Some Puzzles in Oxide Magnetism

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1. Introduction
2. $SrTiO_3$
3. CeO_2 nanoparticles
4. Interlude.

www.tcd.ie/Physics/Magnetism

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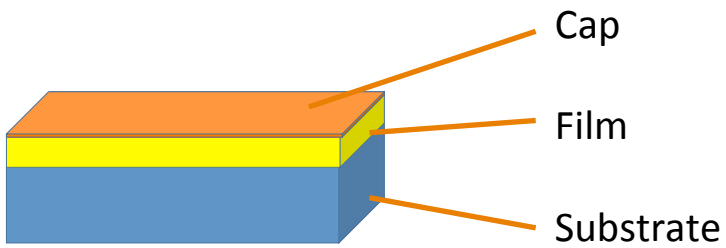
Introduction - Magnetic thin films

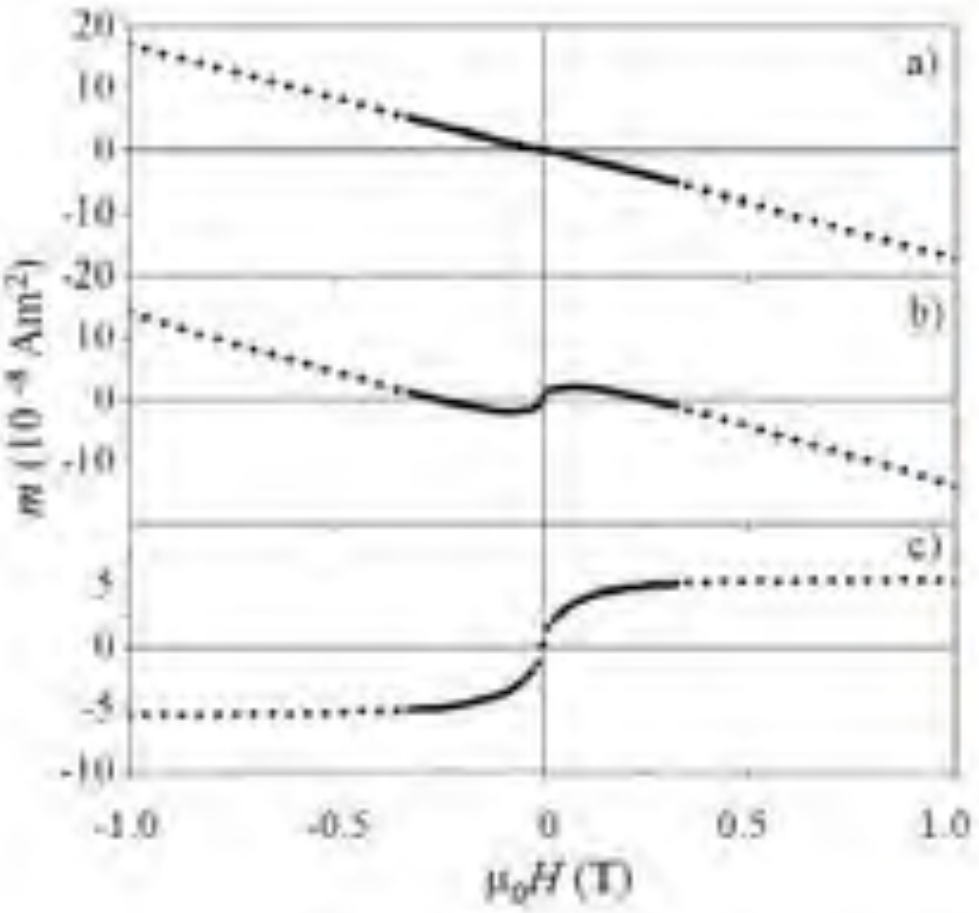
Magnetic thin films

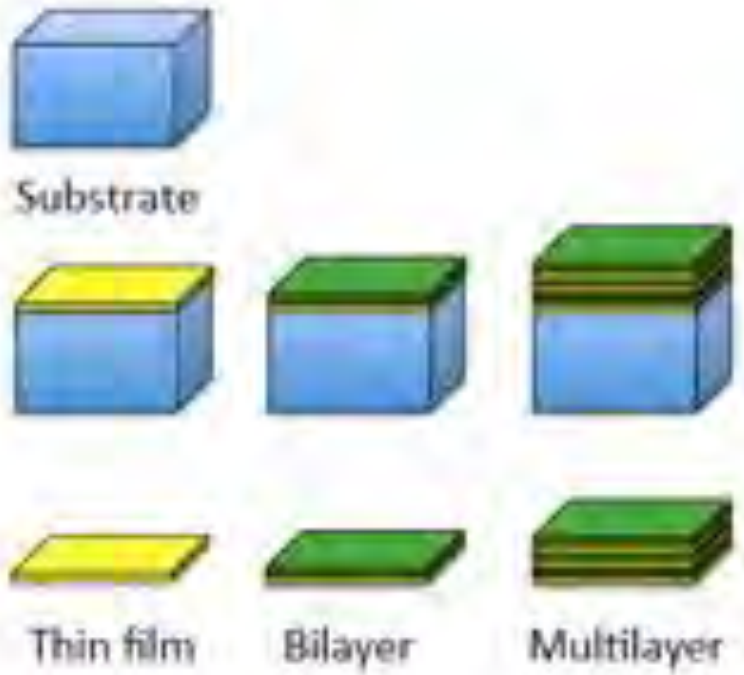


Achievable sensitivity with SQUID magnetometer	10^{-11} Am^2 (10^{12} spins)
Ferromagnetic monolayer 5 x 5 mm^2	~ 10^{-8} Am^2
Moment of oxide substrate 5x5x0.5 mm^2 in 1 T	~ -10^{-8} Am^2
1 ppm of iron in the substrate	~ 10^{-8} Am^2

Table I. Magnetic susceptibility of insulating oxides. Units (SI) are 10^{-6}.

Al_2O_3	MgO	$SrTiO_3$	$LaAlO_3$	TiO_2	SiO_2	YSZ	$MgAl_2O_4$
–18	–11	–7	–18	4	–18	–8	–15





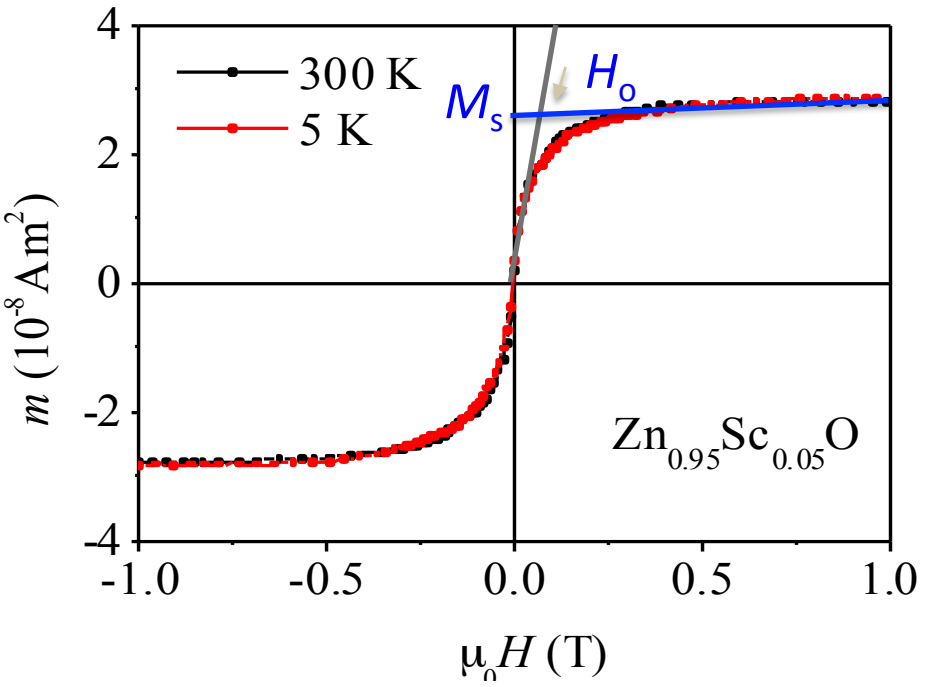
Assume $m_{\text{sample}} = m_{\text{sample on substrate}} - m_{\text{substrate}}$

This is naïve !

How do dilute magnetic oxides behave? Thin films

Material	E_g(eV)	Doping	Moment/T (μ_B)	T_C (K)	Reference
TiO_2	3.2	V – 5%	4.2	>400	Hong et al (2004)
		Co – 7%	0.3	>300	Matsumoto et al (2001)
		Co – 1 -2%	1.4	>650	Shinde et al (2003)
		Fe – 2%	2.4	300	Wang et al(2003)
SnO_2	3.5	Fe – 5%	1.8	610	Coey et al (2004)
		Co – 5%	7.5	650	Ogale et al (2003)
ZnO	3.3	V – 15 %	0.5	>350	Saeki et al (2001)
		Mn – 2.2%	0.16	>300	Sharma et al (2003)
		Fe5%, Cu1%	0.75	550	Han et al, (2002)
		Co – 10%	2.0	280-300	Ueda et al (2001)
CeO_2	3.0	Co – 3.0%	6.3	725	Tiwari et al (2006)
Cu_2O	2.0	Co5%, Al 0.5%	0.2	> 300	Kale et al (2003)
In_2O_3	2.9	Fe – 5 %	1.4	>600	He et al (2005)
		Cr – 2 %	1.5	900	Philip et al (2006)
ITO	3.5	Mn – 5%	0.8	>400	Philip et al (2004)
LSTO	-	Co - 1.5%	2.5	550	Zhao et al (2003)

d^0 magnetism



— Found for doped and undoped oxide thin films and nanoparticles

— At first they were thought to be ferromagnetic dilute magnetic semiconductors (DMS) $Zn_{0.95}Co_{0.05}O$

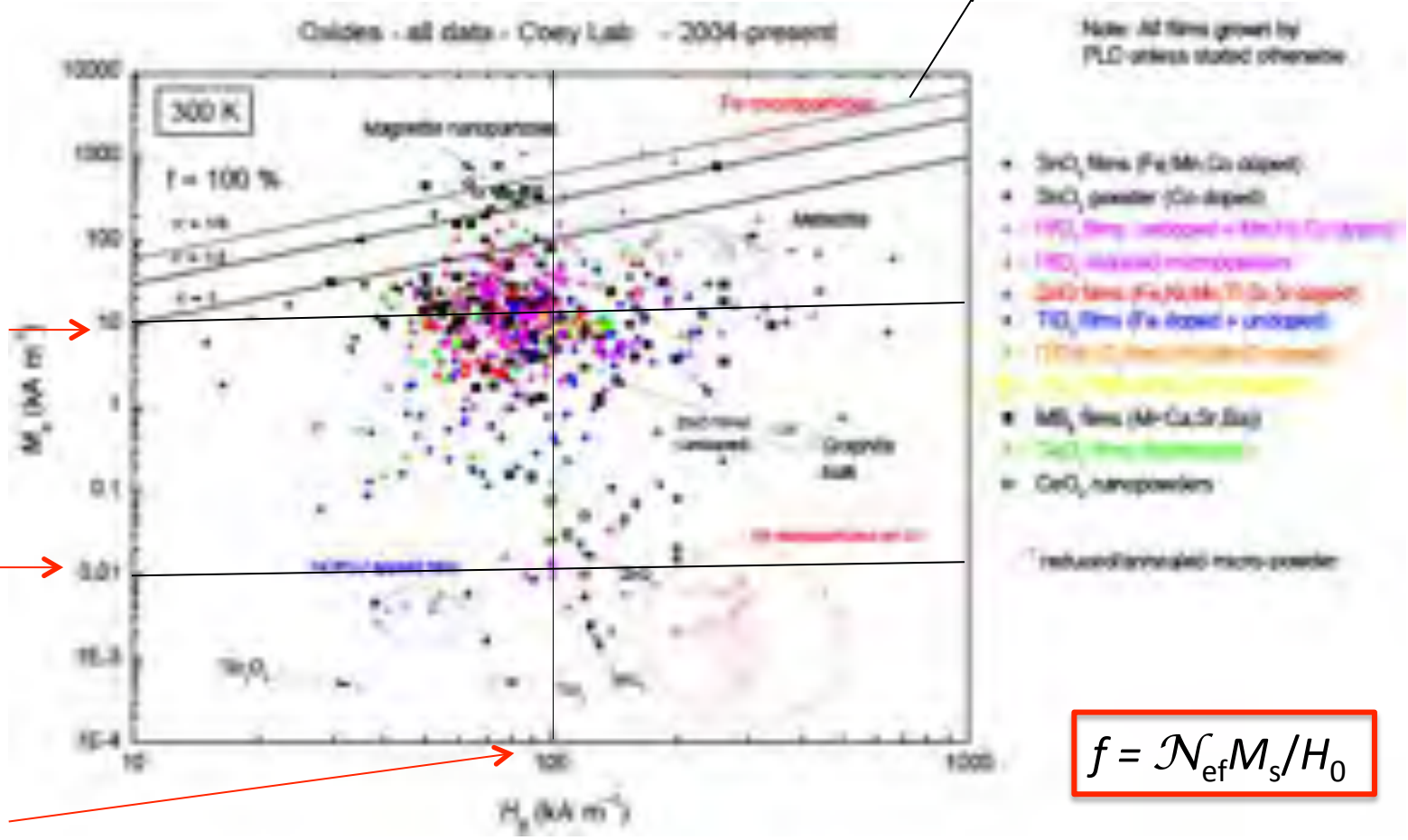
— 3*d* dopants do not order magnetically

— Magnetism is defect-related and *poorly-reproducible*

- Independent of temperature → T_C >> RT
- anhysteretic → dipole interactions
- M_s << H_0 → A tiny volume fraction *f* is 'ferromagnetic'

The syndrome

All Oxide data



$f = \mathcal{N}_{ef} M_s / H_0$

$H_0 = -\mathcal{N}_{eff} M_0$

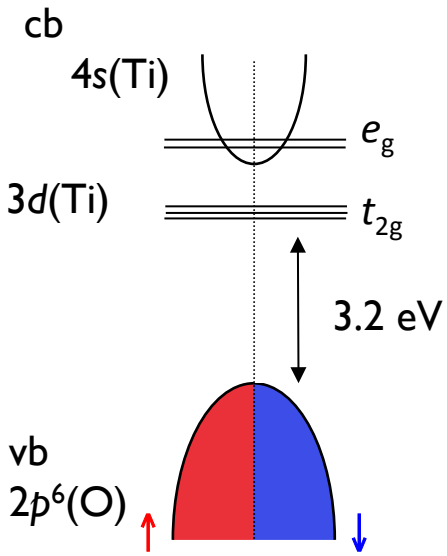
$M_0 \approx 240$ kAm^{-1}

in thin films, only a few % of the volume is ferromagnetic

In nanoparticles, the volume fraction is ~ 10 – 100 ppm

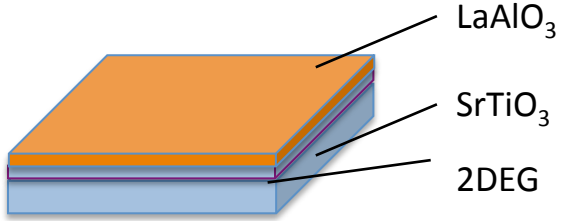
We need a 'fruitfly' system, where data is reproducible, and no extraneous explanation is possible

$SrTiO_3$ – The silicon of oxide electronics. Could it be magnetic?

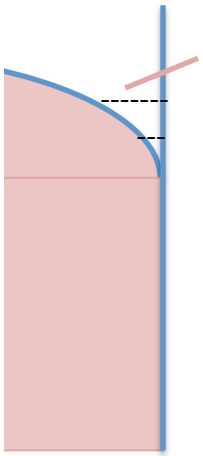


Oxide 2DEG just below the surface of $SrTiO_3$. Two explanations

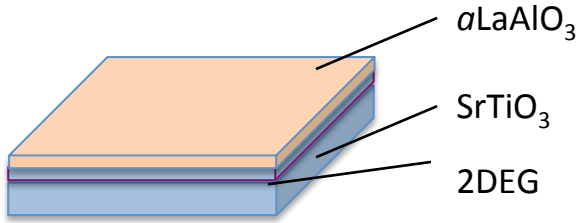
Polar catastrophe



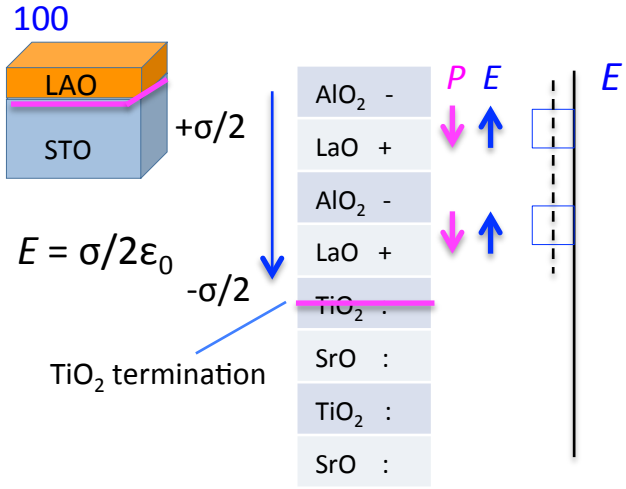
Electronic interface reconstruction
Transfer 0.5e from polar LAO to nonpolar STO (100)



Oxygen vacancies

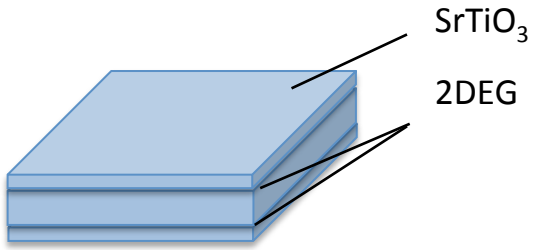


Amorphous, nonpolar LAO works as well! Electrons come from vacancies created by migration of O^{2-} to LAO at the interface.



Charge transfer at the interface needed to avert the polar catastrophe is 0.5e / uc, or ~0.5 Cm^{-2} or 3.3 10^{18} electrons m^{-2}

The 2DEG is confined to a layer ~ 2 nm thick, ~ 2 nm below the STO interface/ surfaces(s)
Essential requirement is *band bending* at the interface for a narrow confining potential.



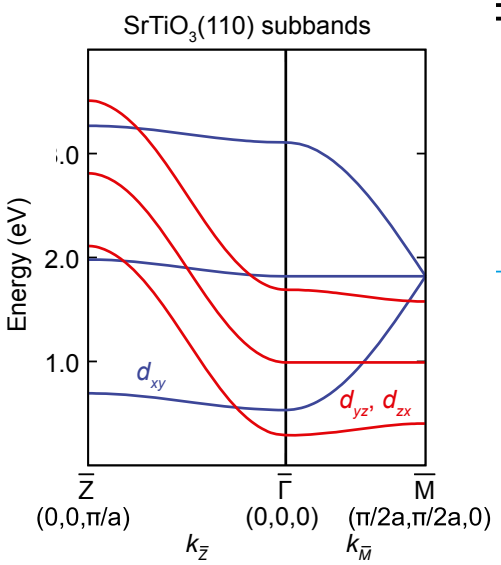
Atomic surface reconstruction for polar cuts of STO (110) and (111). Oxygen vacancies created near the surface.

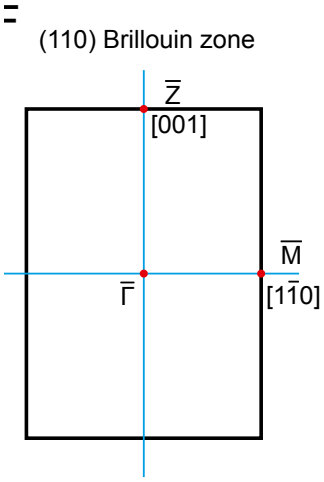
Nakagawa, N. *et al. Nat. Materials* 5, 204-209 (2006). Mainz 25-v-2014 Z. Q. Liu et al, *Phys. Rev. X* **3**, 021010 (2013).

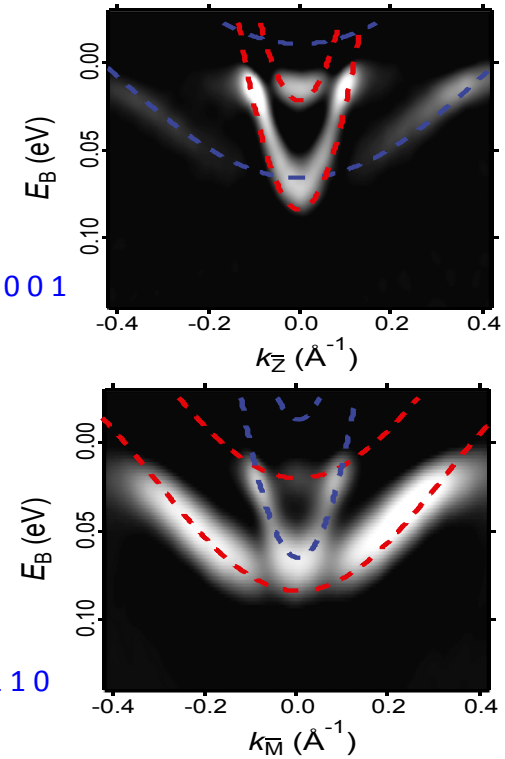
Oxide 2DEG just below the surface of $SrTiO_3$. Is an overlayer needed ?

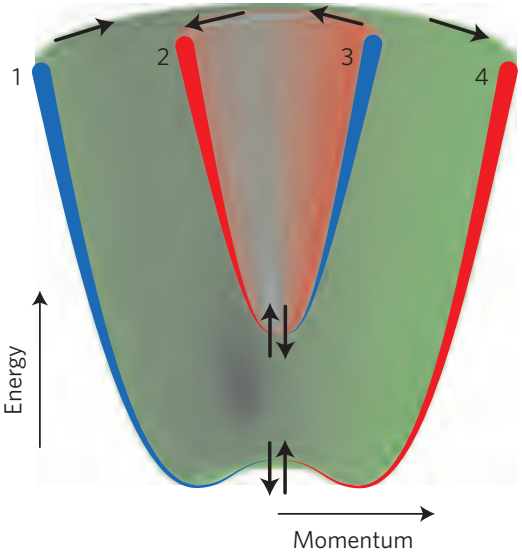
– Single crystals of polar cuts develop a 2DEG at the surface when heated in vacuum.

– ARPES indicates giant Rashba splitting.







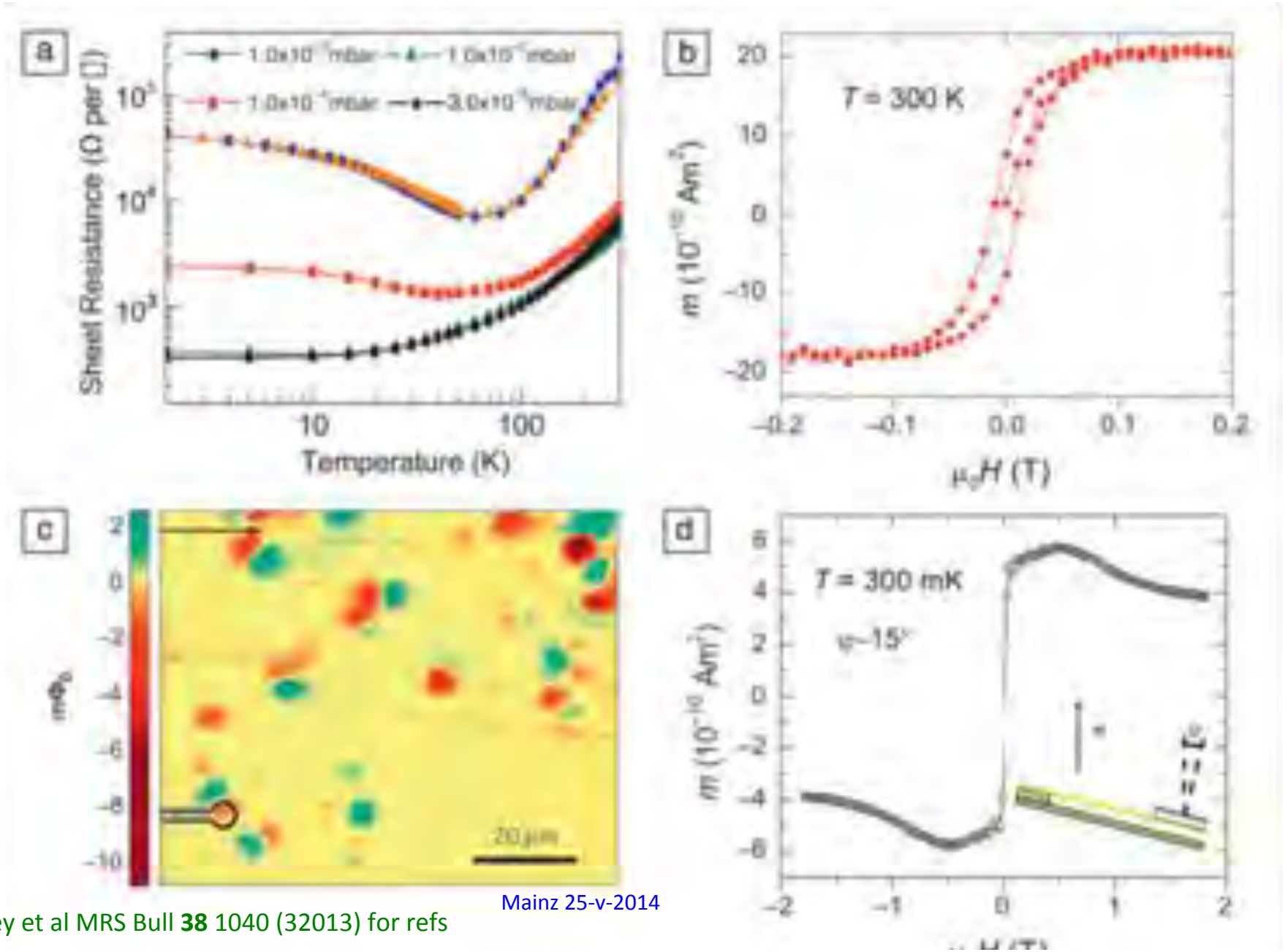


The polar cuts exhibit flat bands, which may be expected to be Stoner-split

Z M Wang, et al *PNAS* **111** 3133 (2014)

F Santander-Syro et al *Nat. Materials* **13** 1085 (2014)

Evidence for magnetism in STO



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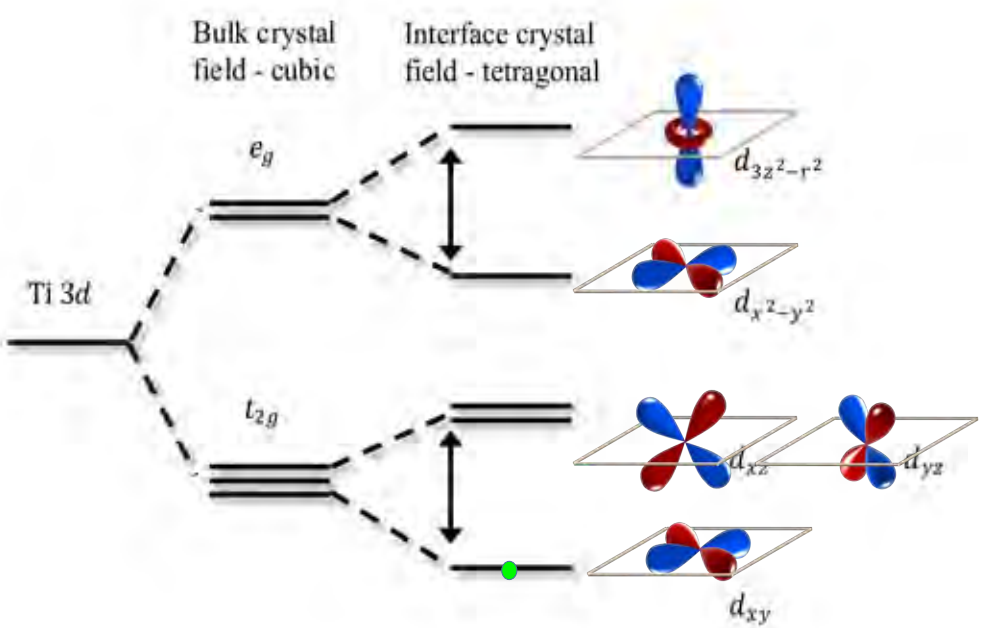
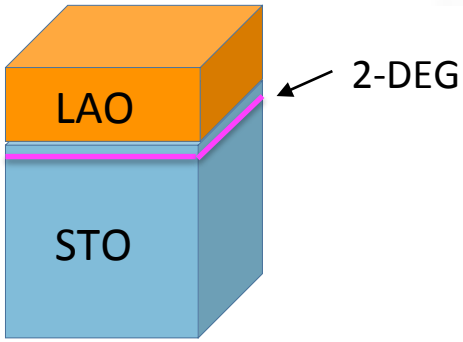
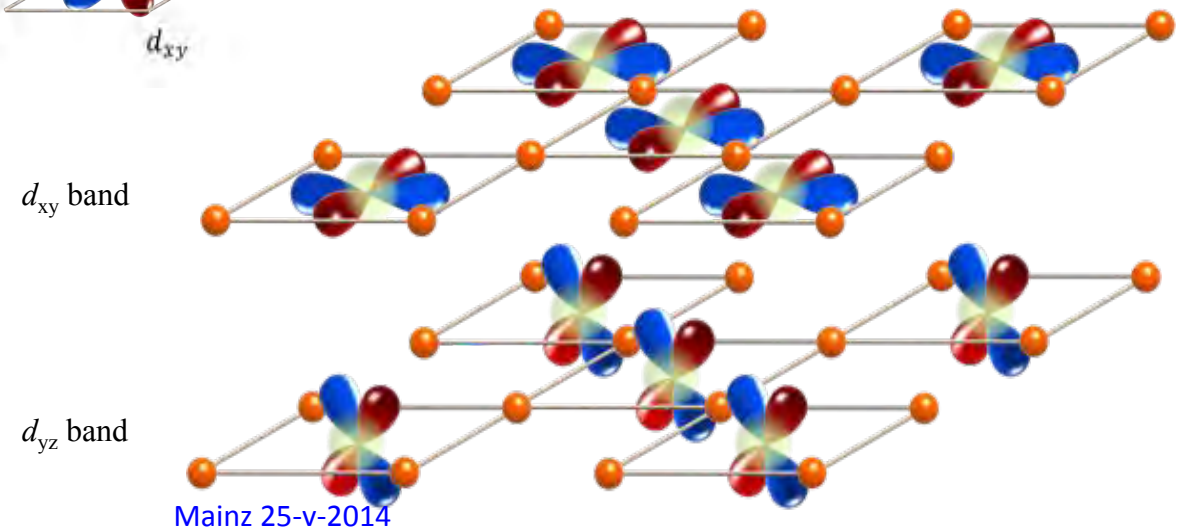
See Coey et al MRS Bull **38** 1040 (32013) for refs

If the 2-DEG at the STO interface is ferromagnetic



- Intrinsic or defect-induced ?
- d_{xy} or $d_{yz/zx}$ (or d_{x2-y2})
- Uniform or inhomogeneous?
- T_C ?





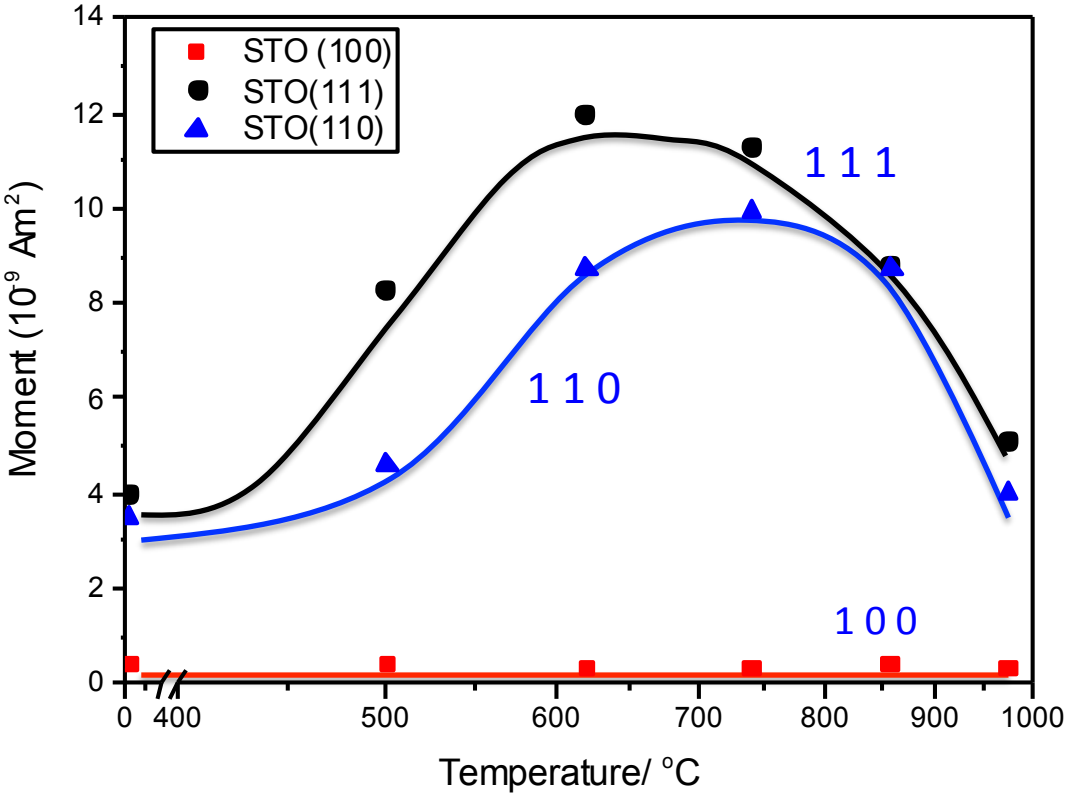
$SrTiO_3$ crystal slices, as received and vacuum

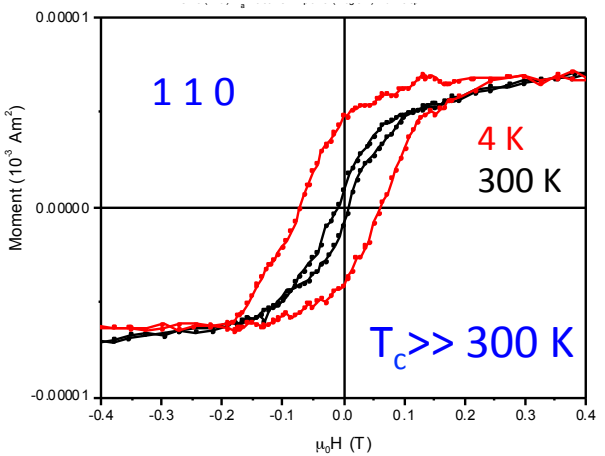
(100) Is non-polar and has no moment.

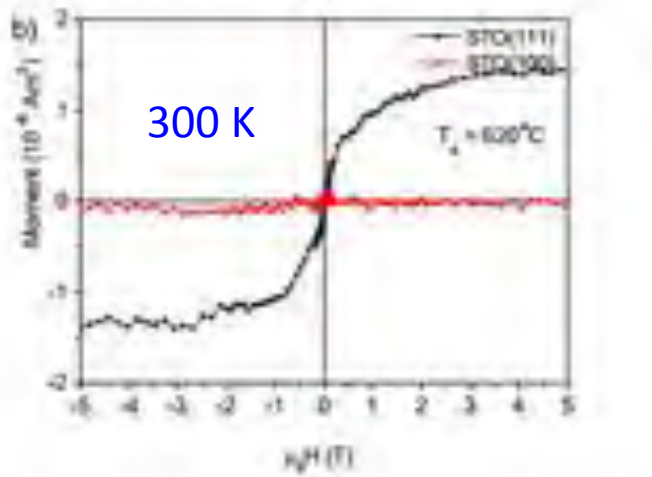
(110) and (111) are polar with flat bands and moments are 14-40 μ_B nm^{-2}.

Magnetization is hysteretic, associated with iron particles at the surface (Scanning laser MS)

Paramagnetic impurity content deduced from Curie Weiss susceptibility is ≤ 0.1 ppm for both



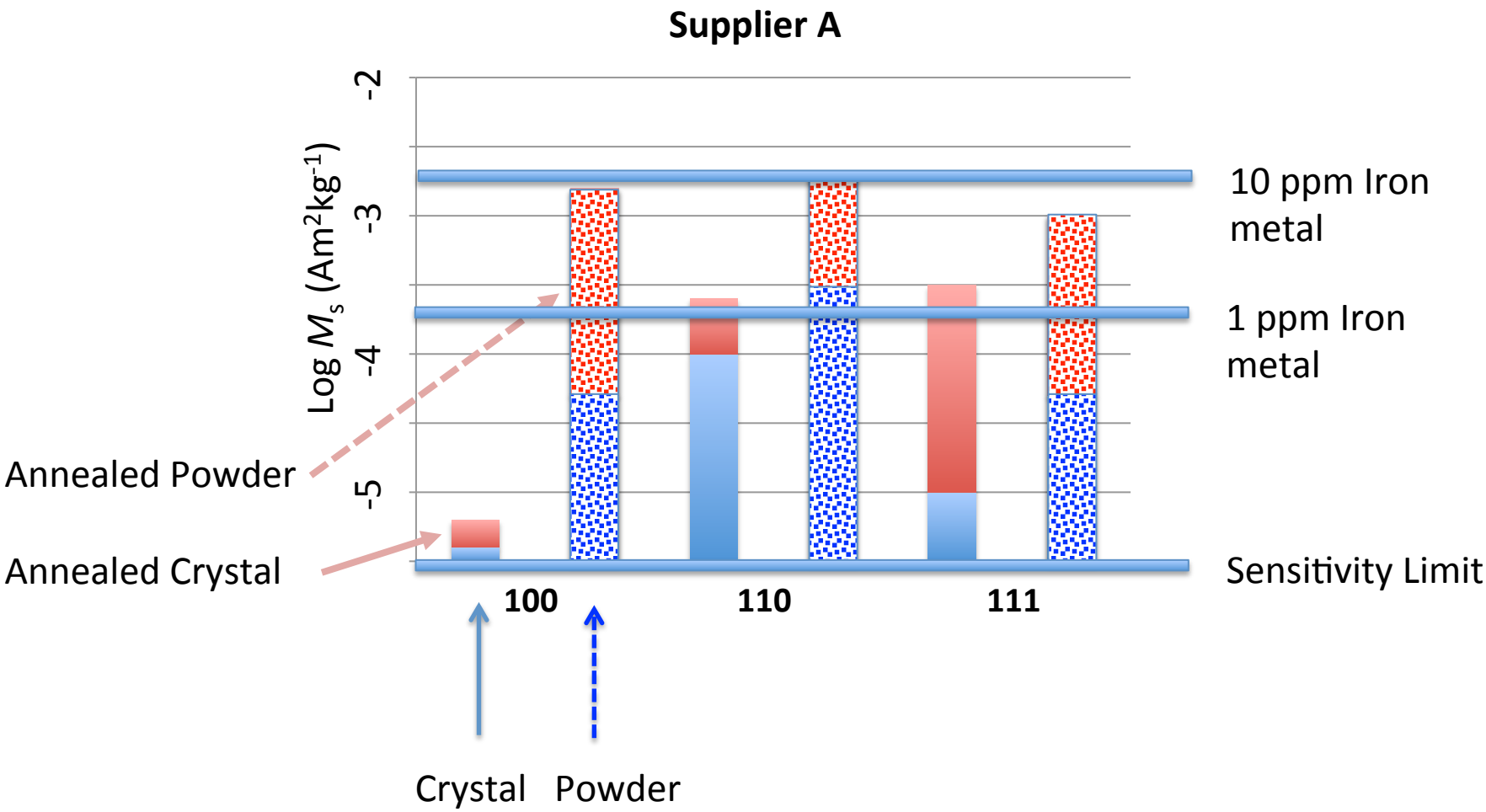


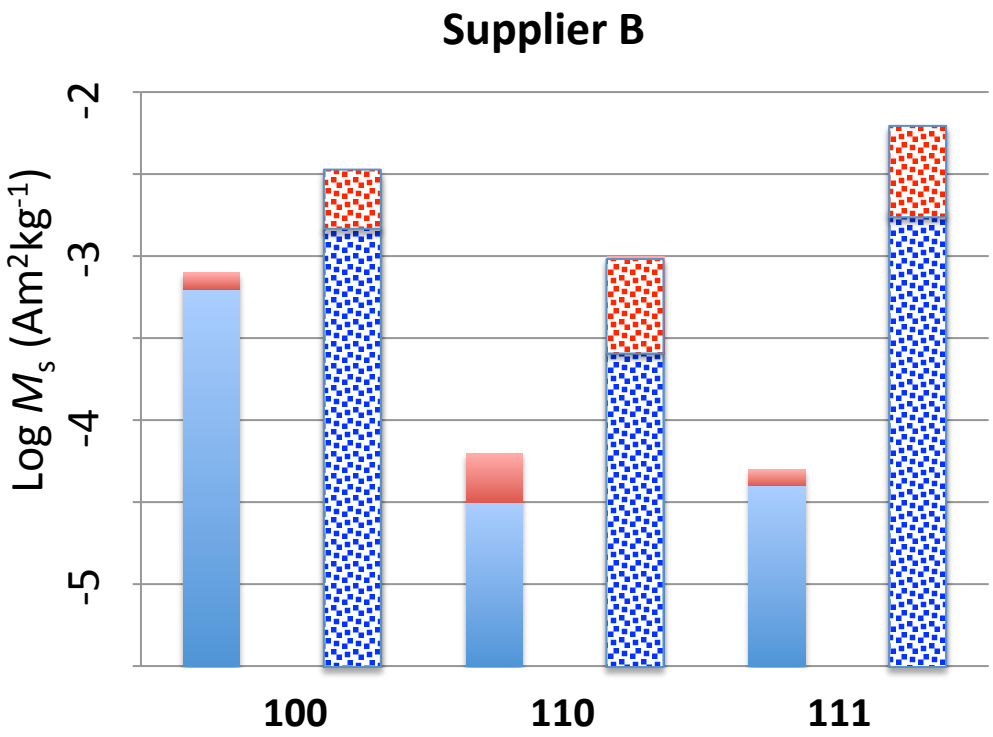


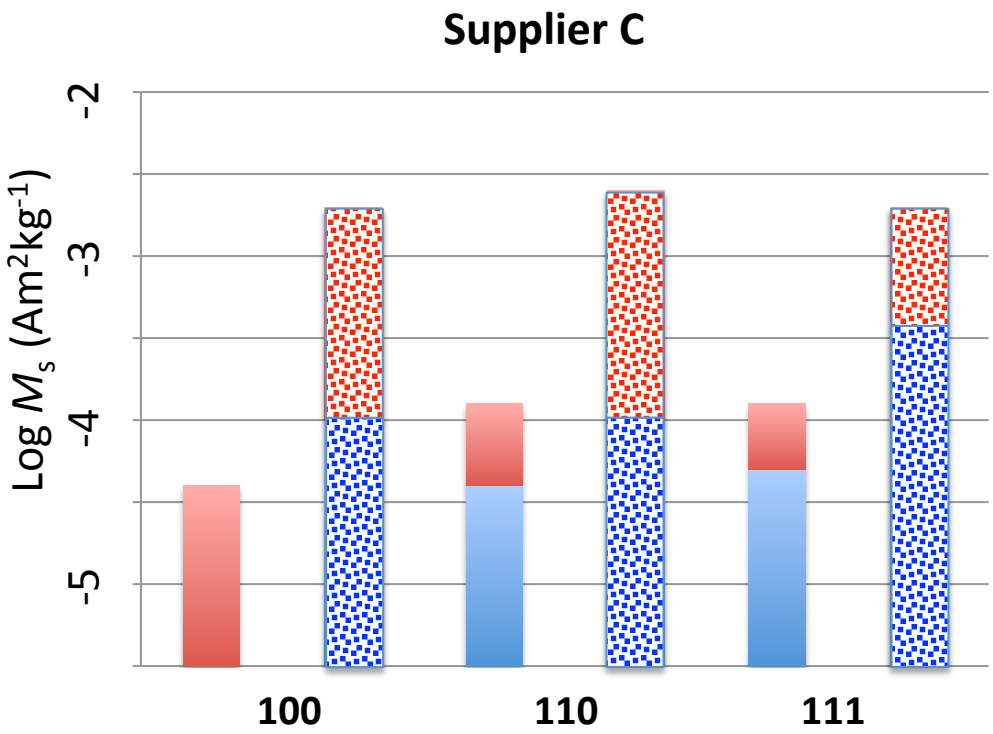
Moment resides at the surface but the magnetization is actually isotropic.

Summary of Magnetization M_s

Crystals of different cuts and their powders ~ 10 µm, before and after vacuum annealing at 750C




Supplier B
Log M_s (Am^{2}kg^{-1})
-2
-3
-4
-5
100
110
111

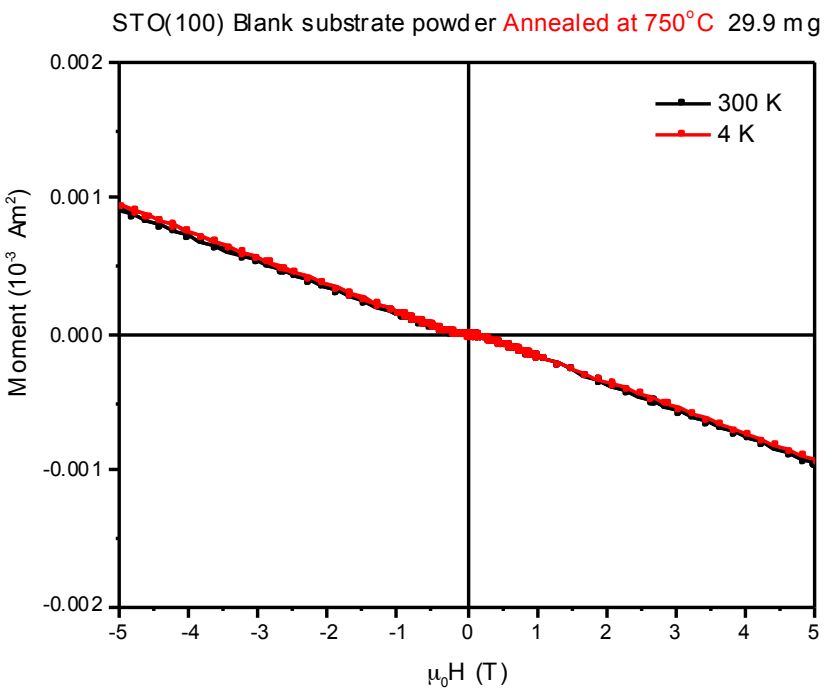


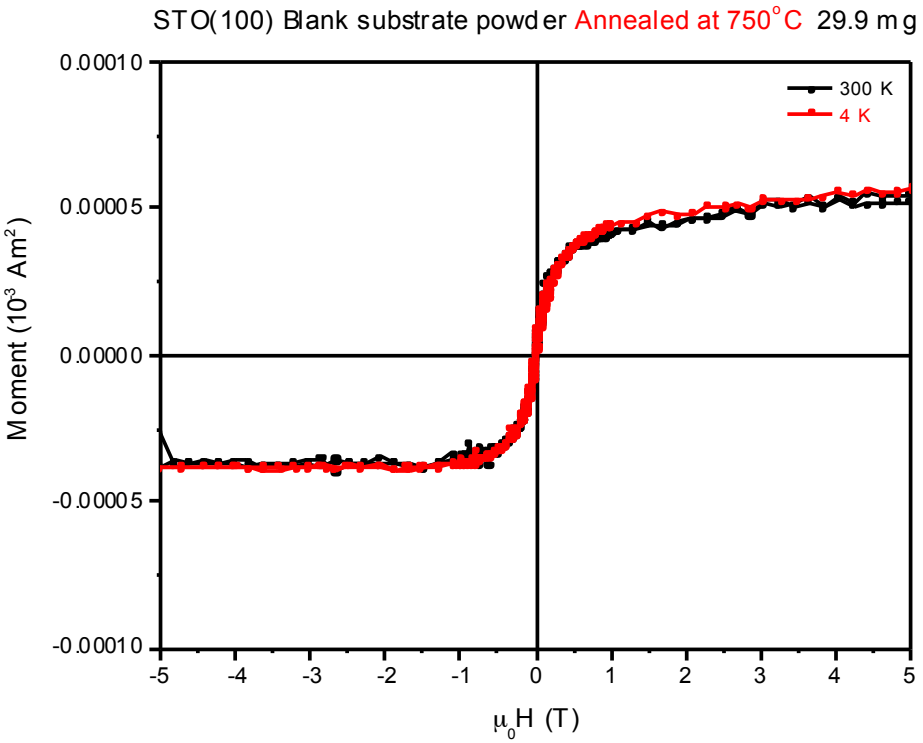
100 crystal has no moment.

On annealing we find 5 $\mu_B nm^{-2}$ (both crystal and powder) ~ 0.7 μ_B per unit cell area

Powdering without annealing gives 0.2 $\mu_B nm^{-2}$

STO !00 annealed powder.





The magnetic signal is identical at 4 K and 300 K. There is no hysteresis !

The syndrome

NB. Spin waves would reduce the moment of an S = 1 ferromagnet with T_C = 1000 K by 5 %

Summary of STO magnetism.

- The surfaces of most crystals from three suppliers are contaminated by ferromagnetic iron-rich particles, probably iron picked up in the polishing process; < 1ppm level. The magnetism is hysteretic.
- Some 100 crystal slices are uncontaminated. These develop a moment on vacuum annealing, especially after reducing to powder form. The moment corresponds to 0.7 μ_B per unit cell area.
- The magnetization curve in anhysteretic and shown no temperature dependence from 5 K to 300 K. The syndrome
- The moment is likely to be related to the surface 2-DEG which is associated with oxygen defects.
- Yes. STO can be magnetic to temperatures far above 300 K.
  The effect is unlikely to be spin-based.

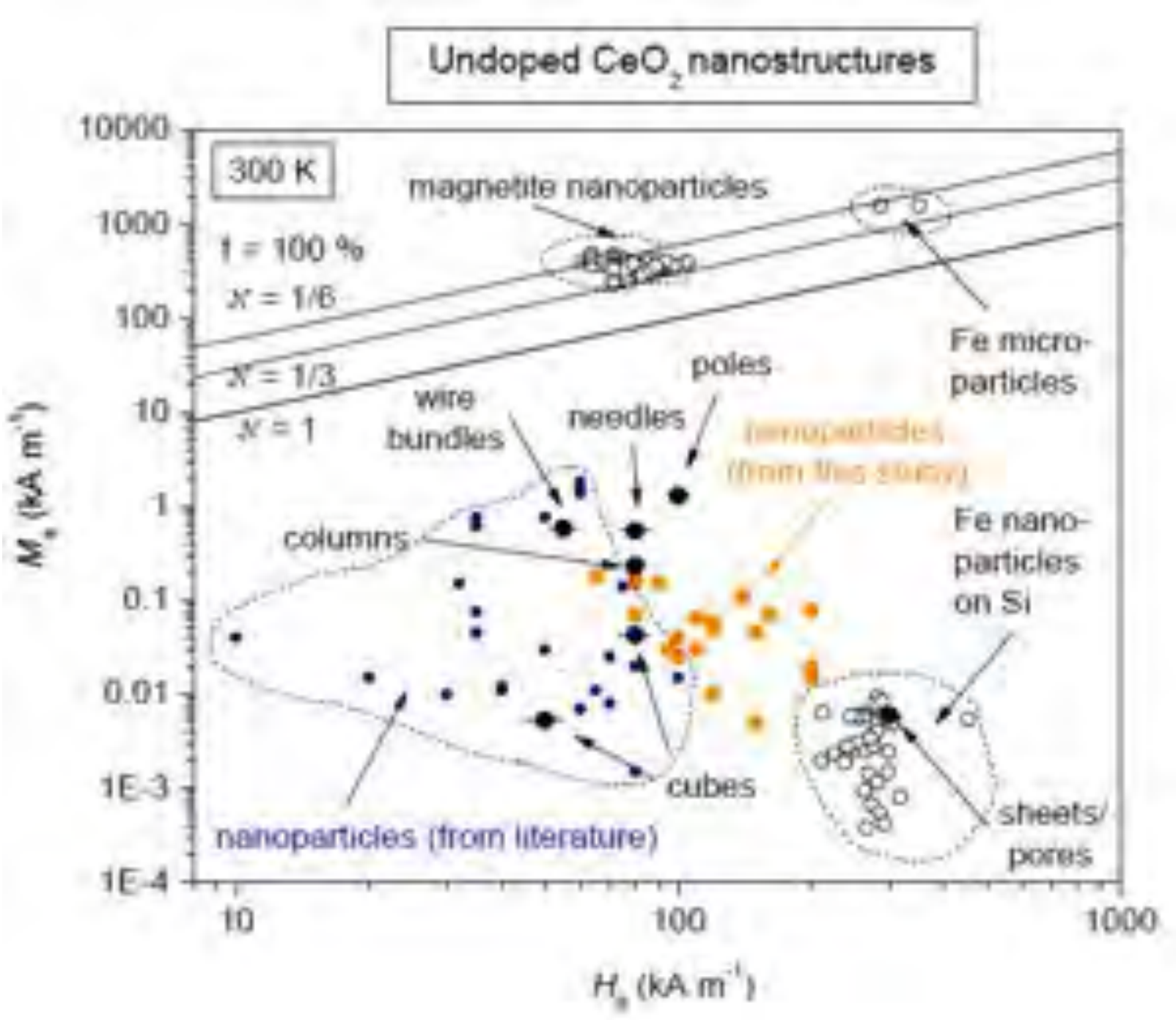
CeO_2 – A fruitfly f^0 system.

CeO_2 nanoparticles Literature

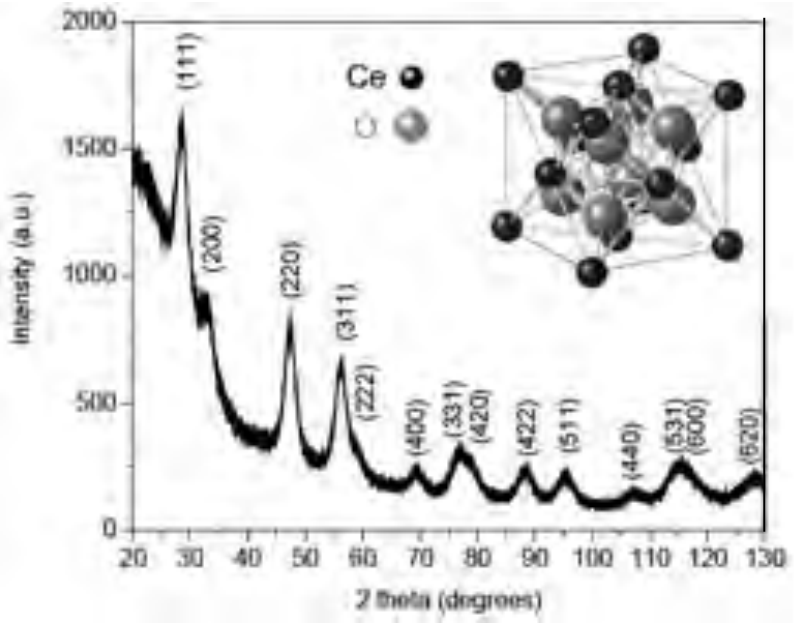
There are many reports that **$CeO_{2-\delta}$ nanoparticles** show stable weak ferromagnetic order, with $M \sim 100$ Am^{-1}

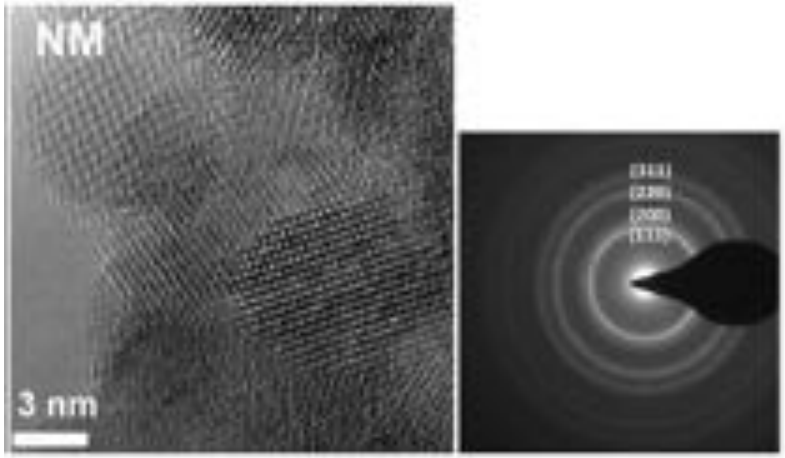
Average radius r_0 (nm)	M_s (Am^{-1})	H_0 (kAm^{-1})	f * (10^{-6})	Surface treatment	Reference
3.5	7	60	39	-	a
7.5	11	40	92	-	a
5×1	550	80	2290	PEG	b
3	40	80	168	Oleic acid	c
3.5	1.5	120	4	Glutamic acid	d
2.7	25	70	120	NH_4OH	e
1.8	760	50	5060	1,2 dodecandiol	f
2.5	150	32	1560	PEG	g
4.6	120	110	364	PVP	h
3.0	140	90	520	-	i
2.0	84(46)	120(38)	233	PEG	Karl Ackland PhD

a) A Sundaresan and C. N. R. Rao, Nano Today **4** 96 (2009)
b) Y. Liu et al, J. Phys. Cond. Matter, **20** 165201 (2008)
c) M. Y. Ge et al, Appl. Phys. Lett, **93** 062505 (2008)
d) X. Chen et al, Nanotechnology, **20** 115606 (2009)
e) M. Li et al, Appl. Phys. Lett, **94** 112511 (2009)
f) S. Y. Chen et al, J. Phys. Chem C **114** 19576 (2010)
g) K. Ackland et al, IEEE Trans Magn. **47** 3509 (2011)
h) S. Phokha et al, Nanoscale Res. Lett. **7** 425 (2012)
i) N. Paunovic et al, Nanoscale **4** 5469 (2012)

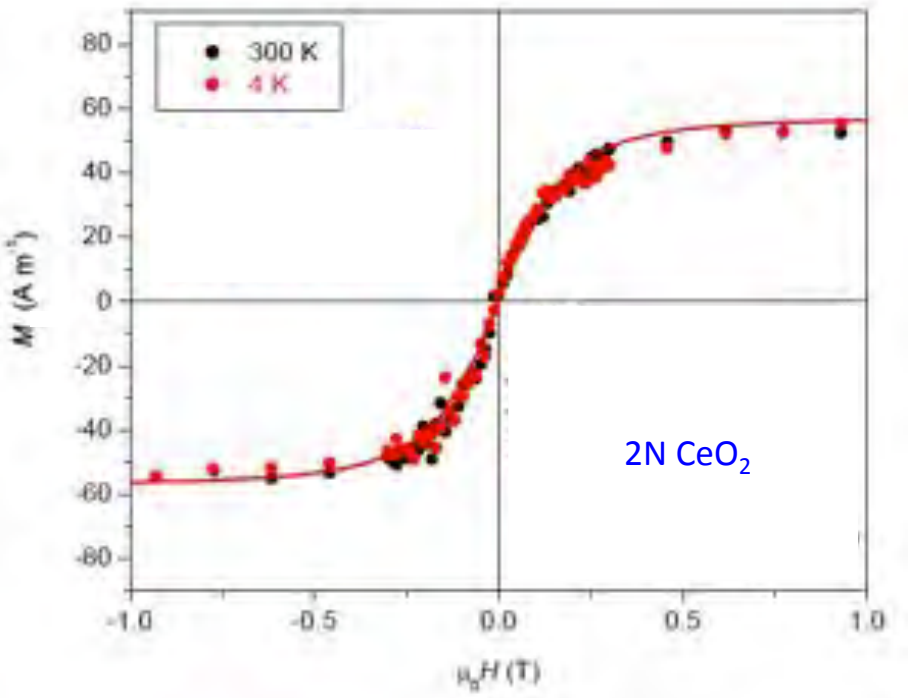

Undoped CeO2 nanostructures
300 K
f = 100 %
x = 1/6
x = 1/3
x = 1
magnetite nanoparticles
Fe micro-particles
poles
wire bundles
needles
columns
Fe nano-particles on Si
cubes
sheets/ pores
nanoparticles (from literature)
10000
1000
100
10
1
0.1
0.01
1E-3
1E-4
10
100
1000
Ms (kA m-1)
Hg (kA m-1)

CeO_2 nanoparticles - Characterization



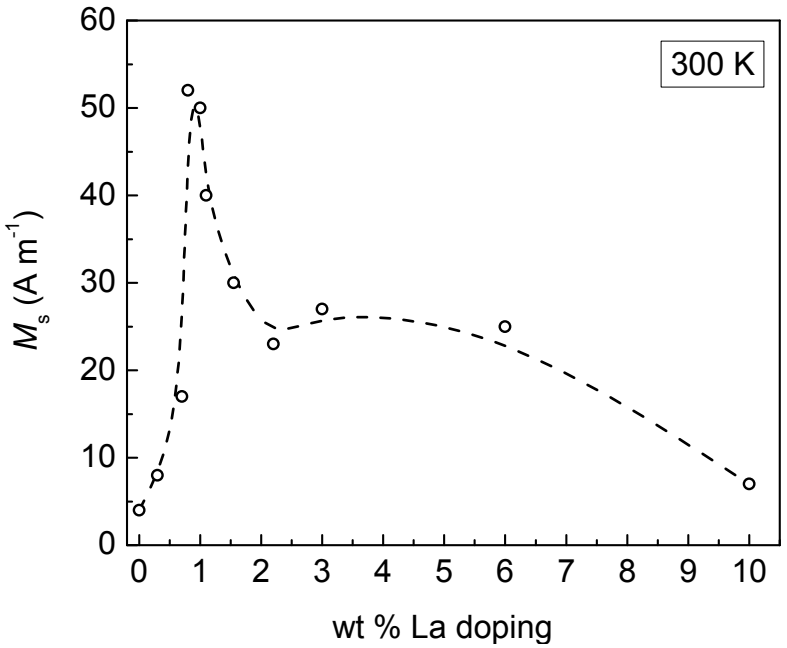


The syndrome



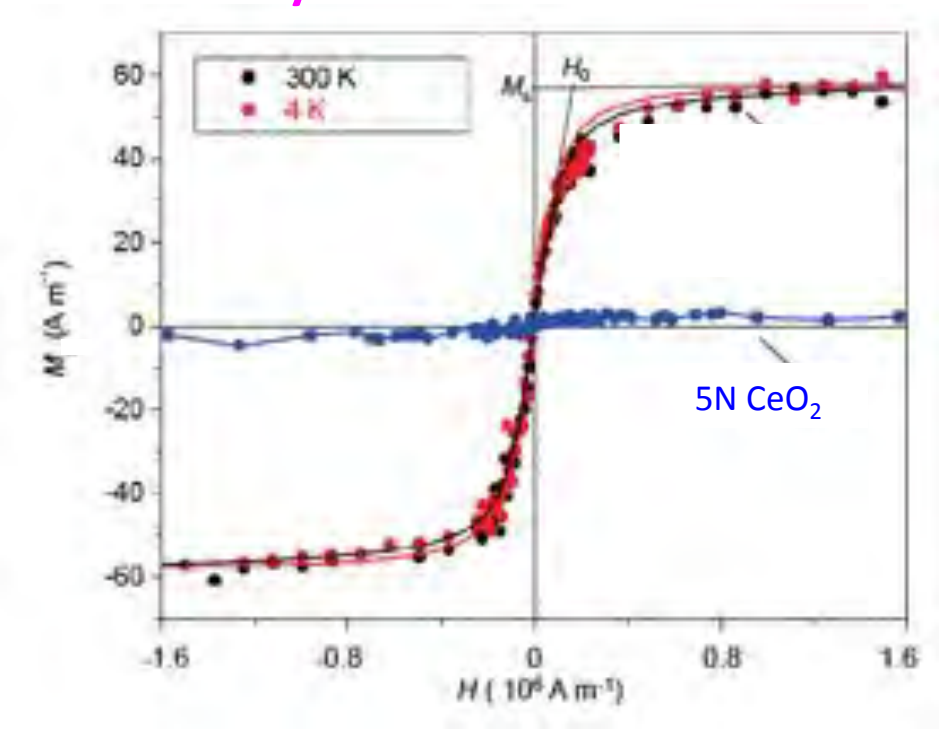
Uniform 4 nm CaF_2-structure nano particles of $CeO_{2-\delta}$ are precipitated from $CeNO_3$ + PEG solution. Moment ~ $0.2\mu_B$/particle (900 Ce)

CeO_2 nanoparticles – La doping



La-doping of 5N pure $CeO_{2-\delta}$ turns on the moment — maximum for 1%

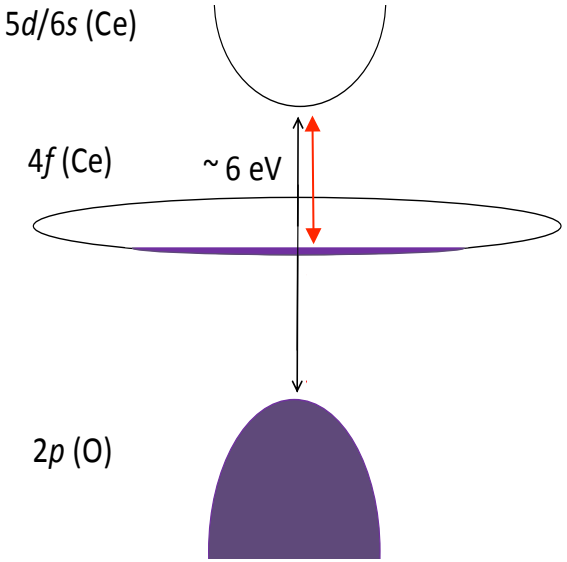
The syndrome



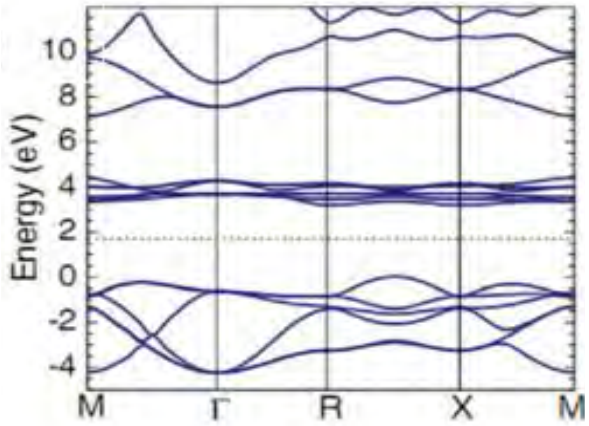
Nanoparticles from 5N precursor are not magnetic, but 2N particles showed 'ferro-magnetic'' signal.

Σ 3*d* impurities < 10 ppm.

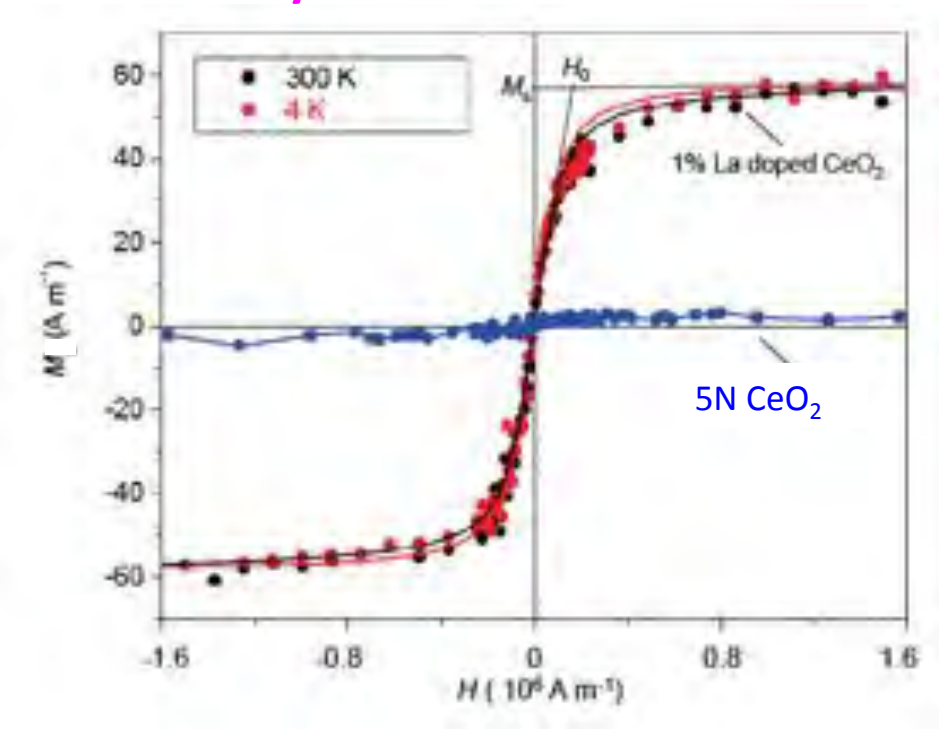
CeO_2 nanoparticles



Any Ce 4*f* electrons are delocalized (~ no Curie-law upturn in susceptibility < 0.4% of Ce).



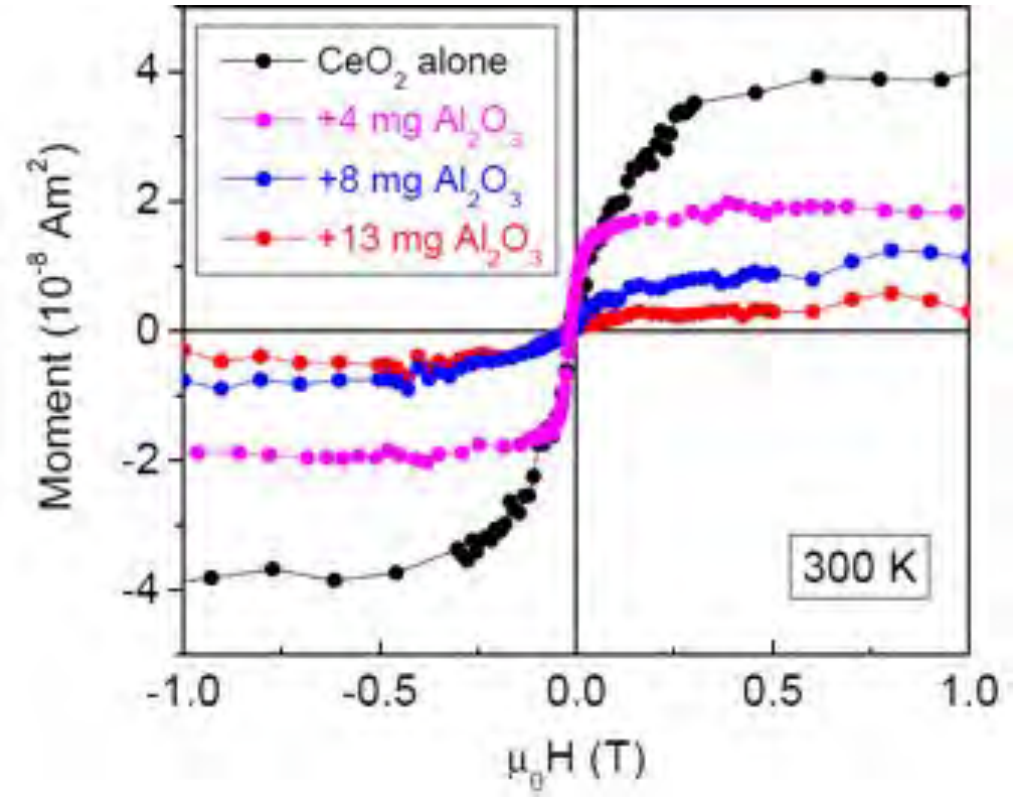
The syndrome



Nanoparticles from 5N precursor are not magnetic, but 2N particles showed 'ferro-magnetic'' signal, due to La impurities

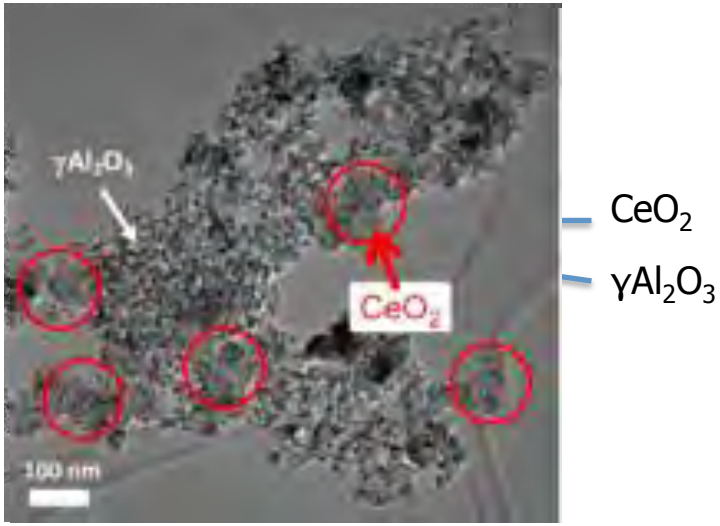
Surfaces of oyygen-deficient nanoparticles are conducting

Effect of dilution– 15nm γAl_2O_3



Progressive dilution with nonmagnetic 15nm γAl_2O_3 nanoparticles makes the moment disappear !

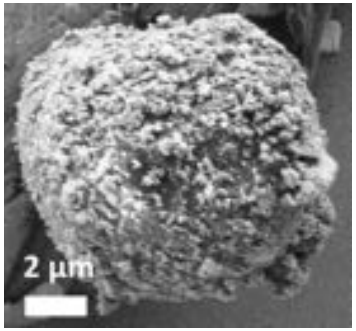
6 x dilution (by volume) reduces moment by 94%

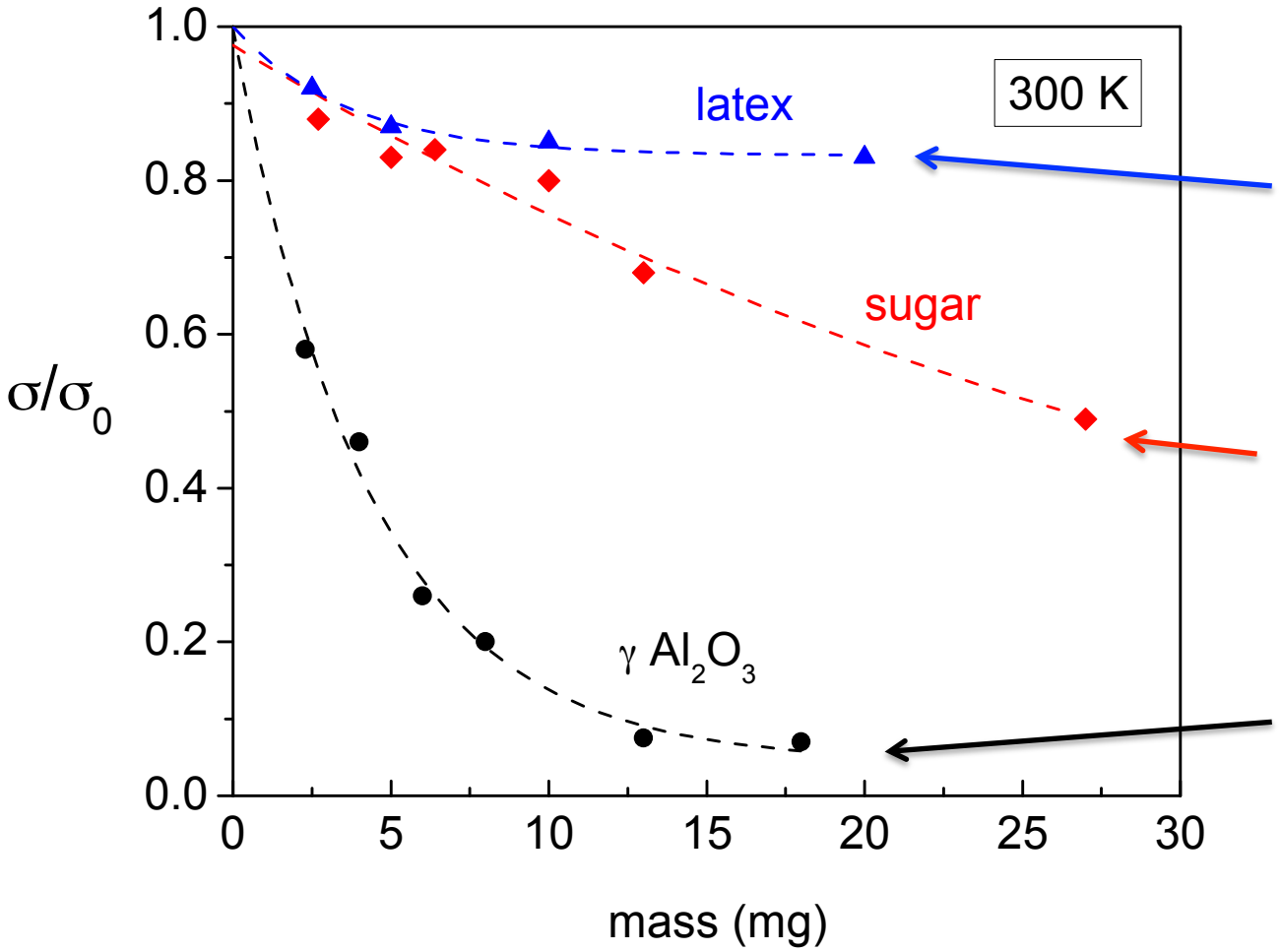


Dilution with 15nm γAl_2O_3 breaks the CeO_2 into clumps < 100 nm in size

Moment is *stable* in time. It diminishes by < 10% in a year

Dilution – Summary





10 µm latex microbeads

1 µm sugar particles

15nm γAl_2O_3

The smallest particles are most effective.

After dissolving the sugar, the moment reappears (increased)

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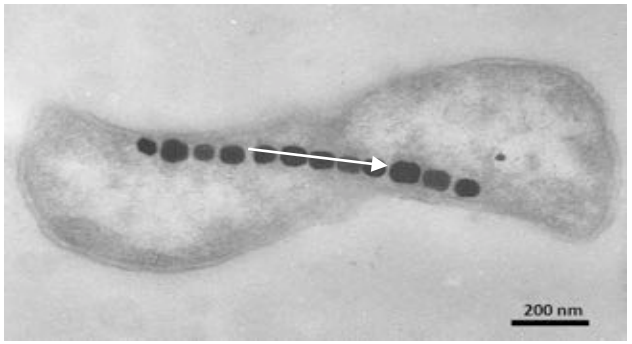
Summary of results

The syndrome seems unprecedented in the literature on magnetism: There is no evidence of superparamagnetism (scaling of M with H/T) and $H_{dipolar}$ is 1000 times too small for superferromagnetism

1. The energy scale is exceptionally large. The absence of temperature dependence from 4 K to 300 K suggests a 'Curie temperature' >1000 K

2. There is a mesoscopic length scale of order 100 nm needed for a collective magnetic response to appear.



Bacterium with ~50 nm Fe_3O_4 nanoparticles
Moment > 1000μ_B/particle

➢ How can we understand it ?

Interlude

Can quantum fluctuations of the vacuum produce observable effects in condensed matter? Siddhartha Sen

– Casimir force
– Lamb shift

– Jaynes-Cummings systems; Resonant optical cavity Ebbesen group; Strasbourg

Can we have effects without a resonant cavity ?

Photons of energy $\hbar\omega$ have wavelength $\lambda = 2\pi c/\omega$

λ is a natural length scale; Energy density $\mathcal{E} = \hbar\omega/\lambda^3$; $\hbar\omega = kT$ gives Stefan-Boltzmann law.

Energy density $\mathcal{E} = \frac{1}{2}\varepsilon_0 E^2$ where electric field $\boldsymbol{E} = \mathbf{u}\sqrt{(2h\omega/\varepsilon_0\lambda^3)}\exp\pm i\omega t$.
Energy of an electron in the field is $-e\boldsymbol{E}.\boldsymbol{x}$, where $\boldsymbol{x}$ is the displacement from =ium.

Zero-point energy $\frac{1}{2}\hbar\omega$ associated with each polarization of em field

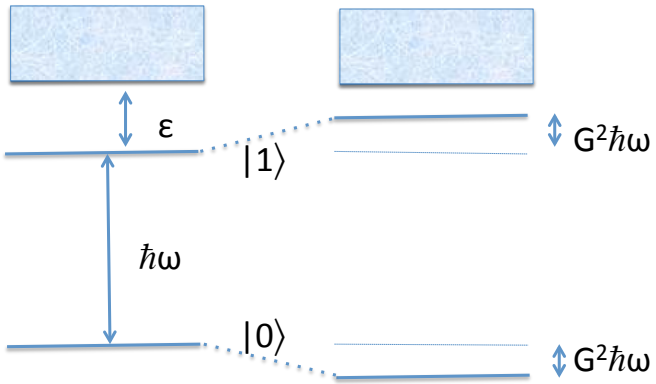
In a theory of the Lamb shift, the effect of the zero-point field is to create a rms displacement of the orbit

$$\delta_L = \sqrt{[2(\alpha/\pi)\ \ln 1/\alpha^2]}\ \lambda_c \qquad \delta_L = 0.52\ \text{pm}$$

fine structure constant

Compton wavelength of electron; 2.43 pm

Toy model; Model condensed matter as an assembly of *N* bound electrons, with ground state $|0\rangle$ and a stable electronic excited state $|1\rangle$ at energy $\hbar\omega$, at an energy ε below the ionization threshold. Ground state energy is lowered by $G^2\hbar\omega$, where $G^2 \propto N$, and $G \ll 1$



One-electron Hamiltonian is

$$\mathcal{H} = \hbar \begin{vmatrix} 0 & \Omega \\ \Omega & \omega \end{vmatrix}$$

where $\hbar\Omega = G\hbar\omega$ is the effect of ZP interaction

NB electrons are considered as *noninteracting*

Calculation of G for an ensemble of *N* such electrons. The occupy a volume of size $R \approx \lambda \approx 100$ nm..

The effect of their interaction with the ZP electric field is to replace *R* by *R'*

$$R' = R + \sqrt{N}\,\delta_L \qquad \text{where } \delta_L = 0.52 \text{ pm}$$

Volume increase is δV.

Energy density is now $\mathcal{E}(V + \delta V)$
Induced change in electic field $\delta\mathbf{E}(V) = \mathbf{E}(V + \delta V) - \mathbf{E}(V) = \mathbf{E}(V)\,(\delta V/2V)$ where $\delta V/V << 1$

The off-diagonal matrix element in the one-electron Hamiltonian $\mathcal{H}$

$$\hbar\Omega = G\hbar\omega = \langle 0|e\boldsymbol{x}.\,\delta\boldsymbol{E}(V)|1\rangle = \sqrt{(2\hbar\omega/\varepsilon_0\lambda^3)}\,\langle 0|e\boldsymbol{x}.\,\boldsymbol{u}|1\rangle$$

Hence $G = G = \sqrt{(\alpha)}(r_1/\lambda)(\delta V/V)$ where $r_1 = \langle 0|\boldsymbol{x}.\mathbf{u}|1\rangle$ (size of excited state orbital)

Expressions for G; 3D; $V \approx \lambda^3$; $\delta V/V = 3\sqrt{(N)}\delta_L/\lambda$ gives $G_3 = 3(r_1\delta_L/\lambda^2)\sqrt{(\alpha N)}$

2G; $V \approx \lambda^2 b$; $\delta V/V = \sqrt{(N)}\delta_L/b$ gives $G_2 = \{r_1\delta_L/b\sqrt{(b\lambda)}\}\sqrt{(\alpha N)}$

Is a realistic solution possible?

Condition $kT < G^2\hbar\omega < \varepsilon$

Suppose T = RT

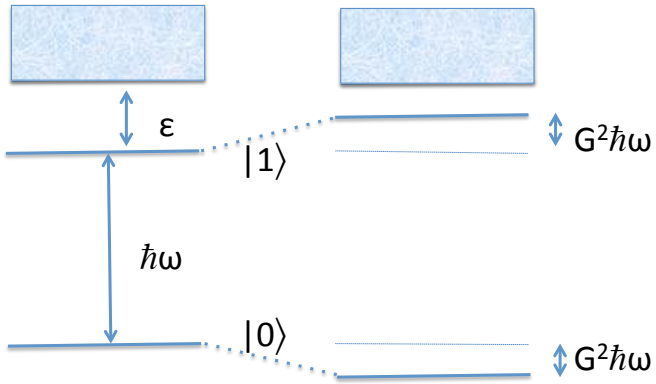


Table 1. Values of parameters for three-dimensional and quasi-two-dimensional systems

$\hbar\omega$ (eV)	λ (nm)	N^{at} $\propto \lambda^3$	N^{surf} $\propto \lambda^2$	G^{RT} $\propto \sqrt{\lambda}$	N_3^{RT} $\propto \lambda^5$	N_2^{RT} $\propto \lambda^2$	N_3^+ $\propto \lambda^3$	N_2^+ $\propto \lambda^2$
1	1240	$1.2\ 10^{11}$	$2.5\ 10^{7}$	0.16	$6.9\ 10^{17}$	$1.2\ 10^{7}$	$9.8\ 10^{6}$	$7.9\ 10^{3}$
2	620	$1.5\ 10^{10}$	$6.2\ 10^{6}$	0.11	$2.2\ 10^{16}$	$3.0\ 10^{6}$	$1.2\ 10^{6}$	$1.9\ 10^{3}$
5	248	$1.0\ 10^{9}$	$1.0\ 10^{6}$	0.07	$2.2\ 10^{14}$	$4.8\ 10^{5}$	$7.8\ 10^{4}$	$3.2\ 10^{2}$
10	124	$1.2\ 10^{8}$	$2.5\ 10^{5}$	0.05	$6.9\ 10^{12}$	$1.2\ 10^{5}$	$9.8\ 10^{3}$	$7.9\ 10^{1}$

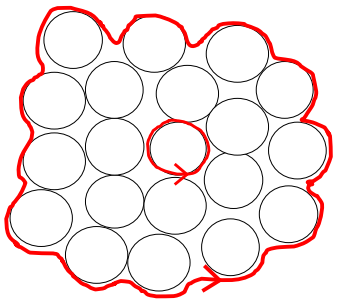
Effects observable at RT may be possible in 2D systems with large surface/interface area; *Never* in 3D systems.

BOTTOM LINE

An explanation

— It has nothing to do with ferromagnetism (No Ce compound has T_c > 15 K!)

— We are looking at giant orbital paramagnetism associated with persistent electric currents in coherent domains > 100 nm is size.



— Quantum field theory envisages such coherent domains due to resonance with vacuum fluctuations of the electromagnetic field. (cf Casimir force), which renormalizes the interaction by $\sqrt{N}$, where N is the number of particles (Ce atoms) in the coherent domain.

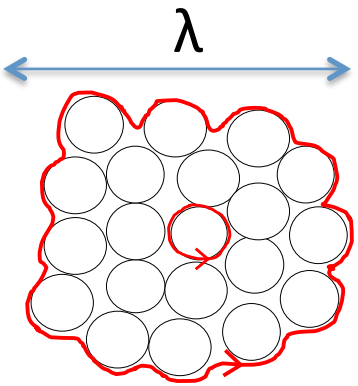
— The theory predicts that the magnetization curve should be of the form

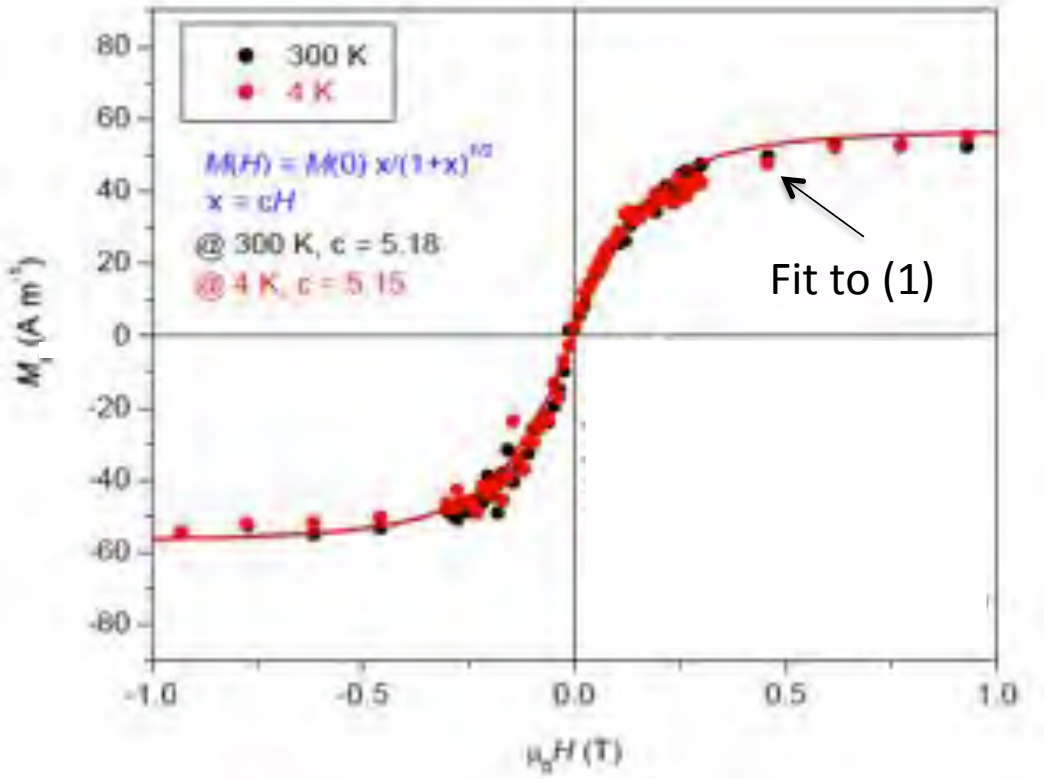
$$M = M_s x/(1 + x)^{1/2} \qquad (1)$$

.

E del Guidice et al, PRL 61 1085 (1985)

An explanation





$x = CB$ (2)

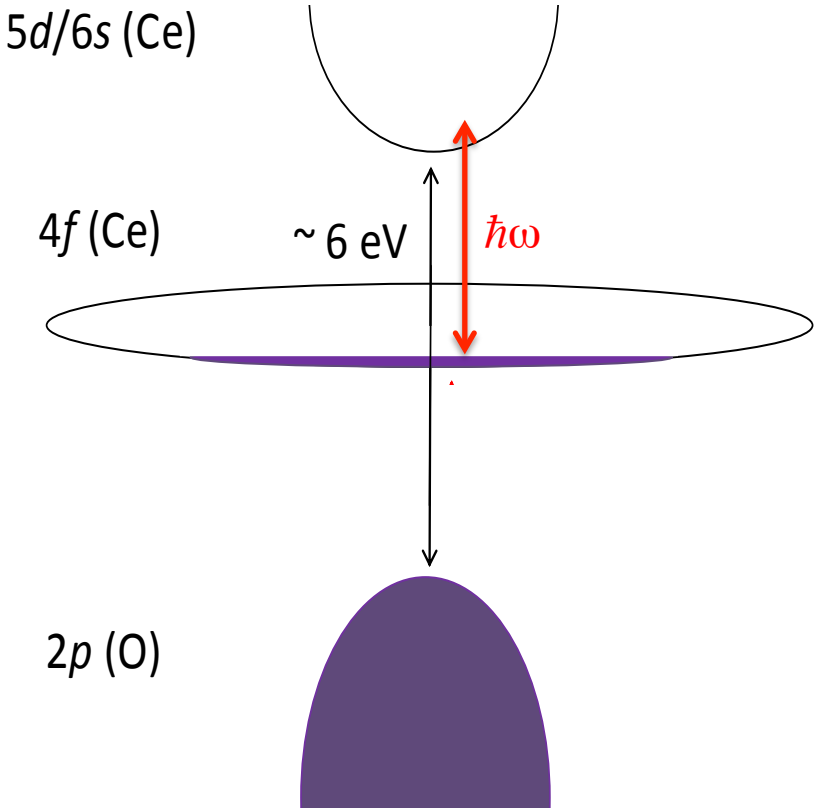
$x = 2V/\hbar\omega$ where $V = mB$
$= (\pi/6)\lambda^3 MB$

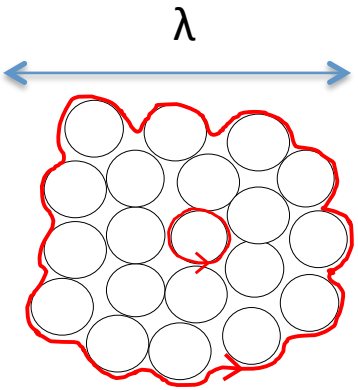
$\lambda = 2\pi c/\omega$ the wavelength of the em radiation is identified with the size of the coherent domain

$$\lambda^4 = 3hcC/\pi M_s \quad (3)$$

— Fitting the magnetization curves gives both the length scale and the energy scale for the system

An explanation





C = 9.4 (7) T^{-1}

M = 58 Am^{-1}

λ = 327 nm

$\hbar\omega$ = 3.8 eV

A coherent domain is 320 nm in size contains $N = 5\ 10^8$ Ce atoms or ~ $5\ 10^5$ nanoparticles with a moment $\mu = 2\ 10^5\ \mu_B$. The moment per nanoparticles in the coherent domain is 2.4 μ_B ➔ 8% of the sample is in the coherent state.

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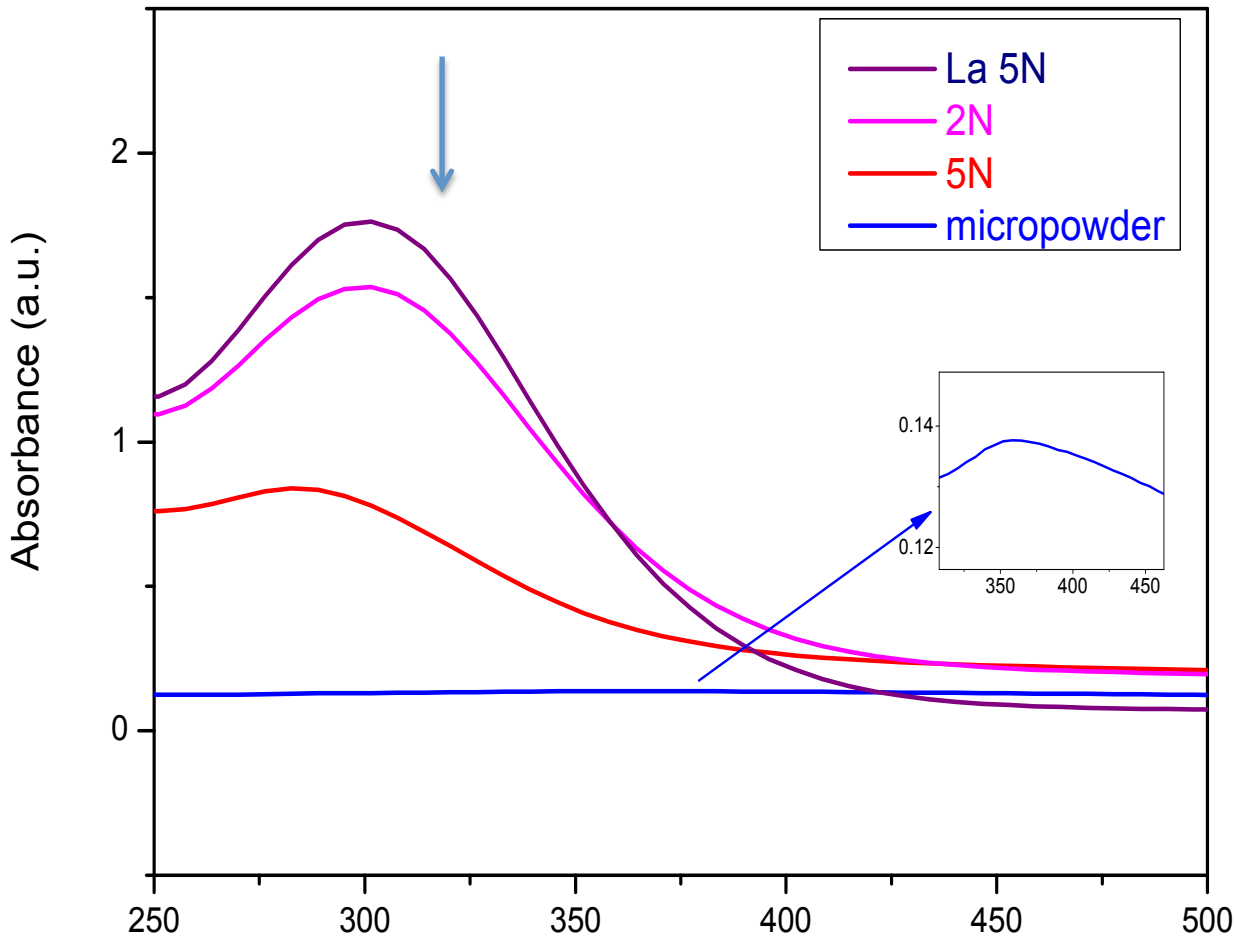
UV absorption spectrum



Summary

- Clusters of 4 nm CeO_2 nanoparticles exhibit *giant orbital paramagnetism.*
- The orbital currents are due to resonant coupling with zero-point fluctuations of the electromagnetic field in coherent domains ~ 300 nm is size.
- This *may* be the first evidence of an influence of these fluctuations in condensed matter.
- The explanation can perhaps be extended to other manifestations of **the syndrome**
- If true, many more manifestations of the effect are anticipated (Water at biological membranes, interfacial nanobubbles……)

Coey-Stamenov Group 2014

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Thank you !

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