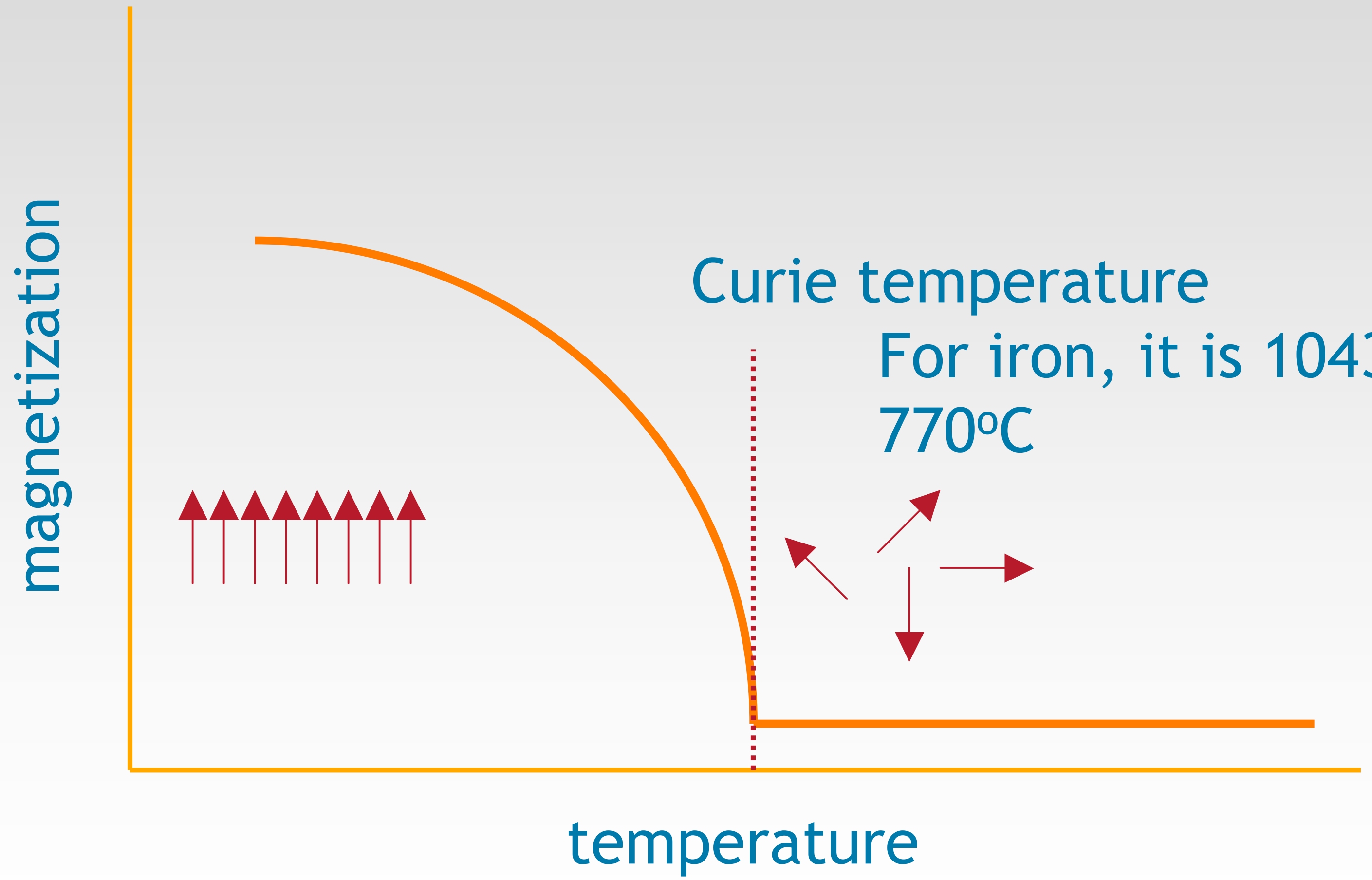
Ferromagnetism: Characterized by a very strong attraction to a magnetic field, and frequently by the material having a memory of being in a magnetic field.

Most materials that we refer to as “magnets” are actually *ferromagnets*, and specifically, hard ferromagnets.

Ferro comes from the phenomenon being associated with iron.

Cooperative Magnetism

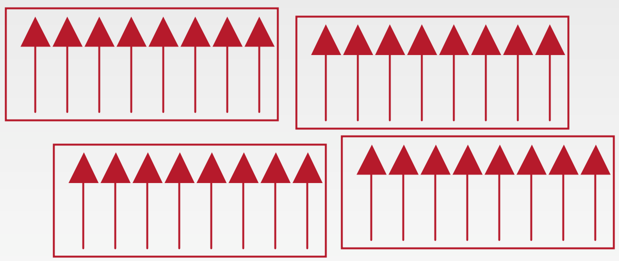
(some) materials are ferromagnetic below their Curie temperatures



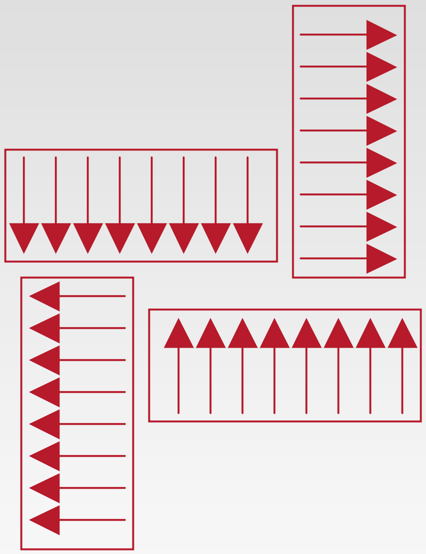
UC SANTA BARBARA engineering

Cooperative Magnetism

Domains are collections of aligned spins (on electrons). They can be aligned (or magnetized) or misaligned (demagnetized)



aligned domains
(magnetized)



misaligned domains
(demagnetized)

Cooperative Magnetism

Domains explain why two pieces of iron don't normally attract each other; iron is a "soft" magnet, and its domains easily demagnetize.

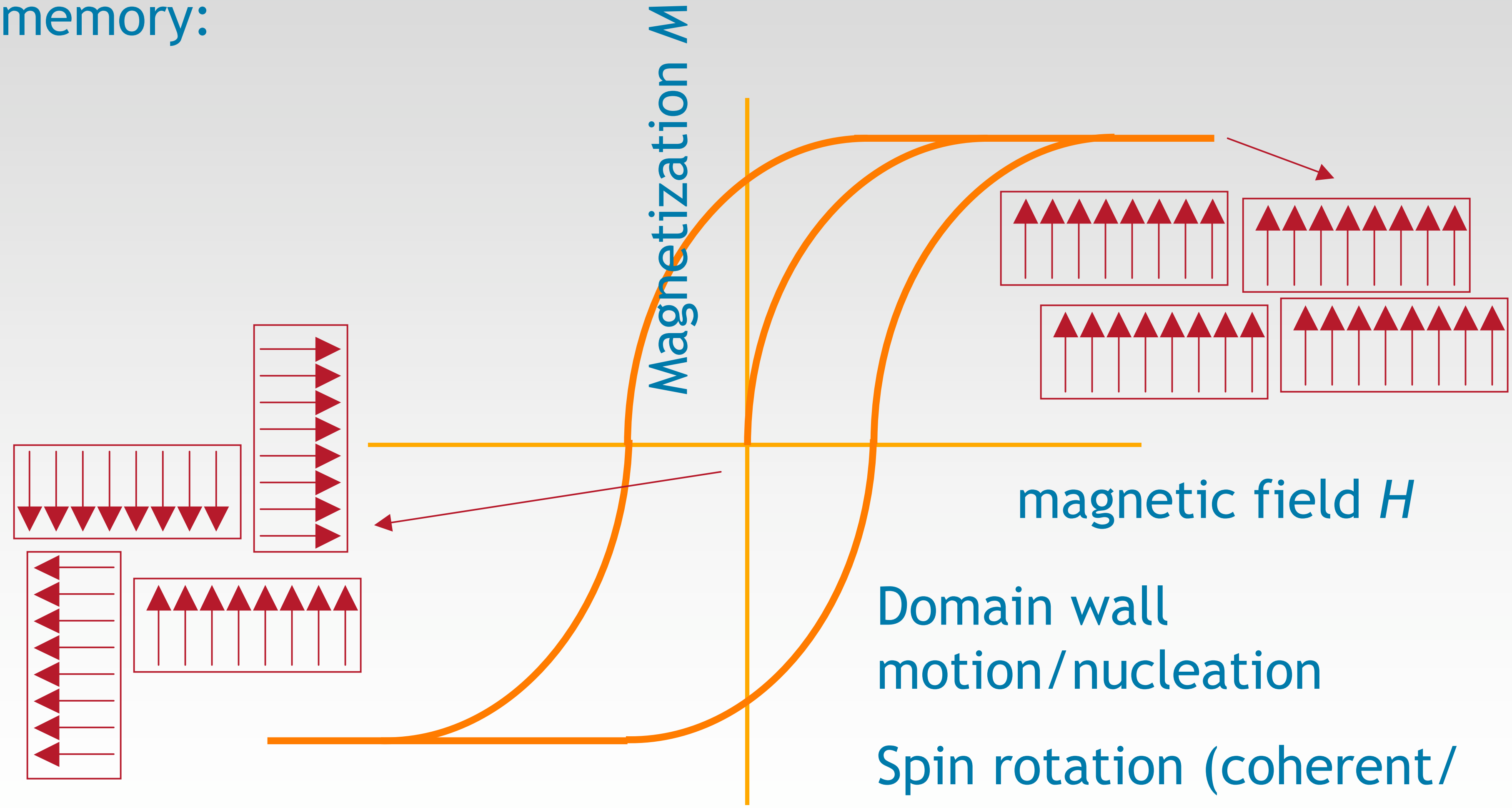
"Hard" magnets such as ferrite, Fe_3O_4 can be demagnetized by heating.

Soft ferromagnets: CoS_2, $La_{0.7}Sr_{0.3}MnO_3$, $ZnFe_2O_4$
Hard feromagnets: $SmCo_5$, $CoFe_2O_4$, Nd-Fe-B, FePt

UC SANTA BARBARA engineering

Cooperative Magnetism

Domains also explain hysteresis, and the notion of magnetic memory:

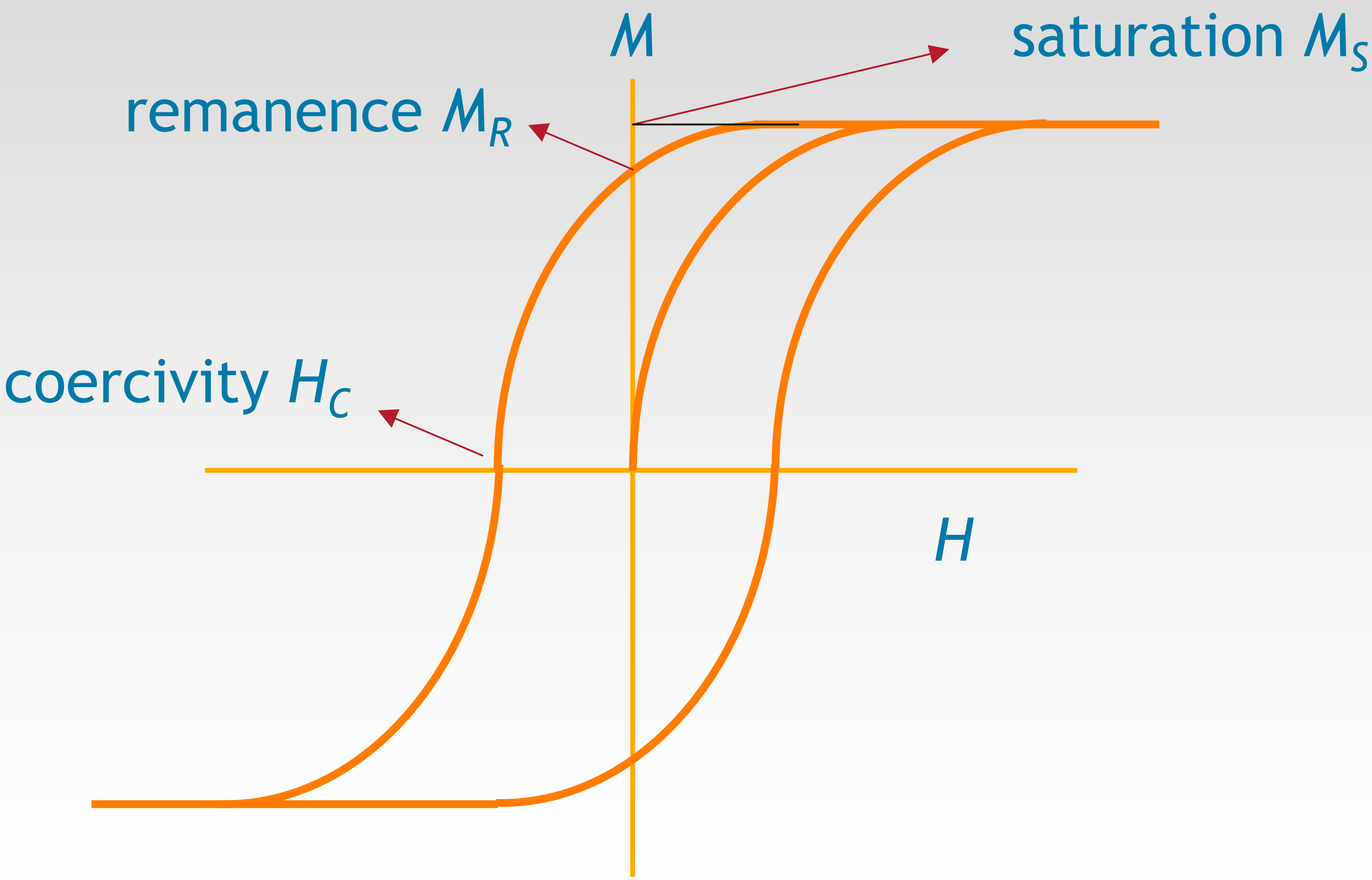


Domain wall motion/nucleation

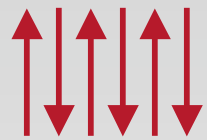
Spin rotation (coherent/incoherent)

Cooperative Magnetism

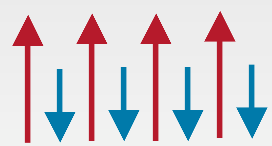
Important terms associated with ferromagnetic hysteresis



Cooperative Magnetism

Antiferromagnets: 

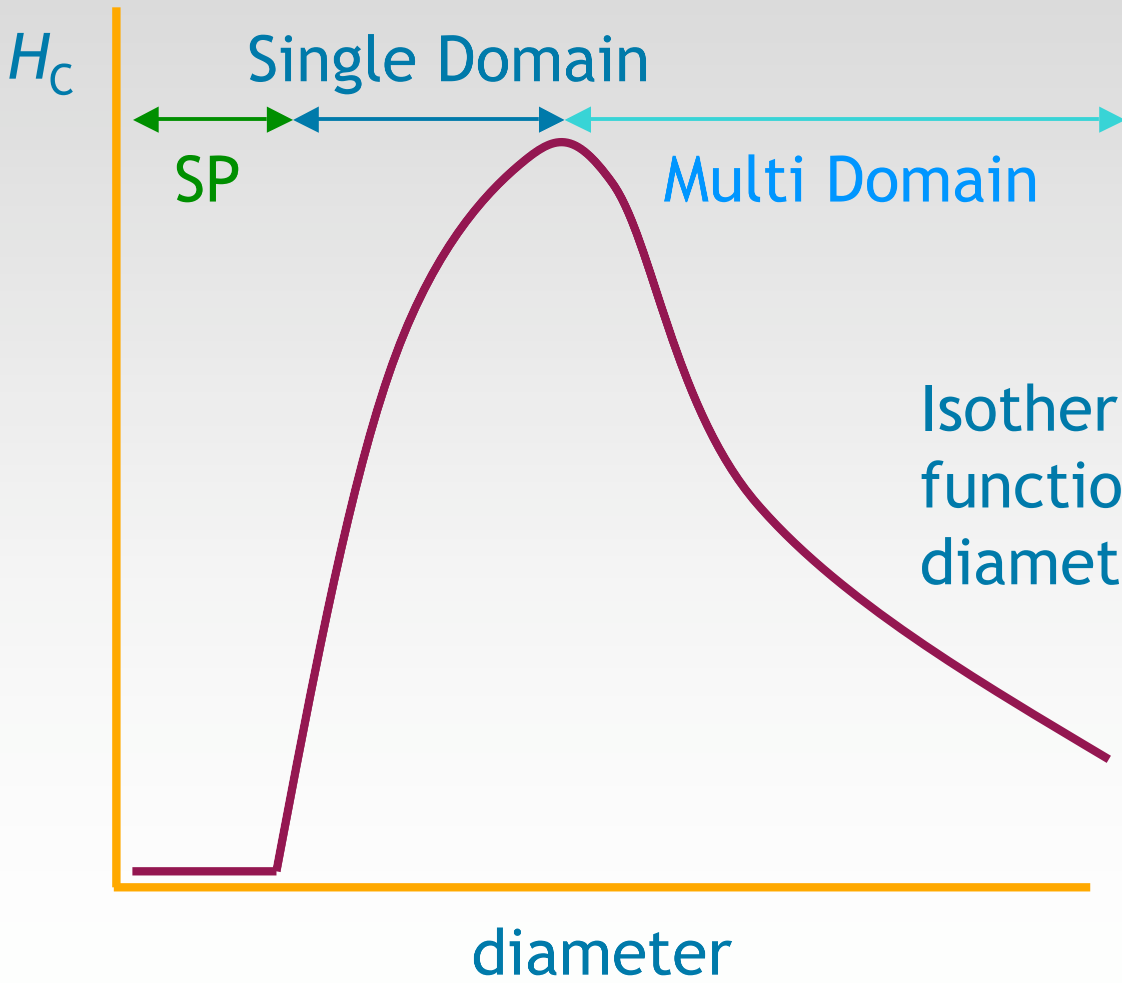
Near-neighbor spins are antialigned. No hysteresis.
Examples: MF_2, MO (M = Mn, Fe, Co, Ni, Cu), IrMn …

Ferrimagnets: 

Near-neighbor spins are antialigned, and are also not compensated (the spins don't cancel). Hysteresis and magnetization like in a ferromagnet.
Examples: Fe_3O_4, $CoFe_2O_4$, $Y_3Fe_5O_{12}$, $BaFe_6O_{19}$ …

Size effects

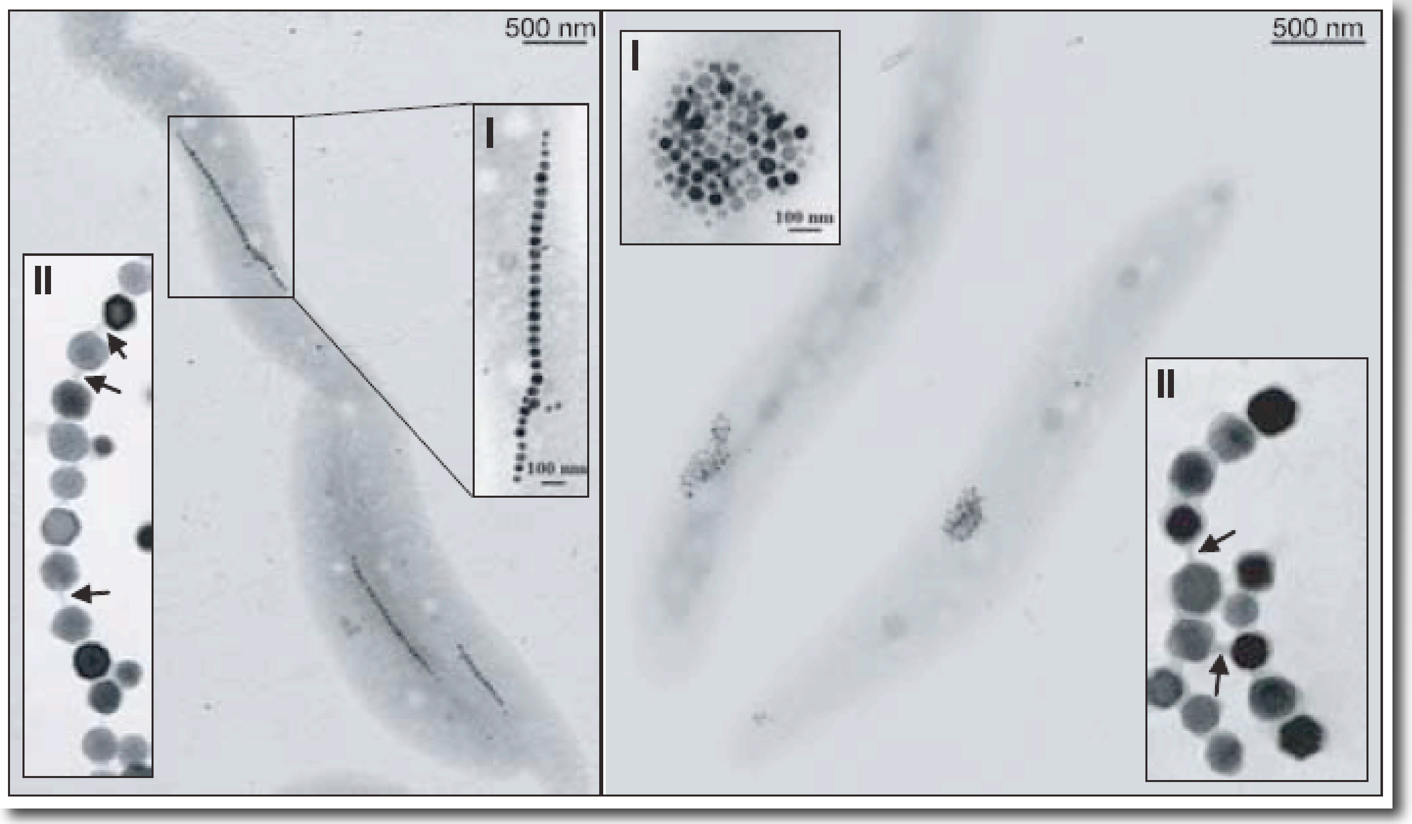
SP: Superparamagnetic



Isotherm of H_c as a function of particle diameter

Size effects

Single-domain ferrite (Fe_3O_4) nanoparticles in magnetotatic bacteria

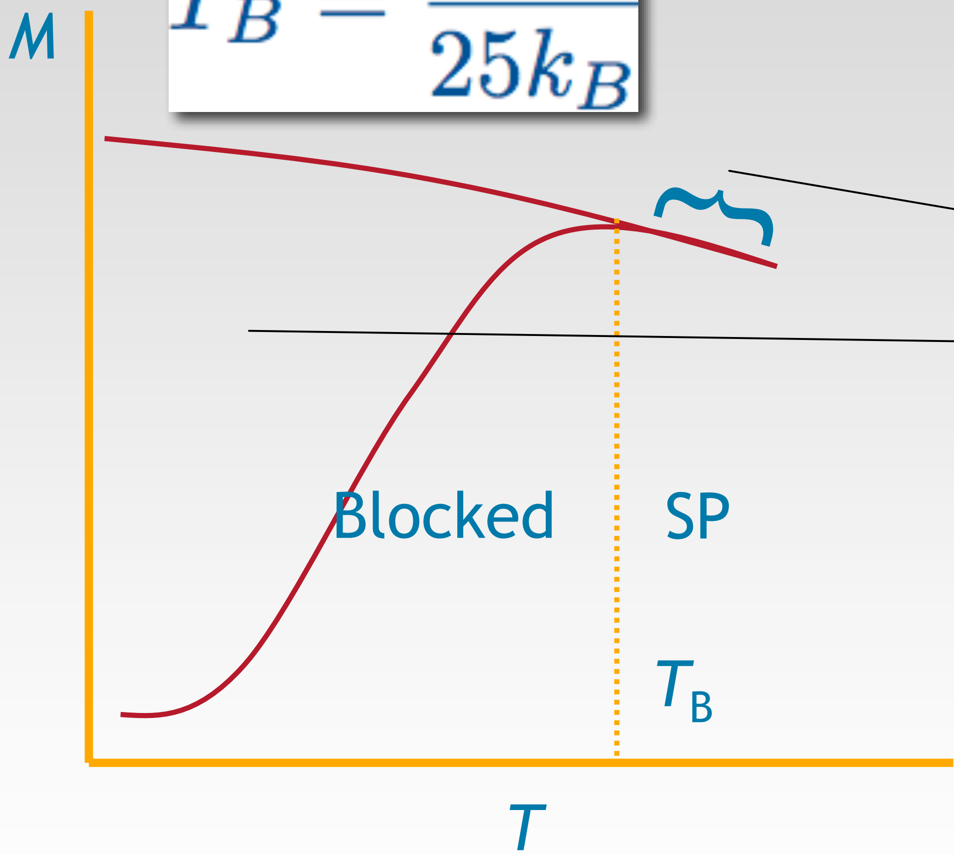


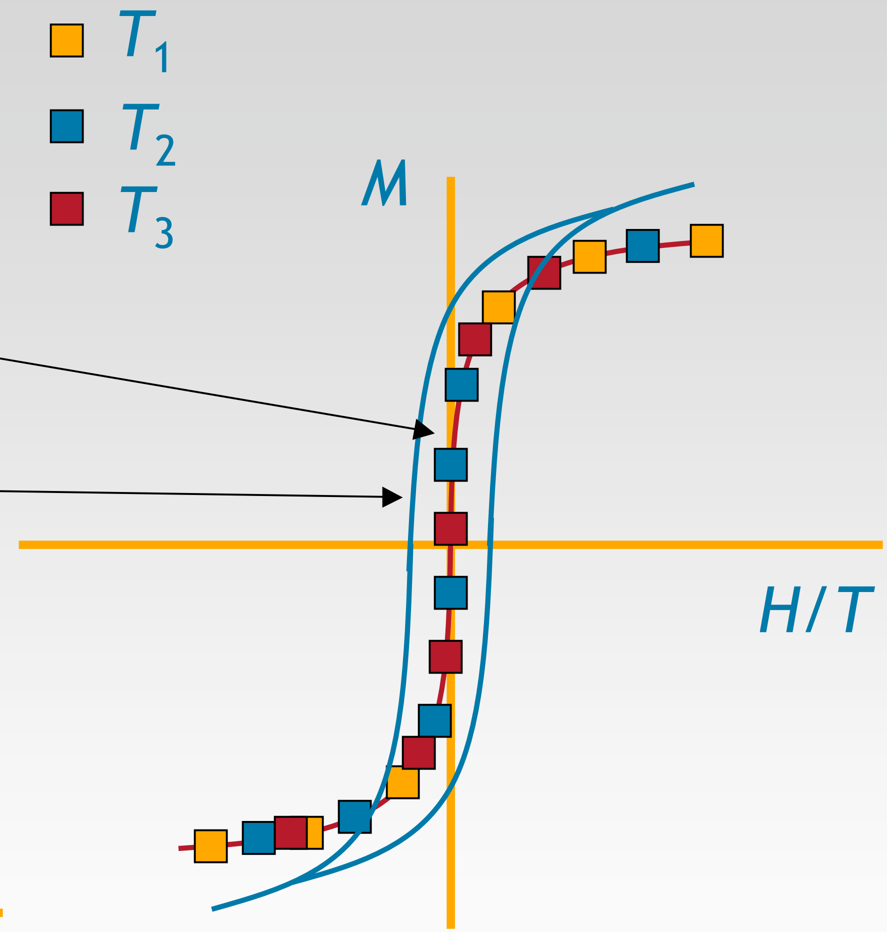
Nature, March 2nd, 2006

Size effects

Superparamagnetism and blocking

$$T_B = \frac{KV}{25k_B}$$





Preparation

Annu. Rev. Mater. Res. 2004. 34:41–81
doi: 10.1146/annurev.matsci.34.052803.090949

SYNTHESIS ROUTES FOR LARGE VOLUMES OF NANOPARTICLES

Ombretta Masala and Ram Seshadri
Materials Department and Materials Research Laboratory, University of California, Santa Barbara, California 93106; email: masala@engineering.ucsb.edu, seshadri@mrl.ucsb.edu

Annu. Rev. Mater. Res. **34** (2004) 41-81: Metals, chalcogenides, main group elements, oxides, pnictides.

UC SANTA BARBARA engineering

Oxide nanoparticles

Oxides can be prepared by

Hydrolysis:

$2M^{3+}(H_2O)_6 \rightarrow M_2O_3 + 9H_2O + 6H^+$ [*eg*. γ-Fe_2O_3]

Metathesis:

$TiCl_4 + Ti(OR)_4 \rightarrow 2TiO_2 + 4RCl$
[Colvin *et al*. *J. Am. Chem. Soc*. **121** (1999) 1613-1614.]

Thermolysis:

$Zn(acac)_2 \rightarrow ZnO$ + products in refluxing dibenzylether

Oxide nanoparticles

Example: $CoFe_2O_4$

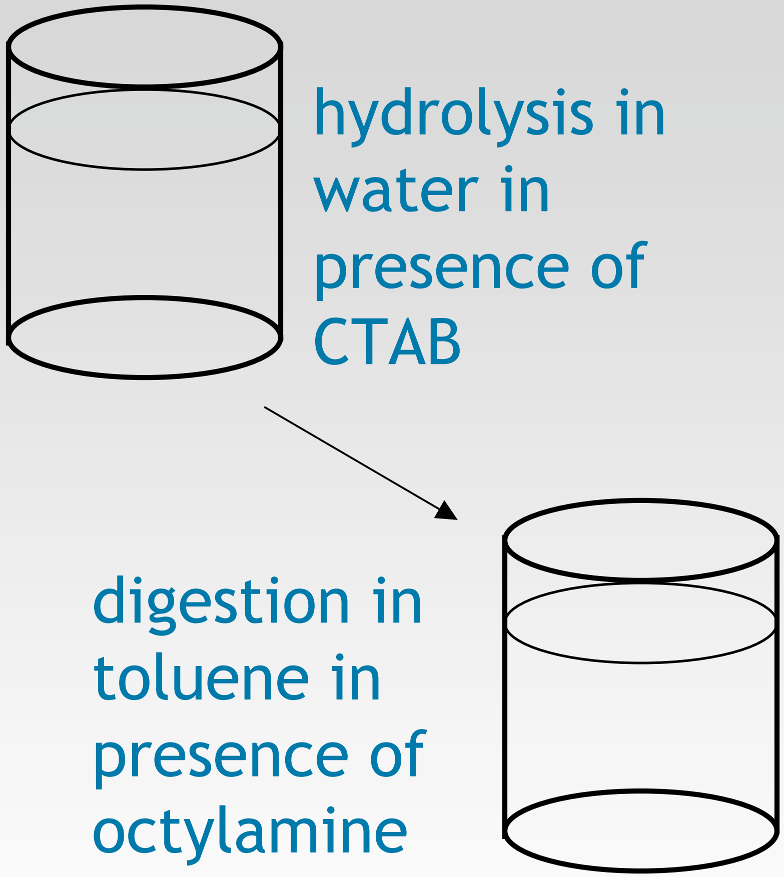
Stoichiometric amounts of **Co(acac)$_2$** and **Fe(acac)$_3$** in benzyl ether

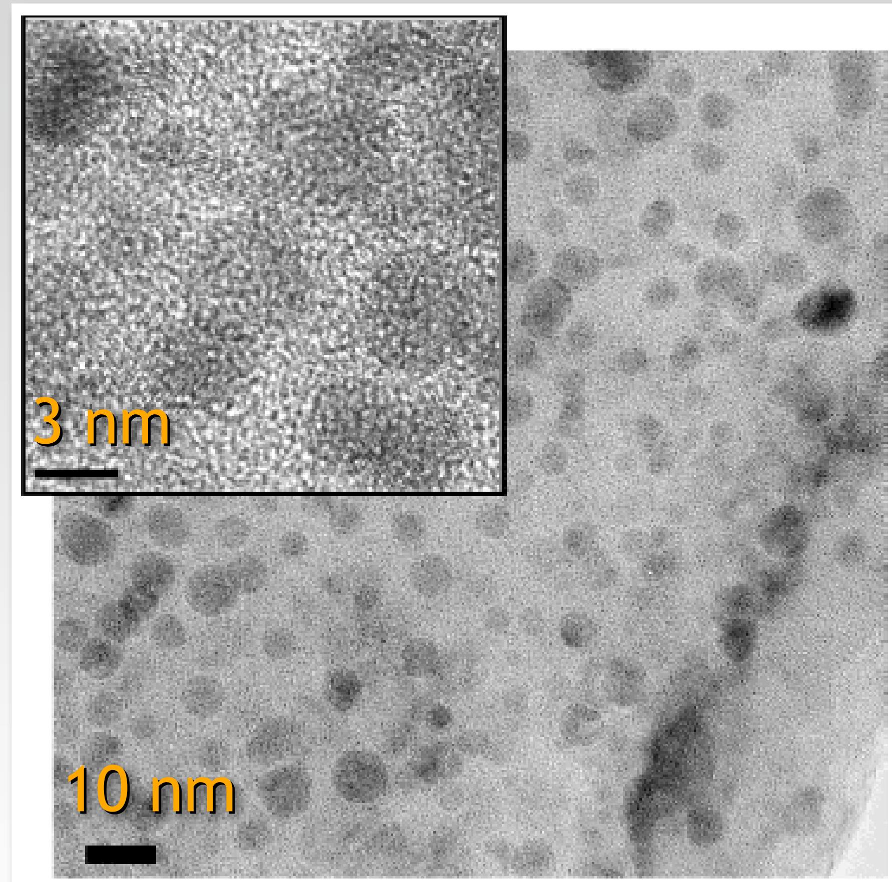
Oleylamine and **oleic acid** as capping agents

200^{o}C and at reflux

Size control by using different amounts of capping agents and different reaction time

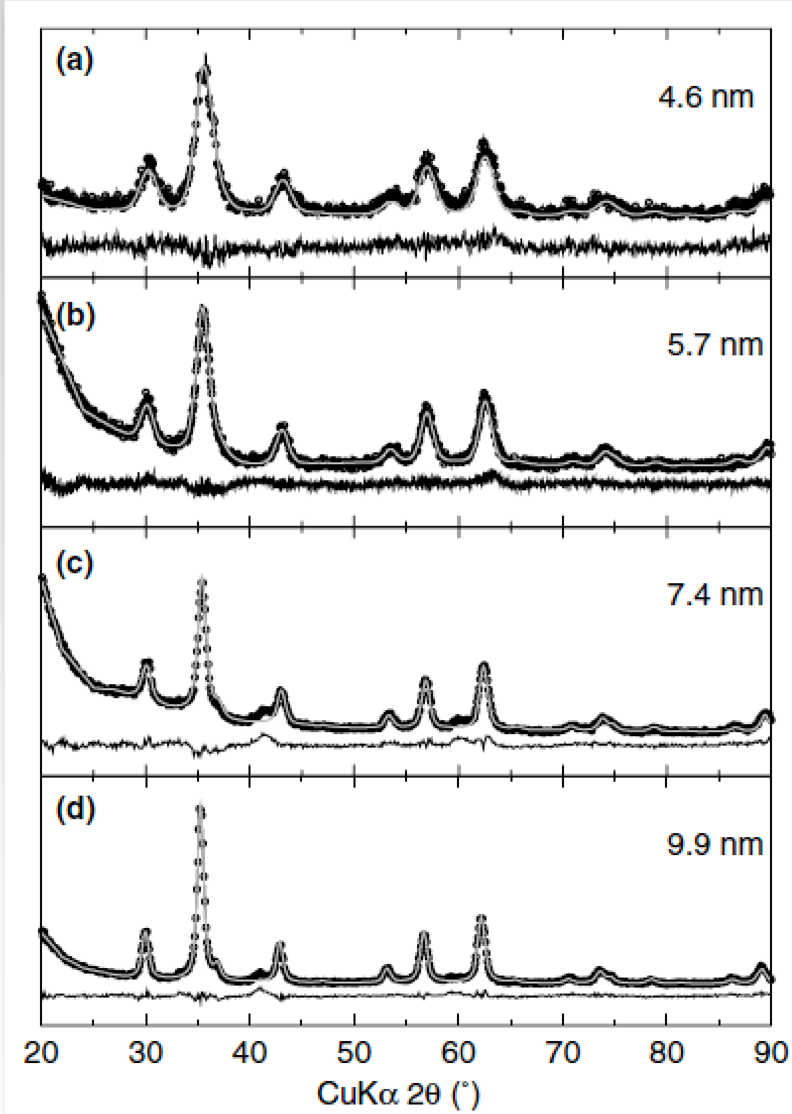
Oxide nanoparticles

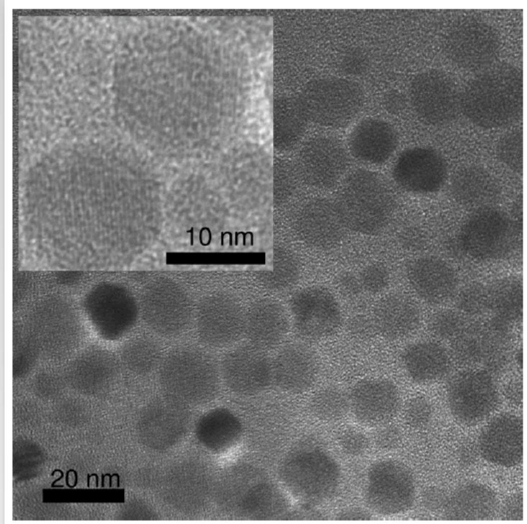




Ghosh et al., *A novel noute to toluene-soluble magnetic oxide nanoparticles: Aqueous hydrolysis followed by surfactant exchange*, *Chem. Mater.* **16** (2004) 118-124.

Oxide nanoparticles: $MnFe_2O_4$



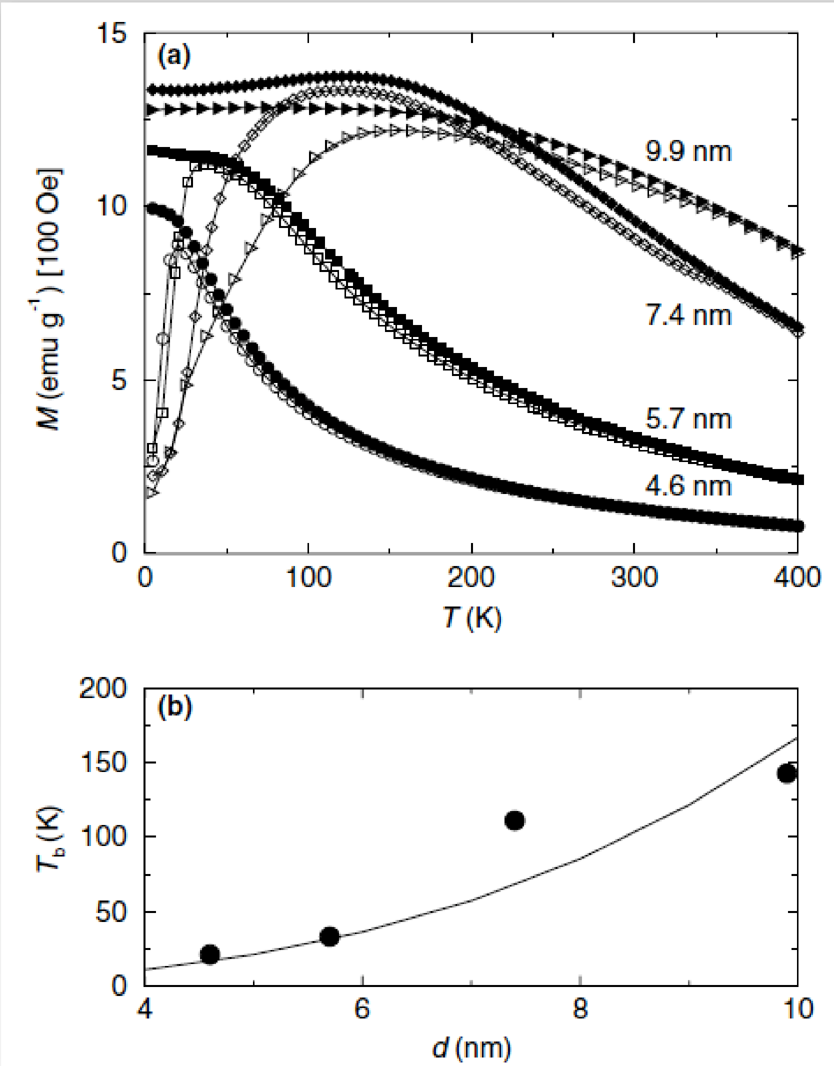


$MnFe_2O_4$ nanoparticles capped with oleic acid and oleyl amine prepared by decomposing $Mn(acac)_2$ and $Fe(acac)_3$ in refluxing dibenzyl ether at 300^{o}C.

Masala and Seshadri, *Chem. Phys. Lett.* **402** (2005) 160.

engineering

Oxide nanoparticles: $MnFe_2O_4$



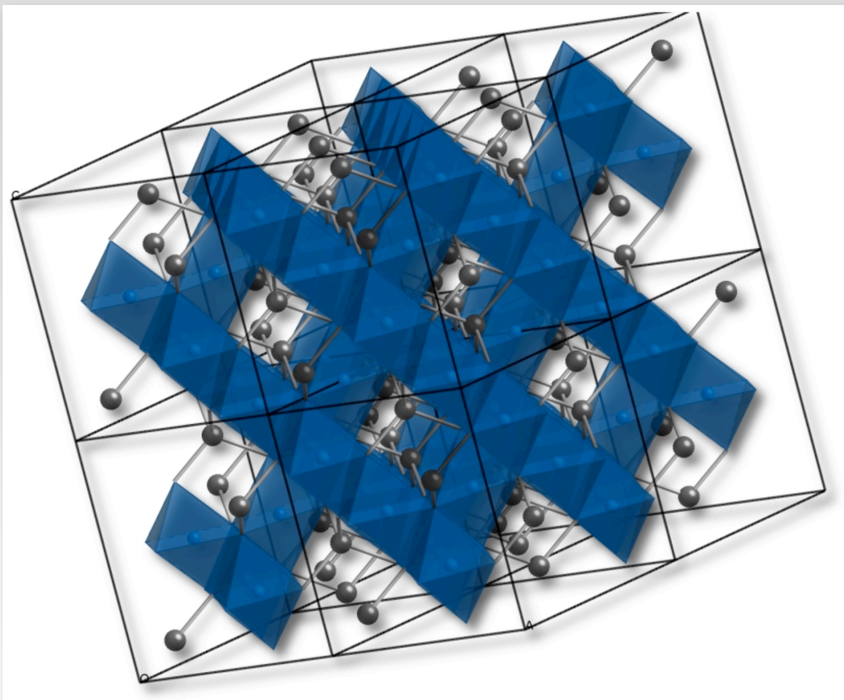
No evidence for a magnetic "dead layer" in well-capped, crystalline nanoparticles.

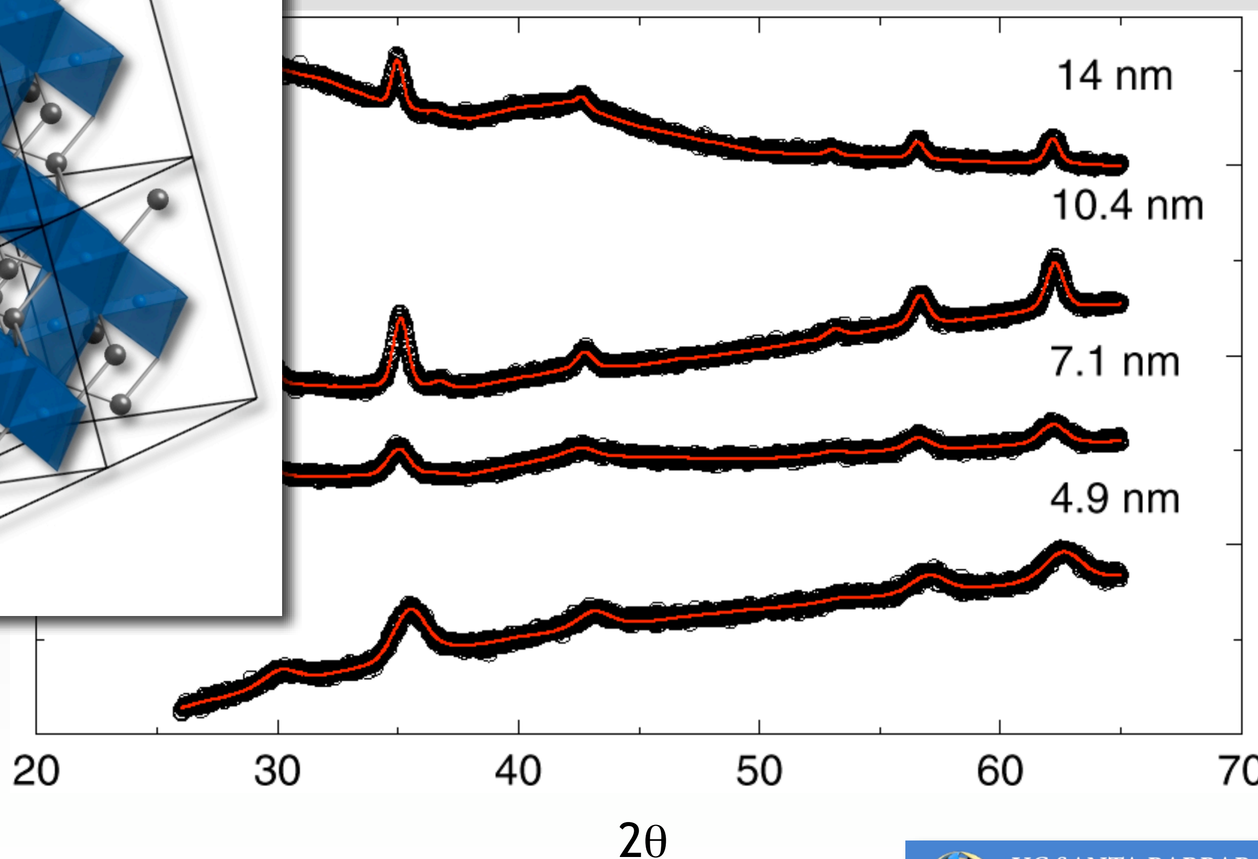
$$T_B = \frac{KV}{25k_B}$$

Masala and Seshadri, *Chem. Phys. Lett.* **402** (2005) 160.

Oxide nanoparticles: $CoFe_2O_4$

X-ray diffraction data and Rietveld refinement: Inverse spinel structure Fe(CoFe)O_4. *Fd-3m* (227)

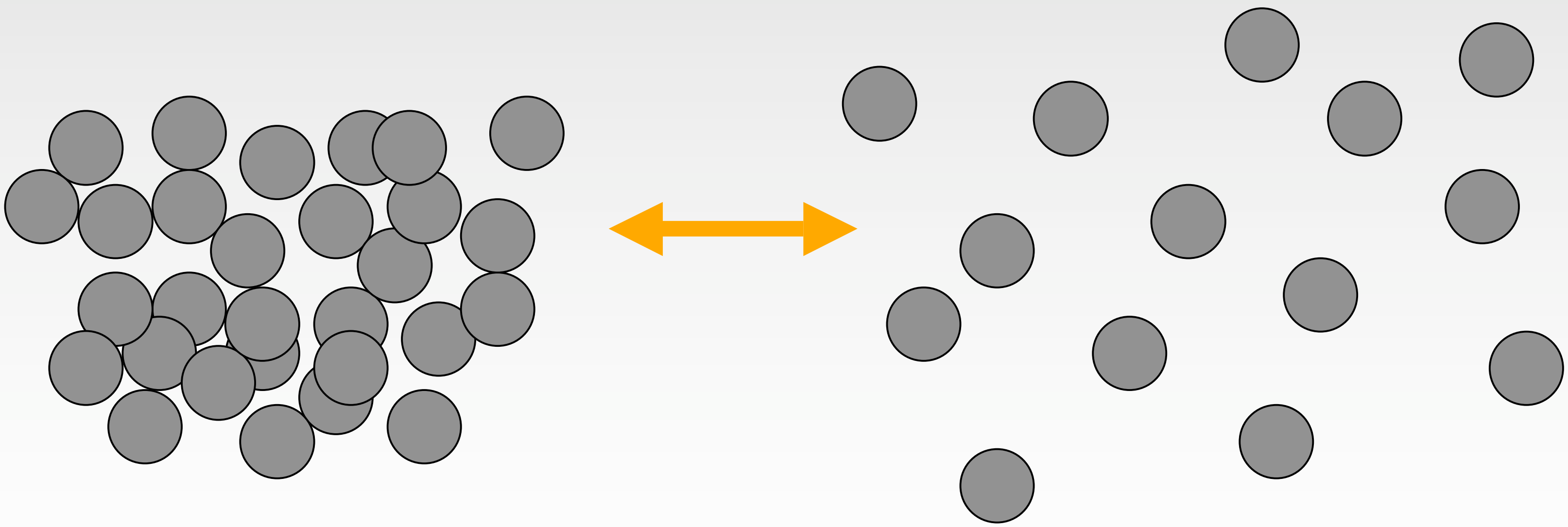




Oxide nanoparticles: $CoFe_2O_4$

Magnetic properties:

Powder **Particles in Wax**

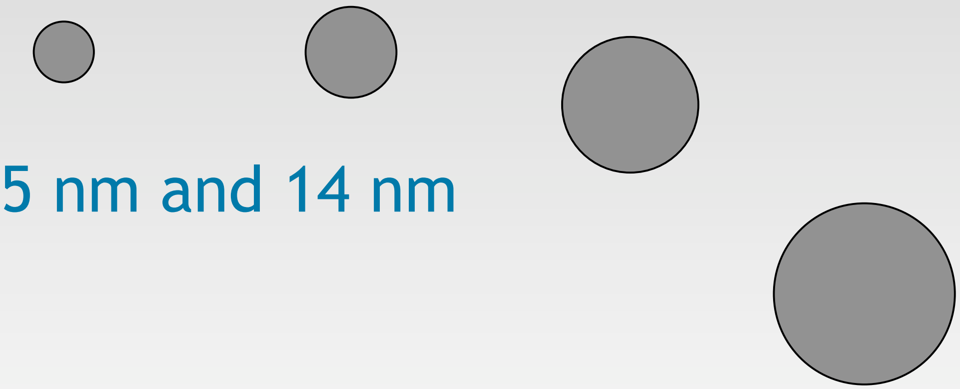


Oxide nanoparticles: $CoFe_2O_4$

Temperature effects:

Hysteresis at low temperature (5K) and at RT (300K)

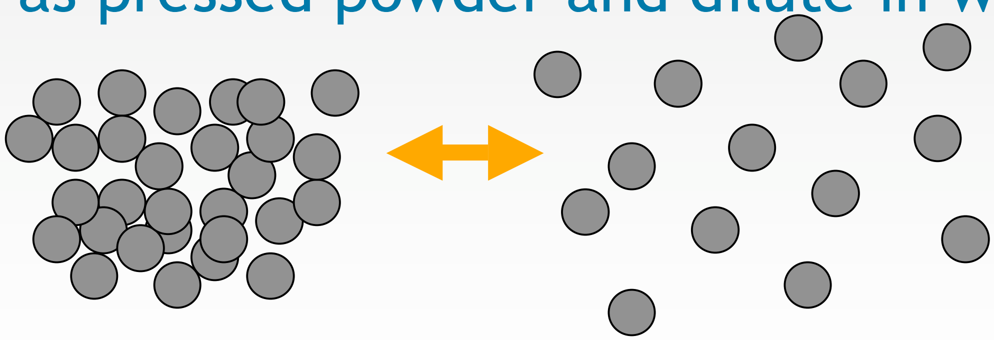
Size effects:



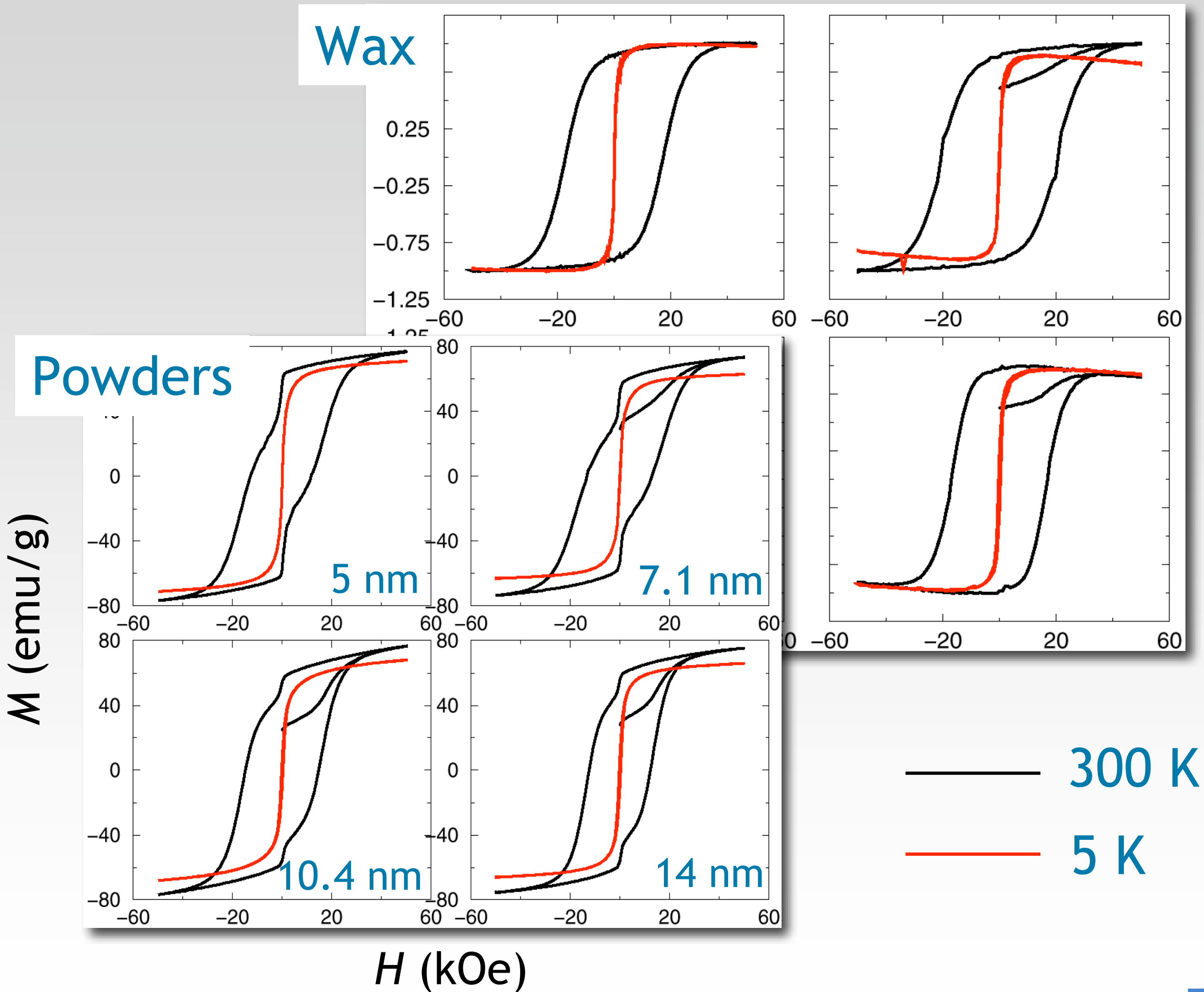
Samples have sizes between 5 nm and 14 nm

Particle interaction effects:

Particles as pressed powder and dilute in wax

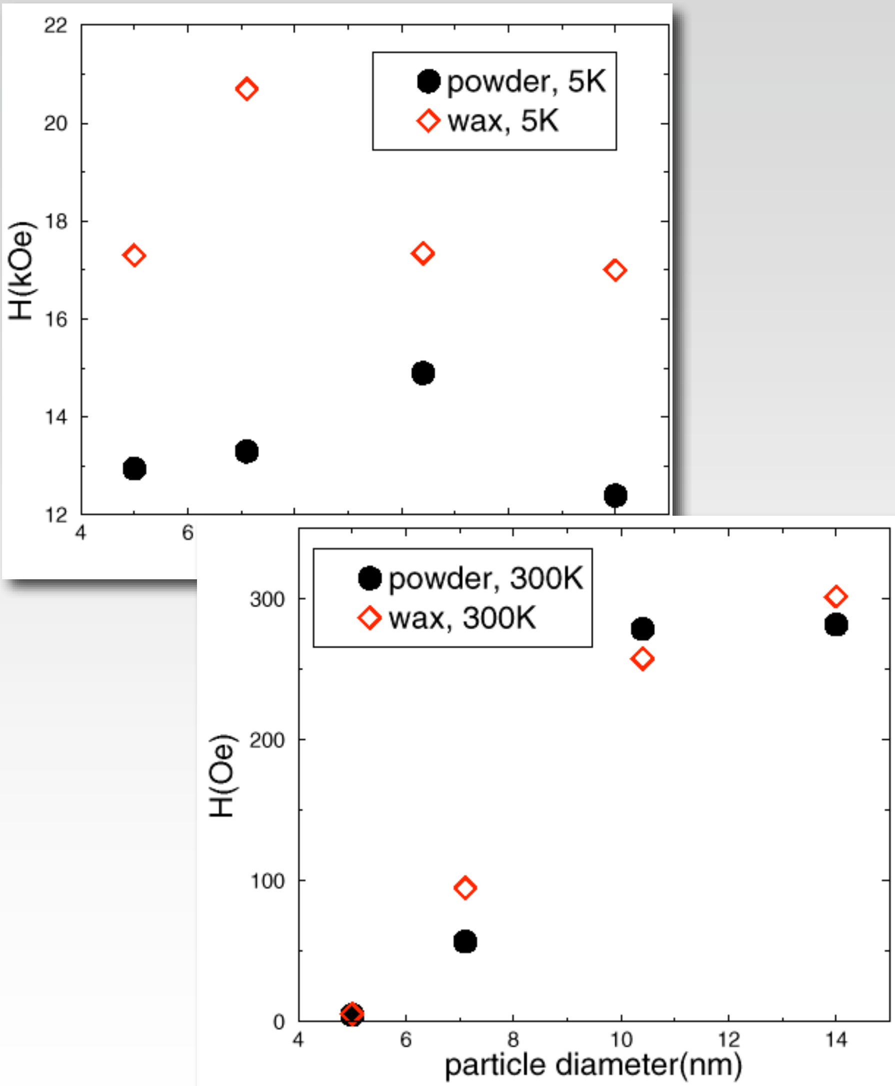


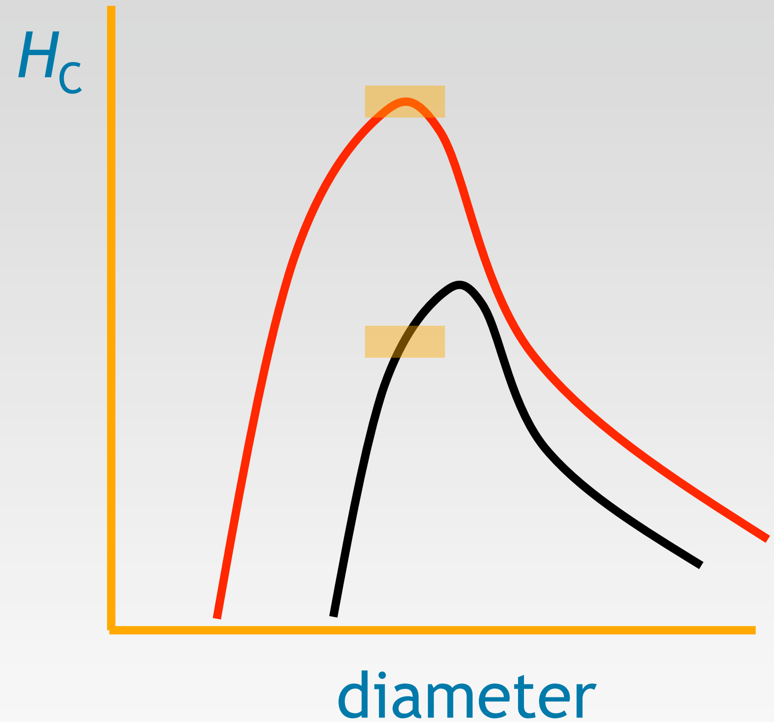
Oxide nanoparticles: $CoFe_2O_4$



UC SANTA BARBARA engineering

Oxide nanoparticles: $CoFe_2O_4$

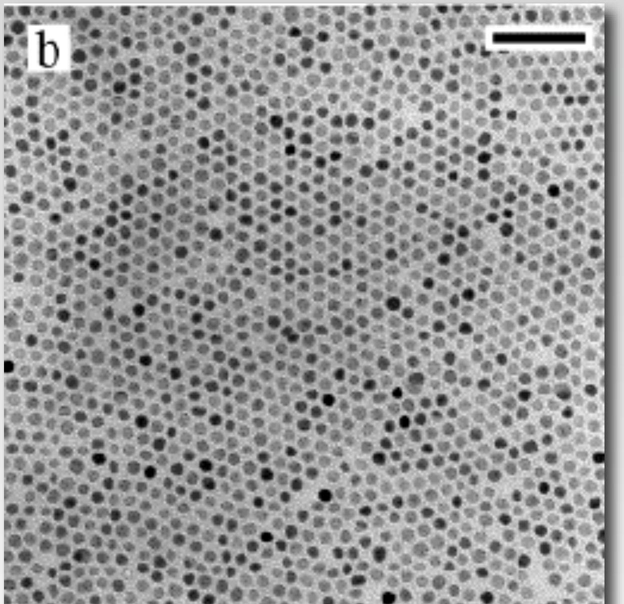




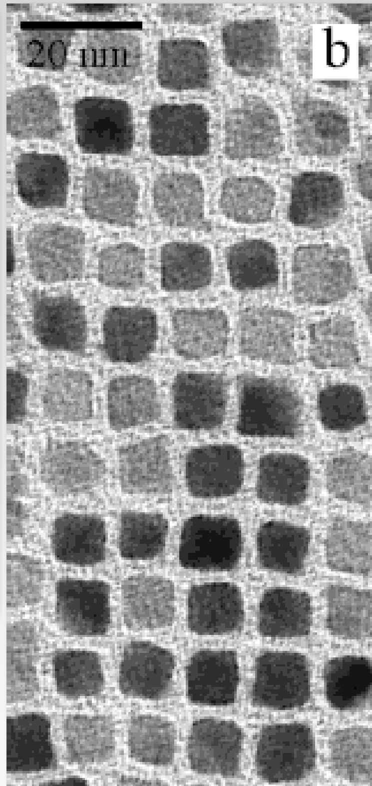
Oxide nanoparticles: $CoFe_2O_4$

- Temperature effects: Coercivity higher at low temperatures
- Size effects: Saturation magnetization does not change with size; coercivity changes with size; blocking temperature increases with size
- Interparticle interaction effect: Coercivity of non-interacting particles is higher. Record at 5 K (near 3 T)
- Shape of hysteresis loop distinct (powder *vs.* wax)
- Blocking temperature increases with dilution
- Remanence ratio increases with dilution

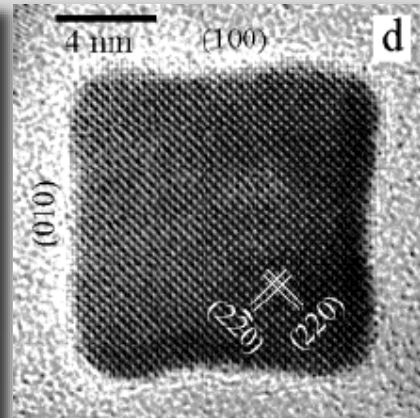
Oxide nanoparticles: $CoFe_2O_4$



7.9 ± 0.5 nm spheres



~9 nm cubes

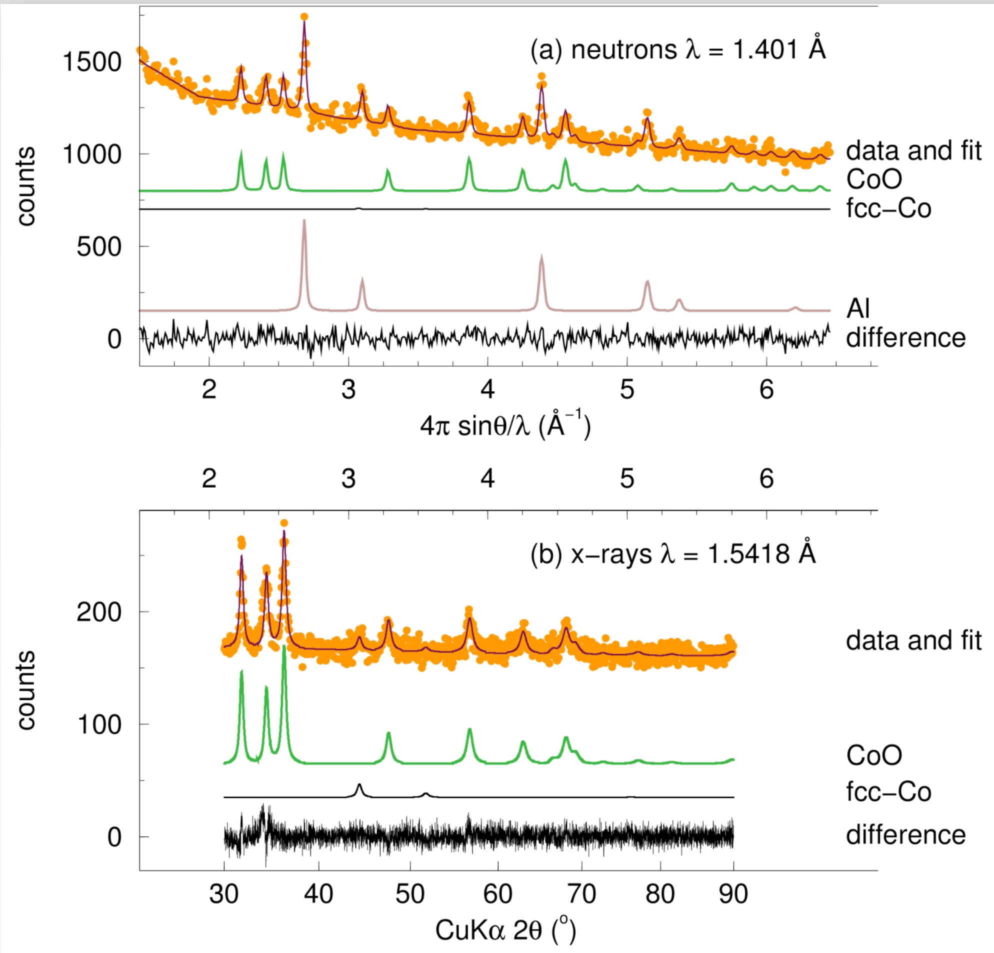


~12 nm cube

Song and Zhang, *J. Am. Chem. Soc.* **126** (2004) 6164.

Oxide nanoparticles: Unusual phases

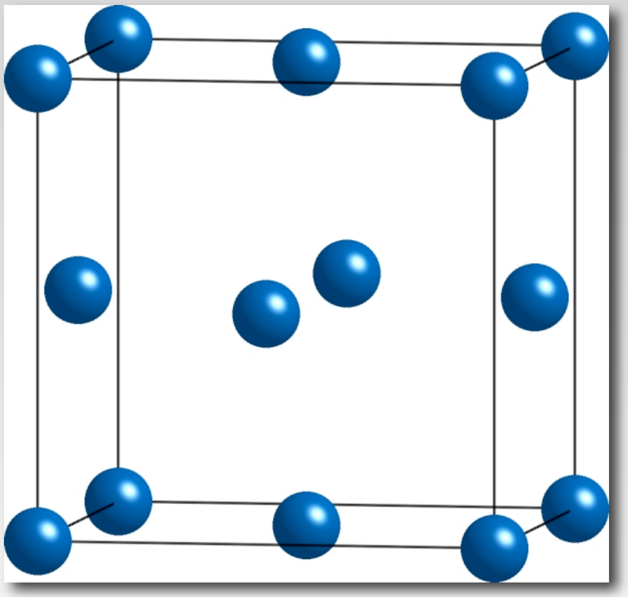
Wurtzite CoO



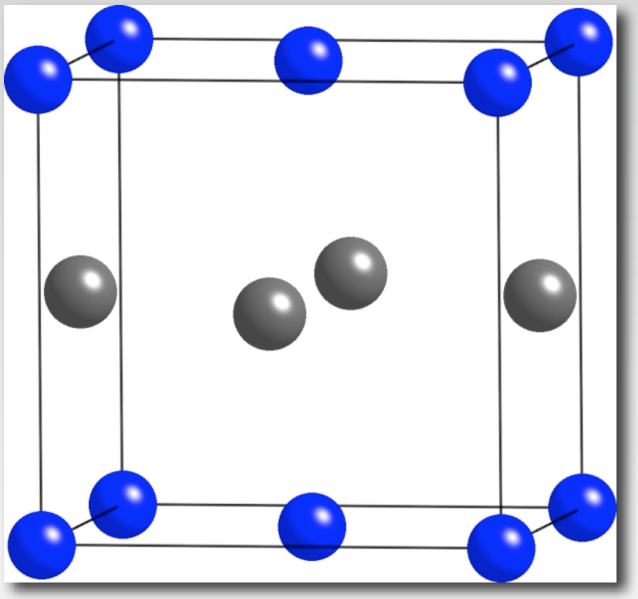
Decomposing Co(acac)$_2$ in refluxing dibenzylether gives CoO in the wurtzite modification.

Risbud *et al. Chem. Mater.* **17** (2005) 834-838.

Intermetallics: FePt



anneal →



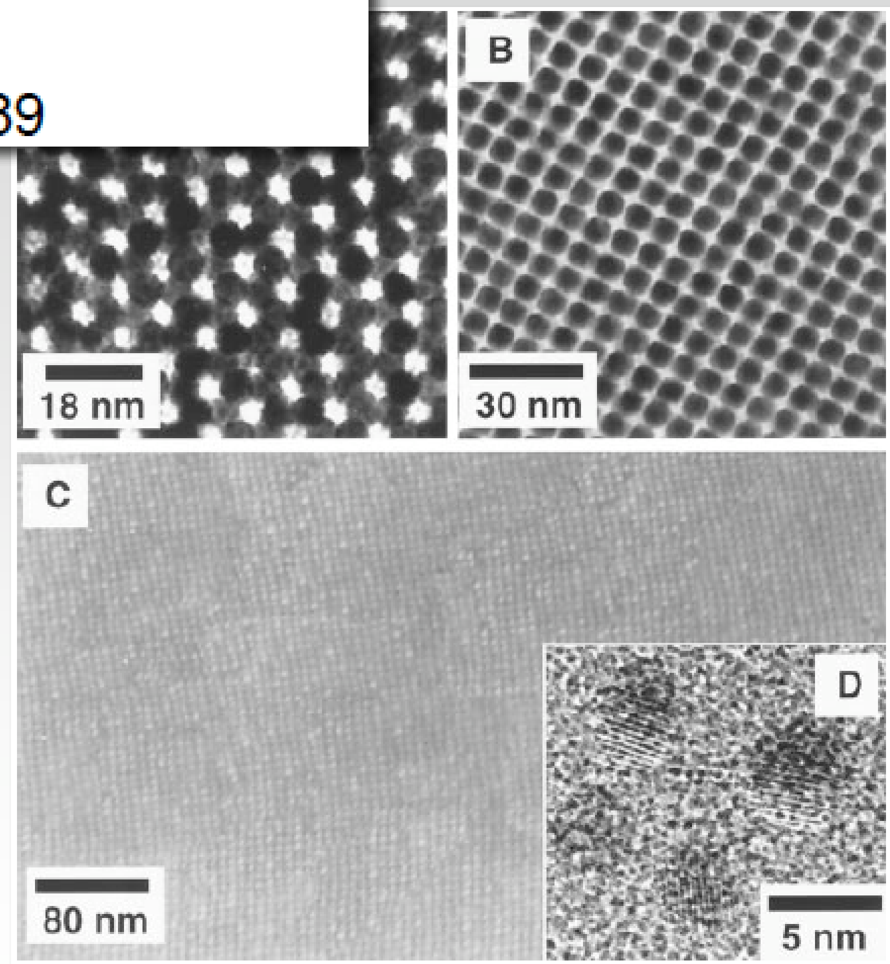
Disordered, *Fm-3m* (225), non-magnetic

Ordered, *P4/mmm* (123), magnetic

Platinum, being heavy, induces spin-orbit coupling, resulting in high *K*

Intermetallics: FePt

Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices
Shouheng Sun, *et al.*
Science **287**, 1989 (2000);
DOI: 10.1126/science.287.5460.1989



Films of nanoparticles annealed to up to 500ºC to induce ordering and coercivity.
5 nm particles are coercive at RT.

Intermetallics: FePt

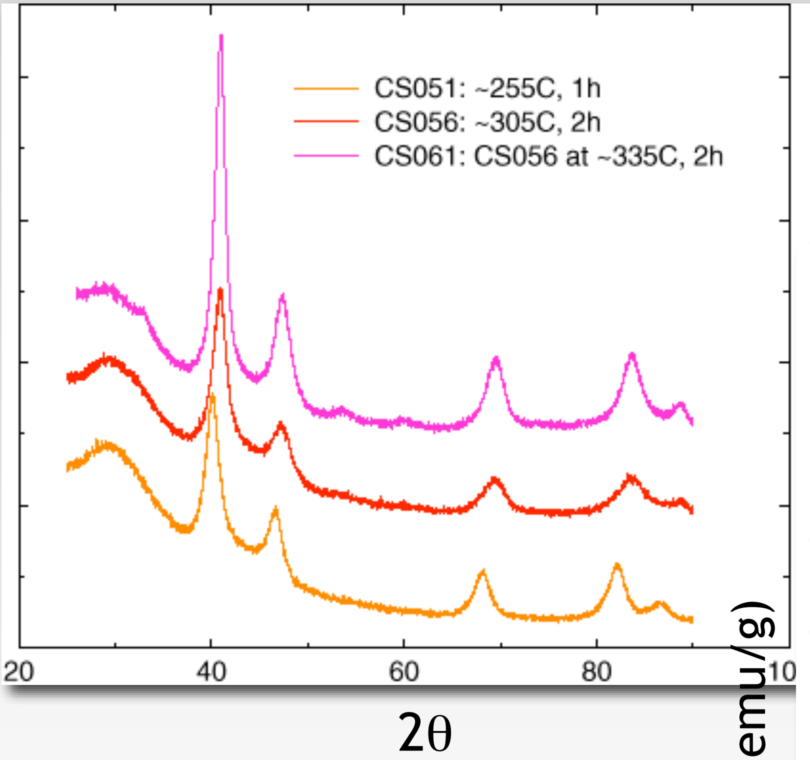
Stoichiometric amounts of $Na_2Fe(CO)_4$ and $Pt(acac)_2$

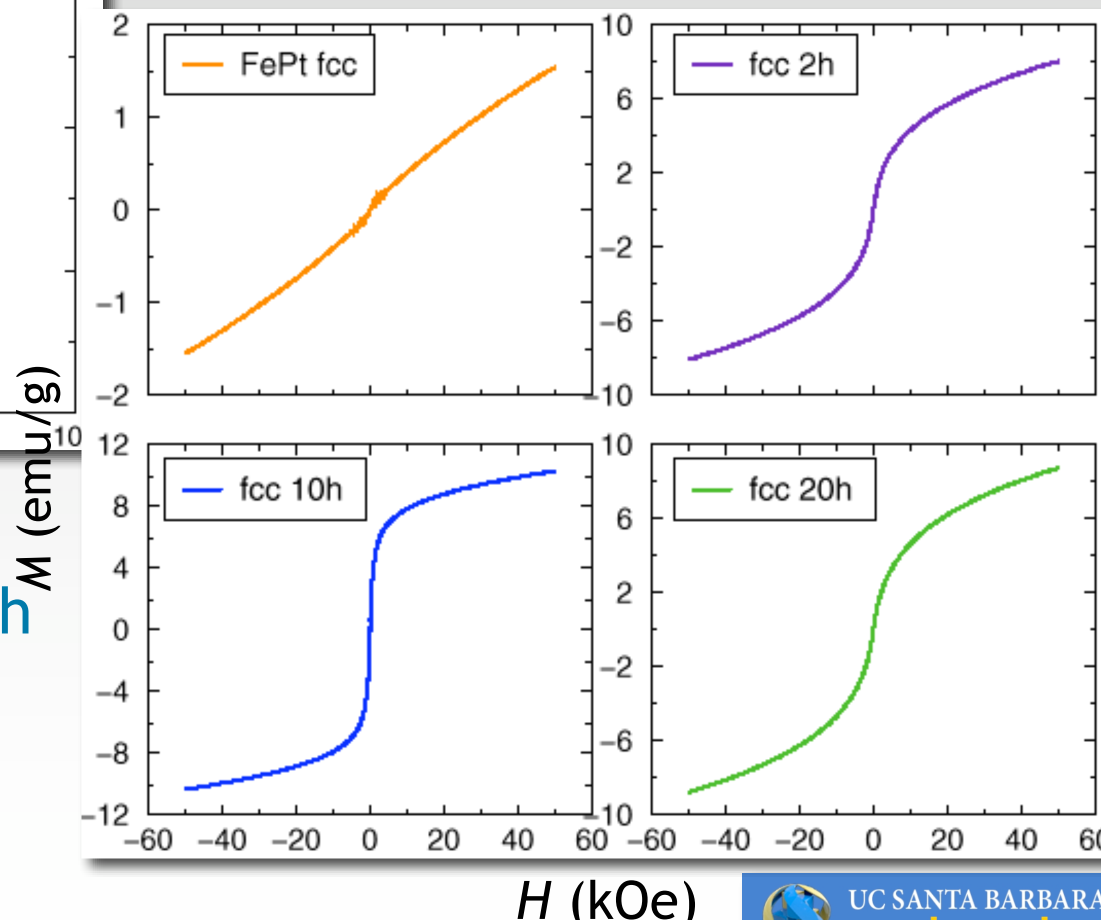
Oleylamine or oleylamine/oleic acid as surfactants

Stir at 70ºC for 1 h, reflux in various solvents

Educts	Solvent	T(ºC)	Time(min)	Phase
reagents	octyl ether	~270	60	fcc
reagents	nonadecane	~310	60	fct
fct sample	tetracosane	~335	120	fct
fcc sample	tetracosane	~336	120	fct
fcc sample	tetracosane	~321	600	fct
fcc sample	tetracosane	~265	1200	fct

Intermetallics: FePt

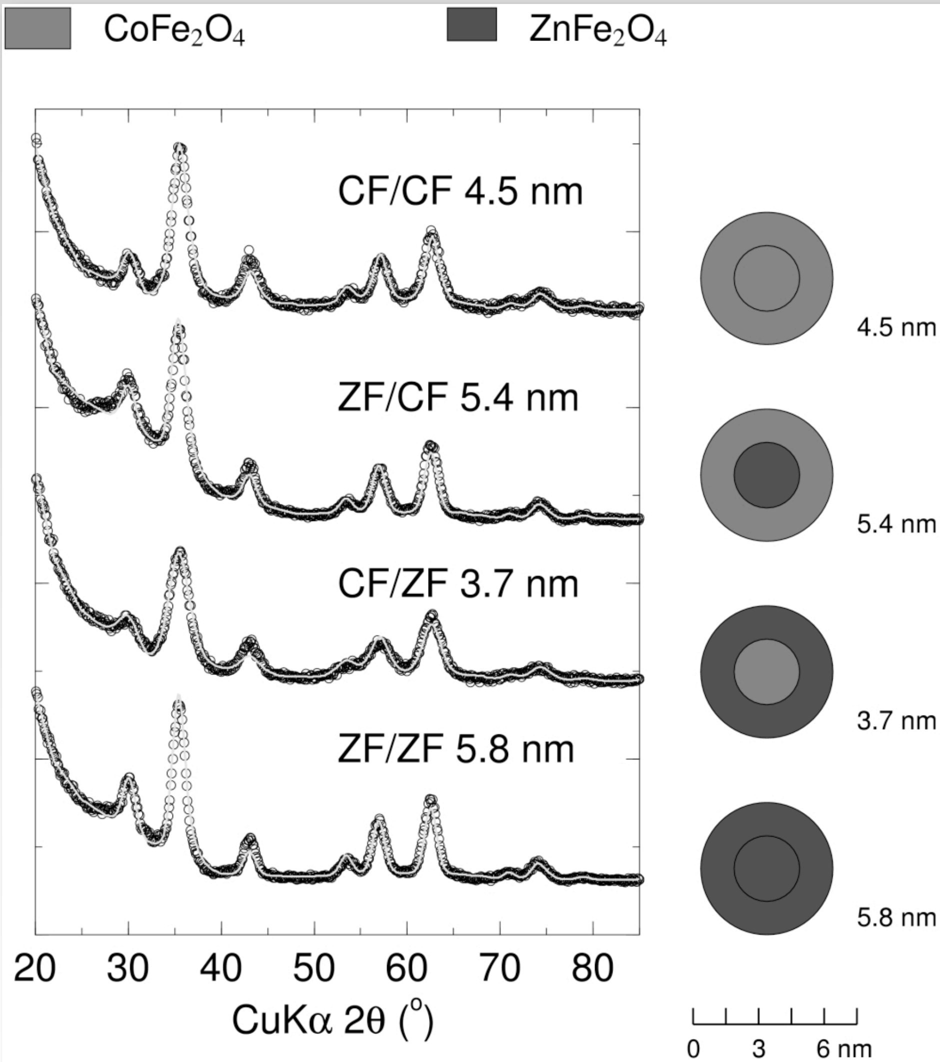




Ordering of atoms in high temperature solvents without increasing particle size.

UC SANTA BARBARA engineering

Oxides: Core/shell magnets; Soft and hard ferrites



Initial experiments:

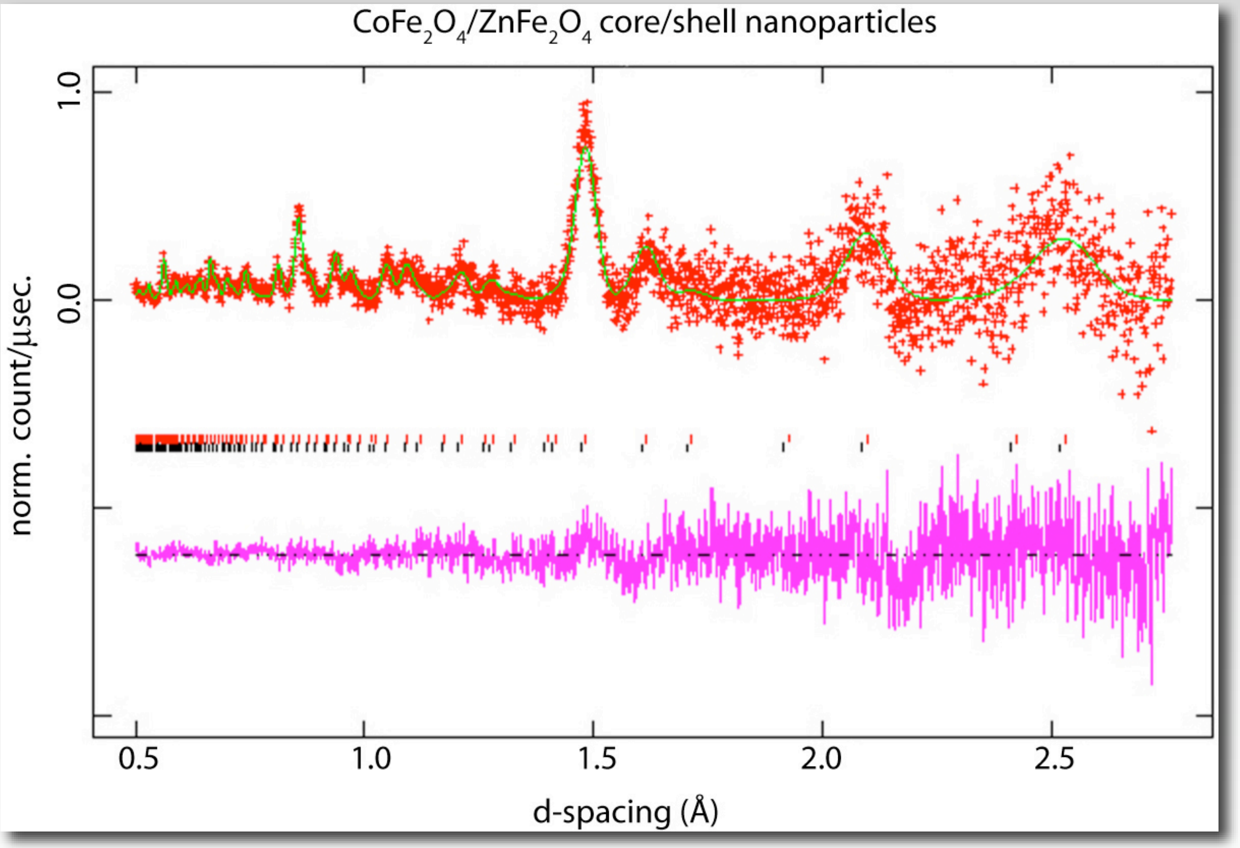
Core grown first (from metal acetylacetonates) and then shell. The idea is to prepare interfaces, such as would be obtained by heteroepitaxy, from solution.

many m^2 of interface rather than mm^2

Spinel $CoFe_2O_4$ is a hard ferrimagnet and $ZnFe_2O_4$ is soft. Lattice parameters are nearly the same.

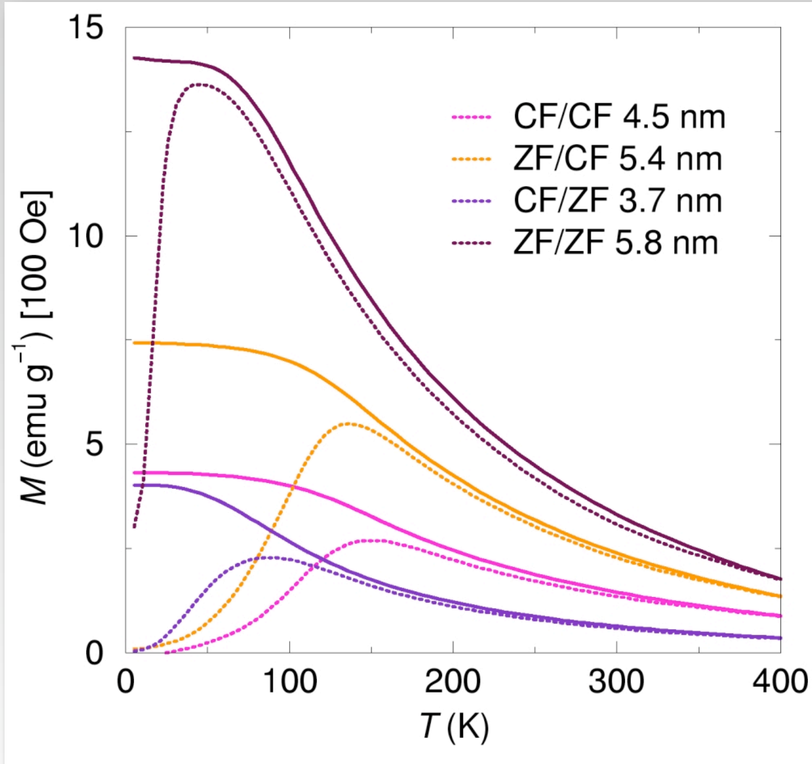
Problem in the characterization: Co, Fe, Zn are nearly indistinguishable by x-rays and by electrons

Oxides: Core/shell magnets; Soft and hard ferrites

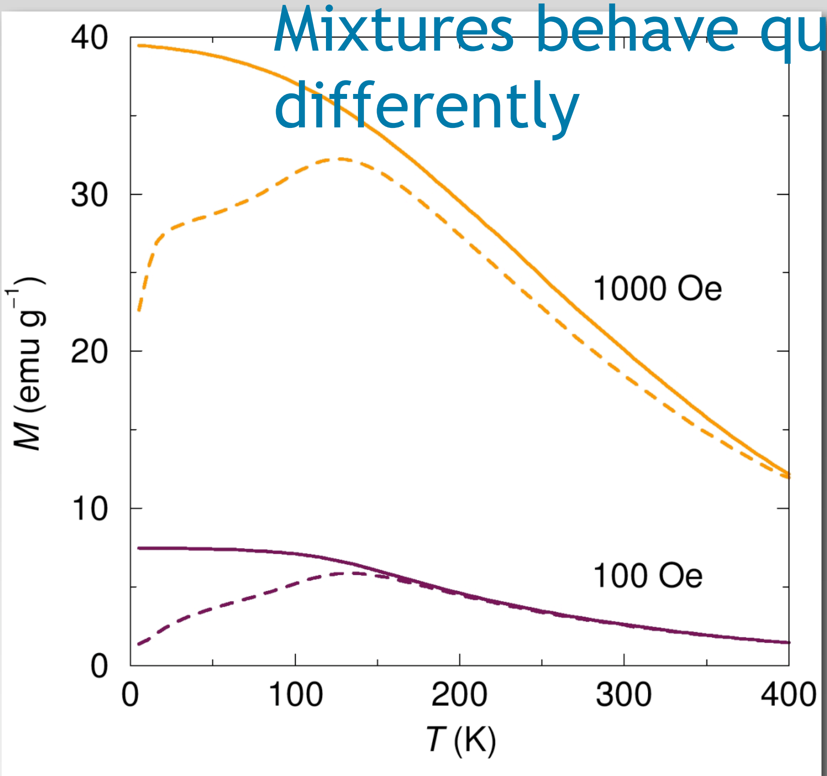


Neutron data from NPDF, Los Alamos, fitted using a two-spinel model.

Oxides: Core/shell magnets; Soft and hard ferrites



Mixtures behave quite differently

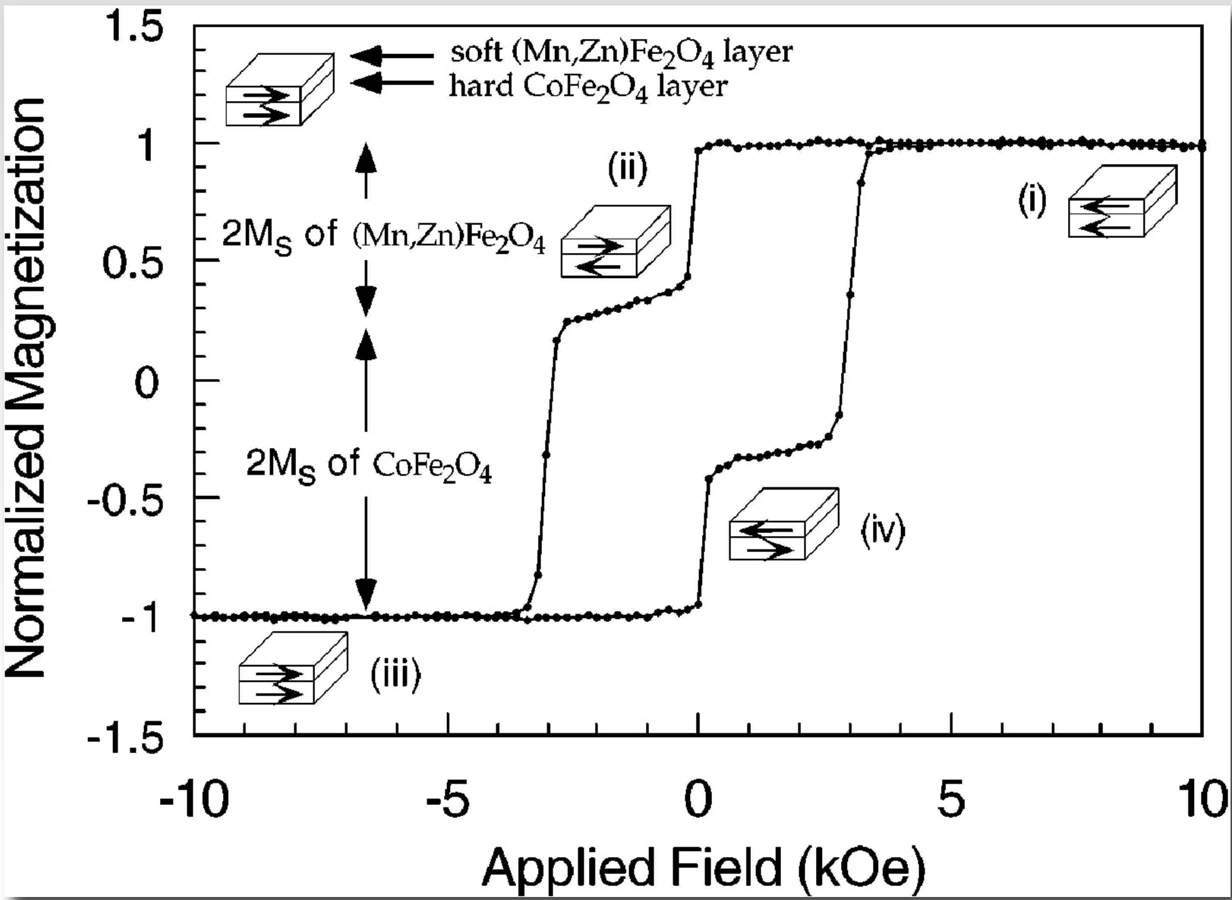


Single blocking temperature: The blocking temperature of the core/shell nanoparticles increases with the amount of hard magnetic material.

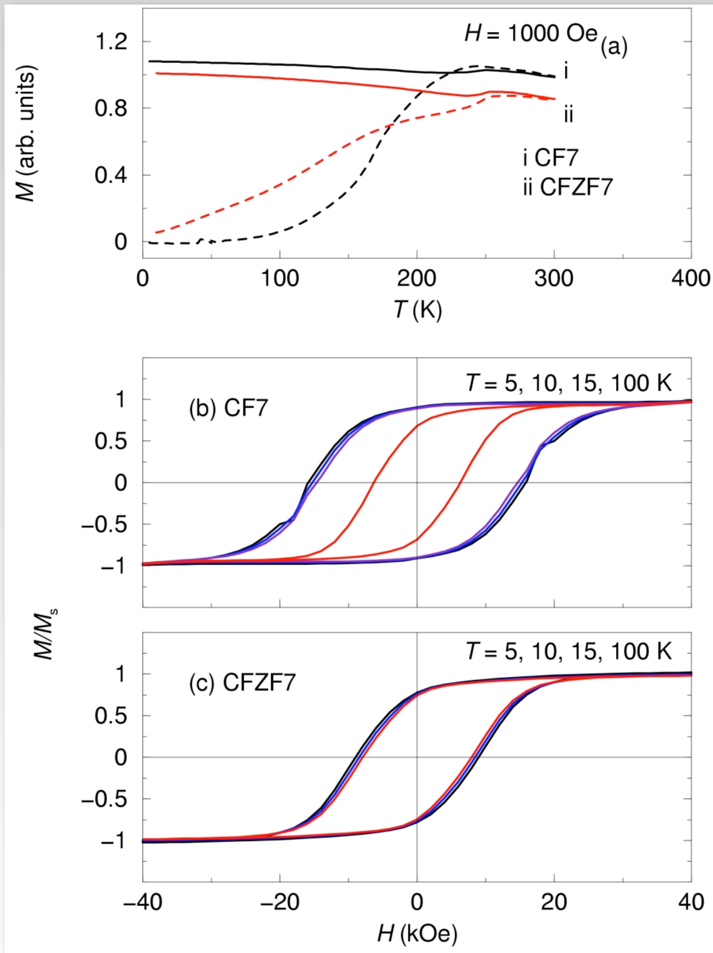
UC SANTA BARBARA engineering

Oxides: Core/shell magnets; Soft and hard ferrites

How should the magnetic interface behave ?
Epitaxial thin film results from Y. Suzuki, *Annu. Rev. Mater. Res.*



Oxides: Core/shell magnets; Soft and hard ferrites



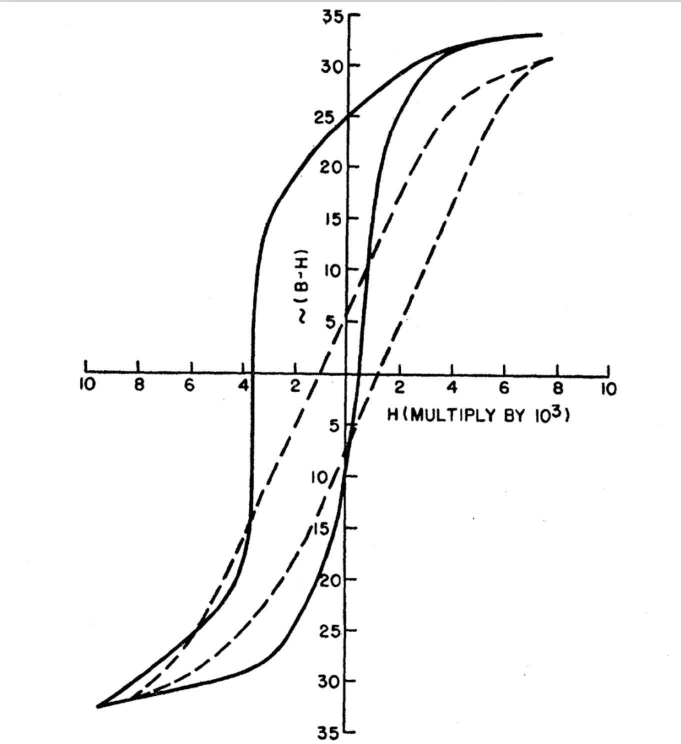
dispersed in wax

Smooth scaling of coercivity with increasing amounts of the soft component.

Masala *et al.*, *Solid State Sci.* **8** (2006) 1015–1022.

Oxides: Core/shell magnets; ferri/antiferro

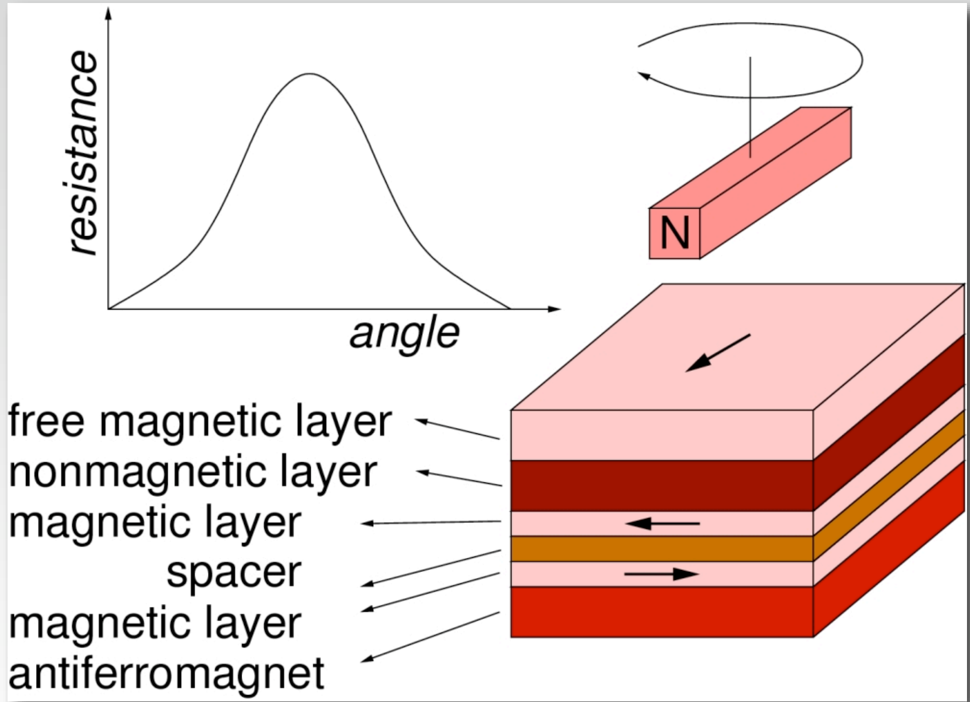
Co/CoO



Hysteresis loops of fine oxide-coated particles of cobalt taken at 77°K. The dashed lines show the hysteresis loop when the material is cooled in the absence of a magnetic field. The solid lines show the hysteresis loop when the material is cooled in a saturating magnetic field.

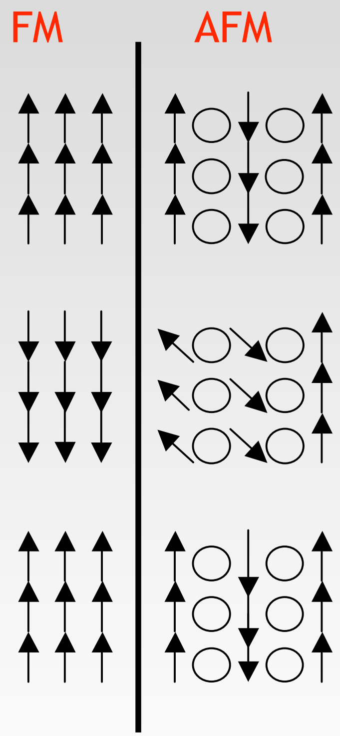
Meiklejohn, Bean, *Phys. Rev.* 102 (1956) 1413.

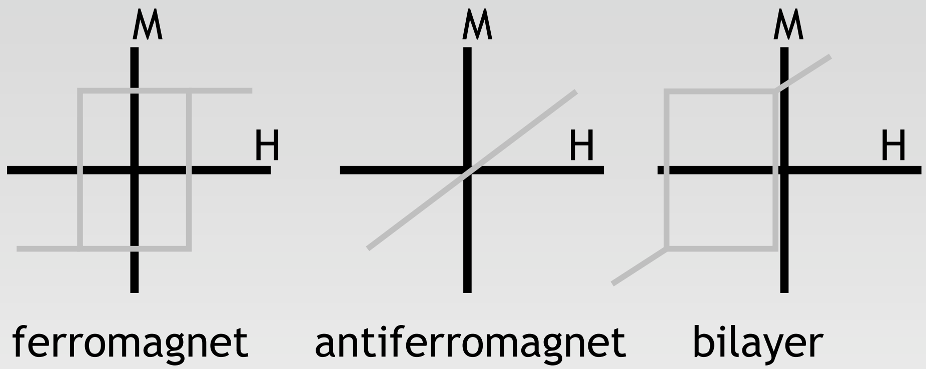
Magnetoresistive angle sensor:



Modified from Grünberg, *Phys. Today* 54 (2001) 34

Oxides: Core/shell magnets; ferri/antiferro





spins of FM are pinned to those of the AFM

additional energy (crystal anisotropy of AFM)

Oxides: Core/shell magnets; ferri/antiferro

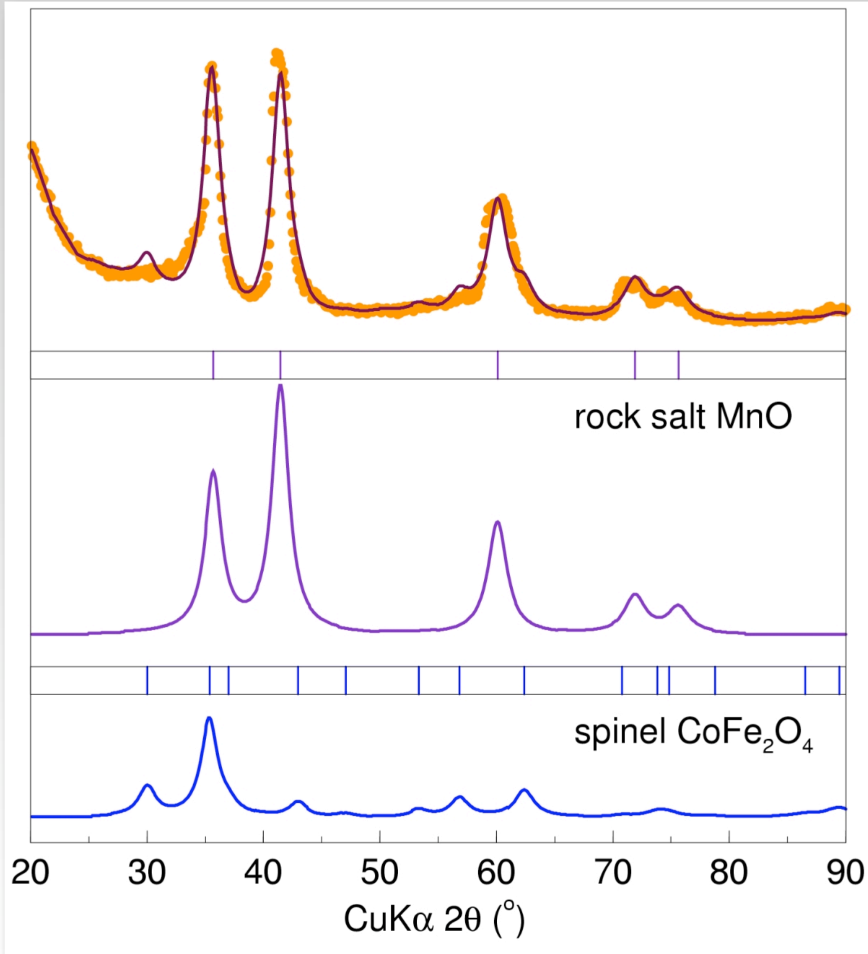
Preparation:

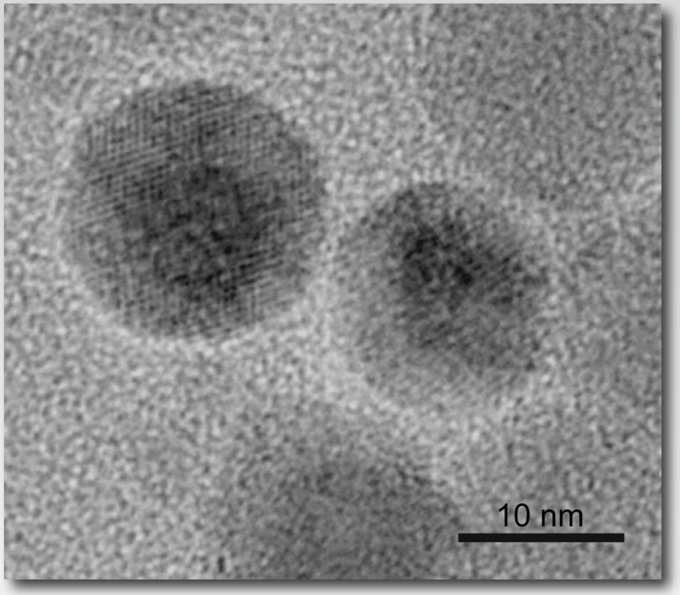
$CoFe_2O_4$ (core), $Mn(acac)_2$

Oleylamine/oleic acid

200^{o}C and reflux in benzyl ether

Oxides: Core/shell magnets; ferri/antiferro



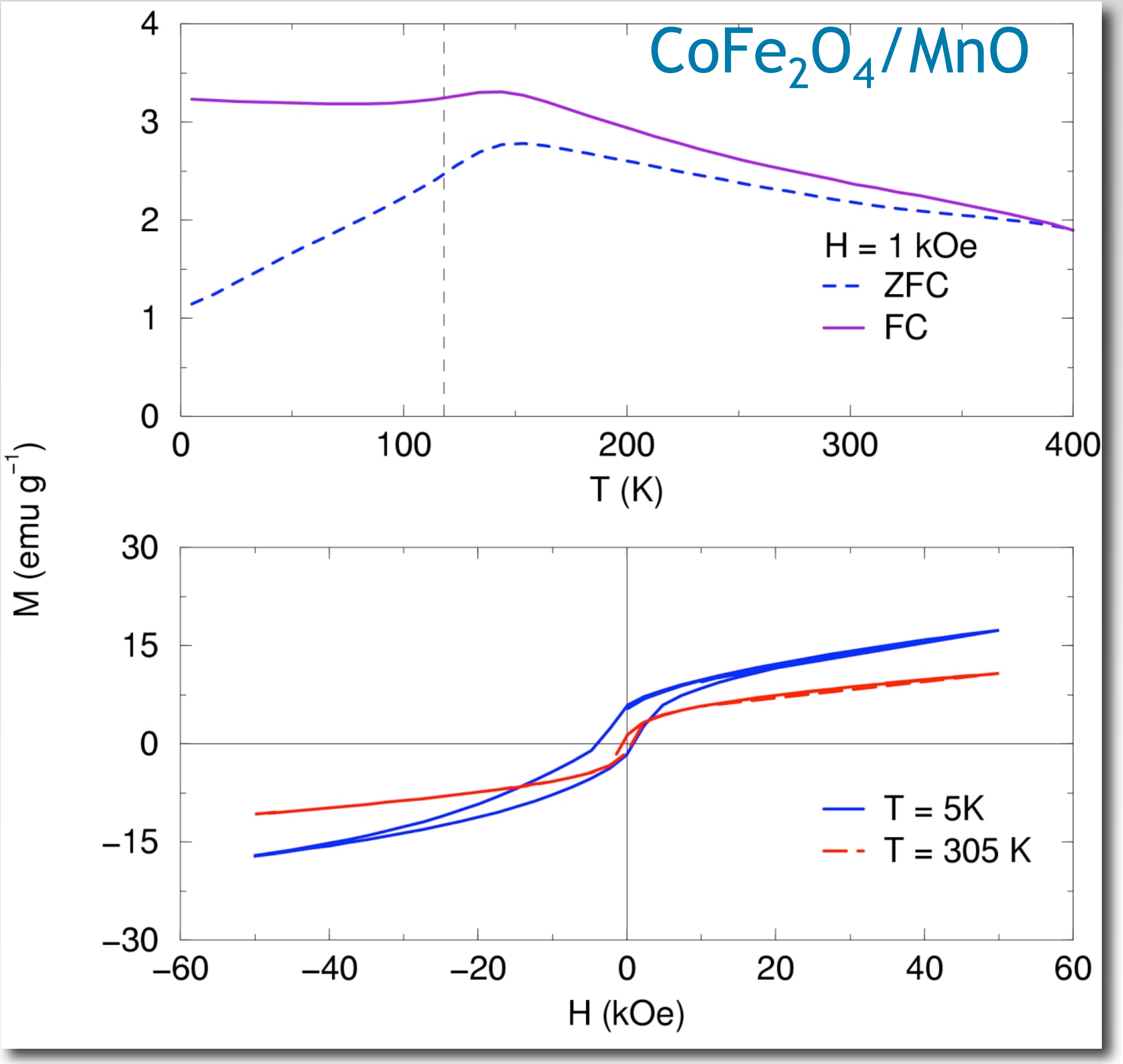


Antiferomagnetic MnO grown over ferrimagnetic $CoFe_2O_4$.

The phases become visible by TEM because they are structurally distinct.

X-ray diffraction indicates the clear presence of two phases; rock salt MnO and spinel $CoFe_2O_4$

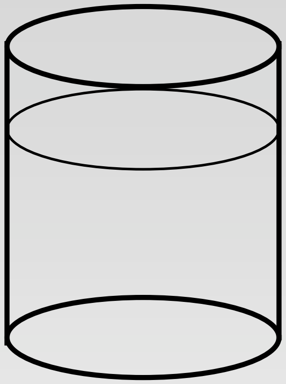
Oxides: Core/shell magnets; ferri/antiferro



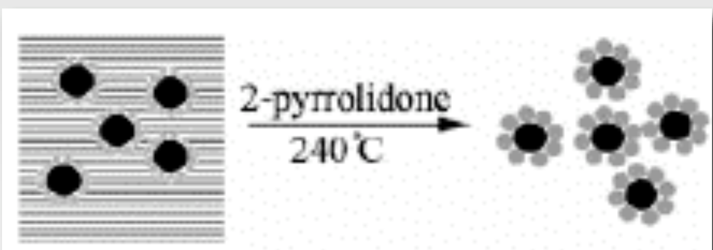
Exchange biasing.

O. Masala and R. Seshadri, *J. Am. Chem. Soc.* **127** (2005) 9354-9355.

Oxides: Molten salt prepn. of complex oxides

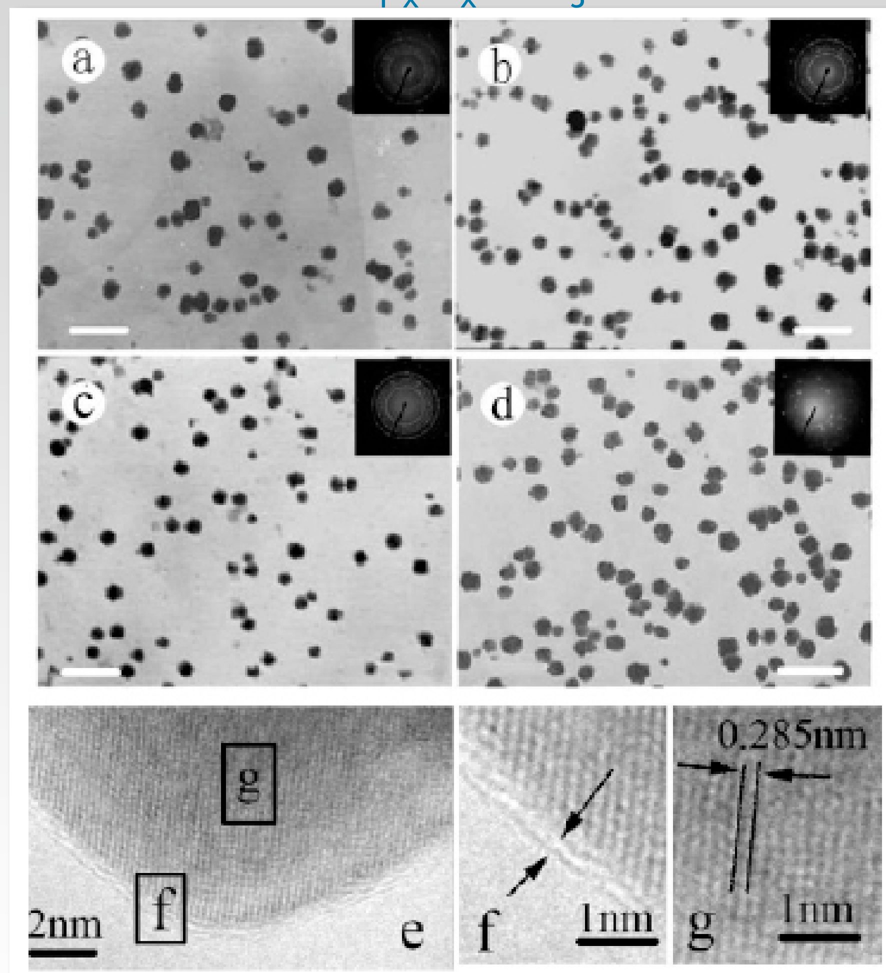


Oxide prepared from nitrates in $NaNO_3/KNO_3$ flux



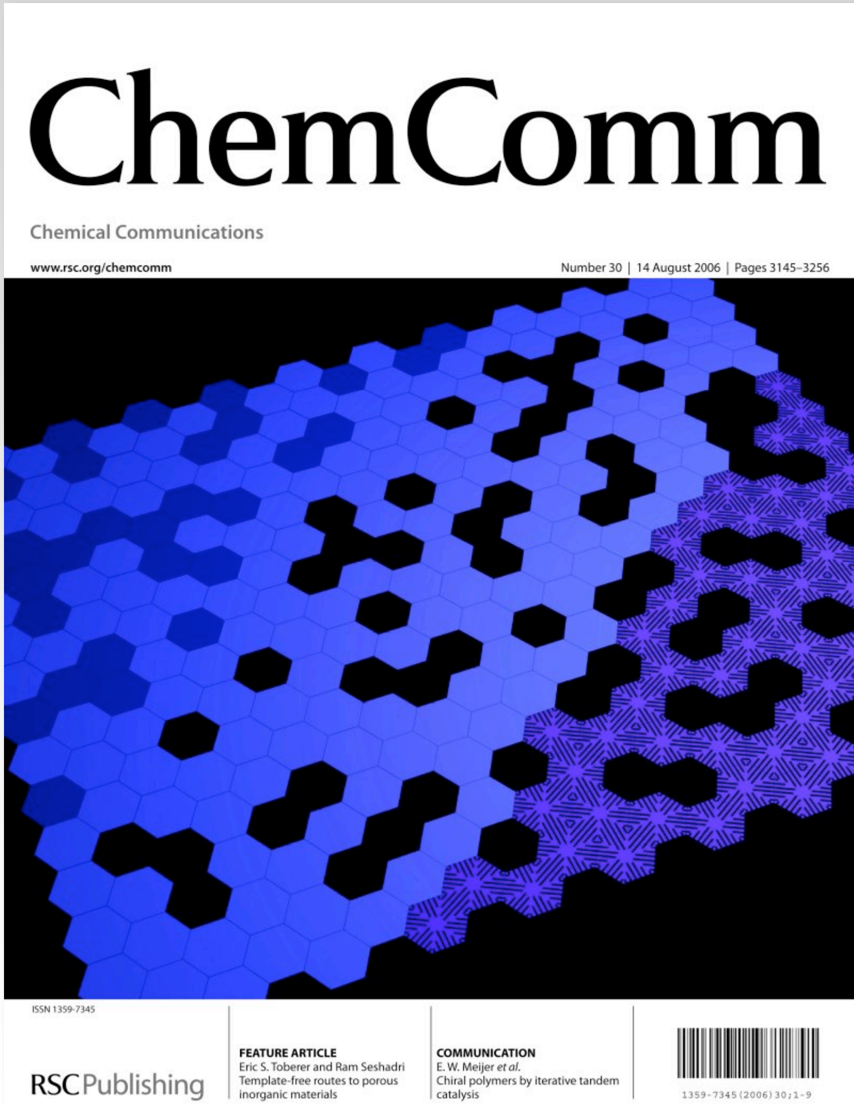
Refluxing in 2-pyrrolidone caps and disperses particles

$La_{1-x}Sr_xMnO_3$



Y. Tian, D. Chen, and X. Jiao, *$La_{1-x}Sr_xMnO_3$ (x = 0, 0.3, 0.5, 0.7) Nanoparticles nearly freestanding in water: Preparation and magnetic properties, Chem. Mater.* **18** (2006) 6088-6090.

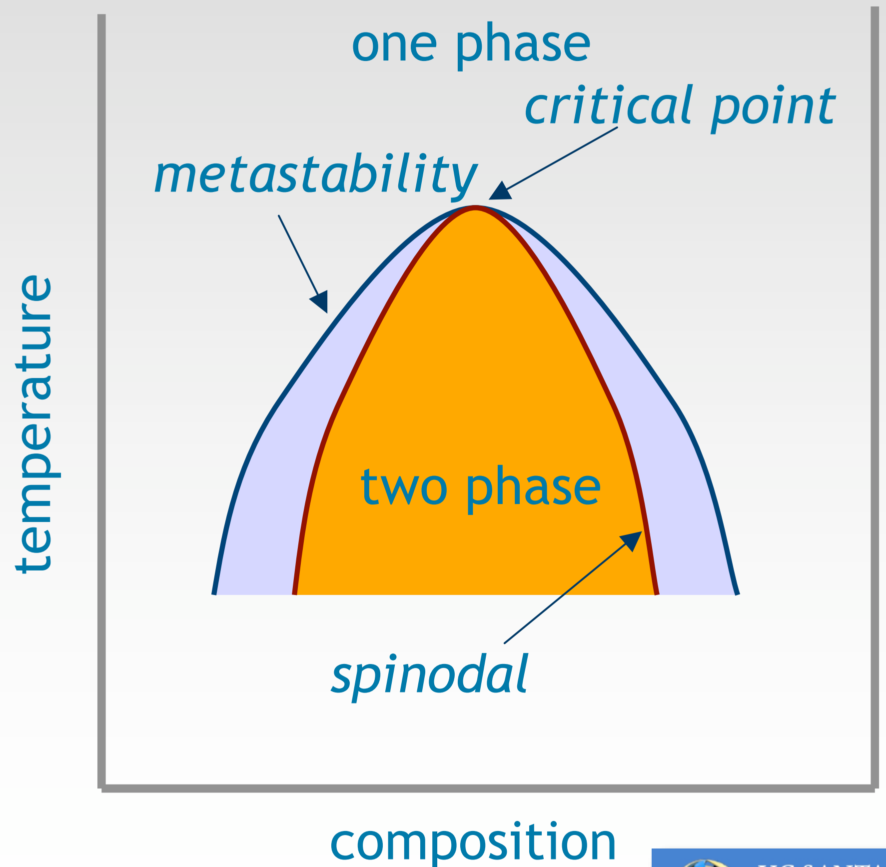
Spontaneously formed magnetic nanocomposites



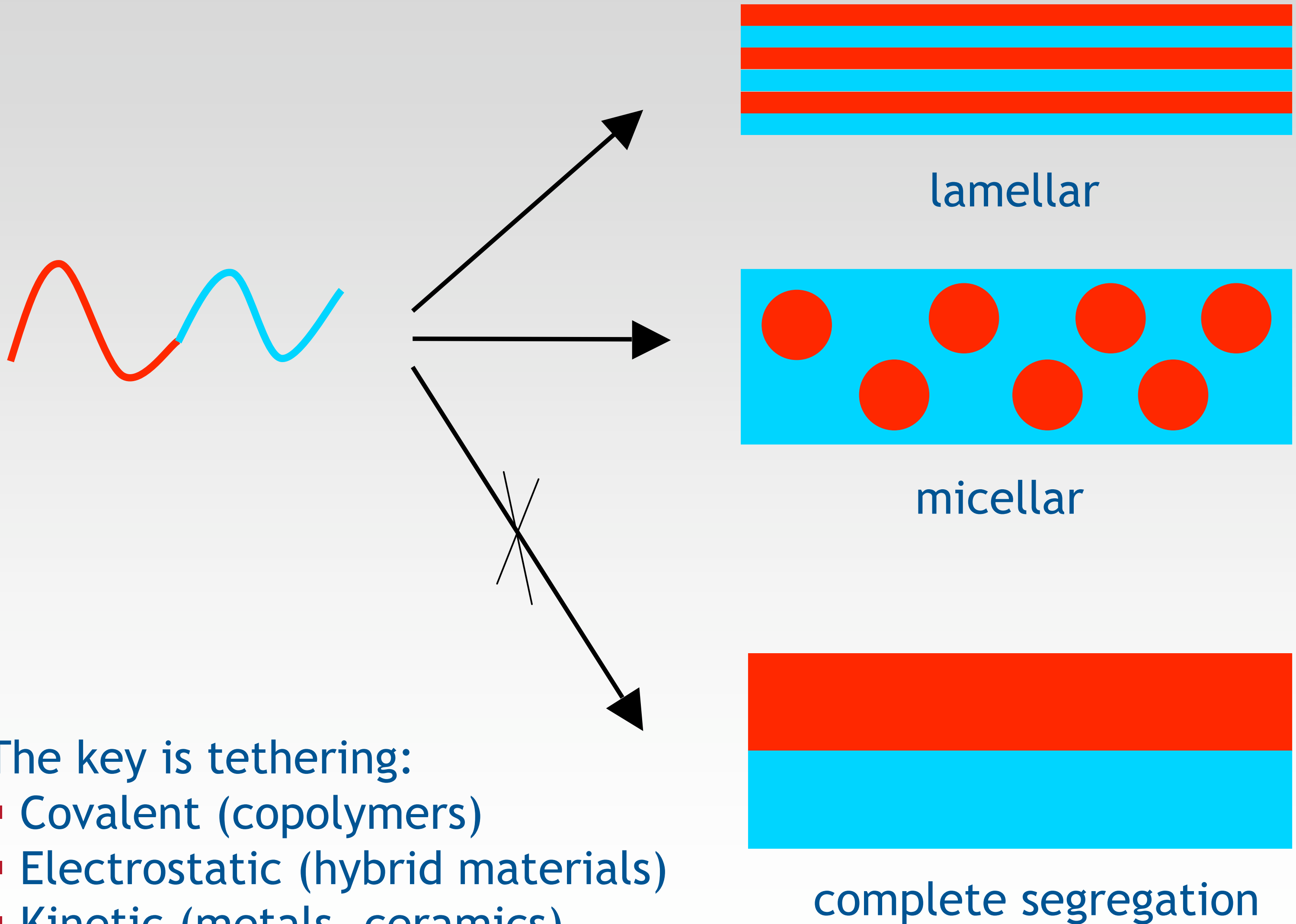
E. S. Toberer and R. Seshadri, Template-free routes to porous inorganic materials, *J. Chem. Soc. Chem. Commun.* (2006) 3159-3165.

Spontaneously formed magnetic nanocomposites

- Phase segregation in block copolymers and polymer melts
- The formation of Raney Ni
- Spinodal decompositions



Spontaneously formed magnetic nanocomposites



The key is tethering:

- Covalent (copolymers)
- Electrostatic (hybrid materials)
- Kinetic (metals, ceramics)

UC SANTA BARBARA engineering

Spontaneously formed magnetic nanocomposites

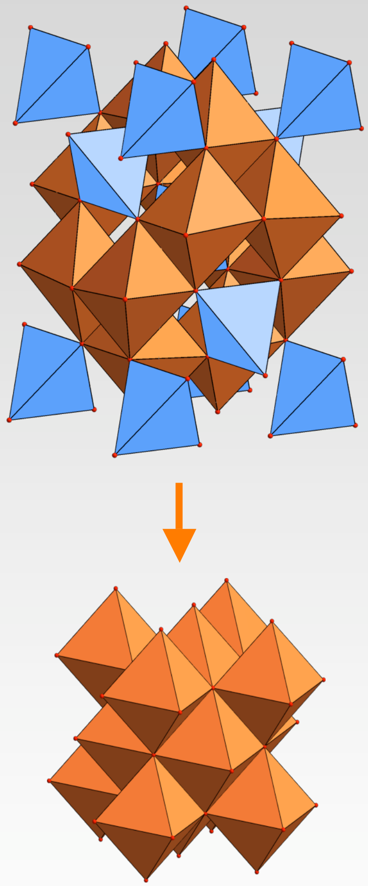
$ZnMn_2O_4$ (hæterolite)
pellet in flowing H_2

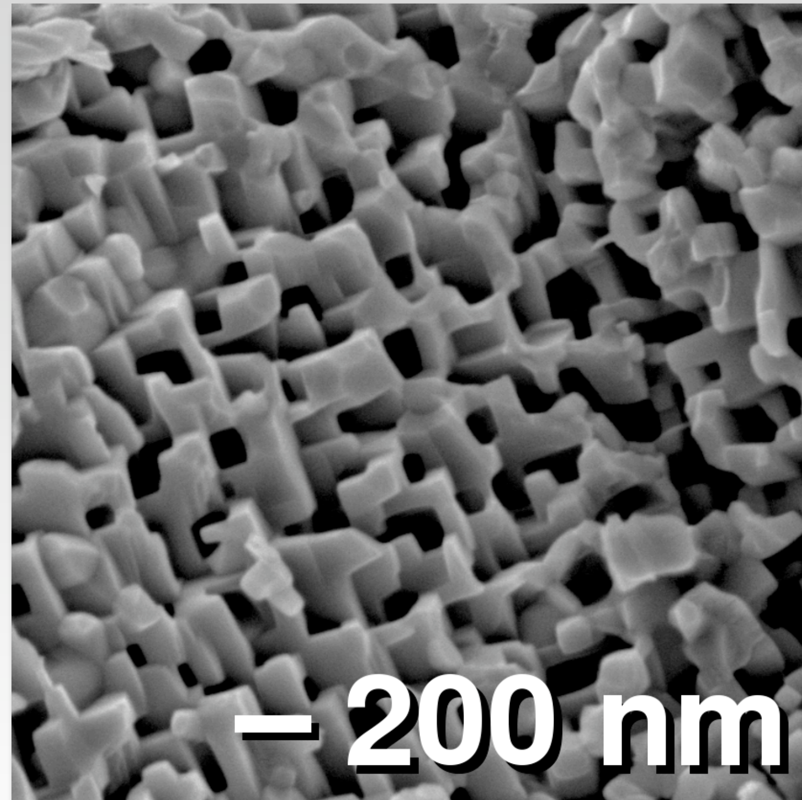
↓ 700 K

$Zn_{0.33}Mn_{0.66}O$

↓ 900 K

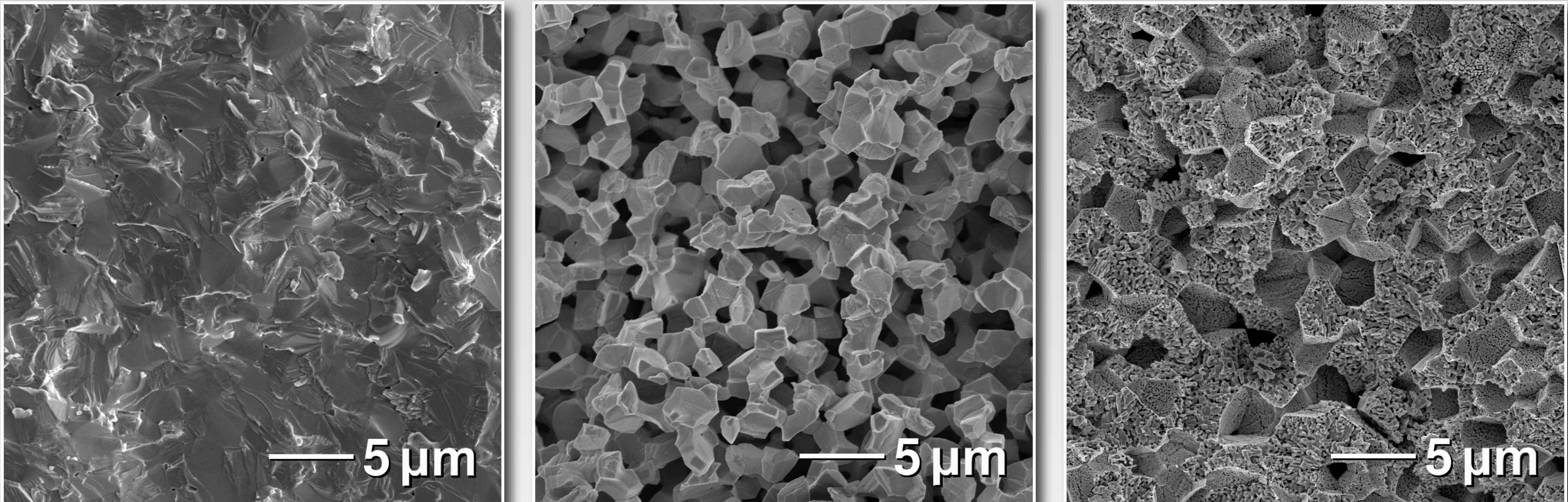
$Zn_{0.1}Mn_{0.9}O$ + Zn(g)



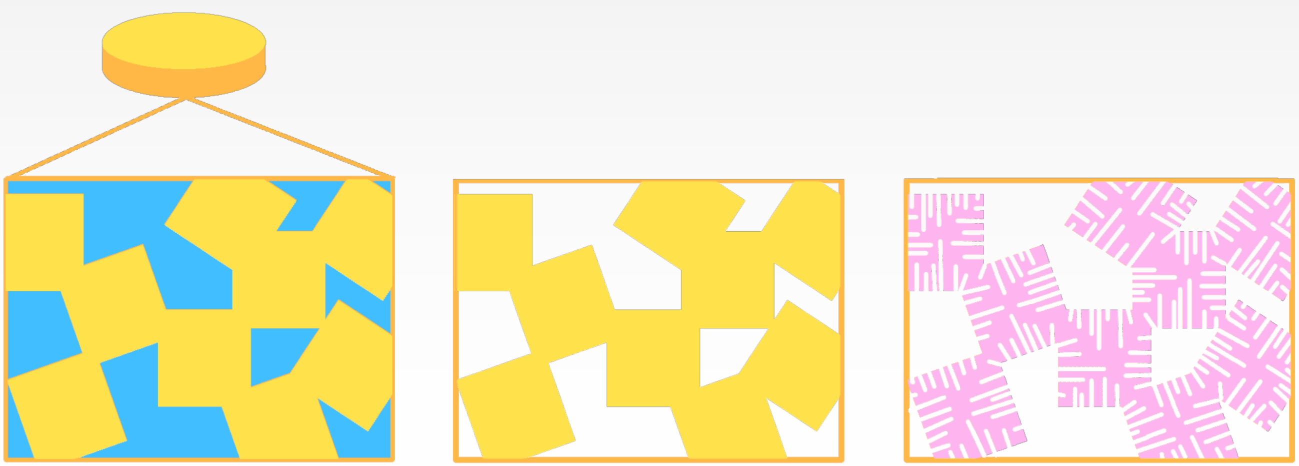


Toberer and Seshadri, *Adv. Mater.* **17** (2005) 2244

Spontaneously formed magnetic nanocomposites



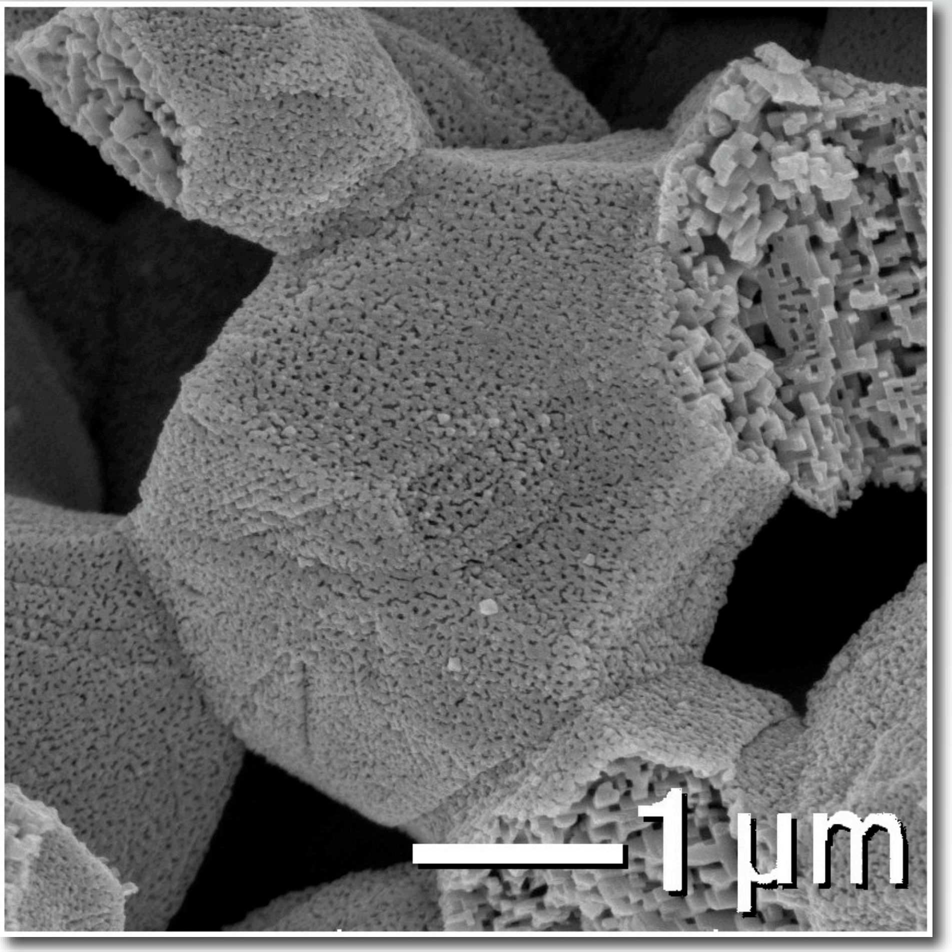
9 ZnO / $ZnMn_2O_4$ → $ZnMn_2O_4$ → rock salt $Zn_{0.1}Mn_{0.9}O$



UC SANTA BARBARA engineering

Spontaneously formed magnetic nanocomposites

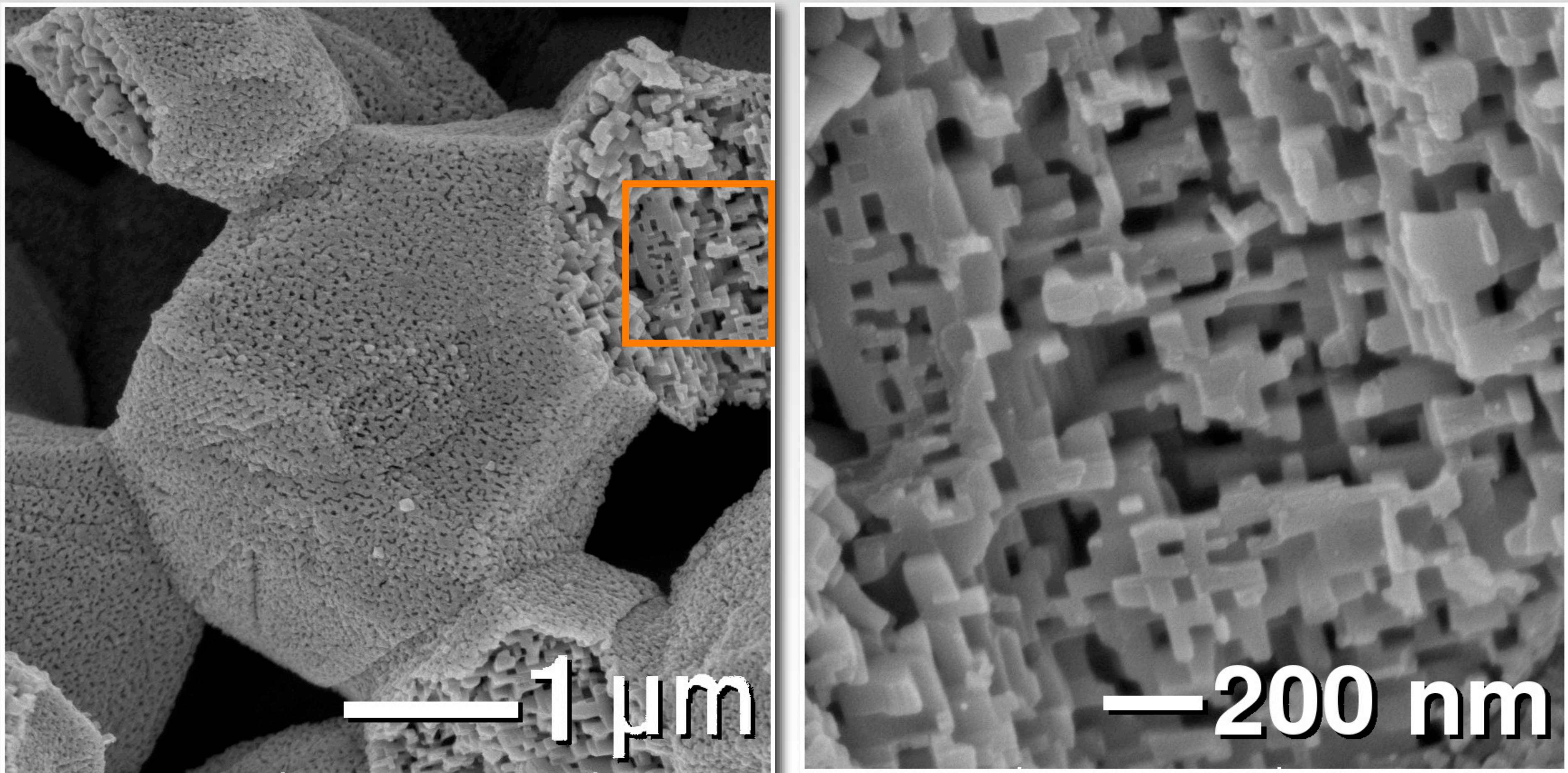
Hierarchically Porous Mn



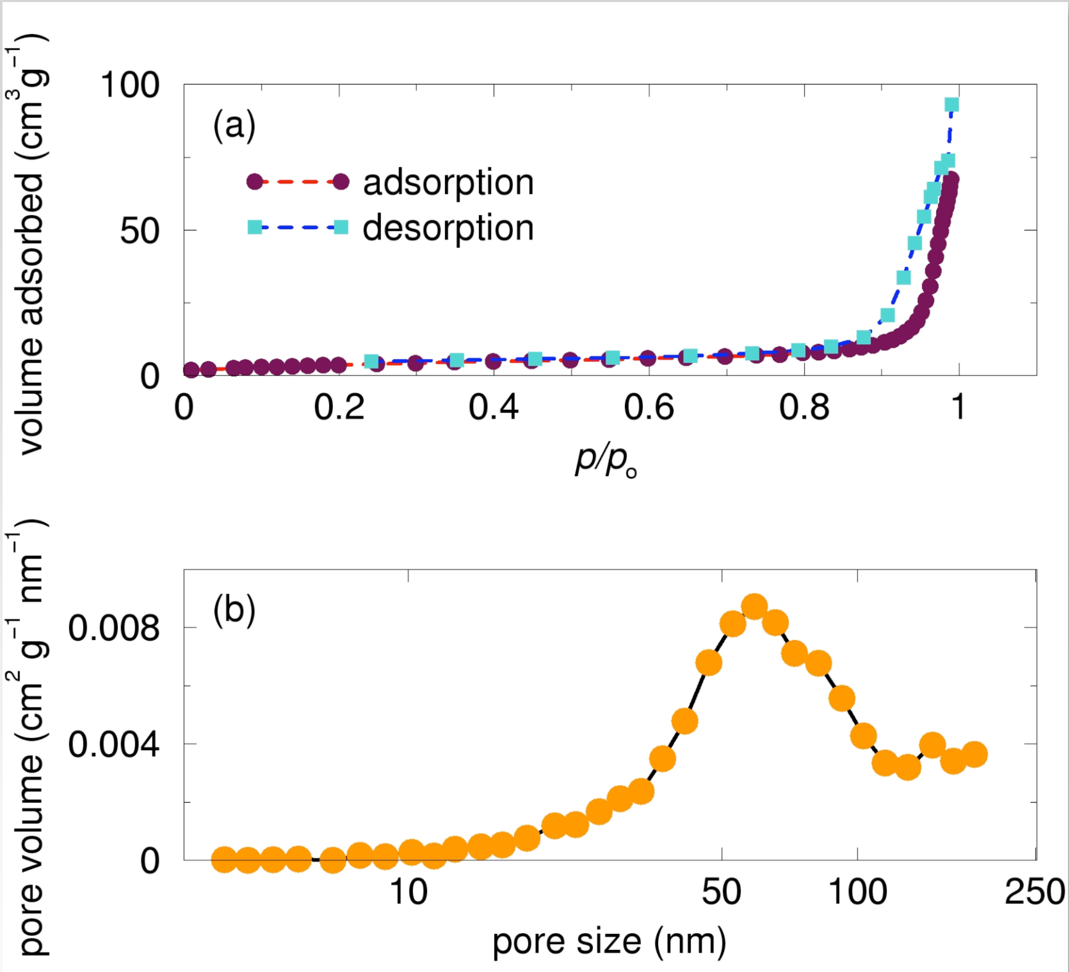
Macropore network remains intact and grains remain well-connected

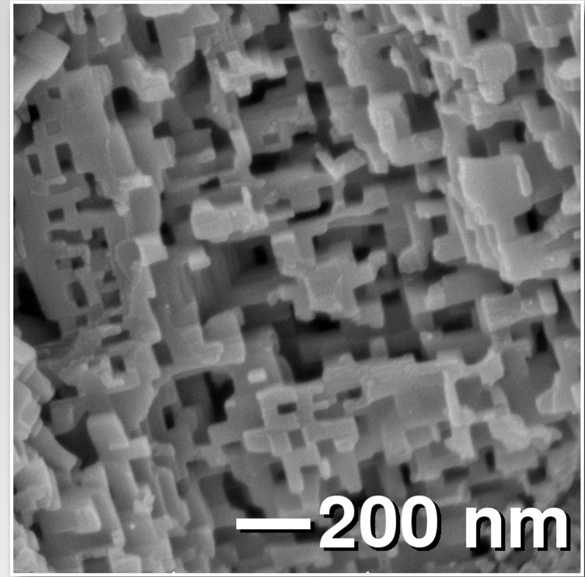
Spontaneously formed magnetic nanocomposites

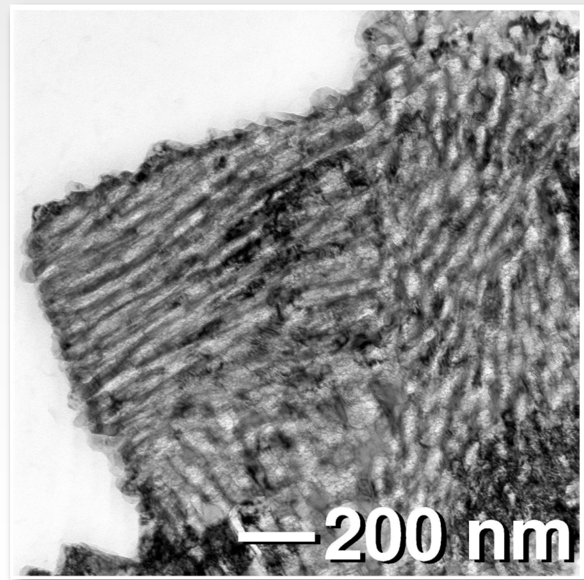
Hierarchically Porous Mn



Spontaneously formed magnetic nanocomposites







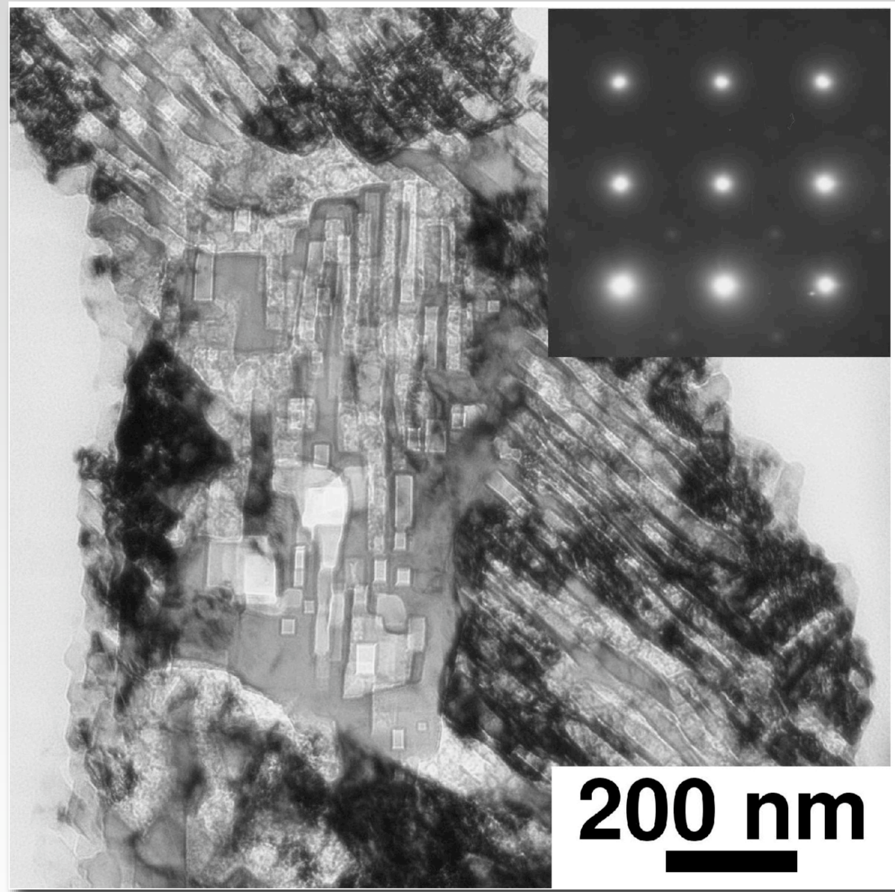
BET, SEM, and TEM suggest ~50 nm pores

Hierarchically Porous Mn

Spontaneously formed magnetic nanocomposites

Hierarchically Porous Mn

TEM: Pore walls are {100} faces; lowest energy faces of rocks salt

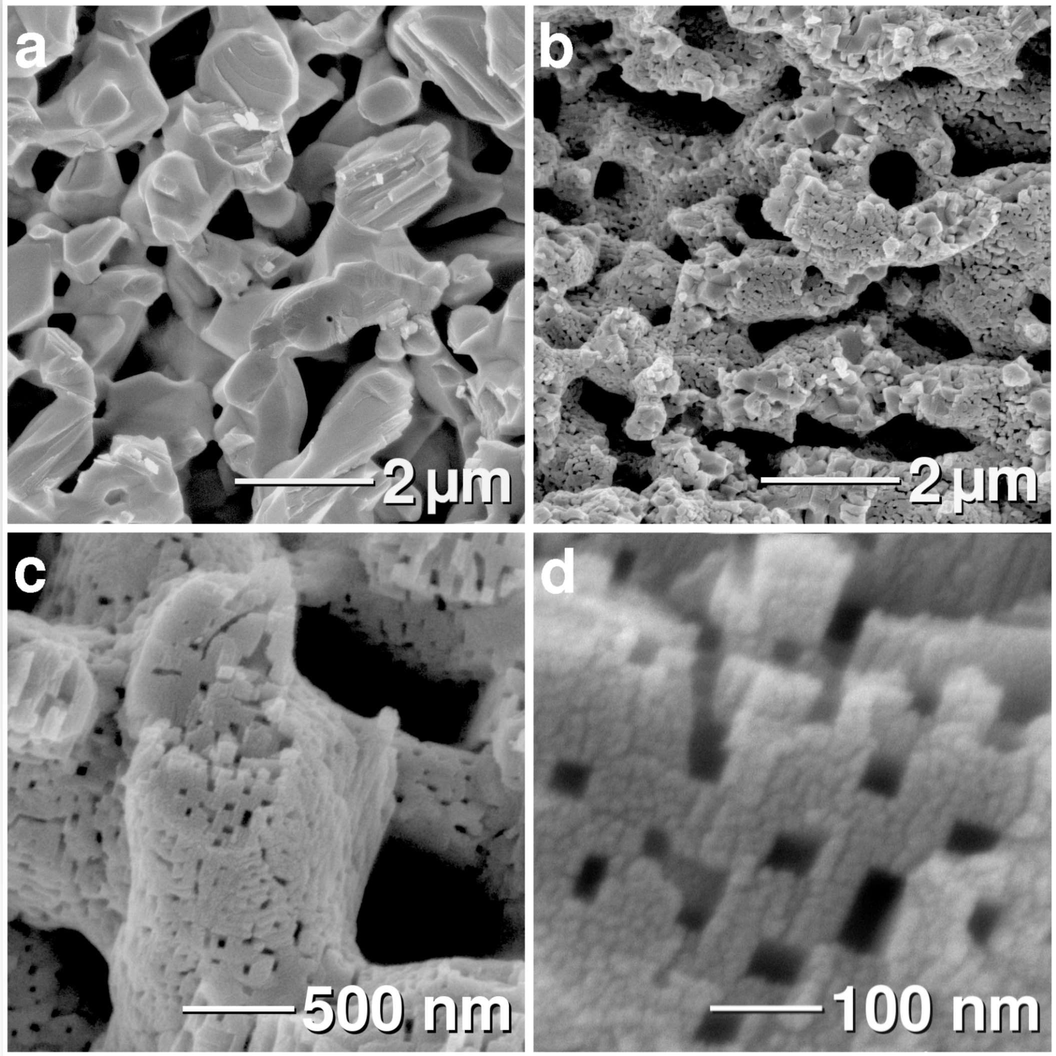


Toberer, Löfvander, and Seshadri, *Chem. Mater.* **18** (2006) 1047.

UC SANTA BARBARA engineering

Spontaneously formed magnetic nanocomposites

Hierarchically Porous Mn



Mn_3O_4	MnO
MnO	MnO

Sintered Mn_3O_4 reduced in 5% H_2/N_2

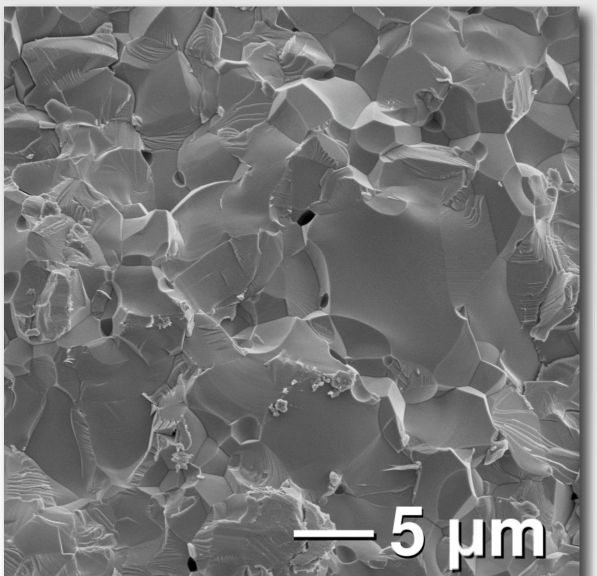
UC SANTA BARBARA engineering

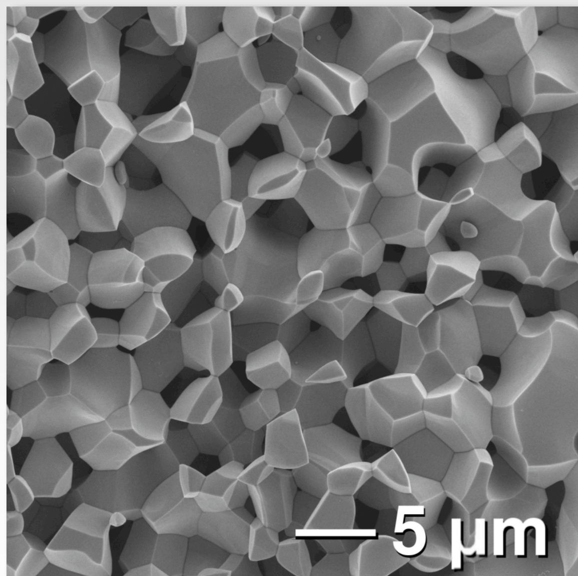
Spontaneously formed magnetic nanocomposites

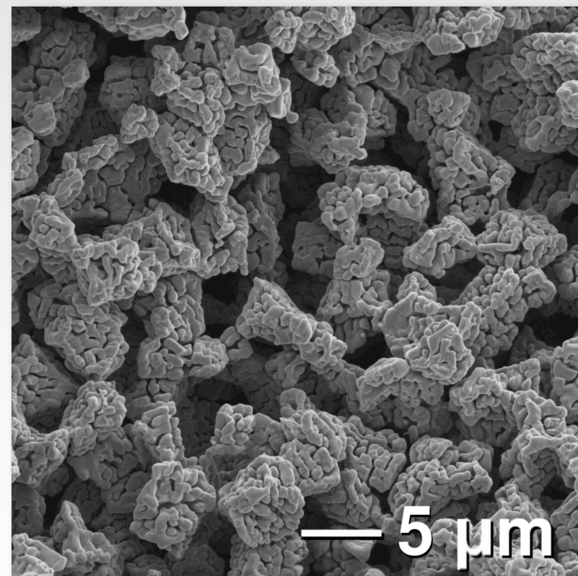
Titania is used in:

- photocatalysis
- Grätzel cells
- water purificaiton
- sensing

3 ZnO/Zn_2TiO_4 → Zn_2TiO_4 → TiO_2

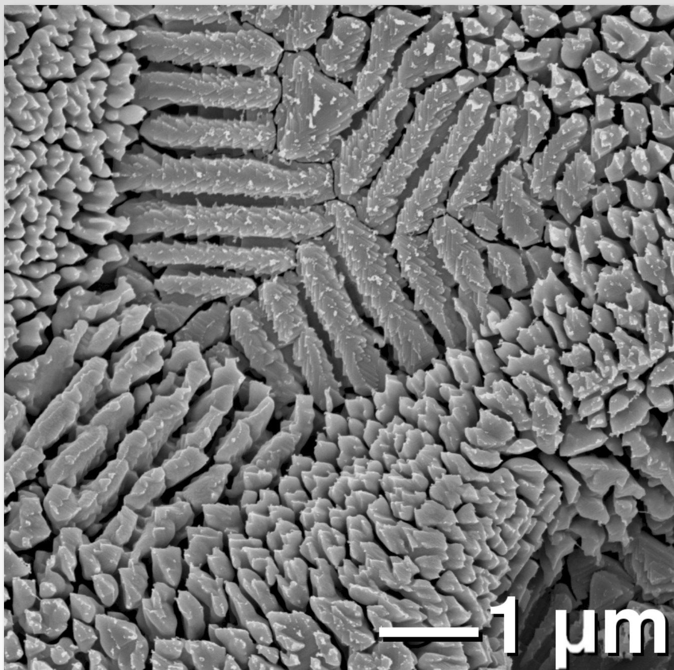


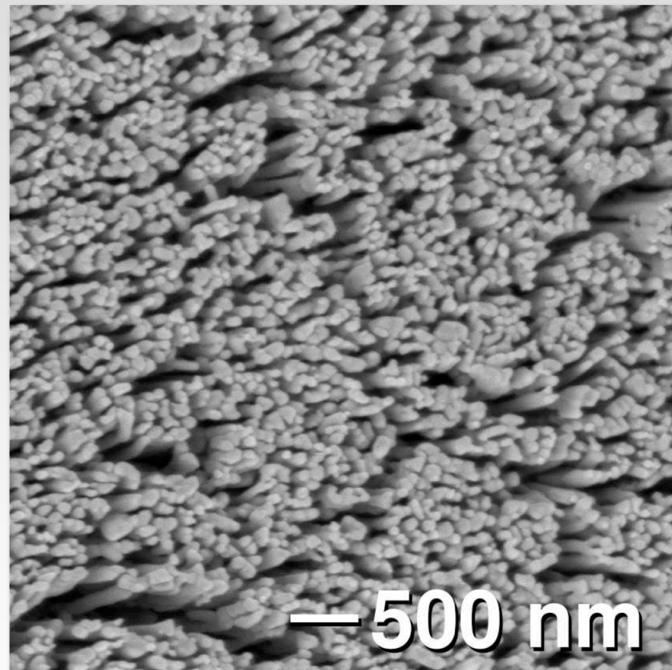




Spontaneously formed magnetic nanocomposites

Interesting morphologies in the intermediate stages of leaching.

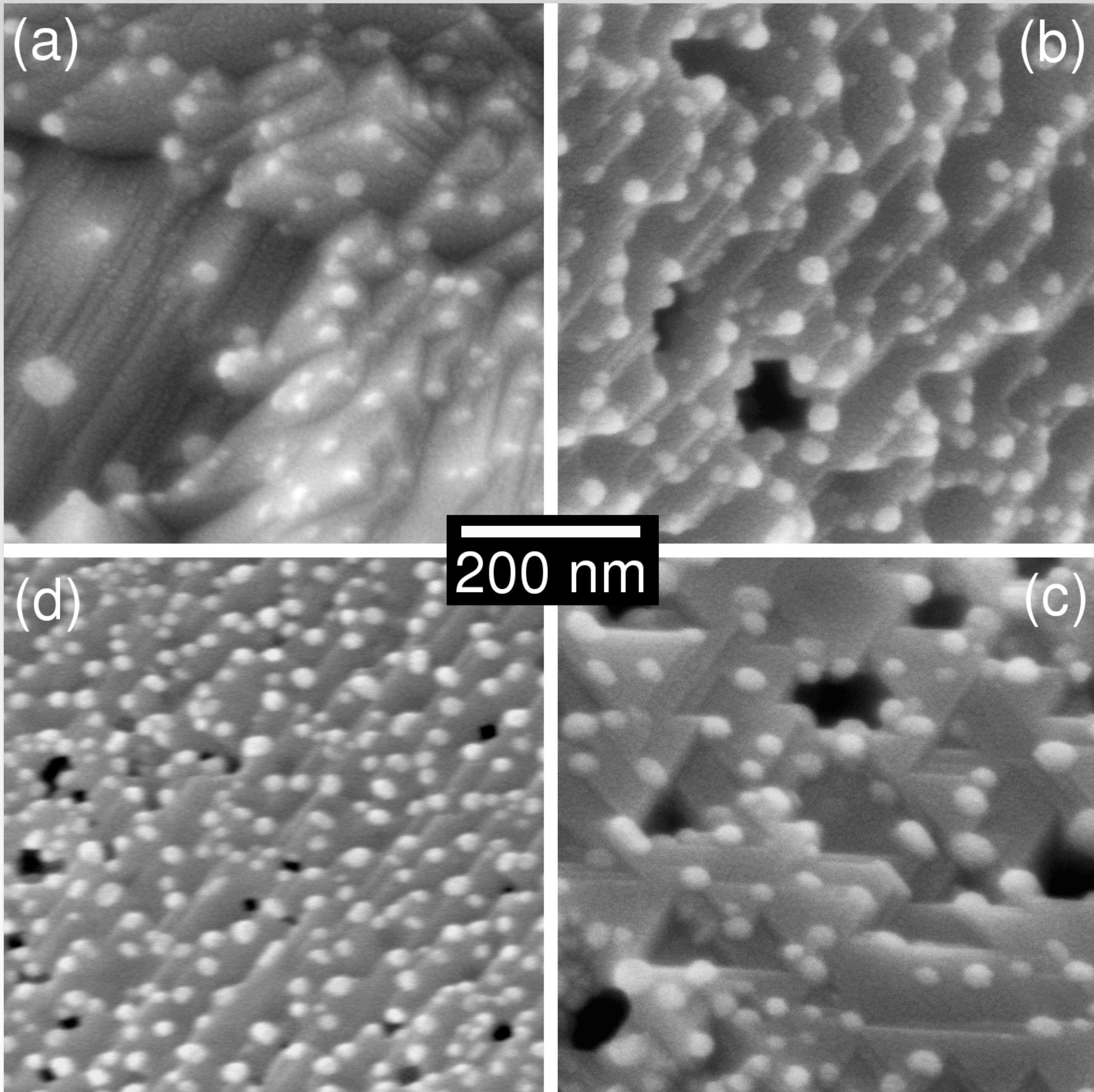




Toberer, Epping, Chmelka, and Seshadri,
Chem. Mater. **18** (2006) 6345.

Other early transition metal oxides (V, Nb, Cr W, …)

Spontaneously formed magnetic nanocomposites

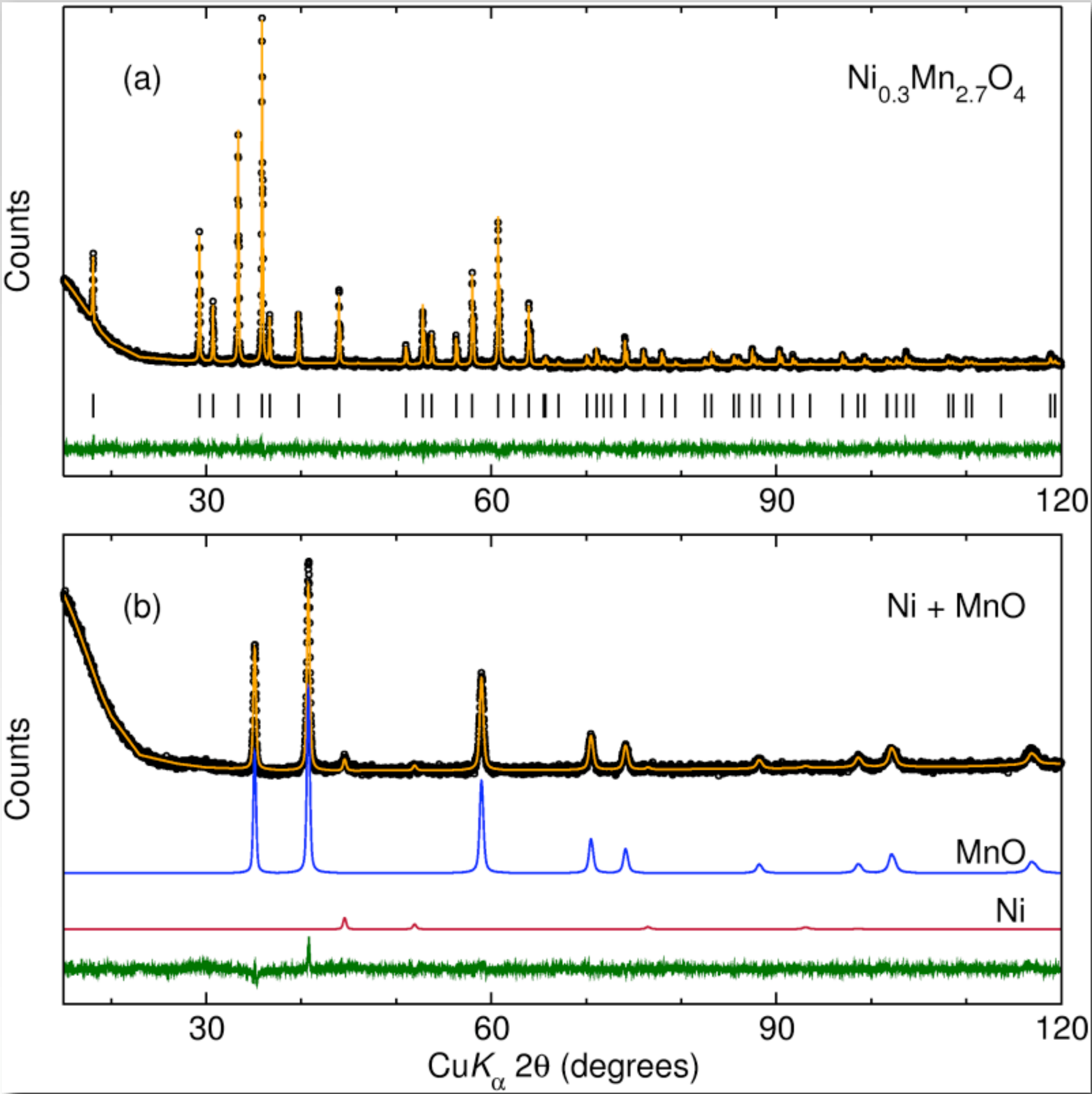


Single-domain Ni nanoparticles on porous MnO, prepared by reducing $Mn_{3-x}Ni_xO_4$. (a) through (d) are increasing x.

$Mn_{3-x}Ni_xO_4 \rightarrow (3-x)MnO + xNi$

UC SANTA BARBARA engineering

Spontaneously formed magnetic nanocomposites

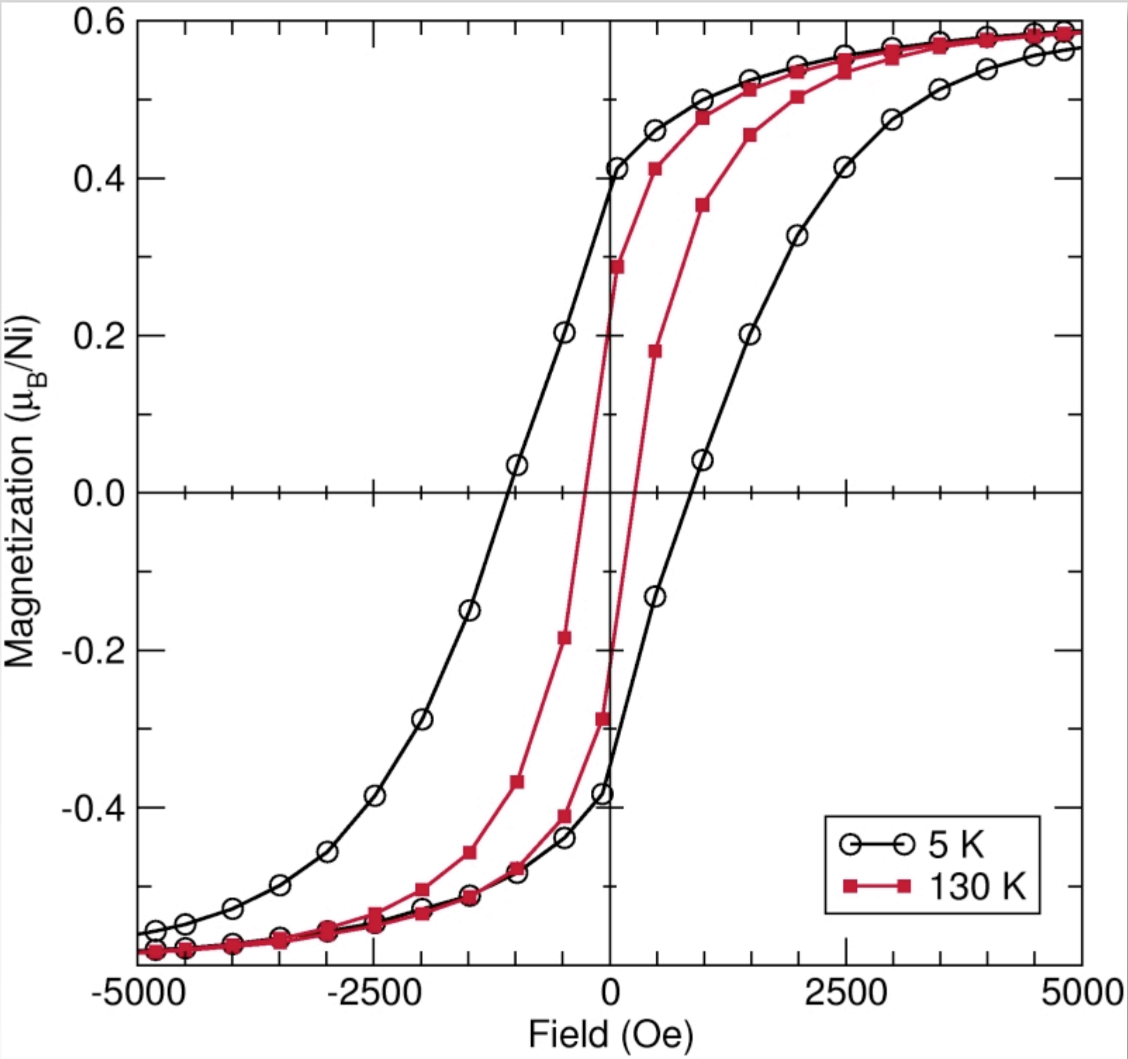


X-ray diffraction confirms the quantitative conversion.

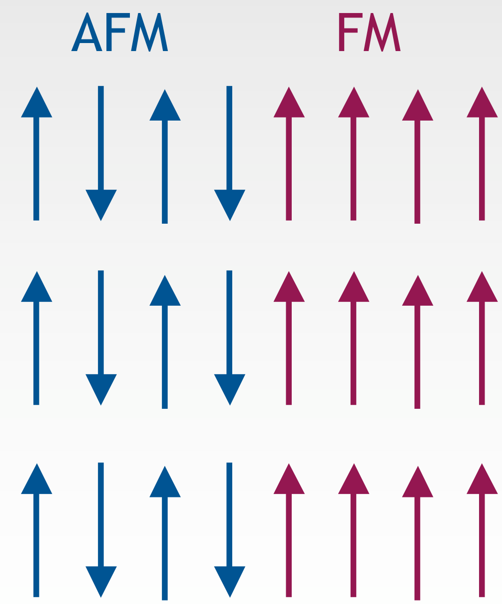
$Mn_{3-x}Ni_xO_4 \rightarrow$ $(3-x)MnO + xNi$

UC SANTA BARBARA engineering

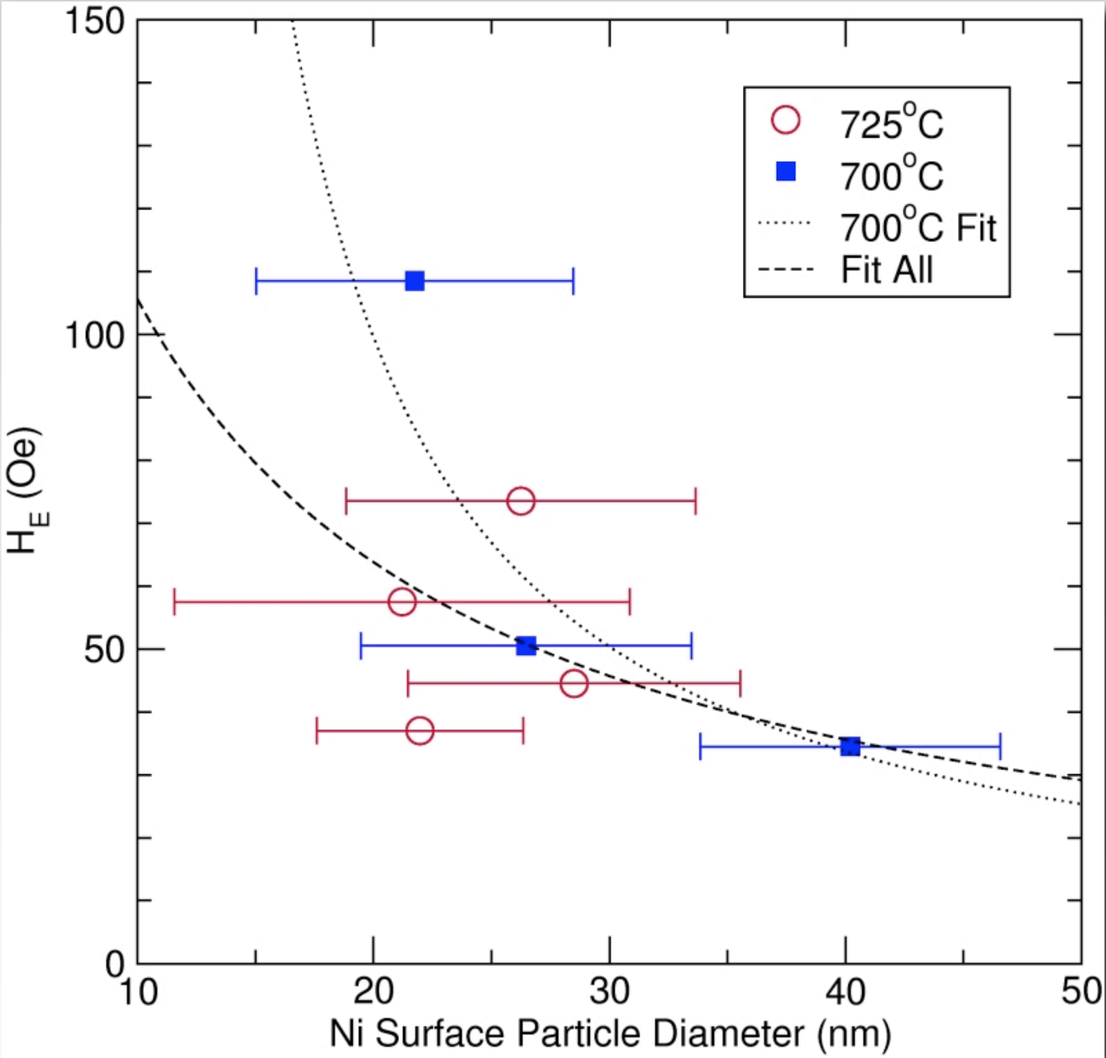
Spontaneously formed magnetic nanocomposites



The Ni loops, after field cooling, are shifted on the field axis because of antiferromagnetic MnO.



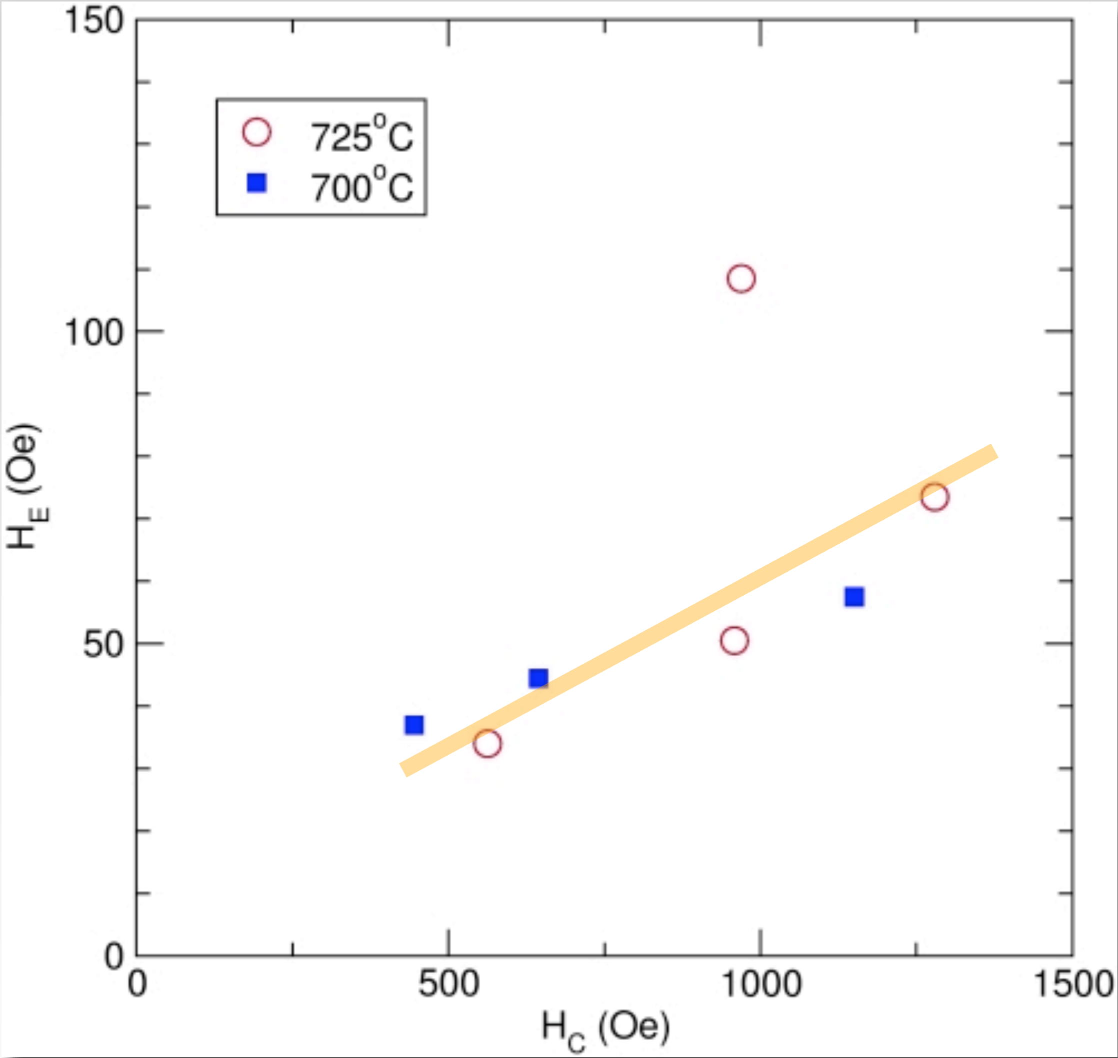
Spontaneously formed magnetic nanocomposites



The extent of exchange biasing (at 5 K) scales with the inverse diameter of the Ni particles.

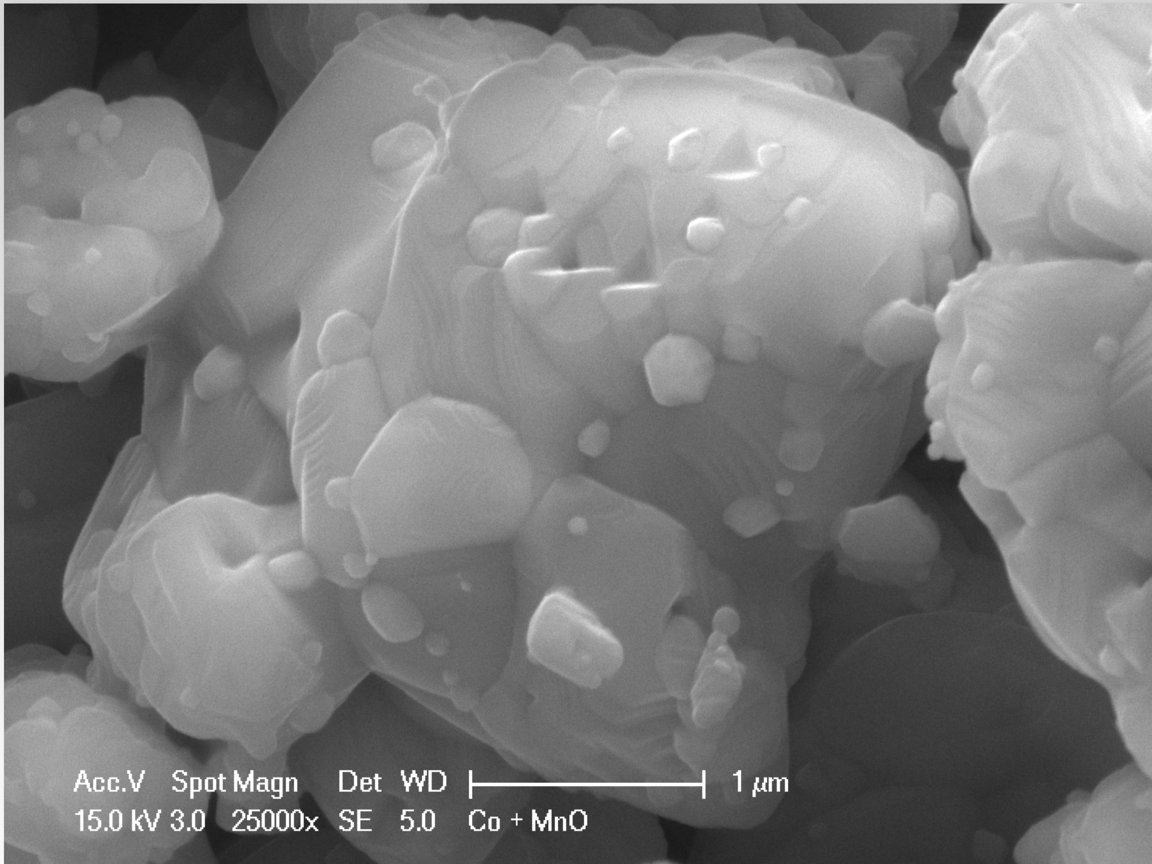
UC SANTA BARBARA engineering

Spontaneously formed magnetic nanocomposites



The coercivity (at 5 K) is increased as well, as the extent of exchange bias increases. A way of hardening soft magnets.

Spontaneously formed magnetic nanocomposites



Other systems: Co on MnO.

In progress: CoO and Cr_2O_3-based systems.

UC SANTA BARBARA engineering

Summary

Much yet to be learned from even simple nanomagnetic systems: For example, size effects on antiferromagnets.

Simple ways of achieving complex magnetic nanoarchitectures

Questions ?