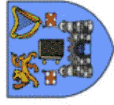


# Magnetism in dilute ferromagnetic oxides and $d^0$ ferromagnetism

**J. M. D. Coey**

Physics Department and CRANN, Trinity College  
Dublin 2, Ireland



Santa Barbara 22-iii-2006

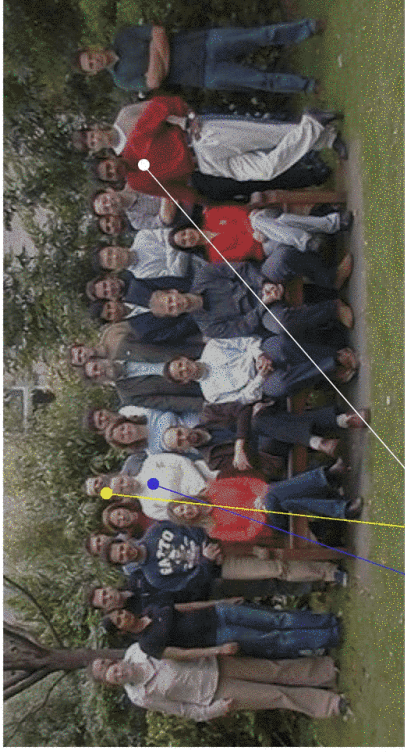


## Outline

- Magnetic order in solids;  $m - J$  paradigm.
- Dilute ferromagnetic oxides, magnetic semiconductors  
ZnO: Sc - Cu, SnO<sub>2</sub>: Ti - Cu
- A model; impurity-band exchange + magnetic polarons
- $d^0$  ferromagnetism; HfO<sub>2</sub>, CaB<sub>6</sub>
- Perspectives; **warning!**

Santa Barbara 22-iii-2006

## Acknowledgements



Dr M. Venkatesan  
 Dr.A. Douvalis  
 Oscar Céspedes  
 Ciara Fitzgerald  
 Plamen Stamenov



Prof J. G. Lunney  
 Des O' Mahony  
 Enrico de Posada  
 Dr Kentaro Nakajima

## 1. The $m$ - $J$ paradigm

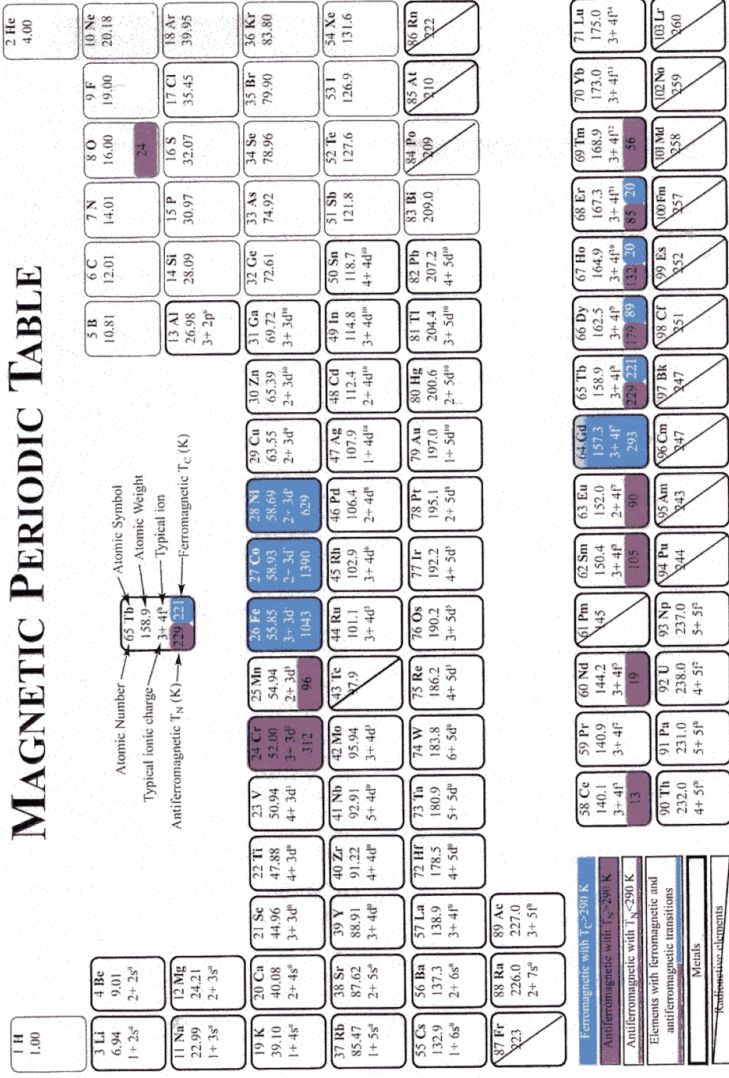
$m$  represents the magnetic moment, mainly localized on the atoms

$J$  represents the exchange coupling of electron spins.

$d^0$  ferromagnetism challenges our understanding of magnetism in solids. It seems to be incompatible with the  $m$ - $J$  paradigm.



# MAGNETIC PERIODIC TABLE

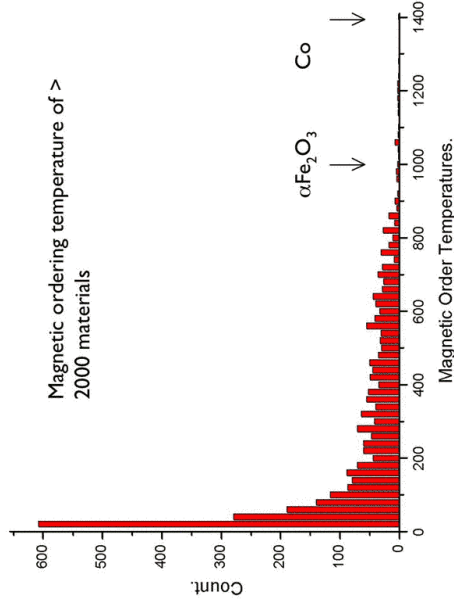


## 2. Dilute ferromagnetic oxides; $T_C > RT$

Material	$E_g$ (eV)	Doping	Moment ( $\mu_B$ )	$T_C$ (K)	Reference
GaN	3.5	Mn – 9%	0.9	940	S. Sonoda et al (2002)
		Cr	-	> 400	M. Hashimoto et al (2002)
AlN	4.3	Cr – 7%	1.2	>600	Wu et al (2003)
		V – 5%	4.2	>400	Hong et al (2004)
TiO <sub>2</sub>	3.2	Co – 1-2%	0.3	>300	Matsumoto et al (2001)
		Co – 7%	1.4	>650	Shinde et al (2003)
		Fe – 2%	2.4	300	Wang et al(2003)
		Fe – 5%	1.8	610	Coey et al (2004)
SnO <sub>2</sub>	3.5	Co – 5%	7.5	650	Ogale et al (2003)
		V – 15 %	0.5	>350	Saeki et al (2001)
ZnO	3.3	Mn – 2.2%	0.16	>300	P. Sharma et al (2003)
		Fe5%,Cu1%	0.75	550	Han et al, (2002)
		Co – 10%	2.0	280-300	Ueda et al (2001)
		Ni – 0.9%	0.06	>300	Radovanovic et al (2003)
Cu <sub>2</sub> O	2.0	Co5%,Al0.5%	0.2	> 300	Kale et al (2003)



# The m-J paradigm



In dilute systems,  $T_c$  usually scales as  $x$  or  $x^{1/2}$ ;

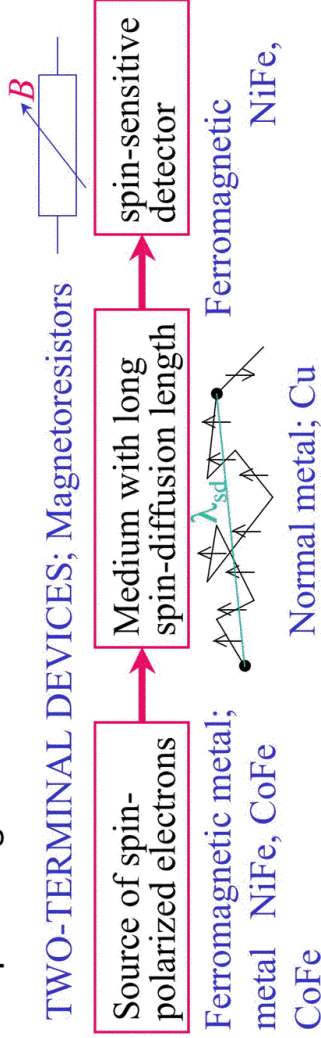
If  $x = 5\%$ ,  $T_c < 50$  K or 250 K

Santa Barbara 22-iii-2006

# Spin Electronics

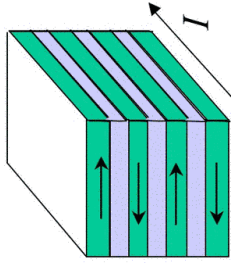
*Conventional electronics has ignored the spin in the electron:*

- Code information into the  $\uparrow$  and  $\downarrow$  channels  $e = 1.6 \cdot 10^{-19}$  C
- Manipulate the  $\uparrow$  and  $\downarrow$  electrons independently  $m = eh/2m = 1 \mu_B$
- Exploit magnetic and electric fields



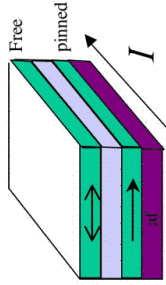
Santa Barbara 22-iii-2006

# Magnetoresistance

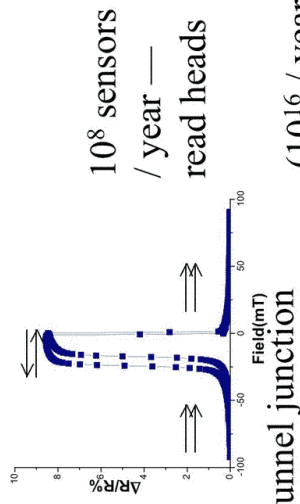


Giant magnetoresistance

*Fert et al*  
1988

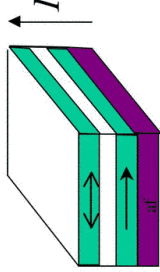


Spin valve



10<sup>8</sup> sensors  
/ year —  
read heads

Magnetic tunnel junction



(10<sup>16</sup> / year  
MRAM)

Santa Barbara 22-iii-2006

Number of Terminals	2	2+	3 / 3+	4 / 4+
Classical Devices	Switch Resistor Diode	Photodiode Varistor	Transistor Filter Amplifier	Wheatstone Bridge 2-gate MOSFET Tetrode Multiplier
Spin Electronic Devices	Spin Switch	Magnetic switch (MTJ) Magnetoresistor Magnetic Photodiode	Spin transistors	Hall Probe Magnetic Gradiometer (bridge)

## Half Metals

— A magnetically-ordered metal with a fully spin-polarised conduction band

$$P = (N^{\uparrow} - N^{\downarrow}) / (N^{\uparrow} + N^{\downarrow})$$

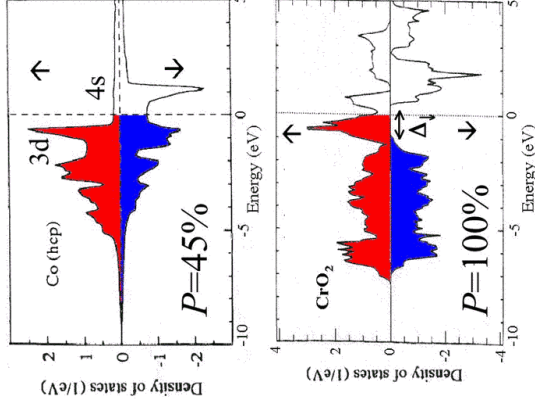
— Metallic for  $\uparrow$  electrons but semiconducting for  $\downarrow$  electrons. Spin gap  $\Delta_{\uparrow}$  or  $\Delta_{\downarrow}$

— Integral spin moment  $n \mu_B$

— Mostly oxides, Heusler alloys, some semiconductors

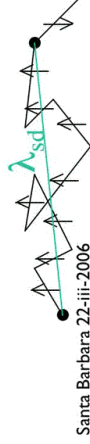
$$MR = 2P / (1 + P^2)$$

Santa Barbara 22-iii-2006



## Spin diffusion lengths (nm)

	$\lambda_{\uparrow}$ (nm)	$\lambda_{\downarrow}$ (nm)	$\lambda_{sd}$ (nm)
semiconductors	200	2000	
semimetals	>50	>500	
s-band metals	30	300	
d-band metals	5.0	0.9	30



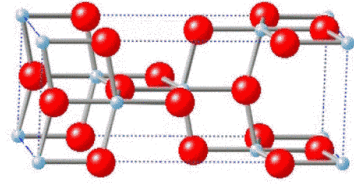
Santa Barbara 22-iii-2006

## Mobility of semiconductors, semimetals and metals

	Curie Point (K)	Mobility ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )
Semiconductors		
Si	-	1400
InSb	-	30000
GaAs	-	8000
(GaMn)As	170	10
Semimetals		
Graphite	-	2000
Bi	-	180000
Metals		
Cu	-	44
Au	-	48
Fe	1044	20
Co	1380	12
Ni	628	16
CrO <sub>2</sub>	392	1.4
Fe <sub>3</sub> O <sub>4</sub>	860	0.2

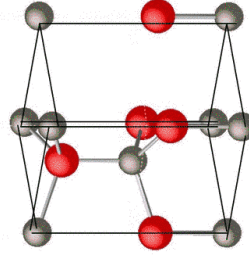
Santa Barbara 22-iii-2006

## Crystal structures



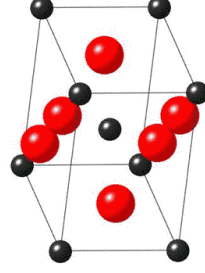
TiO<sub>2</sub>

Anatase Structure  
Spacegroup=I4/amd  
a=3.79Å  
c=9.51Å  
Ti radius=0.62Å  
N radius=1.35Å



ZnO

Wurtzite Structure  
Spacegroup=P63/mc  
a=3.25Å  
c=5.21Å  
Zn radius=0.80Å  
O radius=1.21Å

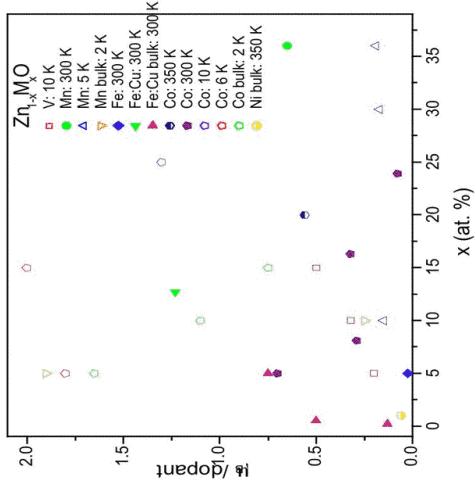
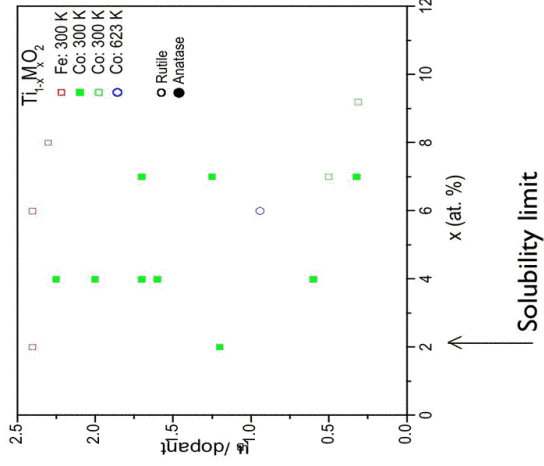


SnO<sub>2</sub>

Rutile Structure  
Spacegroup=P42/mnm  
a=4.75Å  
c=3.18Å  
Sn radius=0.74Å  
O radius=1.35Å

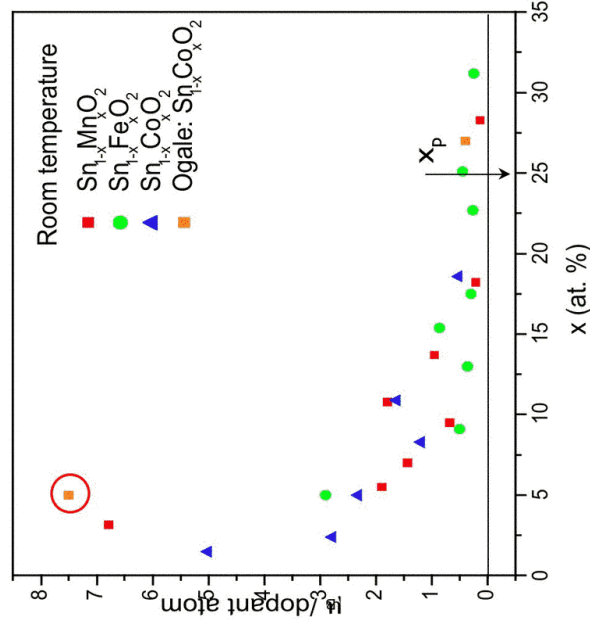
Santa Barbara 22-iii-2006

# Moments in $TiO_2$ and $ZnO$



Santa Barbara 22-iii-2006

# Moments in $SnO_2$



Santa Barbara 22-iii-2006



## The syndrome

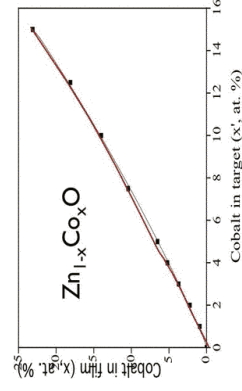
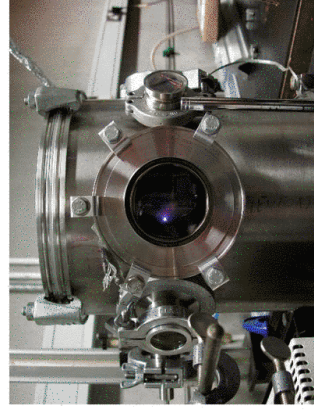
### Dilute magnetic oxide *thin films*:

- i) The oxides are usually *n*-type. They may be partially compensated, semiconducting or insulating.
- ii) The average moment per transition-metal cation  $m_c$  approaches  $x$  (or even exceeds) the spin-only moment at low concentrations  $x$  of magnetic cations. It falls progressively as  $x$  increases.
- iii) The ferromagnetism is already present at concentrations that lie far below the percolation threshold  $x_p$  associated with nearest-neighbour cation coupling.  $T_C$  can be far above RT.
- iv) Properties vary greatly for samples of the same nominal composition prepared by different methods, or by different groups.

Santa Barbara 22-iii-2006

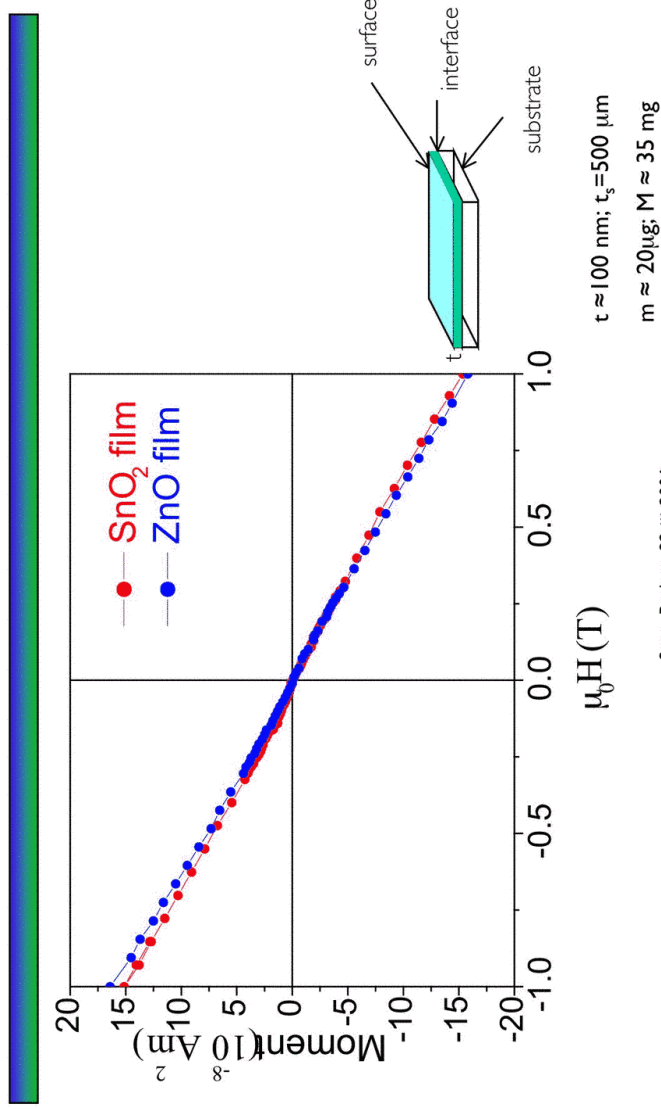
## ZnO : M, M = Sc - Cu

- Ceramic targets were prepared using a solid state reaction technique
- Films were deposited using a KrF excimer laser operating at 248 nm and 10 Hz in vacuum
- Laser fluence on target was  $1.8 \text{ J/cm}^2$
- The target-substrate distance was 35 mm
- Film thickness was monitored during deposition using optical reflectivity.

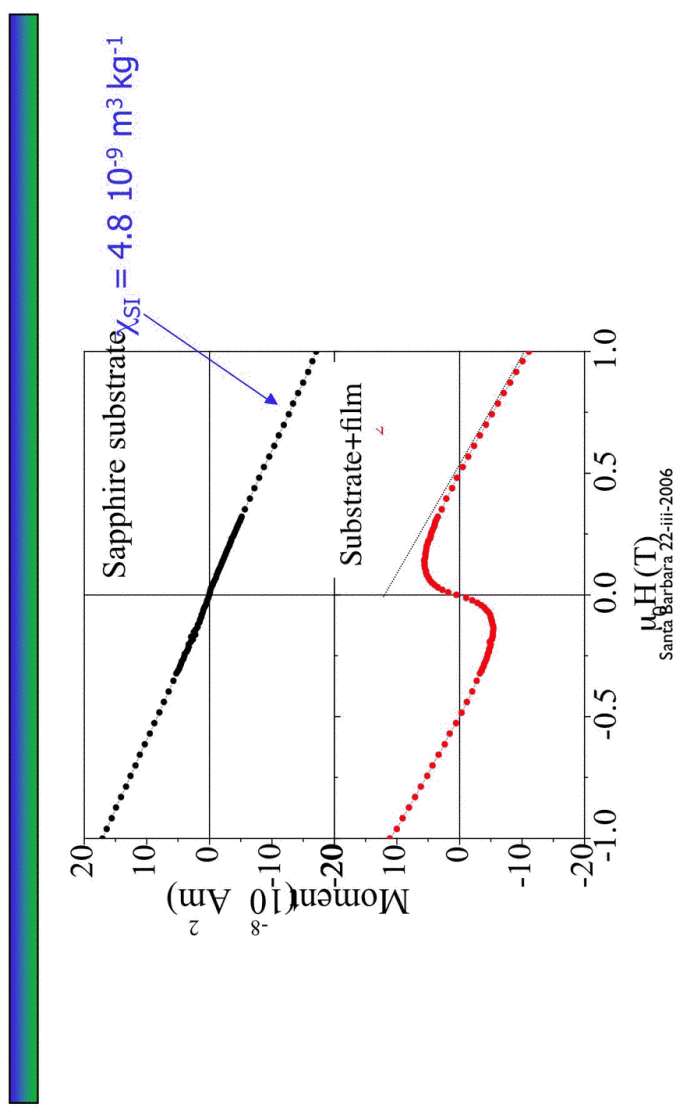


Santa Barbara 22-iii-2006

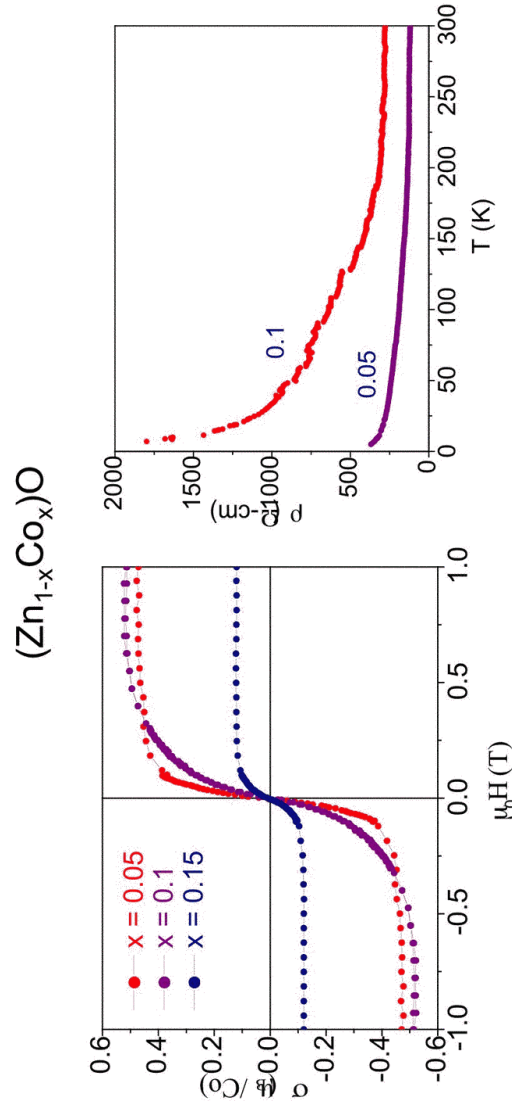
# Undoped SnO<sub>2</sub> and ZnO films



# Data reduction



## ZnO thin films



Santa Barbara 22-iii-2006

## Systematic study of ZnO films

To try to understand the magnetism in these films, we studied:

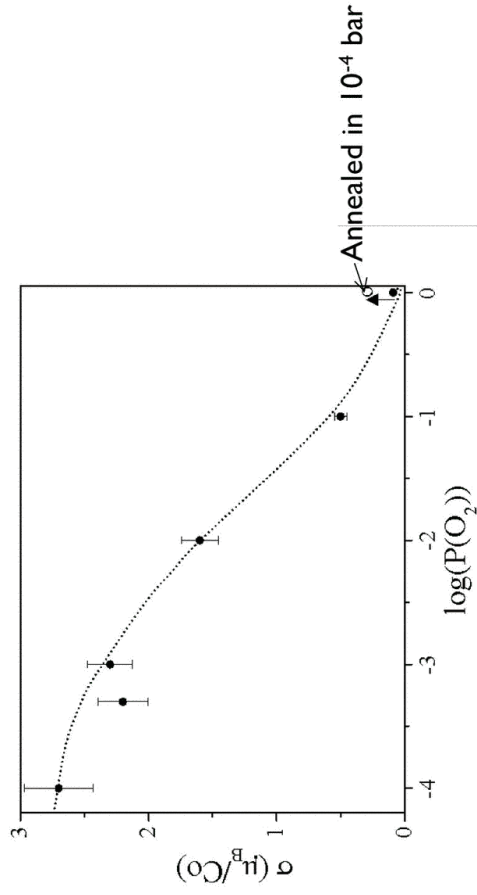
- Magnetism as a function of preparation conditions  $P(\text{O}_2)$
- Magnetism as a function of preparation conditions  $T_{\text{substrate}}$
- Magnetism as a function of dopant concentration  $x$
- Magnetism as a function of film thickness  $t$
- Magnetism as a function of dopant element, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu.
- Magnetism as a function of film orientation.
- Magnetoresistance, undoped and Co-doped, AMR, TMR

magnetism  $\approx$  RT magnetization curve

Venkatesan et al PRL **93** 177206 (2004)

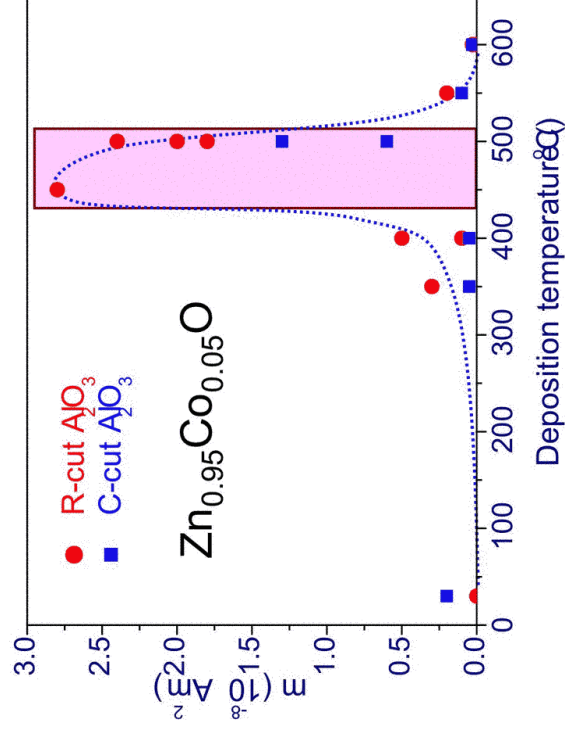
Santa Barbara 22-iii-2006

## Vary oxygen pressure

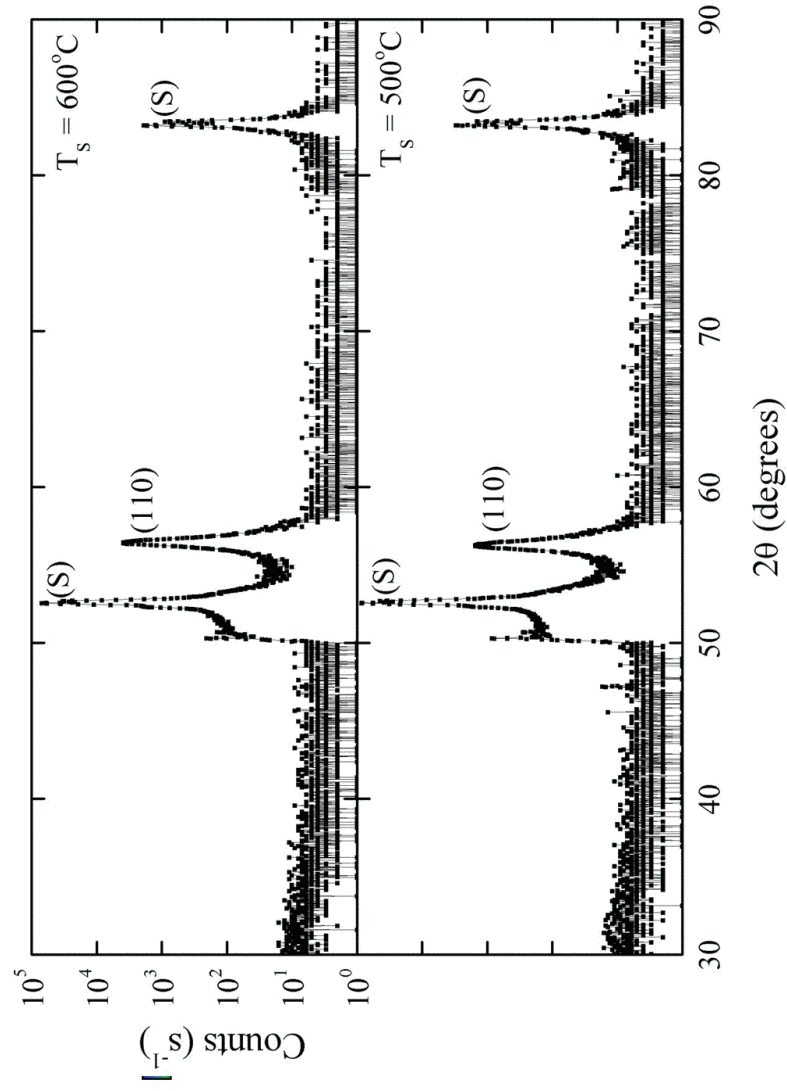


$(Zn_{0.93}Co_{0.07}O)$  produced in different oxygen pressures,  $10^{-4}$  - 1 mbar

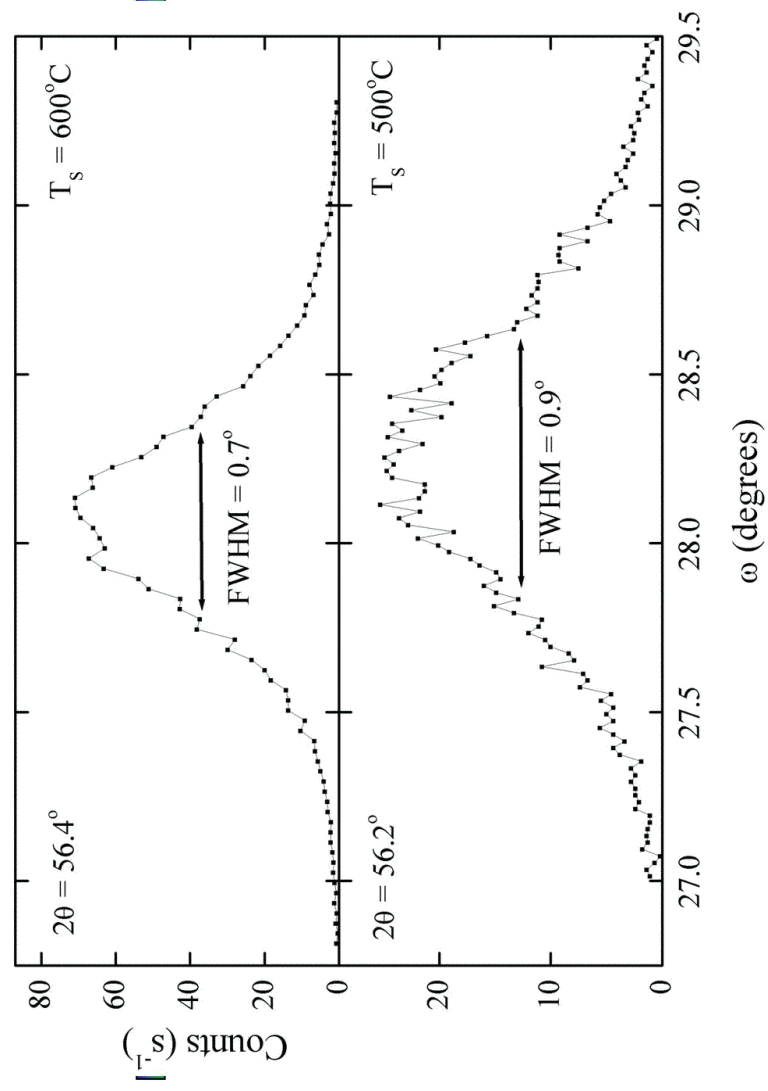
## Vary substrate temperature



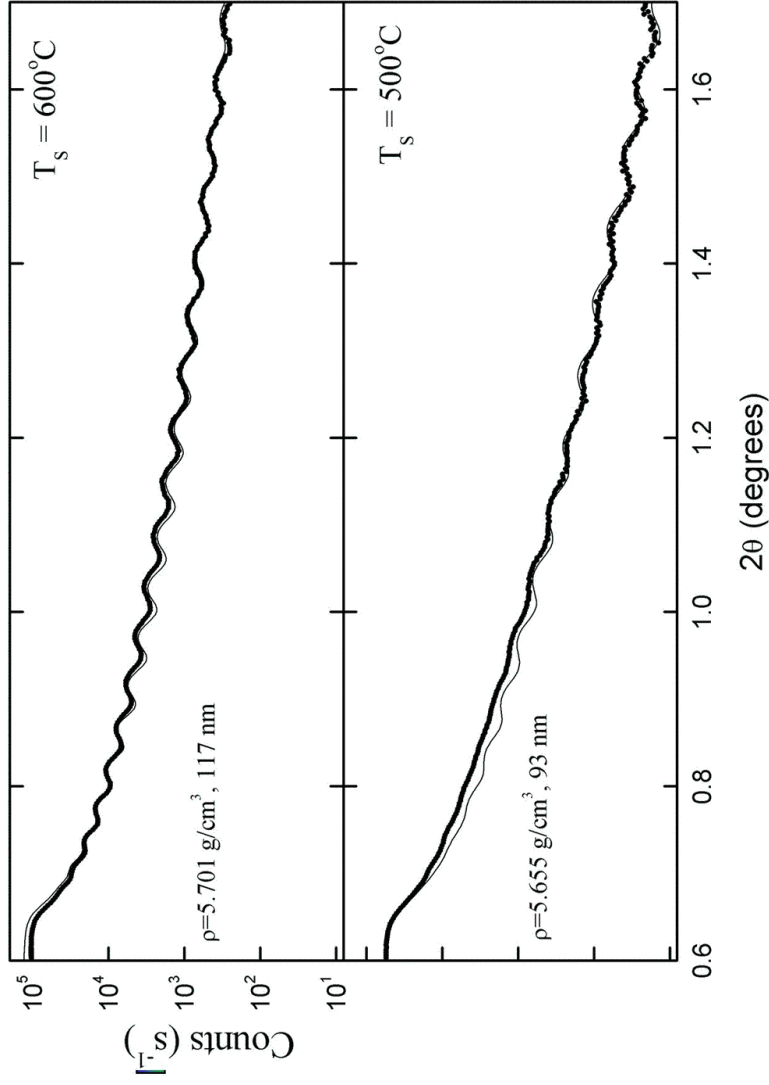




Santa Barbara 22-iii-2006

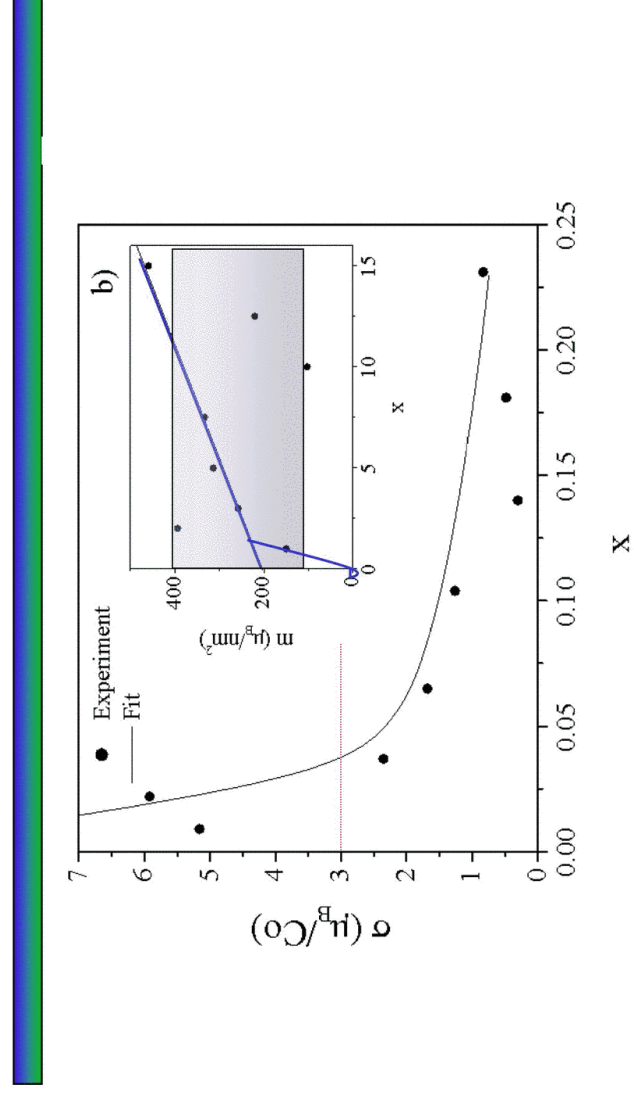


Santa Barbara 22-iii-2006



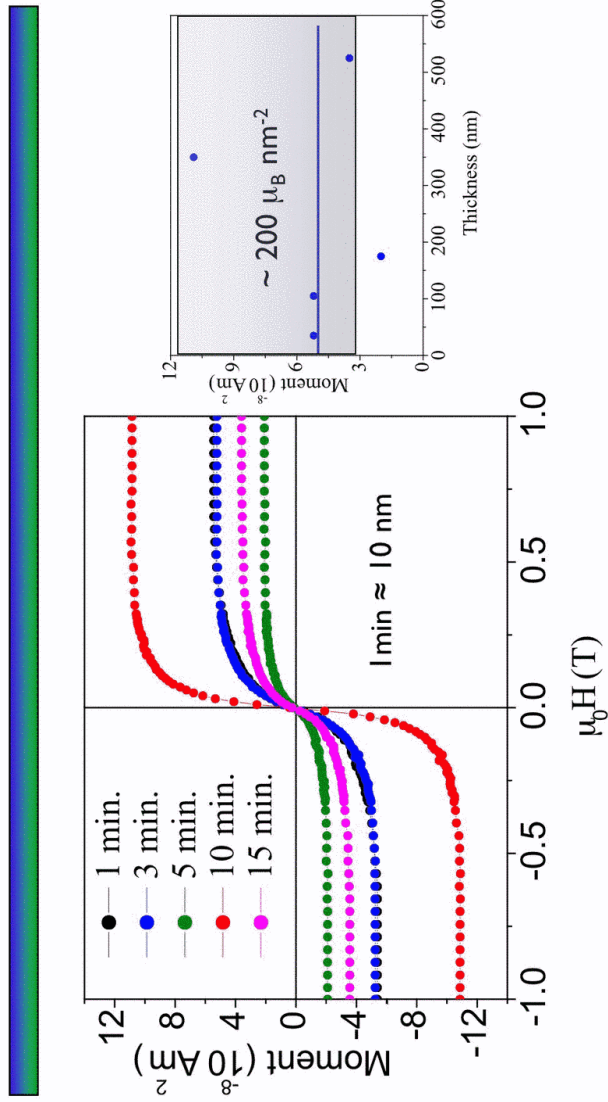
Santa Barbara 22-iii-2006

## Vary composition



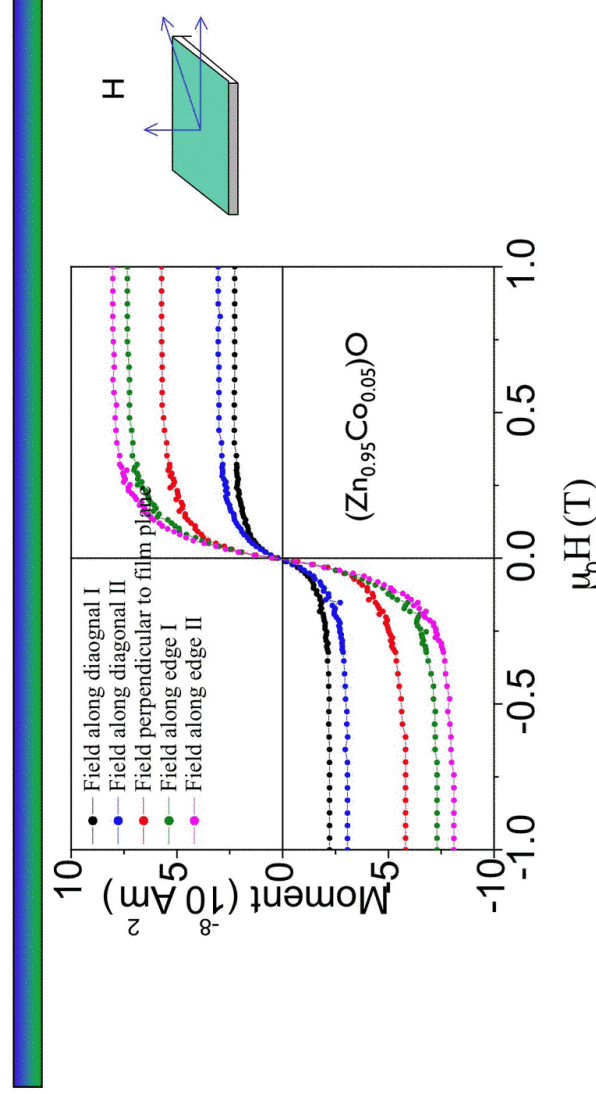
Santa Barbara 22-iii-2006

# Vary thickness



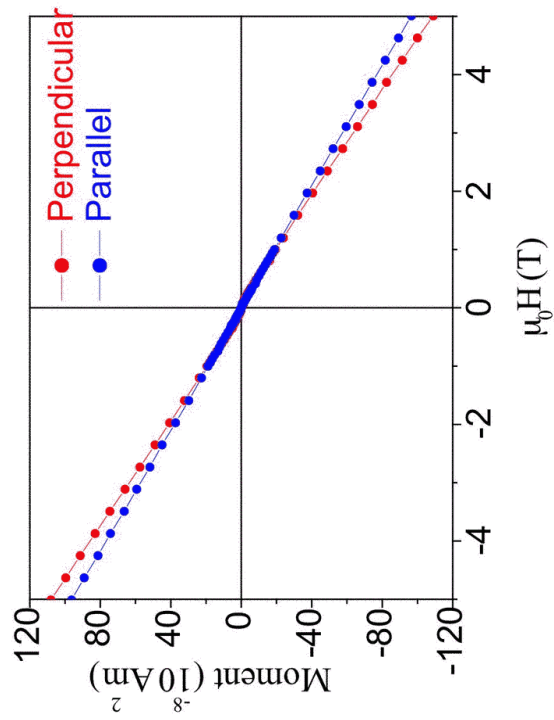
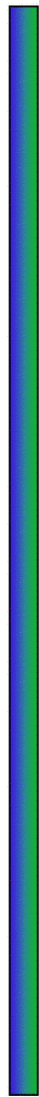
Santa Barbara 22-iii-2006

# Vary orientation

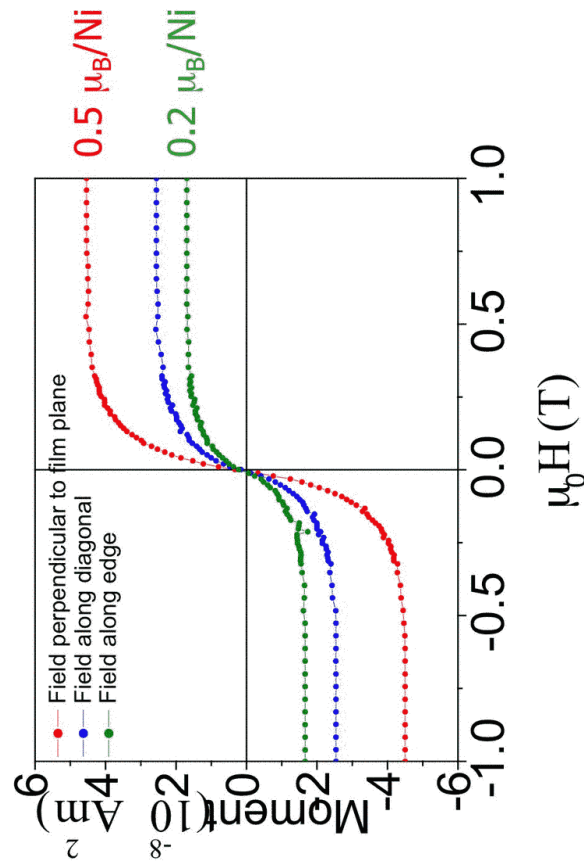


Stamenov and Coey, RSI 77 015106 (2006)

Santa Barbara 22-iii-2006

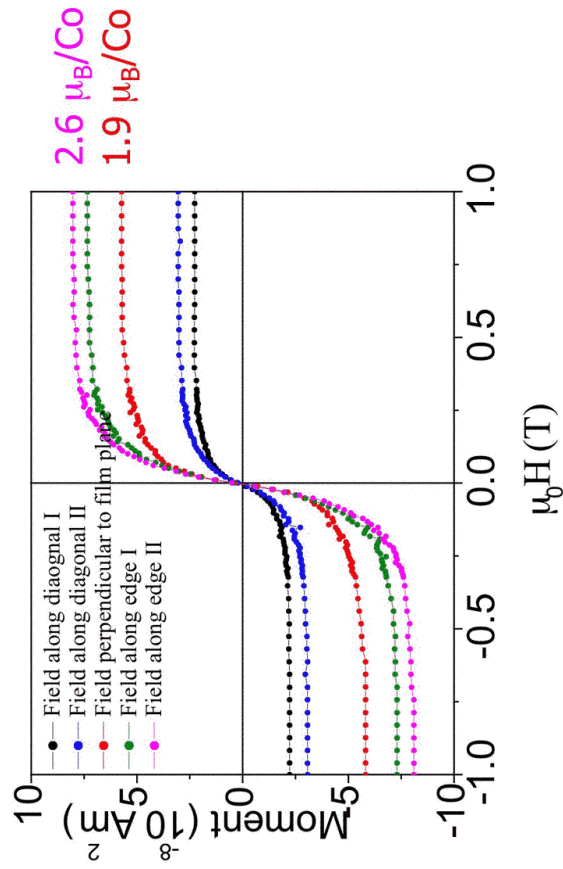


Santa Barbara 22-iii-2006

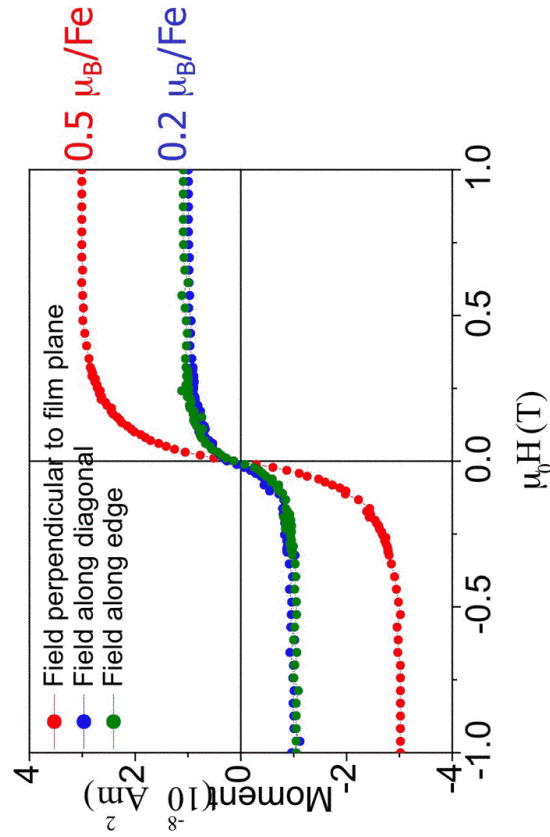


Santa Barbara 22-iii-2006

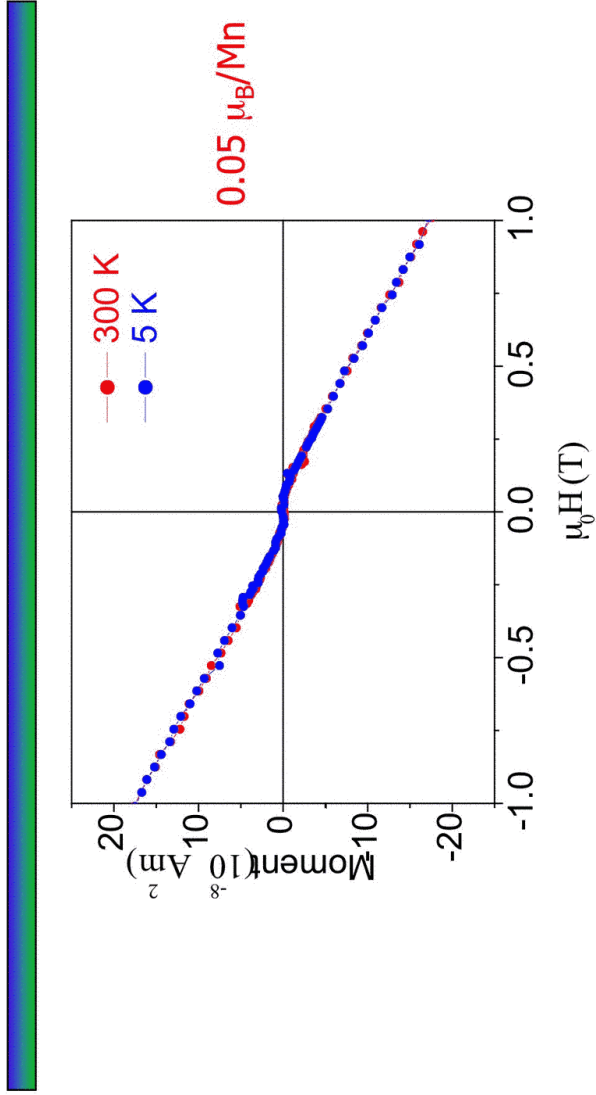




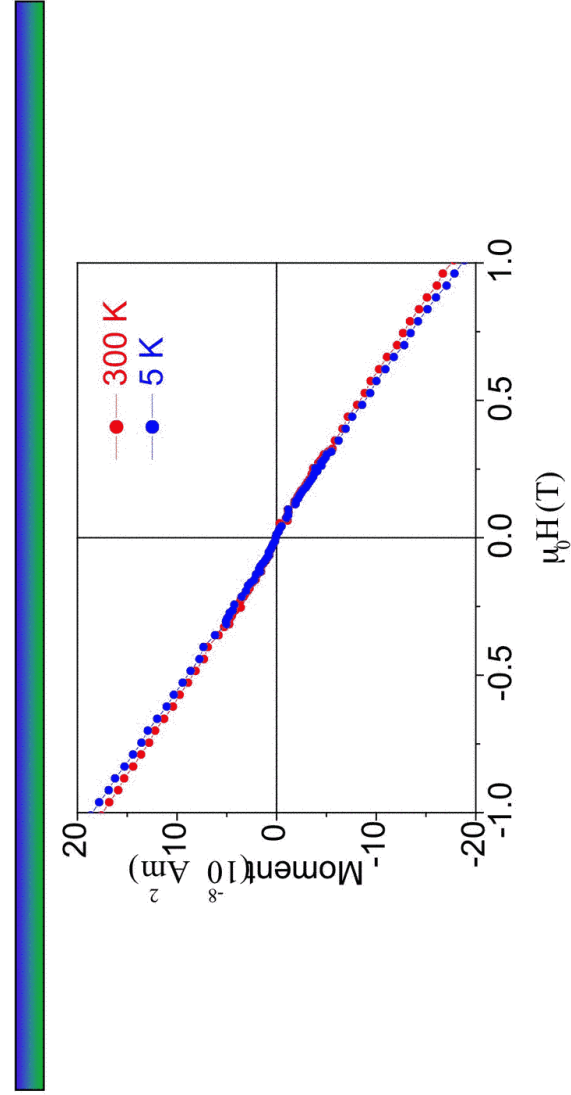
Santa Barbara 22-iii-2006



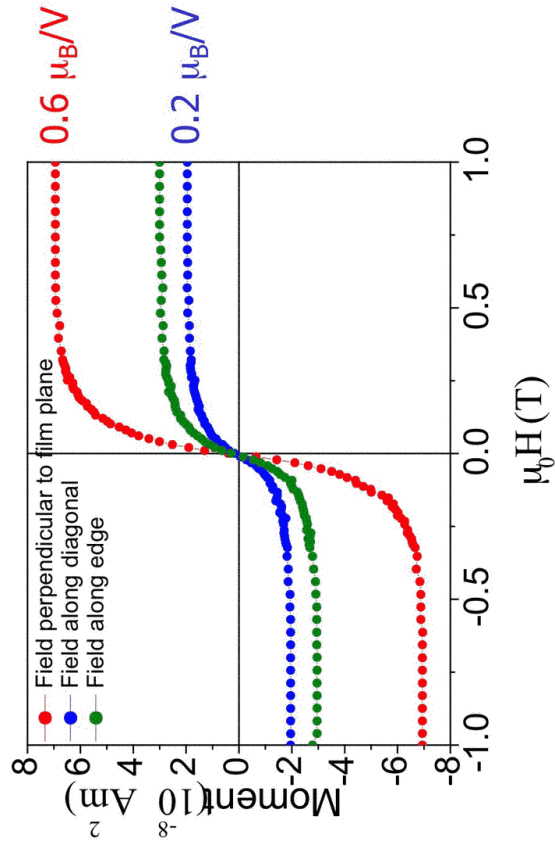
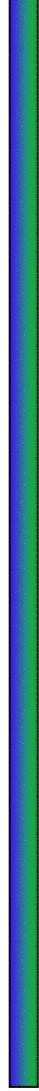
Santa Barbara 22-iii-2006



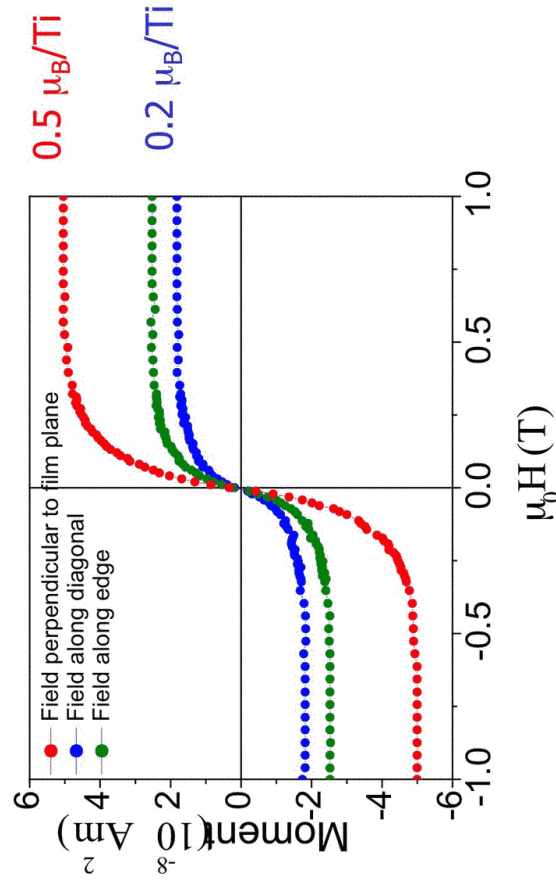
Santa Barbara 22-iii-2006



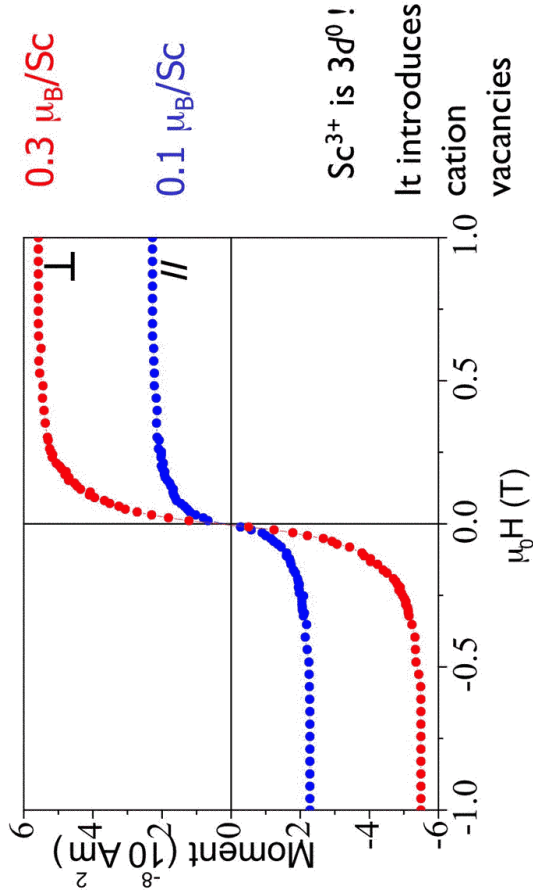
Santa Barbara 22-iii-2006



Santa Barbara 22-iii-2006



Santa Barbara 22-iii-2006



Santa Barbara 22-iii-2006

### MAGNETIC PERIODIC TABLE

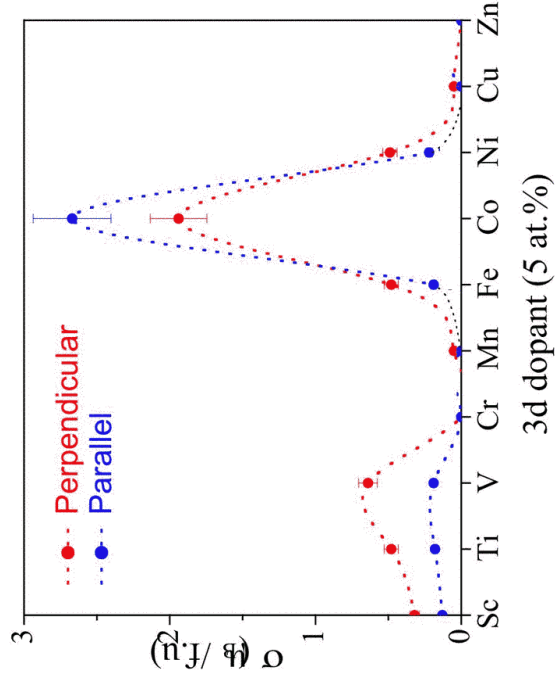
Atomic Number	Atomic Symbol	Atomic Weight	Typical ionic	Antiferromagnetic T <sub>N</sub> (K)	Ferromagnetic T <sub>c</sub> (K)
1 H		1.00			
2 He		4.00			
3 Li		6.94	1+ 2s		
4 Be		9.01	2+ 2s		
5 B		10.81			
6 C		12.01			
7 N		14.01			
8 O		16.00			
9 F		19.00			
10 Ne		20.18			
11 Na		22.99	1+ 3s		
12 Mg		24.21	2+ 3s		
13 Al		26.98			
14 Si		28.09			
15 P		30.97			
16 S		32.07			
17 Cl		35.45			
18 Ar		39.95			
19 K		39.10	1+ 4s		
20 Ca		40.08	2+ 4s		
21 Sc		44.96	3+ 3d		
22 Ti		47.88	4+ 3d		
23 V		50.94	4+ 3d		
24 Cr		52.00	3+ 3d		
25 Mn		54.94	2+ 3d		
26 Fe		55.85	3+ 3d		
27 Co		58.93	2+ 3d		
28 Ni		58.69	2+ 3d		
29 Cu		63.55	2+ 3d		
30 Zn		65.39	2+ 3d		
31 Ga		69.72	3+ 3d		
32 Ge		72.61			
33 As		74.92			
34 Se		78.96			
35 Br		79.90			
36 Kr		83.80			
37 Rb		85.47	1+ 5s		
38 Sr		87.62	2+ 5s		
39 Y		88.91	3+ 4d		
40 Zr		91.22	4+ 4d		
41 Nb		92.91	5+ 4d		
42 Mo		95.94	3+ 4d		
43 Tc		97.9			
44 Ru		101.1	3+ 4d		
45 Rh		102.9	3+ 4d		
46 Pd		106.4	2+ 4d		
47 Ag		107.9	1+ 4d		
48 Cd		112.4	2+ 4d		
49 In		114.8	3+ 4d		
50 Sn		118.7	4+ 4d		
51 Sb		121.8			
52 Te		127.6			
53 I		126.9			
54 Xe		131.6			
55 Cs		132.9	1+ 6s		
56 Ba		137.3	2+ 6s		
57 La		138.9	3+ 4f		
58 Ce		140.1	3+ 4f		
59 Pr		140.9	3+ 4f		
60 Nd		144.2	3+ 4f		
61 Pm		145			
62 Sm		150.4	3+ 4f		
63 Eu		152.0	2+ 4f		
64 Gd		157.3	3+ 4f		
65 Tb		158.9	3+ 4f		
66 Dy		162.5	3+ 4f		
67 Ho		164.9	3+ 4f		
68 Er		167.3	3+ 4f		
69 Tm		168.9	3+ 4f		
70 Yb		173.0	3+ 4f		
71 Lu		175.0	3+ 4f		
72 Hf		178.5	4+ 5f		
73 Ta		180.9	5+ 5f		
74 W		183.8	6+ 5f		
75 Re		186.2	4+ 5f		
76 Os		190.2	3+ 5f		
77 Ir		192.2	4+ 5f		
78 Pt		197.0	2+ 5f		
79 Au		197.0	1+ 5f		
80 Hg		200.6	2+ 5f		
81 Tl		204.4	3+ 5f		
82 Pb		207.2	4+ 5f		
83 Bi		209.0			
84 Po		209			
85 At		210			
86 Rn		222			
87 Fr		223			
88 Ra		226.0	2+ 7s		
89 Ac		227.0	3+ 5f		
90 Th		232.0	4+ 5f		
91 Pa		231.0	5+ 5f		
92 U		238.0	4+ 5f		
93 Np		237.0	5+ 5f		
94 Pu		244			
95 Am		243			
96 Cm		247			
97 Bk		247			
98 Cf		251			
99 Es		252			
100 Fm		257			
101 Md		258			
102 No		259			
103 Lr		260			

Legend:

- Antiferromagnetic with T<sub>N</sub> > 290 K
- Antiferromagnetic with T<sub>N</sub> < 290 K
- Antiferromagnetic with T<sub>N</sub> < 290 K
- Elements with ferromagnetic and antiferromagnetic transitions
- Metals
- Nonmetallic elements

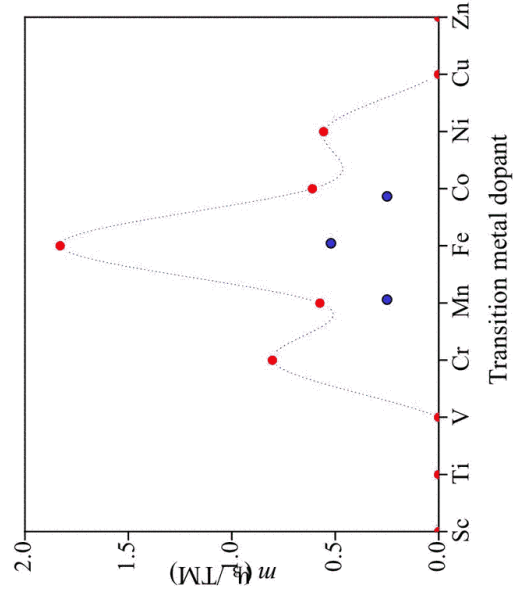


## Summary of anisotropy for ZnO



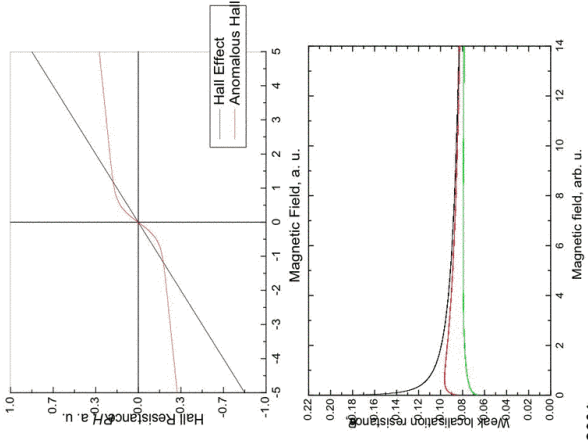
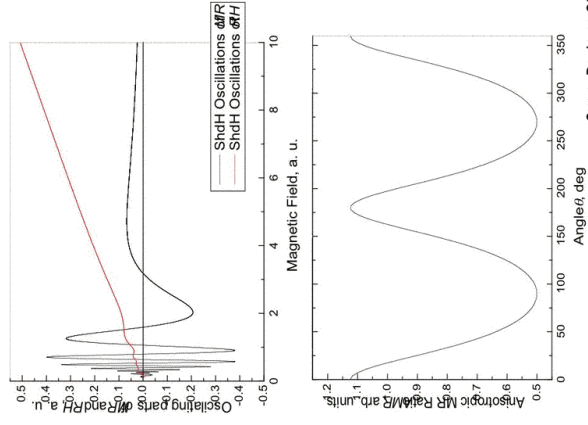
Santa Barbara 22-iii-2006

## Summary of anisotropy for SnO<sub>2</sub>



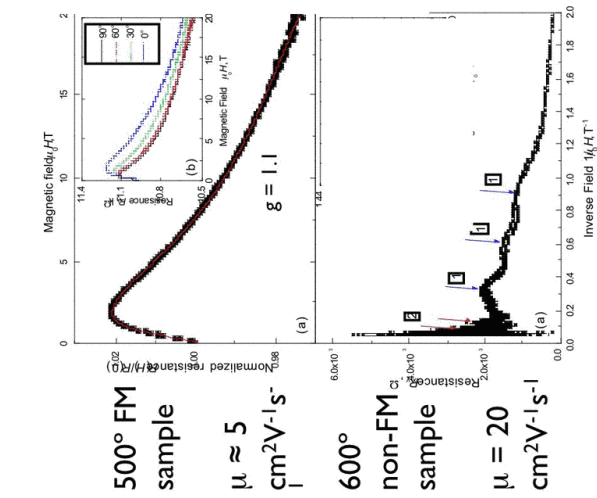
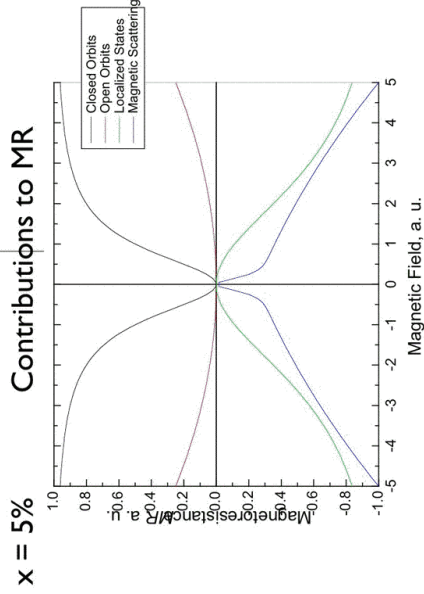
Santa Barbara 22-iii-2006

# The MR Zoo – Hall, ShdH, AMR & WL



Santa Barbara 22-iii-2006

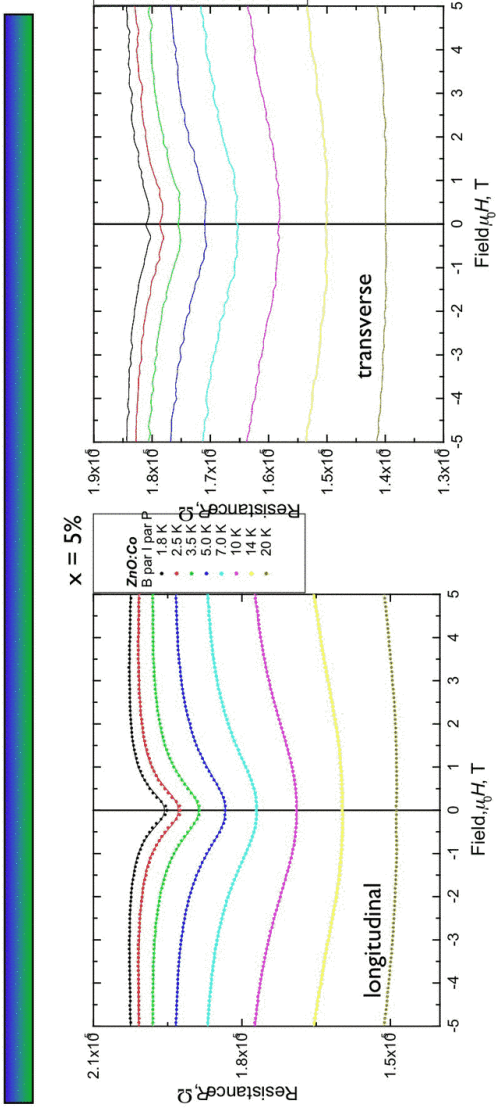
# Magnetoresistance of ZnO - Co



Transport is explained in terms of

- i) Open and closed orbits (positive  $B^2$  MR)
- ii) Ionized impurity scattering  $\approx -B^2$
- iii) Magnetic scattering  $\approx -M^2$

# Magnetoresistance of ZnO - Co

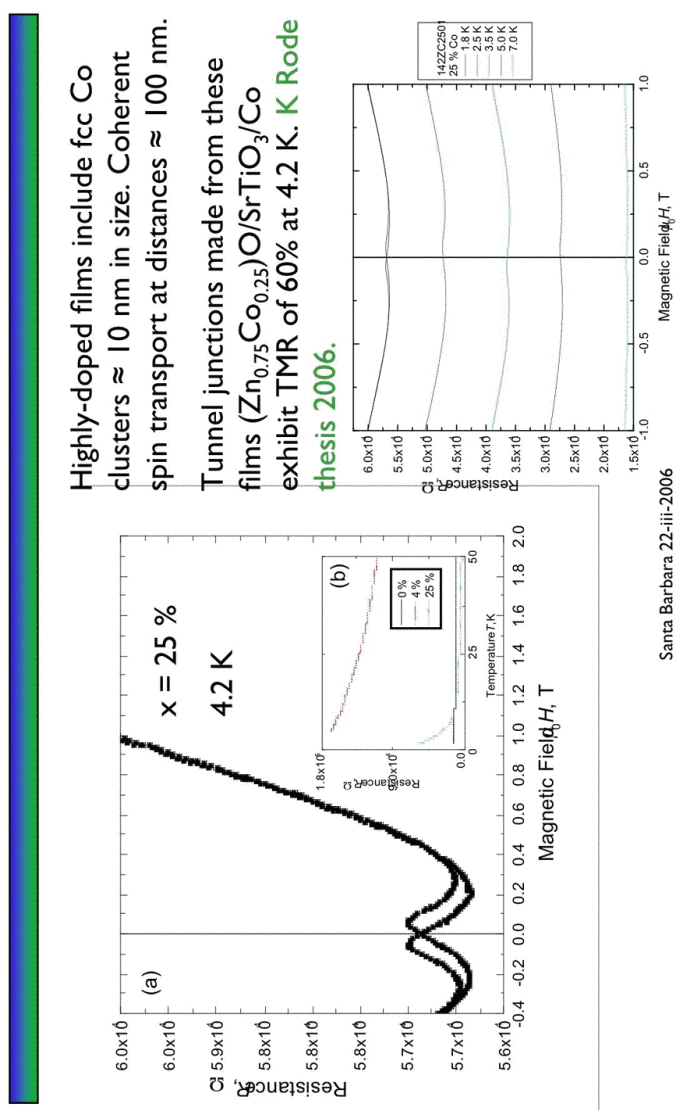


Magnetization-related magnetoresistance visible only below 20 K. Nonmagnetic scattering is dominant.

$$\sigma \approx 10 \Omega^{-1} \text{cm}^{-1}$$

Santa Barbara 22-iii-2006

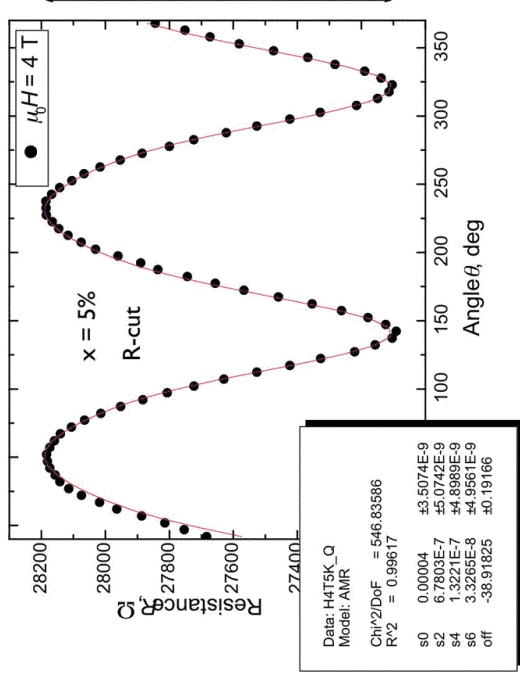
# Magnetoresistance of ZnO - Co



Highly-doped films include fcc Co clusters  $\approx 10$  nm in size. Coherent spin transport at distances  $\approx 100$  nm. Tunnel junctions made from these films ( $\text{Zn}_{0.75}\text{Co}_{0.25}\text{O}/\text{SrTiO}_3/\text{Co}$ ) exhibit TMR of 60% at 4.2 K. **K Rode thesis 2006.**

Santa Barbara 22-iii-2006

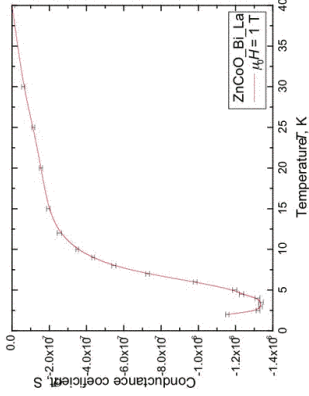
# Anisotropic magnetoresistance of ZnO-Co



Large AMR, up to 15% at low temperature.

Possible d-states at E<sub>F</sub> or spin-split s band.

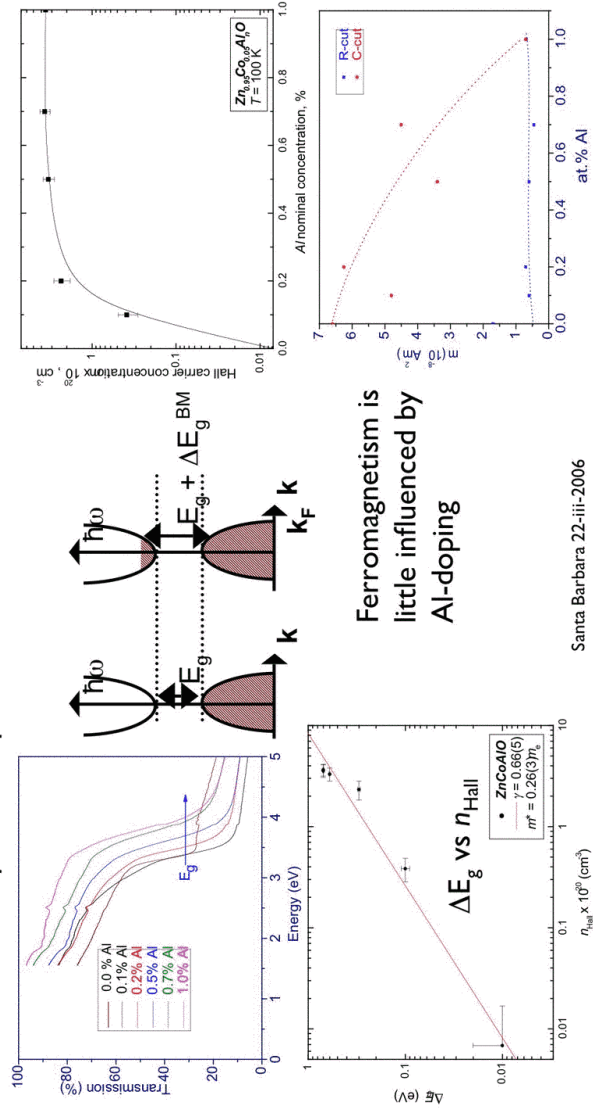
4 % Terms up to 6th order in cos θ.



Santa Barbara 22-iii-2006

# Al co-doped ZnO-Co

5% Co-ZnO doped with up to 1 % Al exhibits a Moss-Burstein shift.



Ferromagnetism is little influenced by Al-doping

Santa Barbara 22-iii-2006

## ZnO-Co Conclusions

- o There is evidence of intrinsic ferromagnetism in this system
- o The conduction electrons are only *weakly coupled* to the magnetism. Magnetoresistive effects appear only below 30 K. No anomalous Hall effect is observed.
- o There is band-edge magnetic circular dichroism
- o The magnetic ordering is little influenced by conduction electron concentration.
- o The mechanism leading to magnetic order is an open question.

Santa Barbara 22-iii-2006

## Origin of the magnetism I

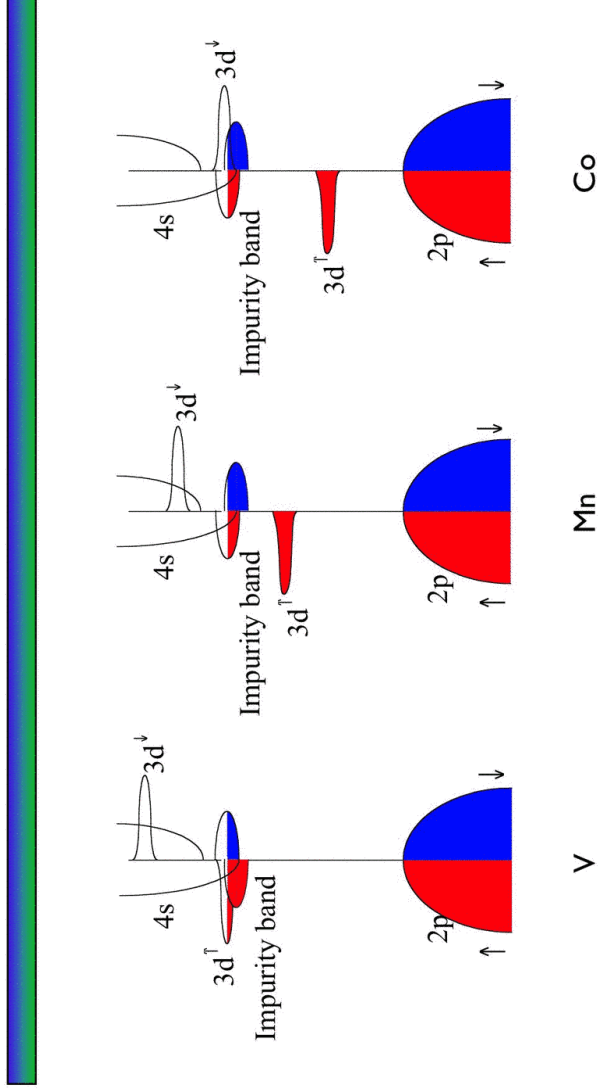
The weakly-hysteretic ferromagnetism in doped ZnO *cannot* be explained by secondary ferromagnetic impurity phases:

- No ferromagnetic phases exist for which the moment exceeds the spin-only value - typical moments in oxides are  $< 1.5 \mu_B$  per transition metal,
- No ferromagnetic phases exist in the d<sup>0</sup> systems Zn-Sc-O or Zn-Ti-O,
- No known ferromagnets show such anisotropy of the magnetization at room temperature.

Santa Barbara 22-iii-2006



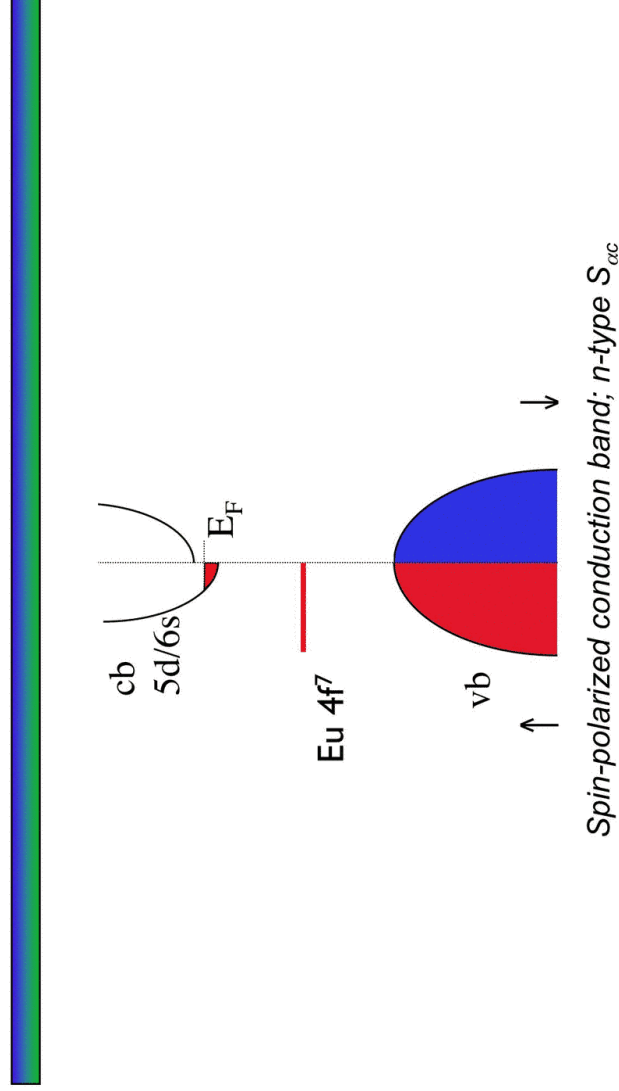
# An idea



Distinguish 3d-dopants and defects; Impurity band is due to defects

Santa Barbara 22-iii-2006

# Magnetic semiconductors; n-type

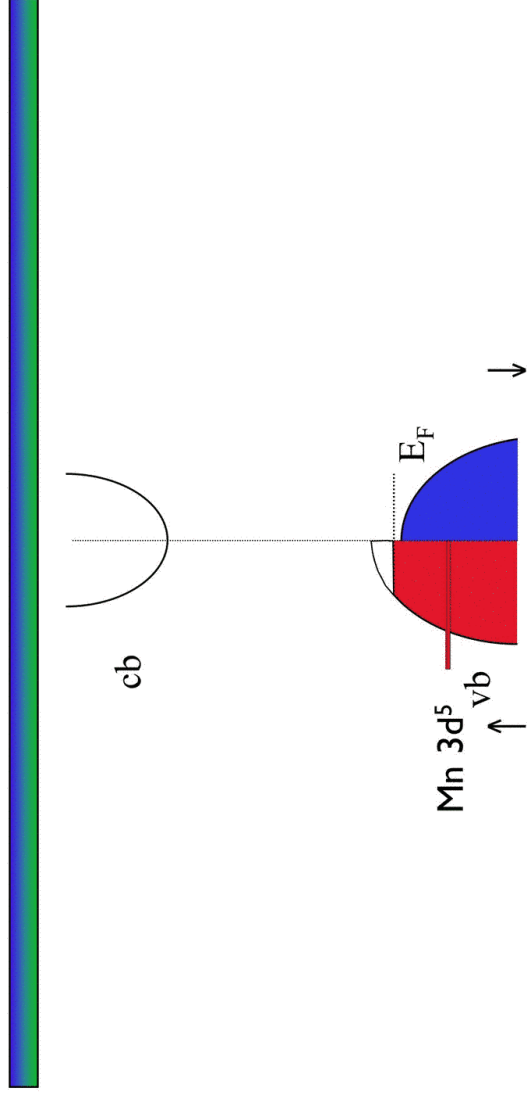


Spin-polarized conduction band; n-type S<sub>cc</sub>

Example EuO

Santa Barbara 22-iii-2006

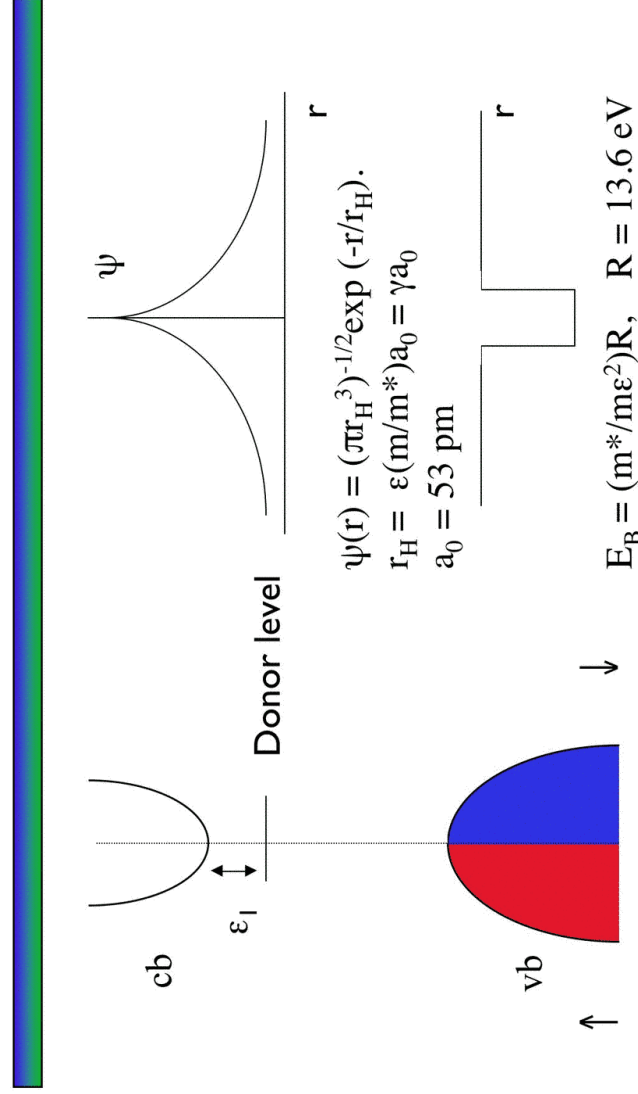
# Magnetic semiconductors; p-type



Spin-polarized valence band; p-type  $S_{cv}$   
 Example  $(\text{Ga}_{1-x}\text{Mn}_x)\text{As}$

Santa Barbara 22-iii-2006

# Doped semiconductor



$$\psi(r) = (\pi r_H^3)^{-1/2} \exp(-r/r_H).$$

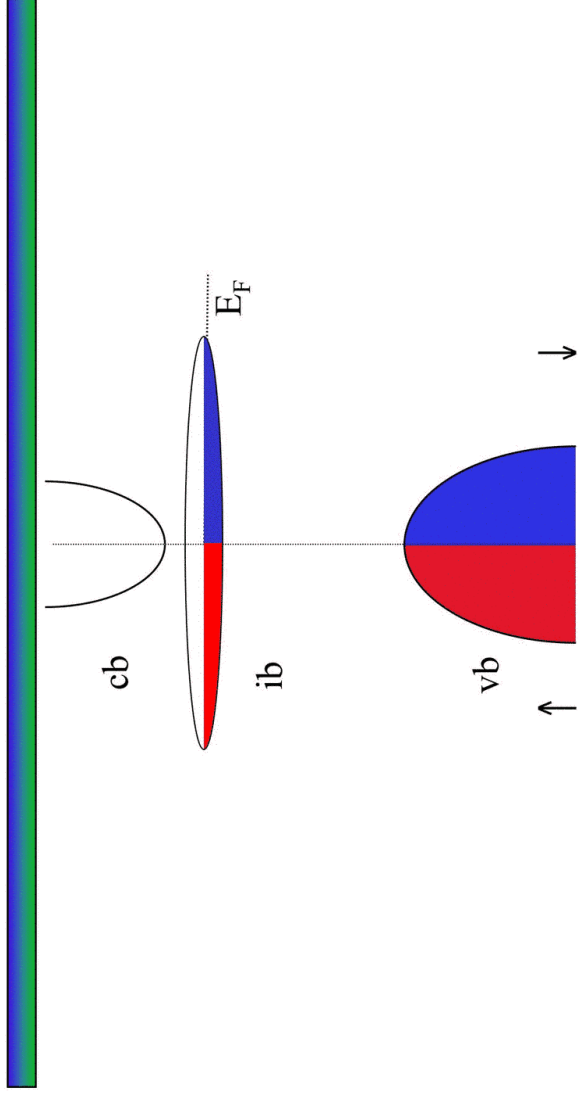
$$r_H = \epsilon(m^*/m^*)a_0 = \gamma a_0$$

$$a_0 = 53 \text{ pm}$$

$$E_B = (m^*/m\epsilon^2)R, \quad R = 13.6 \text{ eV}$$

Santa Barbara 22-iii-2006

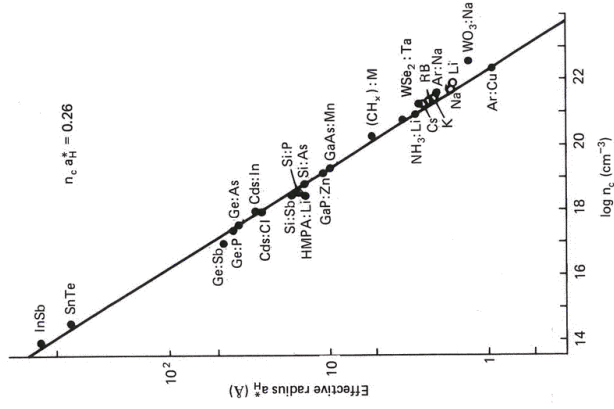
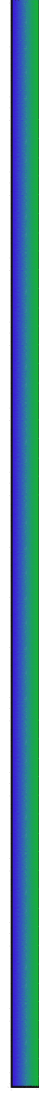
# The impurity band



Donors form an impurity band

Santa Barbara 22-iii-2006

# The impurity band

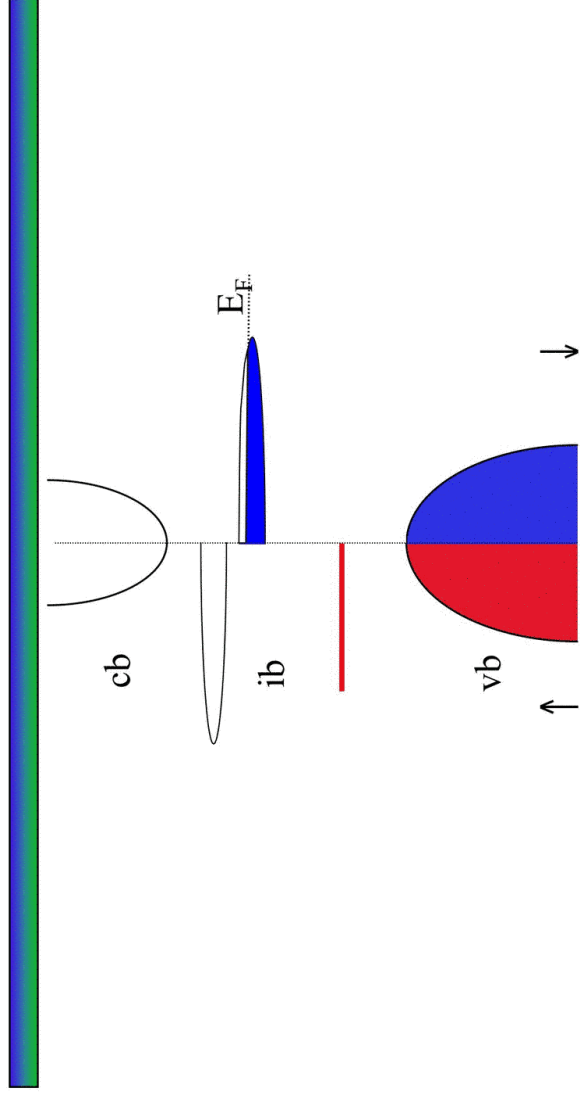


Metal-insulator transition occurs when  $(n^{crit})^{1/3} r_H \approx 0.26$  (1)

This is an Anderson transition due to the random potential creating a mobility edge, not a Mott transition due to electron correlation

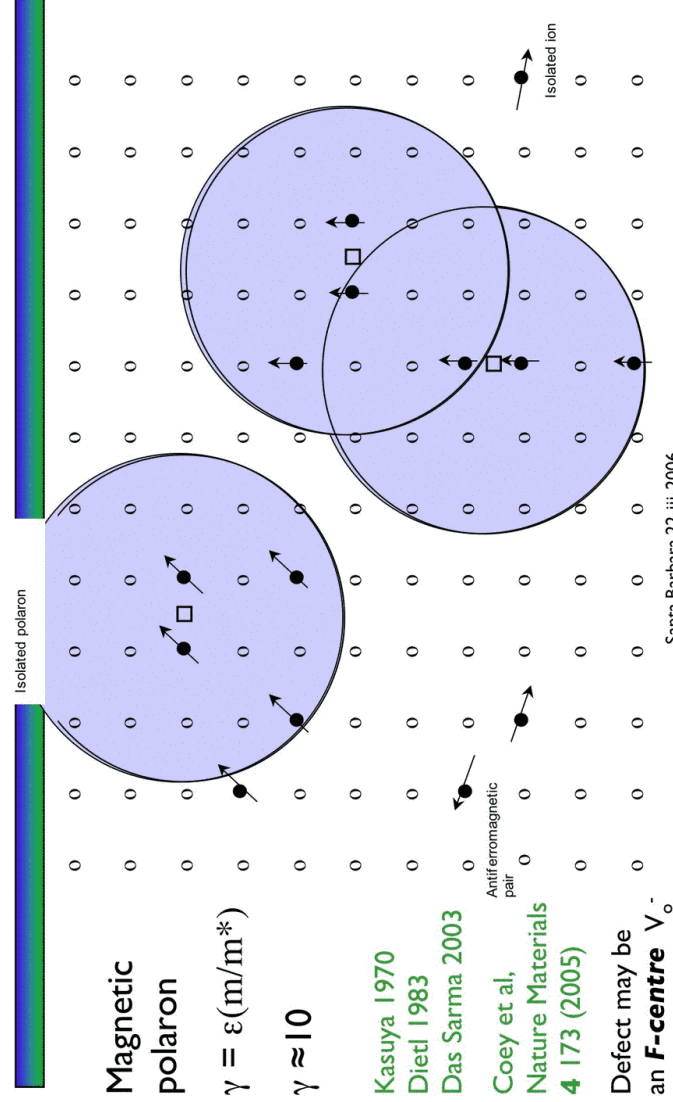
Santa Barbara 22-iii-2006

# Spin-split impurity band



Spin-polarized impurity band  $S_{\beta i}$   
 Santa Barbara 22-iii-2006

# 3. A Model; Magnetic polarons



Magnetic polaron

$\gamma = \epsilon(m/m^*)$

$\gamma \approx 10$

- Kasuya 1970
- Dietl 1983
- Das Sarma 2003

Coey et al, Nature Materials 4 173 (2005)

Defect may be an **F-centre**  $V_o^-$

## Metal insulator transition in the impurity band

An oxide  $AO_n$ , with donor concentration  $\delta$  per cation, where  $\delta \ll 1$ .

$\delta^{\text{crit}} = n^{\text{crit}}/n_O$ , where the oxygen density  $n_O$  is approximately  $6 \times 10^{28} \text{ m}^{-3}$  for oxides with a close-packed oxygen lattice.

We define  $\gamma = \epsilon(\text{m/m}^*)$  so that  $r_H = \gamma a_0$ , where  $a_0$  is the Bohr radius, 0.052 nm,  $\epsilon$  is the dielectric constant and  $m^*$  is the effective mass; so the condition  $(n^{\text{crit}})^{1/3} r_H \approx 0.26$  becomes

$$\gamma^3 \delta^{\text{crit}} \approx 2.2$$

Santa Barbara 22-iii-2006

## Some numerical values

	a	c	Z	$n_c$	$\epsilon$	$m^*/m$	$\gamma a_0$	$V_c$	$n_O^{\text{crit}}$	$\delta^{\text{crit}}$	$x_p$
	pm	pm		$10^{28}$			nm		$10^{23}$	$10^{-6}$	
				$\text{m}^{-3}$					$\text{m}^{-3}$		
ZnO	wurtzite	335	2	3.94	4.0	0.28	0.76	27	480	1200	0.17
TiO <sub>2</sub>	anatase	379	4	2.93	9.0	1.0	0.4	2284	4.3	7.3	0.17
SnO <sub>2</sub>	rutile	474	2	2.80	3.9	0.24	0.86	39	240	430	0.25

Santa Barbara 22-iii-2006

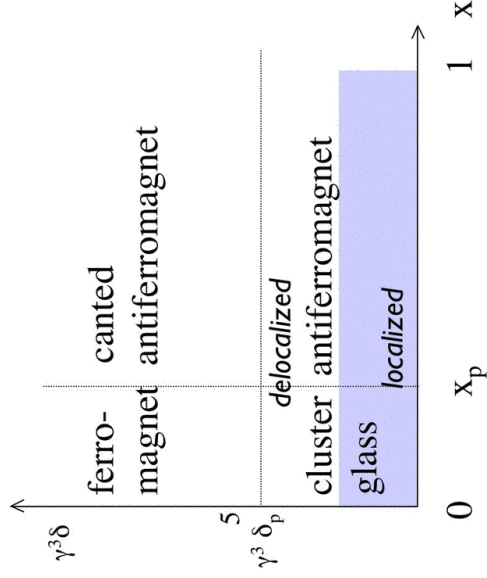


# Percolation

For randomly-packed spherical objects with radius  $r_H$ , percolation occurs when they occupy roughly 16% of space  
 $(4/3)\pi r_H^3 n \approx 0.16$   
 or  $n^{1/3} r_H \approx 0.34$ .

$$\gamma^3 \delta_p \approx 4.3$$

General formula for a doped oxide



Santa Barbara 22-iii-2006

# Exchange

Exchange coupling between a hydrogenic electron and an ion core



Exchange is represented by a molecular field acting on the donor electron,

$$H_W = J_{sd} \langle S_z \rangle / 2 \mu_0 \mu_B \rho^3, \text{ where } \rho = r_H / r_c$$

In the ordered state, the electron will be highly spin polarized because it interacts with many magnetic cations.

For example, if  $\epsilon = 10$  and  $x = 0.2$ , the number of cations interacting with a single electron is  $\nu = 5$ , assuming  $n_c = 4 \times 10^{28} \text{ m}^{-3}$ . The maximum magnetic energy associated with the donor is then  $\nu \Delta E_{\text{ex(max)}} = 105 \text{ K}$ , independent of the size of the orbital.

Santa Barbara 22-iii-2006

## Curie Temperature

The Curie temperature  $T_C$  is estimated using the *molecular field approximation*. The effective field acting on the cation spins  $\mathbf{S}$  is

$$H_W' = J_{sd} N \langle S_z \rangle / 2 \mu_0 \mu_B \rho^3.$$

$N$  is the number of donor electrons interacting with a cation. Hence

$$\langle S_z \rangle / S = \mathcal{B}_S(J_{sd} N \langle S_z \rangle / 2 k_B T \rho^3) \quad (1)$$

and

$$\langle S_z \rangle / s = \tanh(J_{sd} v \langle S_z \rangle / 2 k_B T \rho^3). \quad (2)$$

$\mathcal{B}_S(x)$  is the Brillouin function. Close to  $T_C$ , the equations are linear;

$$\mathcal{B}_S(x) \approx [(S+1)/3S]x \text{ and } \tanh x \approx x.$$

The number of cations within a donor orbit  $v = (4/3)\pi r_H^3 n_c x$ , hence

$$T_C = [(S+1)s^2 x \delta / 3]^{1/2} J_{sd} \omega_c / k_B$$

Santa Barbara 22-iii-2006

## Curie Temperature

Here  $\omega_c$  is the volume fraction of the oxide occupied by cations (typical value 8 %)  $\times$  the oxygen packing fraction  $f_O$

$$T_C \propto J_{sd} x^{1/2} \delta^{1/2}$$

This is surprising, because it shows that it is pointless to look for a very high dielectric constant. It is sufficient that  $\gamma = \epsilon / \epsilon_0 > 4$ .

The problem is that  $T_C$  is *at least an order of magnitude too low!*

If the charge density in the magnetic polaron is uniform, and  $J_{sd} \approx 1.5$  eV,  $T_C$  in a sample where  $x = 0.1$ ,  $\delta = 0.01$ ,  $S = 3/2$  will not exceed 18 K! Since exchange is  $J_{sd} \mathbf{S}_d \cdot \mathbf{s} |\psi(\mathbf{r})|^2 \Omega$ , we need to increase the donor electron density in the vicinity of the magnetic cations.

Santa Barbara 22-iii-2006

## Curie Temperature

Delocalised electrons: replace (2) by  $\langle s_z \rangle / s = J_{sd} \langle S_z \rangle / \epsilon_F \rho^3$ ,

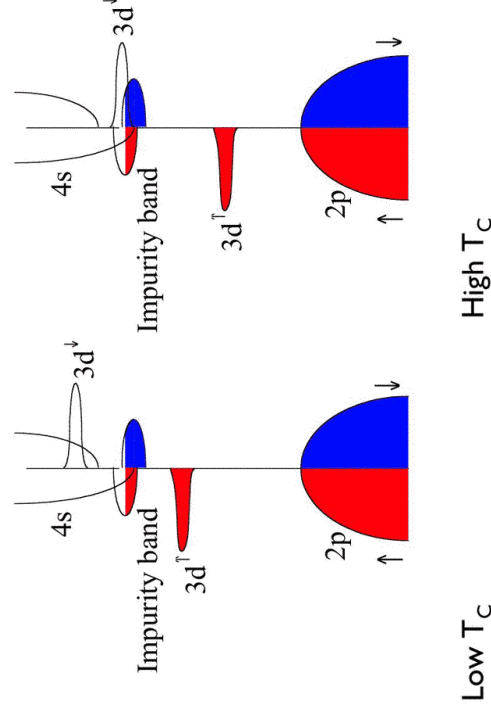
$$T_C = (S+1) s^2 n x \delta / J_{sd}^2 \omega_c^2 / 3 \epsilon_F$$

Here  $T_C \propto J_{sd}^2 x \delta$ , but in the example with  $\epsilon_F = 0.1$  eV,  $T_C < 1$  K

The *only* option to increase T significantly is to boost the donor electron density  $|\psi(\mathbf{r})|^2$  in the vicinity of the cation. Assume  $\psi(\mathbf{r})$  is constant for  $r < r_c$ . An upper limit is  $\sqrt{\Omega} |\psi|^2 = 1$ , i.e. distribute the donor electrons entirely over the cations. This gives  $T_c < 3600$  K. Hence we need to redistribute  $\sim 15\%$  of the donor electrons over the cations. Rescale  $J_{sd}$  by  $(r_{\text{eff}}/r_c)^3$ ;  $r_{\text{eff}} \sim 0.20$  nm.

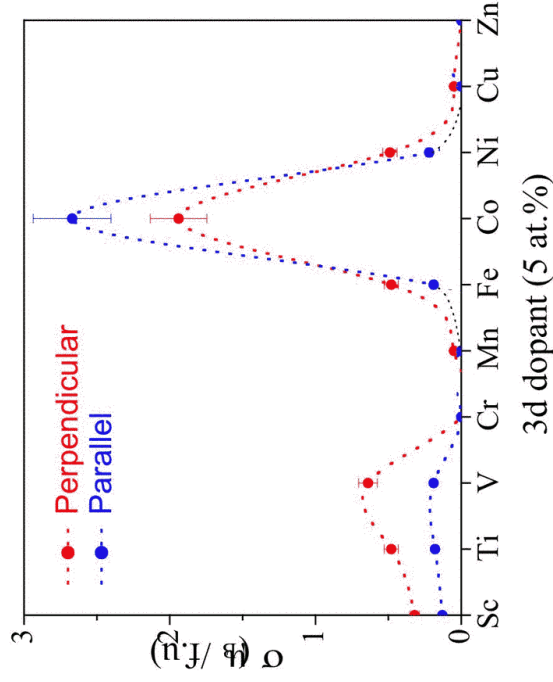
Santa Barbara 22-iii-2006

## Band structure for high $T_C$



Santa Barbara 22-iii-2006

## Evidence from ZnO:M



Santa Barbara 22-iii-2006

## RKKY Interaction

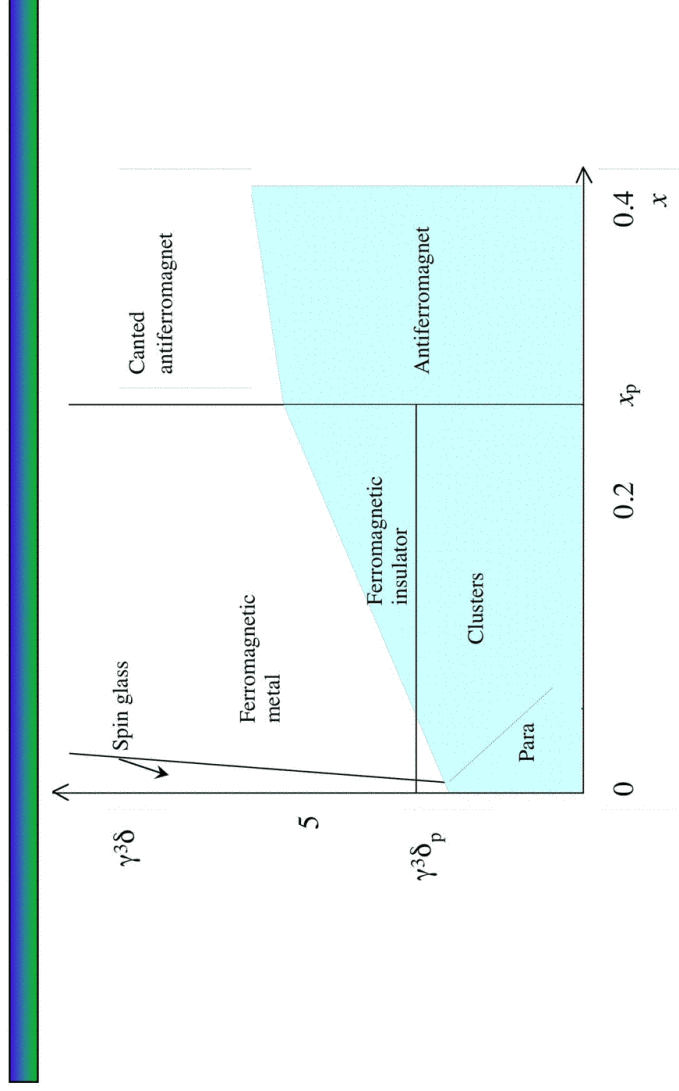
The RKKY interaction is always ferromagnetic at low electron densities. At higher densities, the interaction will provide as many negative as positive exchange bonds, and the system becomes a spin glass. The RKKY function  $F(\xi) = [(\xi \cos \xi - \sin \xi)/\xi^4]$  first changes sign at  $\xi = 2k_F r = 4.49$ . The condition for ferromagnetism  $x > 2.6 n\delta$ , is easily satisfied. The Curie temperature in the molecular field approximation considering only z nearest-neighbour sites is  $T_C = 2zJ_{\text{RKKY}}S(S+1)/3k_B$  where  $J_{\text{RKKY}}$  is  $-[(J_{\text{sd}}^2 m^* k_F^4 n^2)/(32\pi^3 n_O^2)]F(\xi)$ . In the small- $\xi$  limit,  $F(\xi) \approx 1/3\xi$ .

$$T_C \approx z m^* \delta x^{1/3} J_{\text{sf}}^2 S(S+1) / (96\pi^3 h^2 n^{1/3} n_c^{2/3} k_B)$$

Taking  $z = 12$  and the same values  $J_{\text{sf}}$ ,  $S$ ,  $n$ ,  $x$  and  $\delta$  as before, we find  $J_{\text{RKKY}} = 0.23$  K, and  $T_C = 16$  K.

Santa Barbara 22-iii-2006

## Phase Diagram

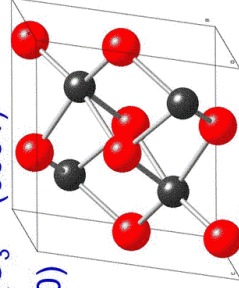


## 4. d<sup>0</sup> ferromagnetism - HfO<sub>2</sub>

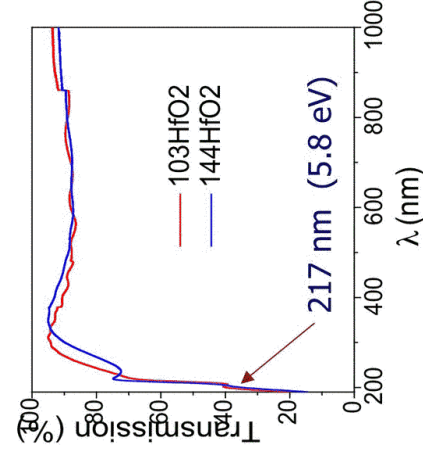
Monoclinic insulating oxide; bandgap is 5.8 eV. Main potential use is as a high- $k$  dielectric in CMOS circuits. Hf<sup>4+</sup> is an ion with a [Ne] closed-shell configuration

46 films were deposited.

- 25 films on R-cut Al<sub>2</sub>O<sub>3</sub> (1102)
- 6 films on C-cut Al<sub>2</sub>O<sub>3</sub> (0001)
- 7 films on YSZ (100)
- 8 films on Si(100)



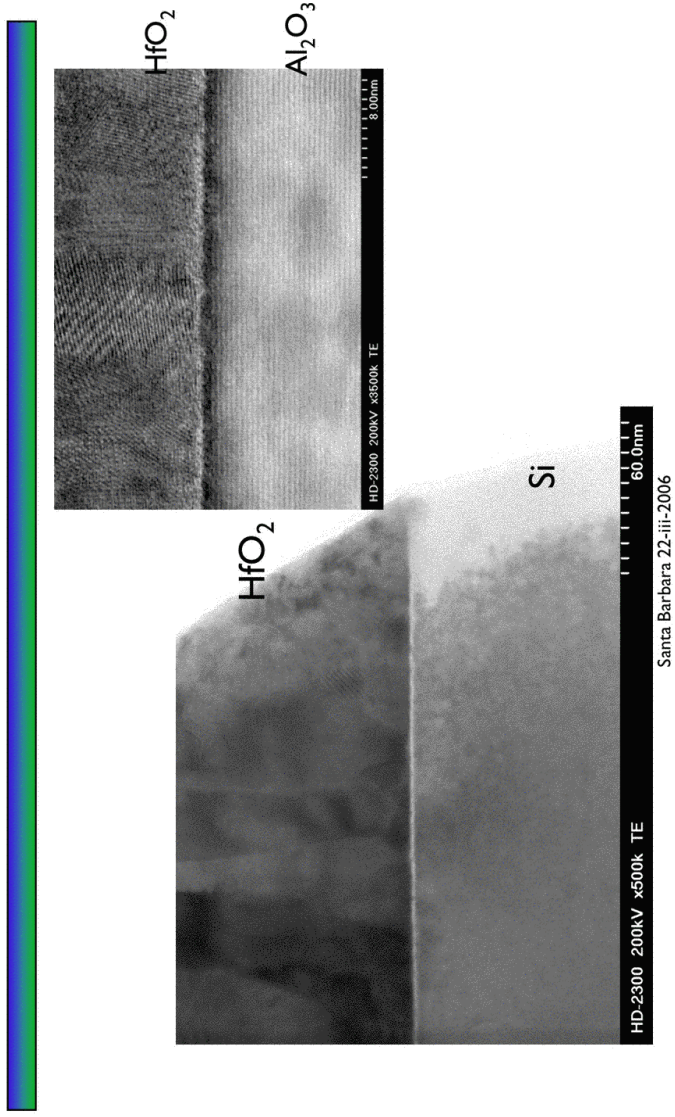
M Venkatesan et al Nature  
**430** 630 (2004); Coey et al,  
 Phys Rev B **72** 024450 (2005)



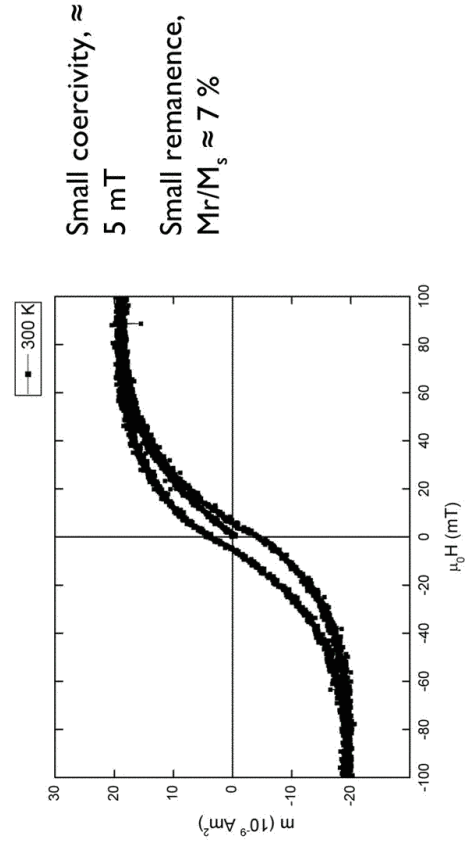




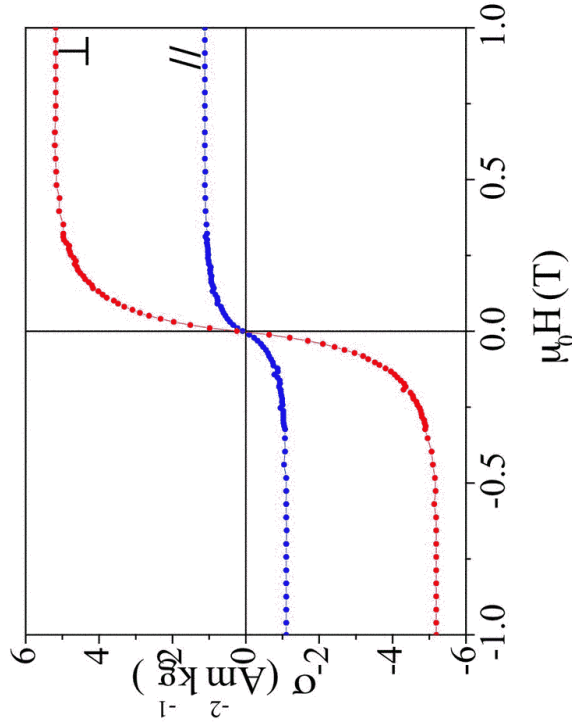
# HfO<sub>2</sub> - STEM



# HfO<sub>2</sub> - Magnetization

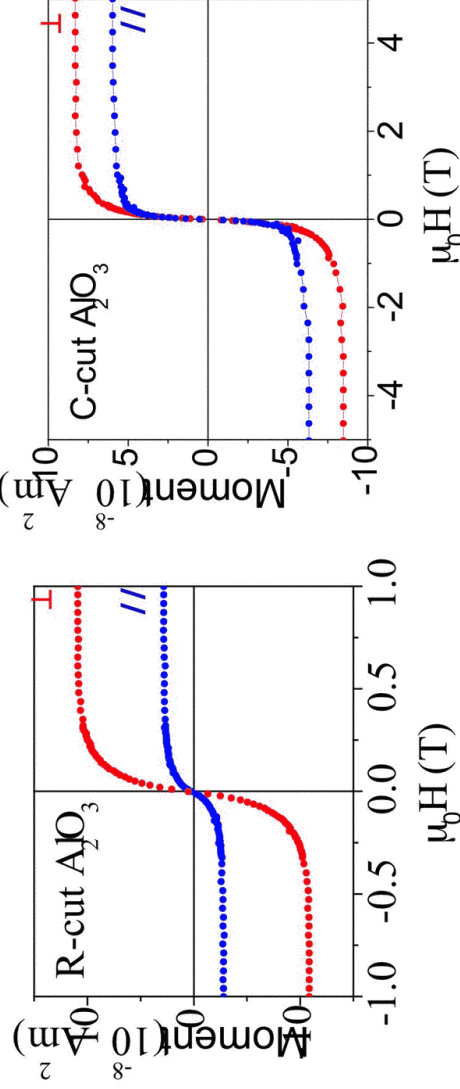
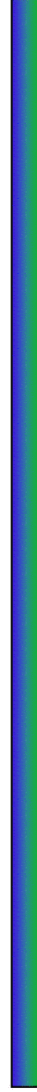


## HfO<sub>2</sub> - Anisotropy



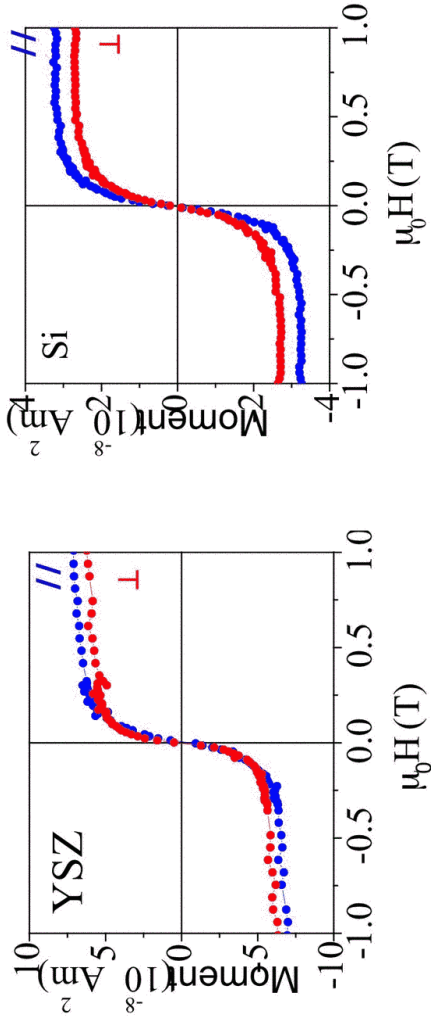
Santa Barbara 22-iii-2006

## HfO<sub>2</sub> films on different substrates



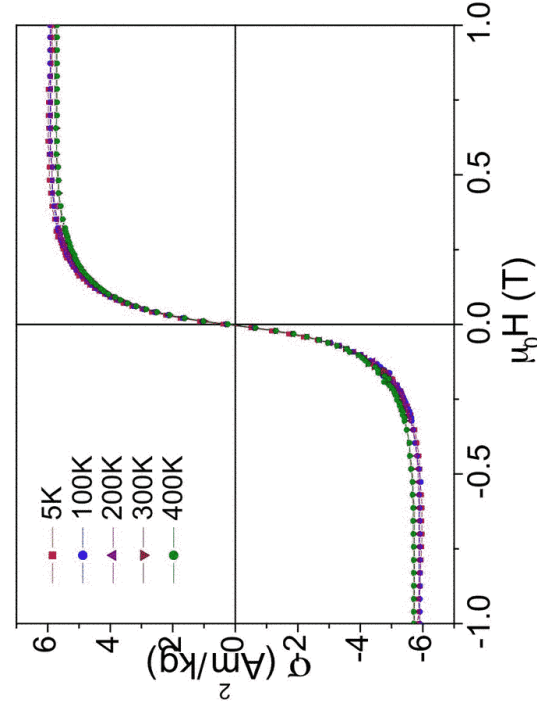
Santa Barbara 22-iii-2006

## *HfO<sub>2</sub> films on different substrates*



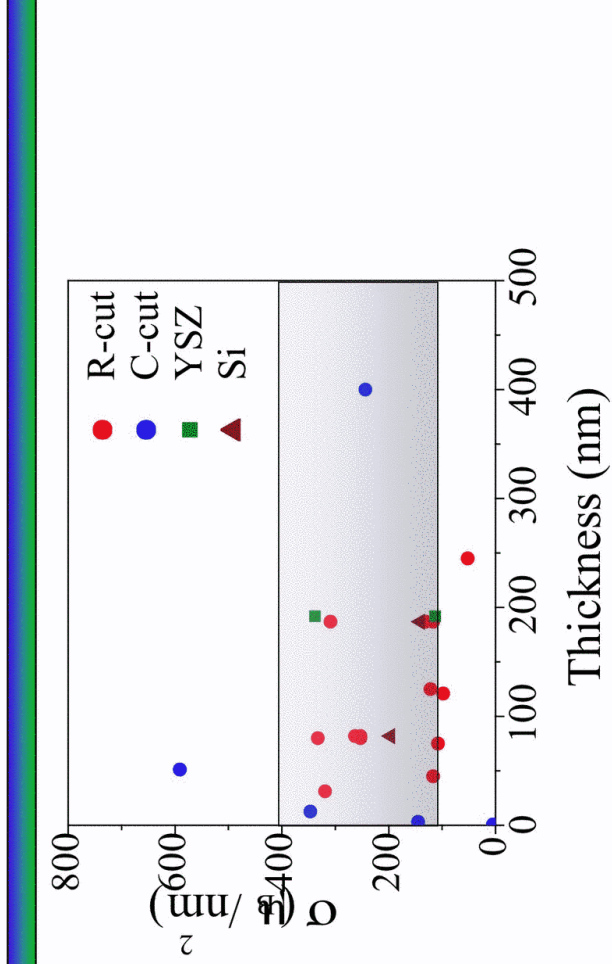
Santa Barbara 22-iii-2006

## *HfO<sub>2</sub> - Magnetization vs T*



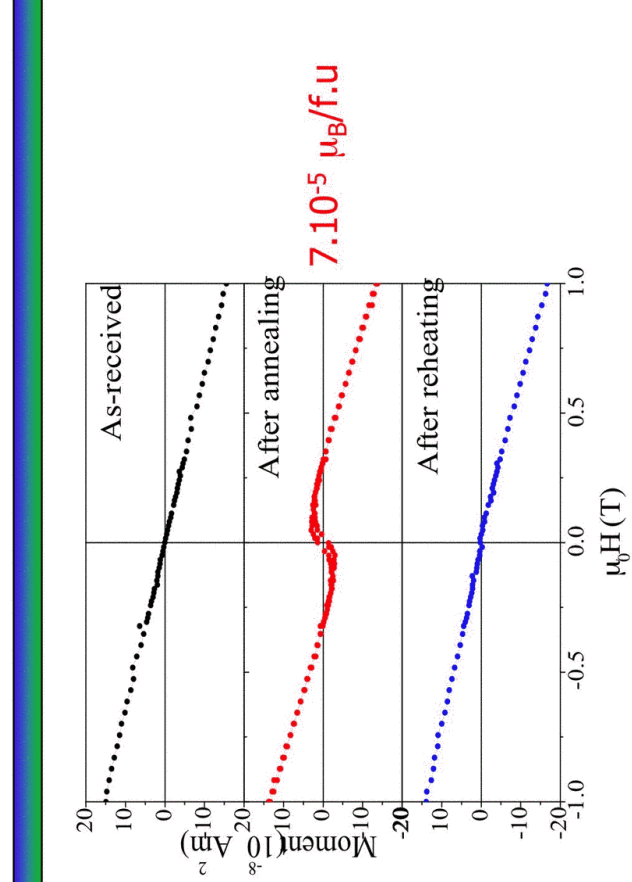
Santa Barbara 22-iii-2006

### *HfO<sub>2</sub> - Moment vs t*



Santa Barbara 22-iii-2006

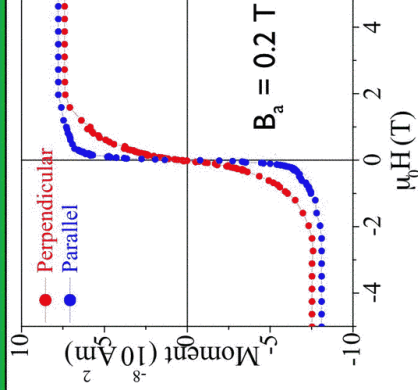
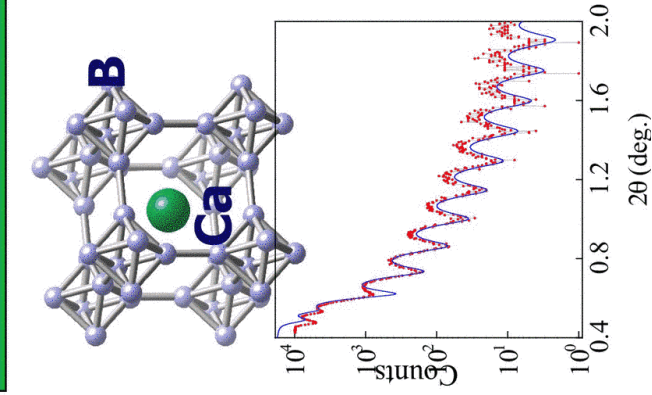
### *HfO<sub>2</sub> powder, heat treated*



Santa Barbara 22-iii-2006



## CaB<sub>6</sub> thin films



Amorphous hexaboride films show little anisotropy of the saturation magnetization. But there is clear anisotropy of the slope of the initial magnetization curve.

Assuming this is due to shape anisotropy of an interface layer of thickness  $t$ ,  $M_s \approx B_a/\mu_0 \Rightarrow t \approx 15$  nm.

Santa Barbara 22-iii-2006 [Dornales et al APL 85 6377 \(2004\)](#)

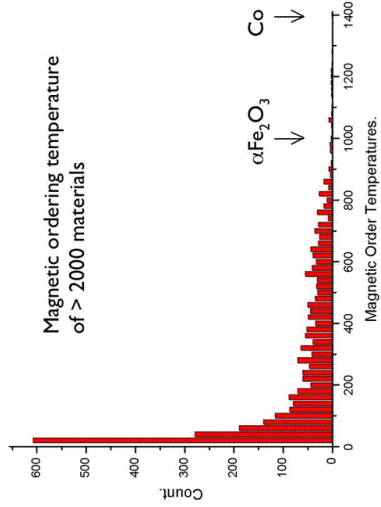
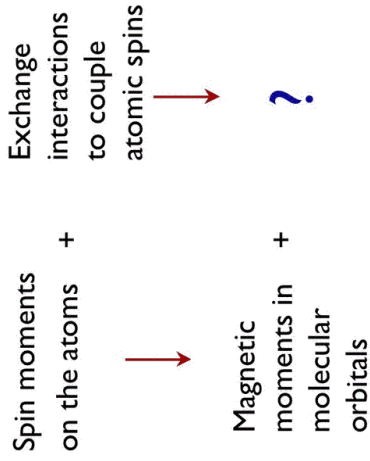
## The syndrome revisited

### Magnetic oxide thin films:

- i) The oxides may be insulators or semiconductors; the semiconductors are usually  $n$ -type. They may be partially compensated, semiconducting or insulating.
- ii) The moment does not depend obviously on the film thickness or doping level when  $x < x_p$ . It is often 100 - 400  $\mu_B \text{nm}^{-2}$
- iii) The ferromagnetism is already present in some undoped films, and in all films at concentrations that lie far below the percolation threshold associated with nearest-neighbour cation coupling.  $T_C$  can be far above RT.
- iv) The magnetism is highly anisotropic, in a way unrelated to the dopant, but dependent on the film/substrate combination

# The *m-J* paradigm revisited

## The *m-J* paradigm



$$T_C \approx x \text{ or } \sqrt{x}$$

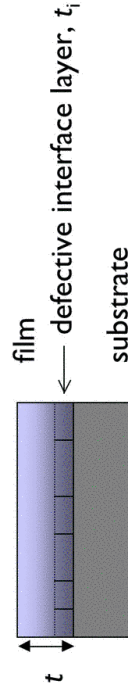
Hence there is no chance of exchange giving  $T_C > 350$  K for a uniform sample with  $x = 5\%$

Santa Barbara 22-iii-2006

# Origin of the magnetism II

There are two sources of magnetism in these films:

- One associated with 3d dopant cations, when they are present
- The other associated with defects in the oxide film.

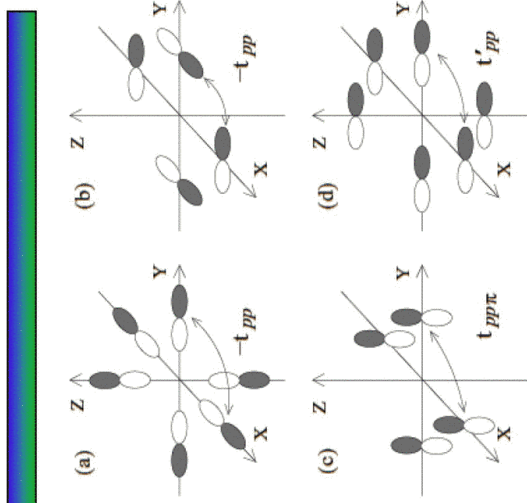


The defects may lie near the interface with the substrate

Santa Barbara 22-iii-2006



# V<sup>0</sup> centre in CaO



$$t_{pp} = 1/2(t_{pp\sigma} - t_{pp\pi})$$

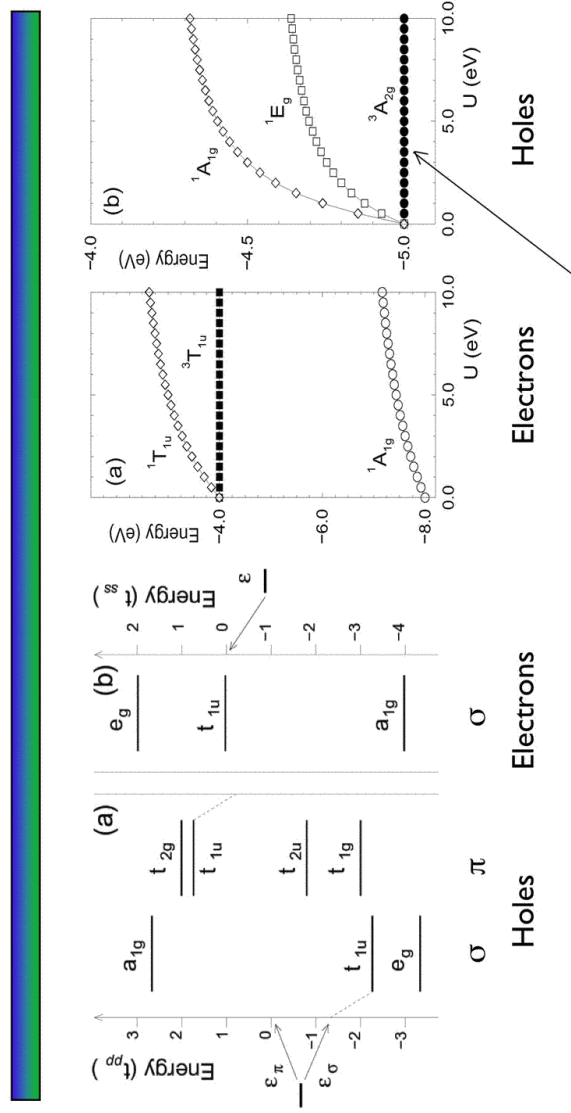
$$t'_{pp} = 1/2(t_{pp\sigma} + t_{pp\pi})$$

FIG. 1: An artists concept of the oxygen  $\sigma$  (a) and  $\pi$  (b,c) bonding orbitals relative to the O-vacancy bond direction surrounding a Ca vacancy. Also shown are the definitions of the hopping integrals (b)  $t_{pp}$ , (c)  $t'_{pp}$ , and (d)  $t''_{pp}$  given in terms of electrons.

Elifimov et al PRL **89** 216403 (2002)

Santa Barbara 22-iii-2006

# Vacancy centres in CaO



Triplet two-hole state

Santa Barbara 22-iii-2006

## Conclusions

- The dilute doped oxides such as ZnO:Co and SnO<sub>2</sub>:Mn show remarkably high Curie temperatures at a few % transition-metal doping.
- There are two sources of magnetism; **dopants** and **defects**.
- A new ferromagnetic exchange mechanism involving a spin-split impurity band is proposed
- In some cases, the defects in a layer at the interface (?) are spontaneously magnetized
- The defect magnetism is very anisotropic, with much orbital character. **It is a new type of magnetism in solids**

Santa Barbara 22-iii-2006

## Conclusions

- It is unclear how this new type of ferromagnetism will contribute to spin electronics. The materials have high Curie temperature and are transparent, but the magnetically-active defect layers are very thin, so devices must be structured on the 10 nm scale..
- It is a challenge to experimentalists to identify and control the defects responsible for ferromagnetism, especially in d<sup>0</sup> systems. and to identify the moments with nanoscale structural probes and element - specific magnetic measurements.
- We need a new paradigm - molecular triplet-based (bosonic ?) ferromagnetism ??
- **Warnings !!** Data may be hard to reproduce exactly. Beware of artefacts ! Moments decay in time when  $x \ll x_p$

Santa Barbara 22-iii-2006