Dilute magnetic oxides

J. M. D. Coey

School of Physics and CRANN, Trinity College Dublin

Ireland.

1. How should they behave?
2. How do they behave ?
3. What is the explanation ?
   5 models

Comments and corrections please: jcoey@tcd.ie

www.tcd.ie/Physics/Magnetism

Dilute magnetic oxides

General formula is $(M_{1-x}T_x)_nO$

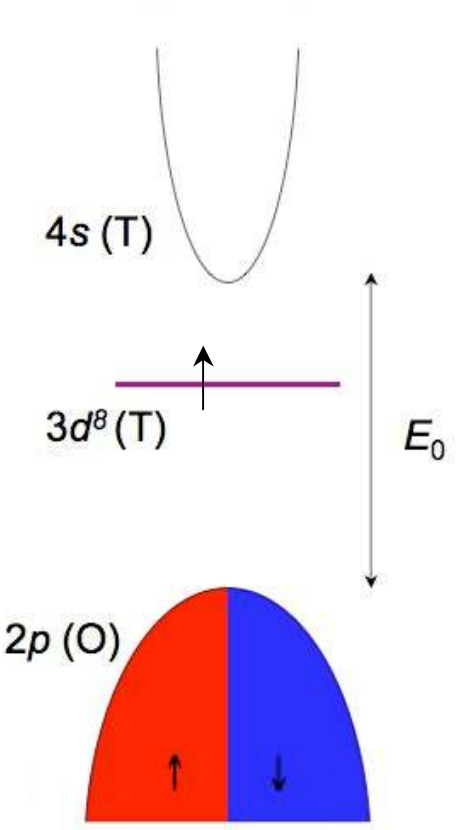
n is an integer or rational fraction x is < 0.1

Examples: $(Zn_{0.98}Co_{0.02})O$

$(Sn_{0,95}Mn_{0.05})O_2$

$(Ti_{0,99}Fe_{0.01})O_2$

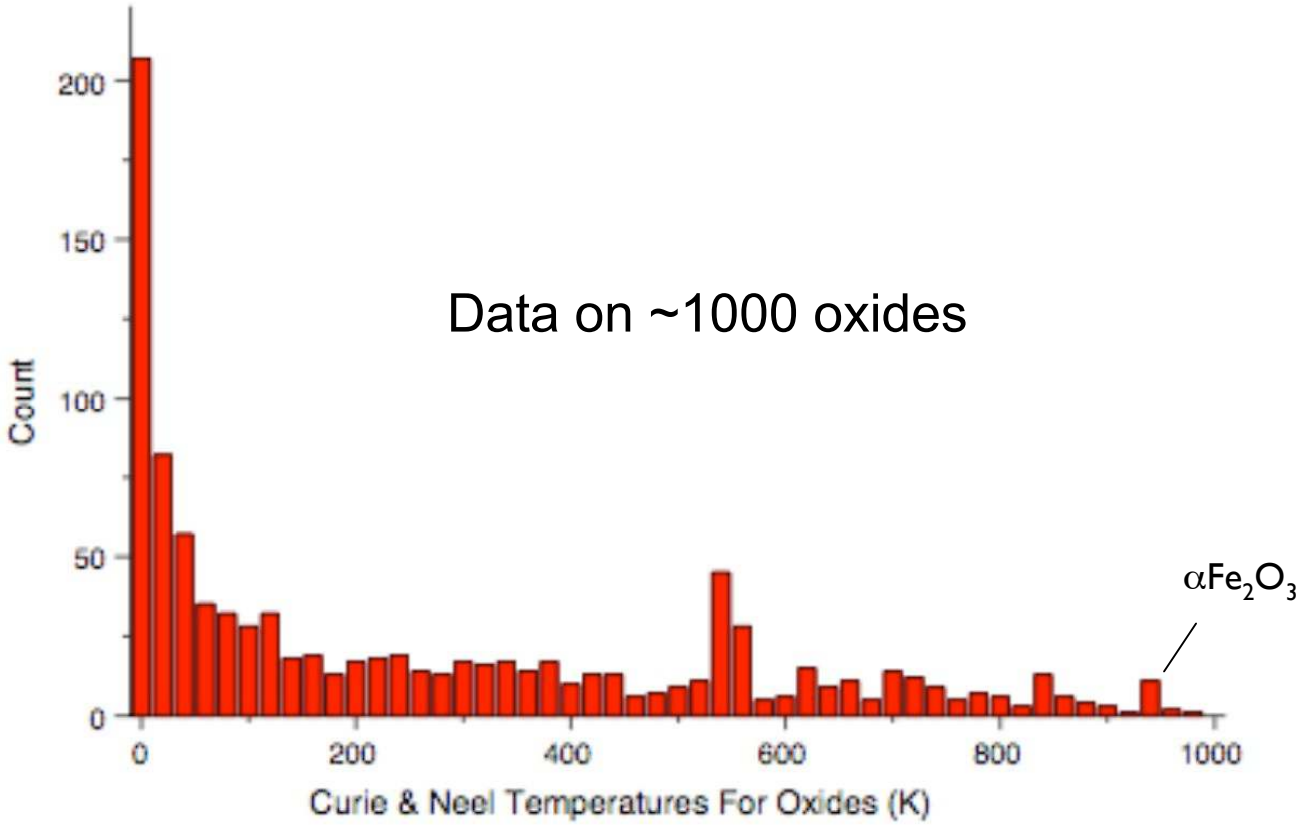
$(In_{0.98}Cr_{0.02})_2O_3$ etc. etc



~ 1000 papers have been published on these materials since 2001.
Samples are usually thin films or nanoparticles.
Oxides may be semiconducting, insulating or metallic.

Many people thought they were dilute magnetic semiconductors (DMS) like $(Ga_{0.93}Mn_{0.07})As$.

1. How should a dilute magnetic oxide behave?



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

e.g $T_C = 2ZxJS(S+1)/3k_B$

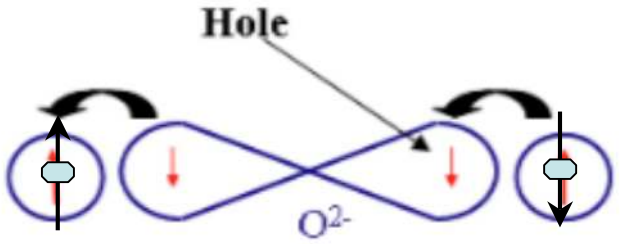
No oxide has $T_C > 1000$ K If $x = 5\%$, $T_C < 50$ K or 250 K

Exchange in oxides

Superexchange

$\mathcal{H} = -2J \Sigma_{i>j} \boldsymbol{S}_i . \boldsymbol{S}_j$

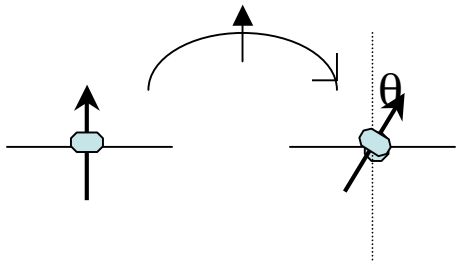
$J \approx t^2/U$



Direct, double exchange

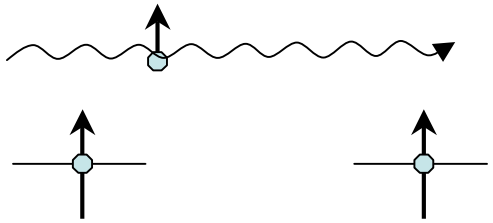
$t_{eff} = t \cos(\theta/2)$

$d^n + d^{n+1} \rightarrow d^{n+1} + d^n$

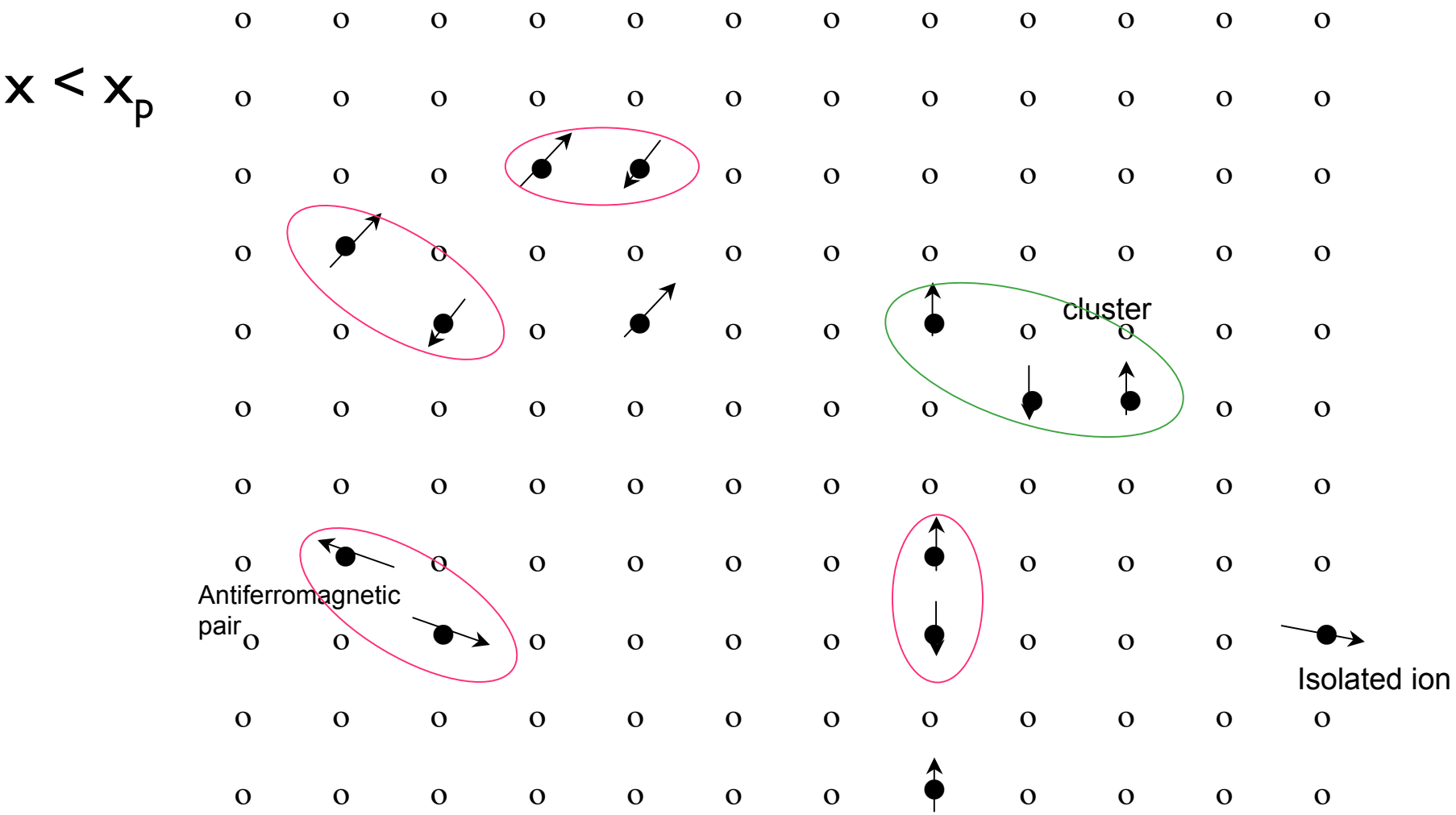


Indirect exchange

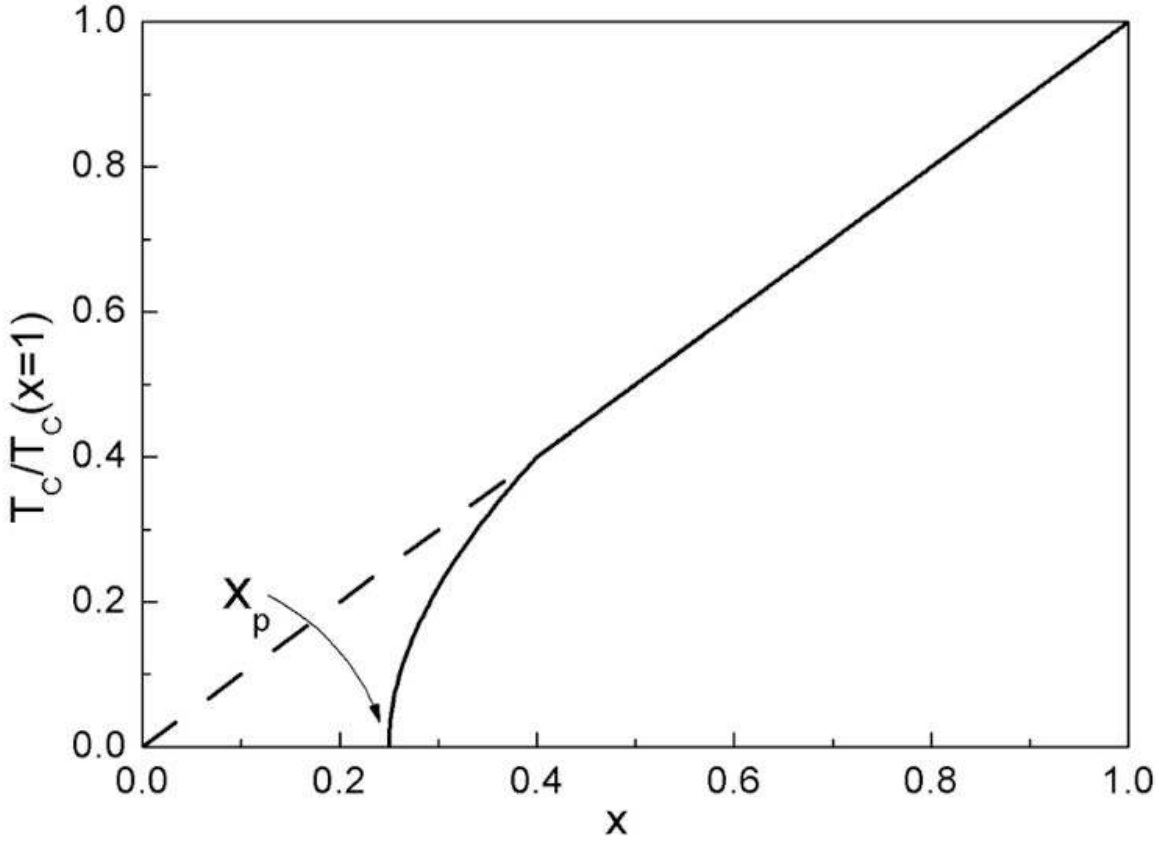
s - S coupling, via conduction band electrons or valence band holes



A dilute magnetic oxide



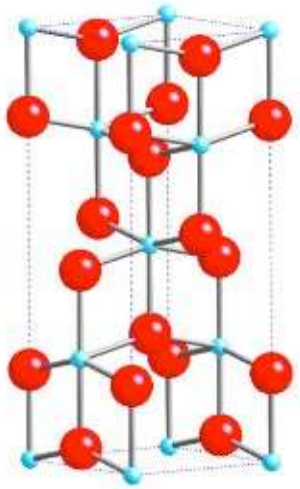
Percolation



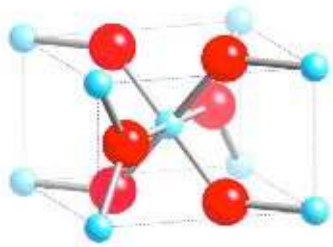
No magnetic order is possible below the percolation threshold x_p.

$x_p \approx 2/Z$ where Z is the cation coordination number

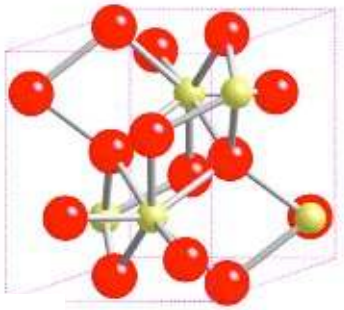
Some oxide structures



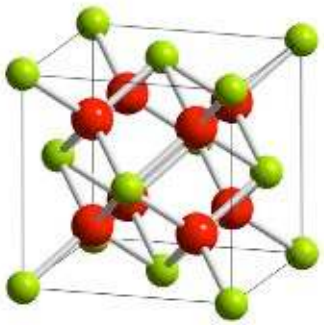
TiO_2



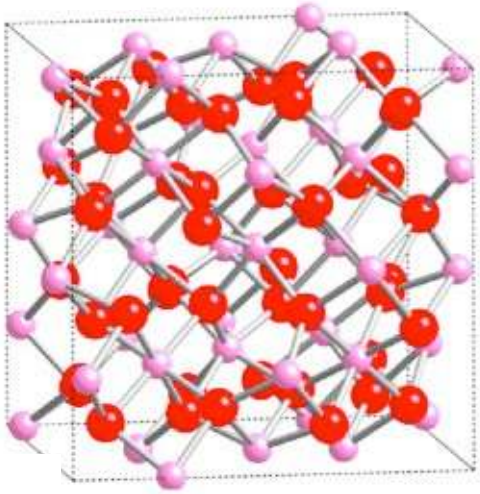
SnO_2



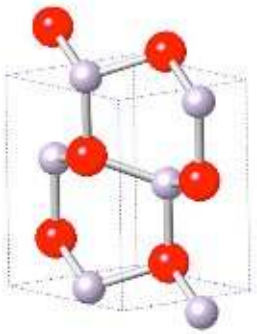
HfO_2



CeO_2



In_2O_3

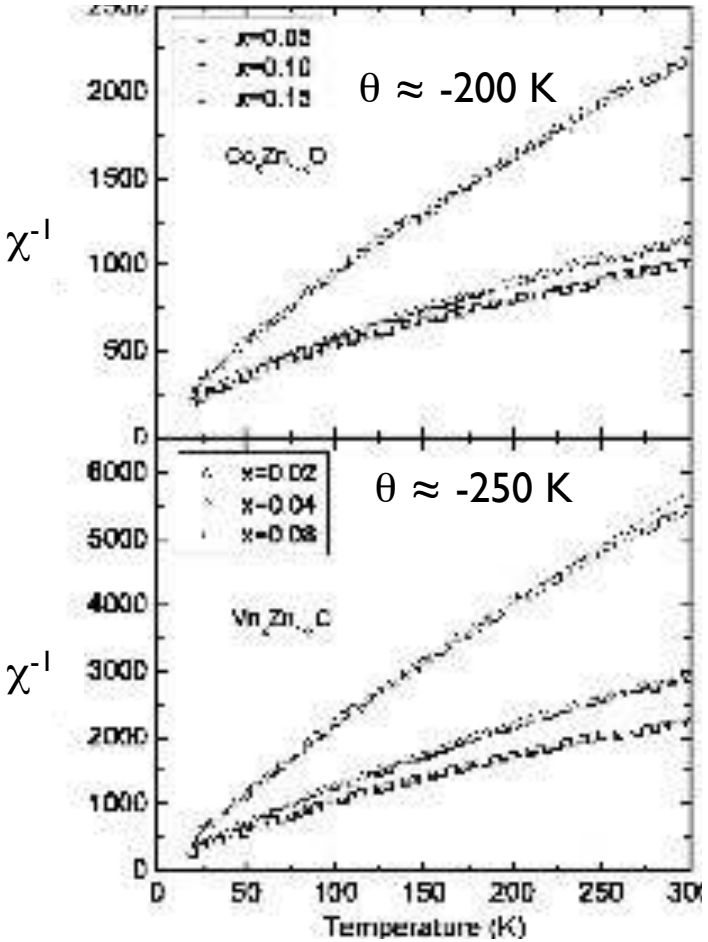


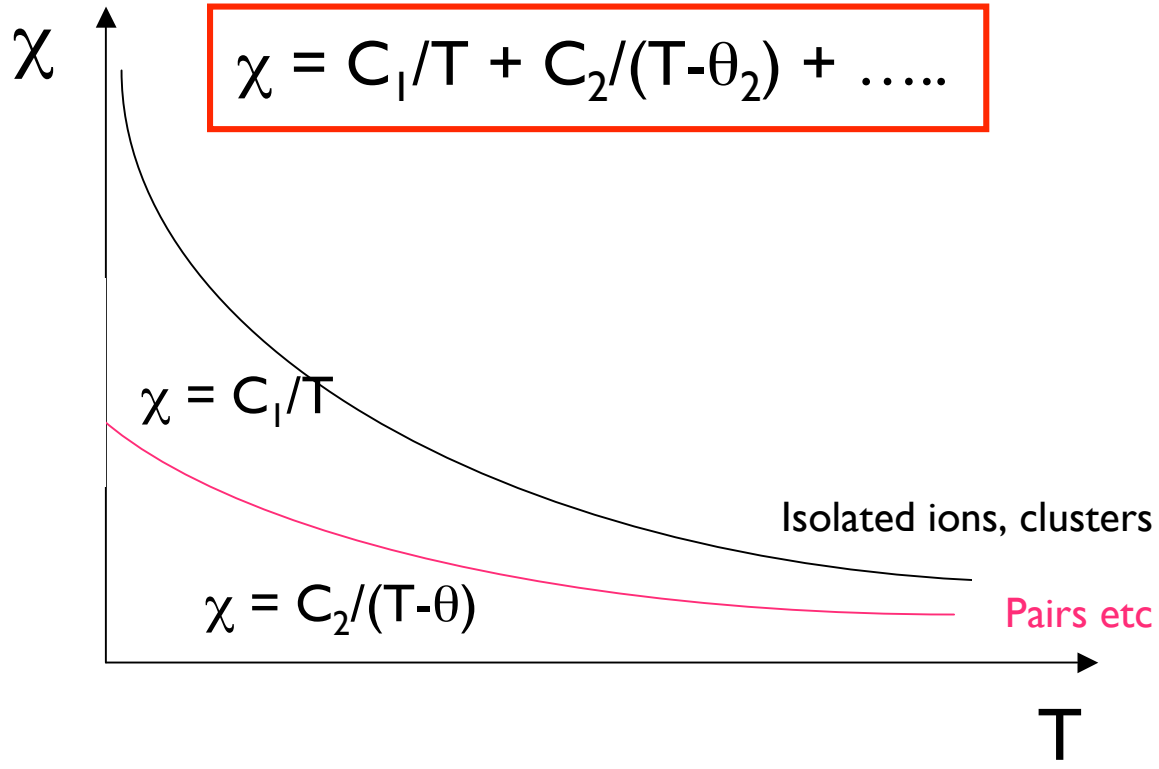
ZnO

No magnetic order is possible below the percolation threshold x_p.

$x_p \approx 2/Z$ where Z is the cation coordination number. $x_p \approx$ 12 - 18 %

Susceptibility – Normal behaviour





Lawes *et al*, Phys Rev B **71**, 045201 (2005)
Rao and Deepak, J. Mater Chem **15** 573 (2005)

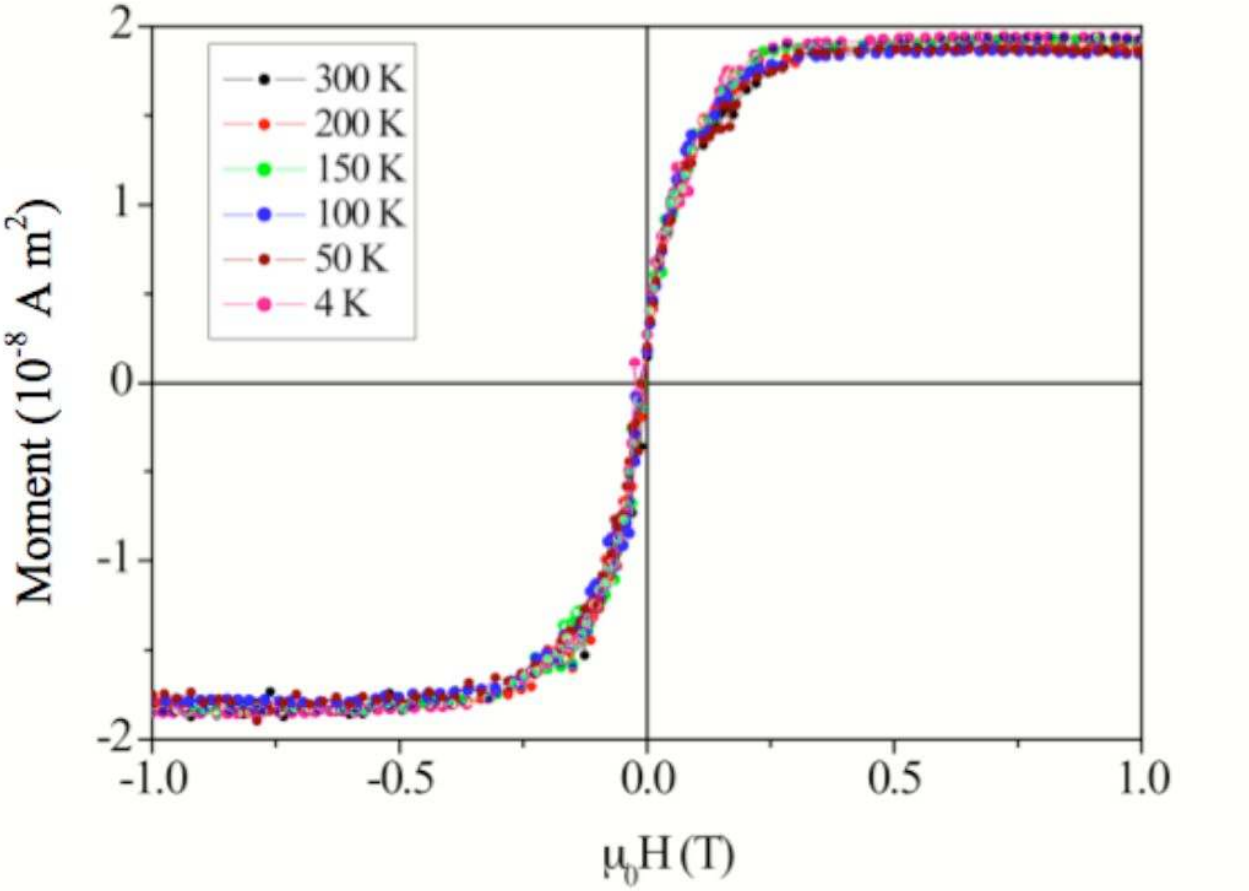
2. How do dilute magnetic oxides behave?

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		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)

These amazingly high ferromagmetic Curie temperatures are found for

— thin films deposited on a substrate

— nanoparticles and nanocrystallites

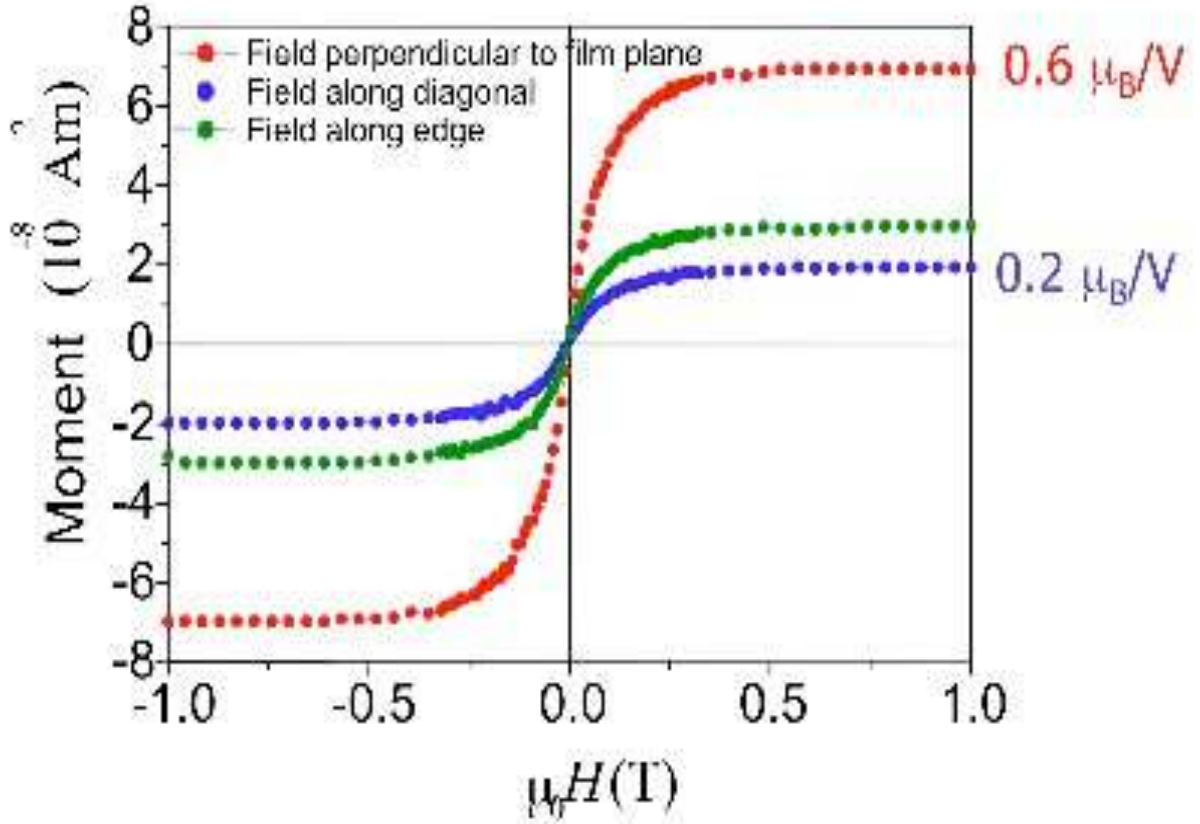


Ferromagnetic magnetization curves of a thin film of 5% Mn-doped ITO

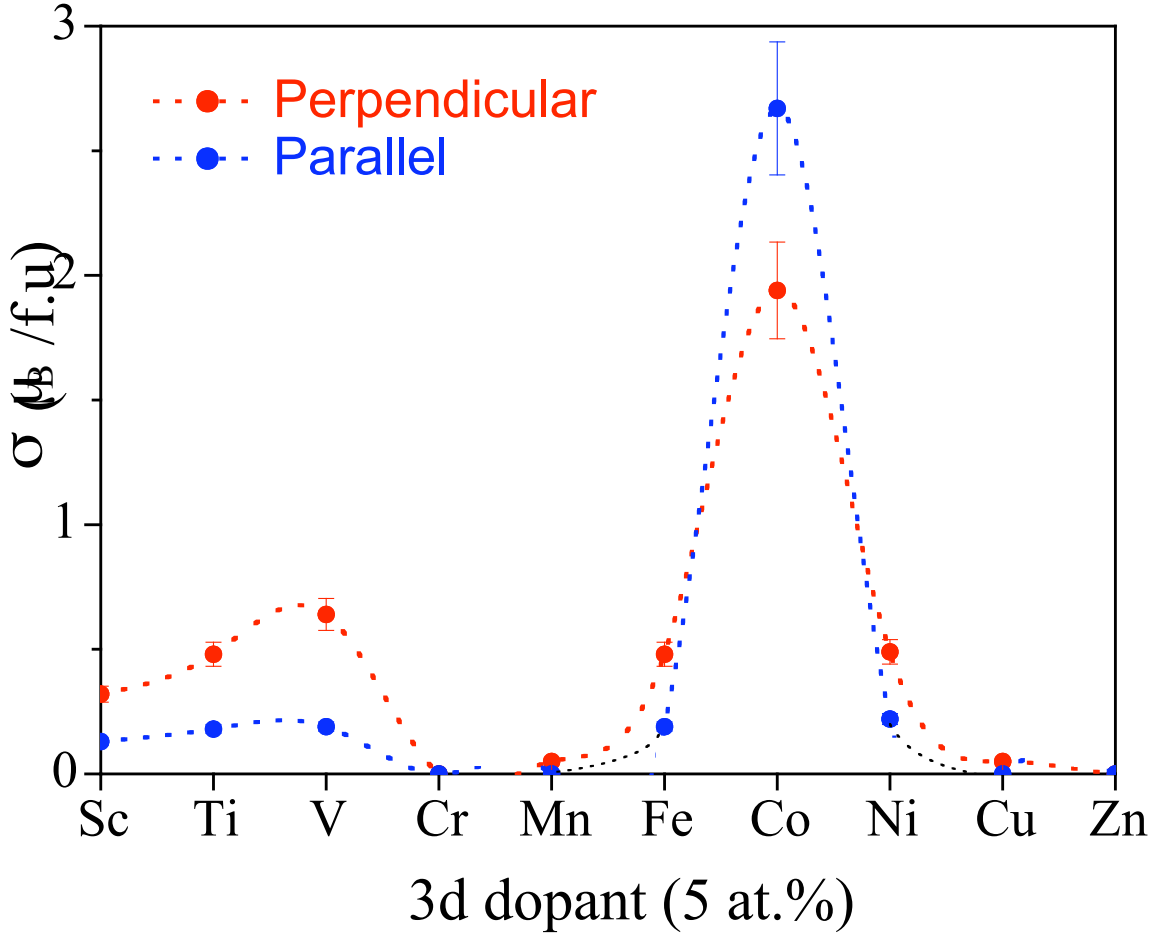
Sometimes:

— the moment per 3*d* dopant exceeds the spin-only moment for the ion

— the magnetic moment of the film is hugely anisotropic



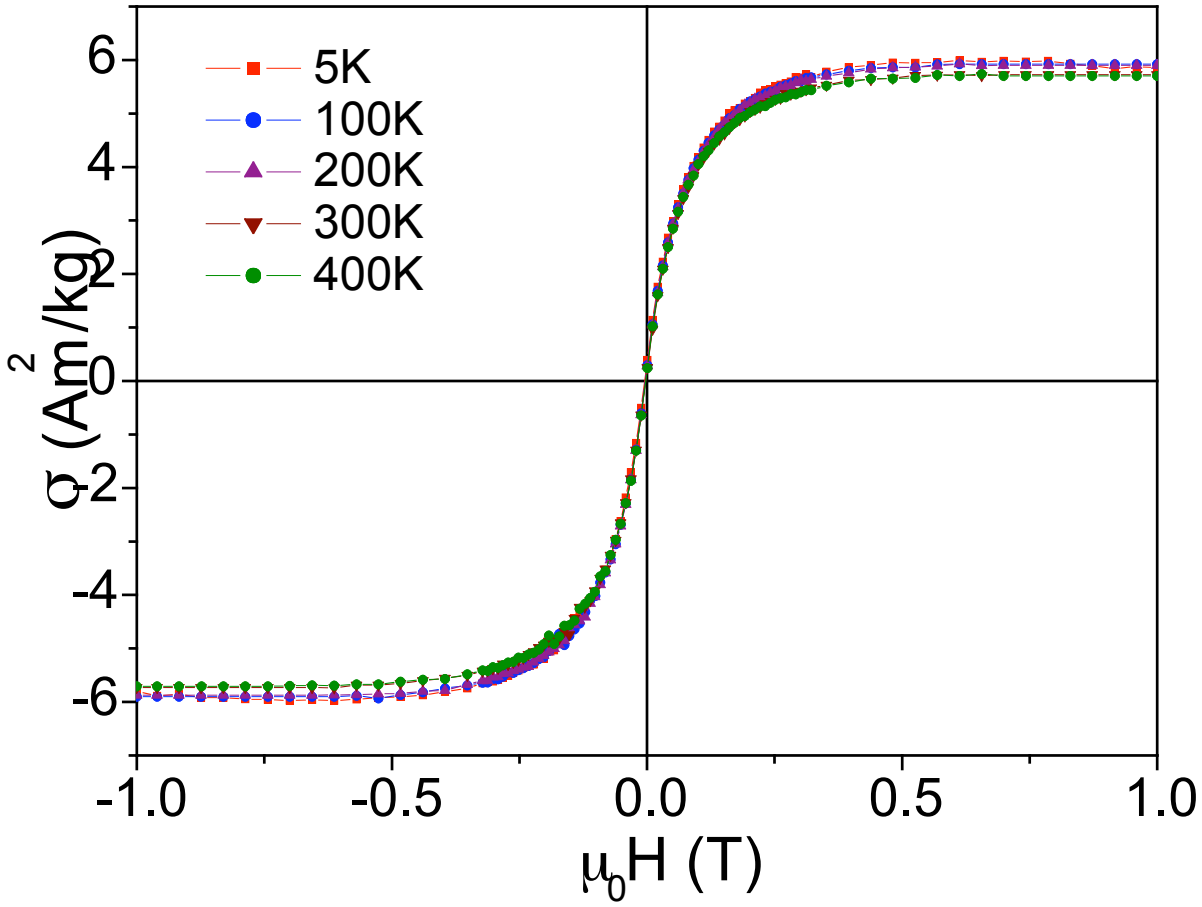
Ferromagnetic magnetization curves of a thin film of 5% V-doped ZnO



Magnetic moments measured in thin film of 5% T-doped ZnO

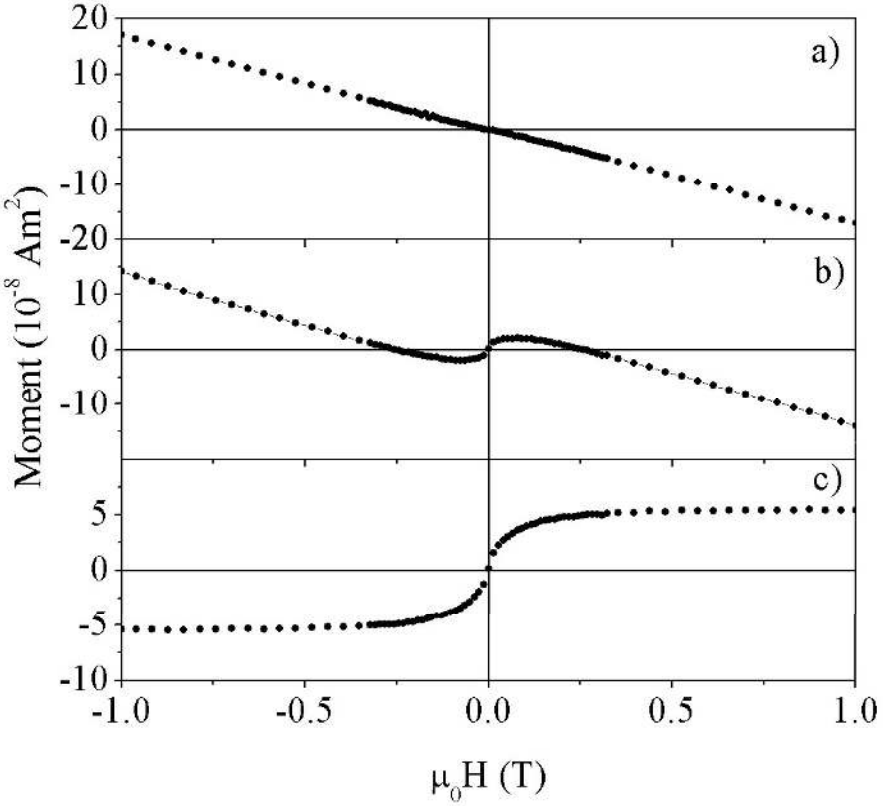
d^0 ferromagnetism

Thin films and nanoparticles of *undoped* oxides sometimes show the same behaviour !



Magnetization curves of thin films of *undoped* HfO_2

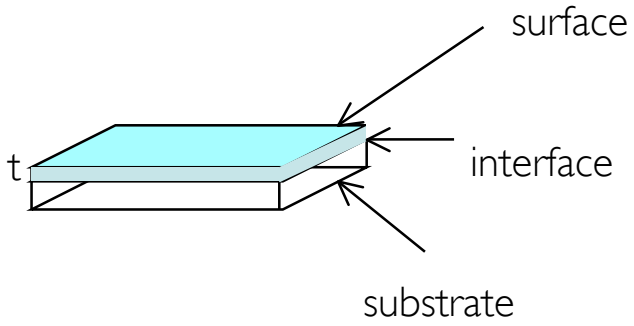
Data reduction



Sapphire substrate

Substrate + film

film



t ≈ 100 nm t_s=500 μm

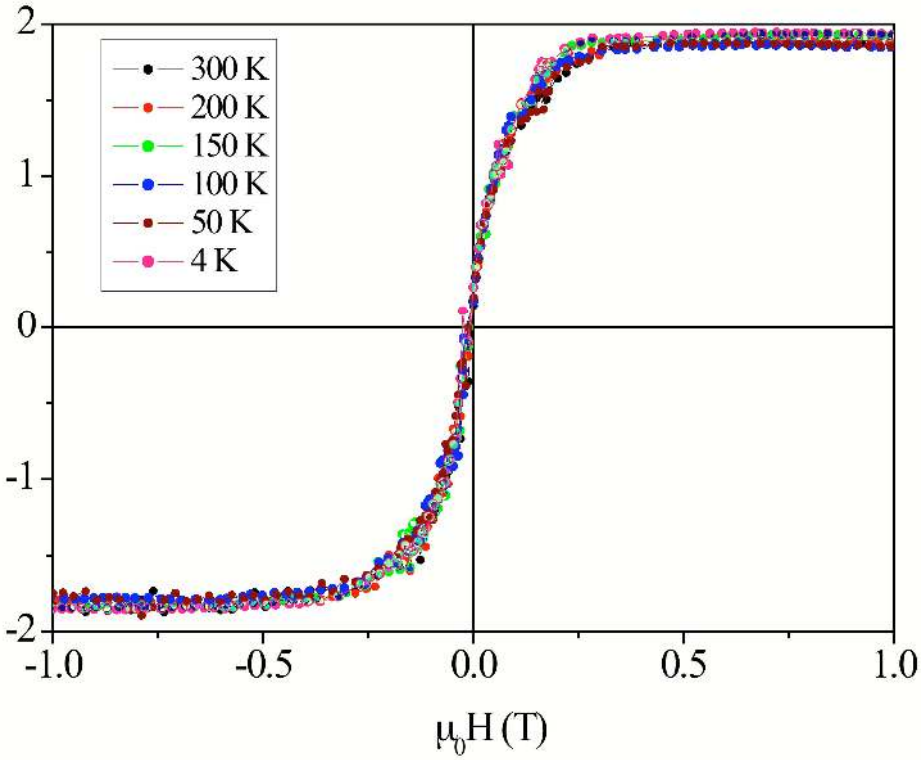
m ≈ 10μg M ≈ 35 mg

film substrate

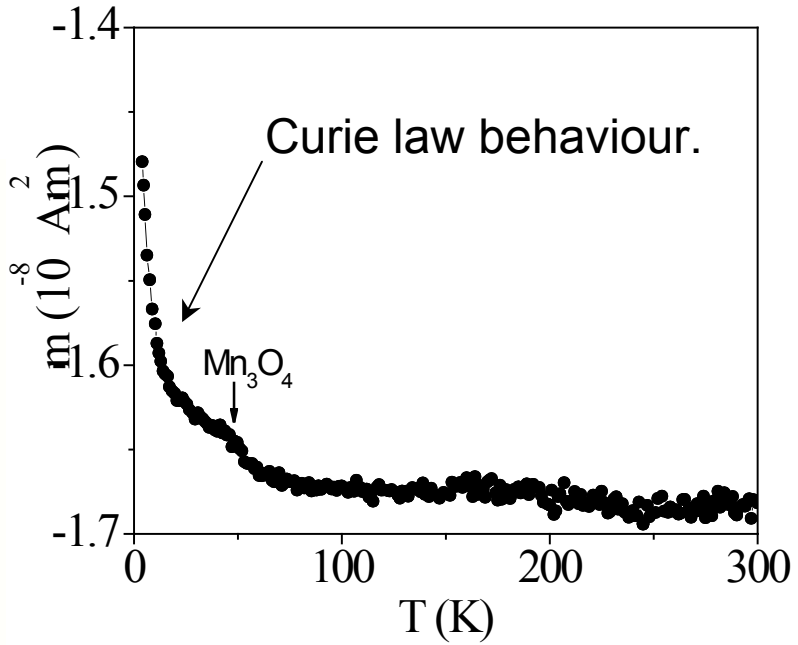
Warning ! The masses of the thin films are *very* small ≈ 10 μg; volumes are ≈ 2 10^{-12} m^3, moments are < 10^{-7} A m^2, M < 50 kA m^{-1}.

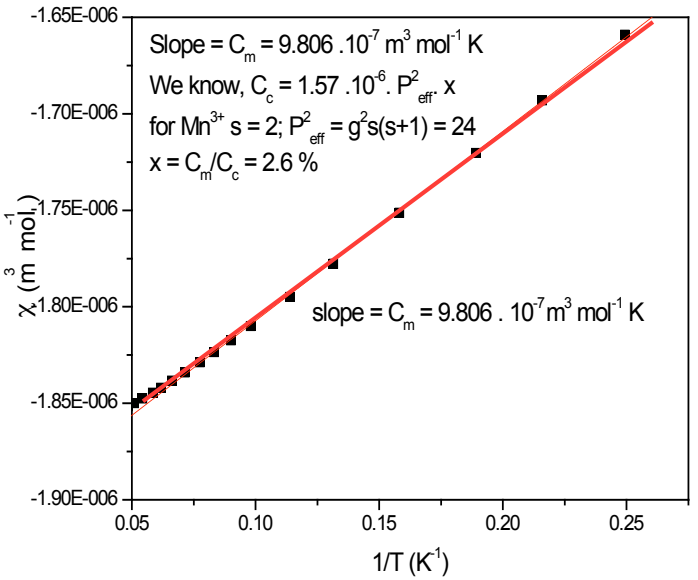
Beware of contamination A 1-μg speck of magnetite could produce such a moment.

Low-temperature susceptibility

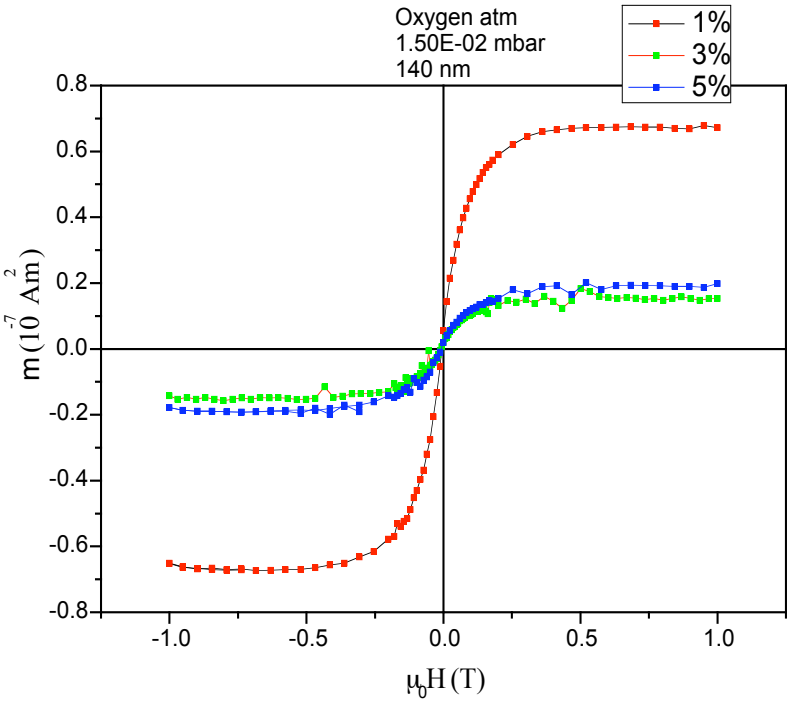


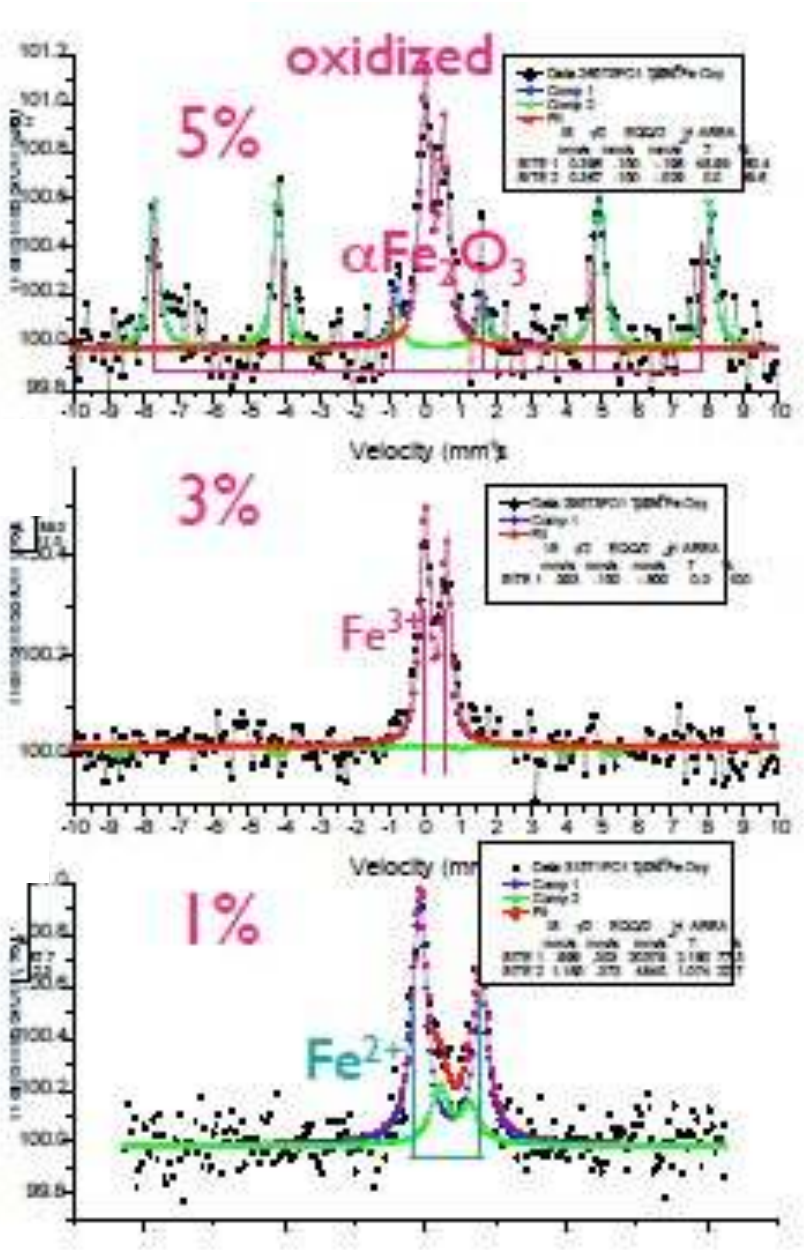
Magnetization curves for 5% Mn-doped ITO films at different temperatures.



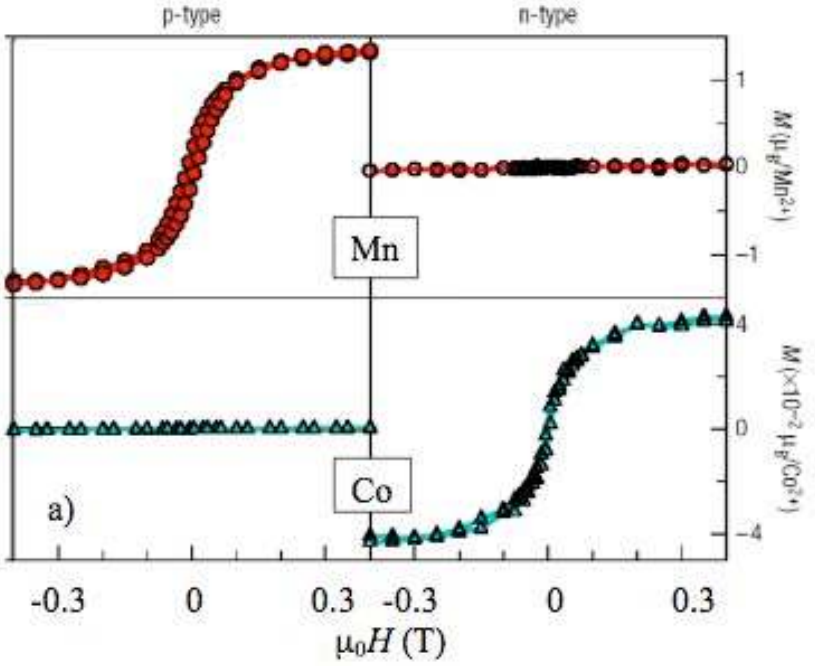


TiO_2 rutile films doped with ^{57}Fe — Mössbauer spectra

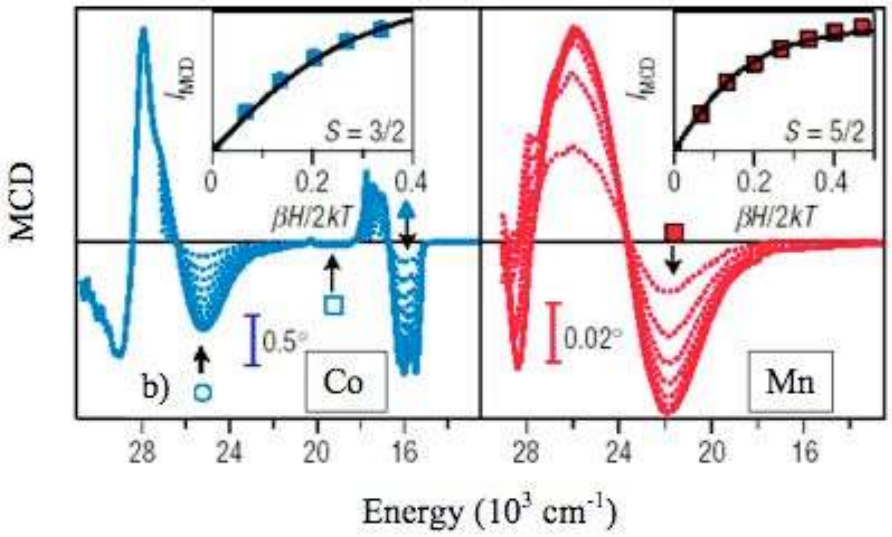




Deposited in 1 mbar oxygen



Development of magnetism in n-type ZnO with Co or p-type ZnO with Mn.



MCD spectra and the magnetic field dependence of the intensity of he MCD signal (insets) recorded at different energies in ZnO doped with Co (left) and Mn (right)

Kittilstved et al., Nat Mater (2006).

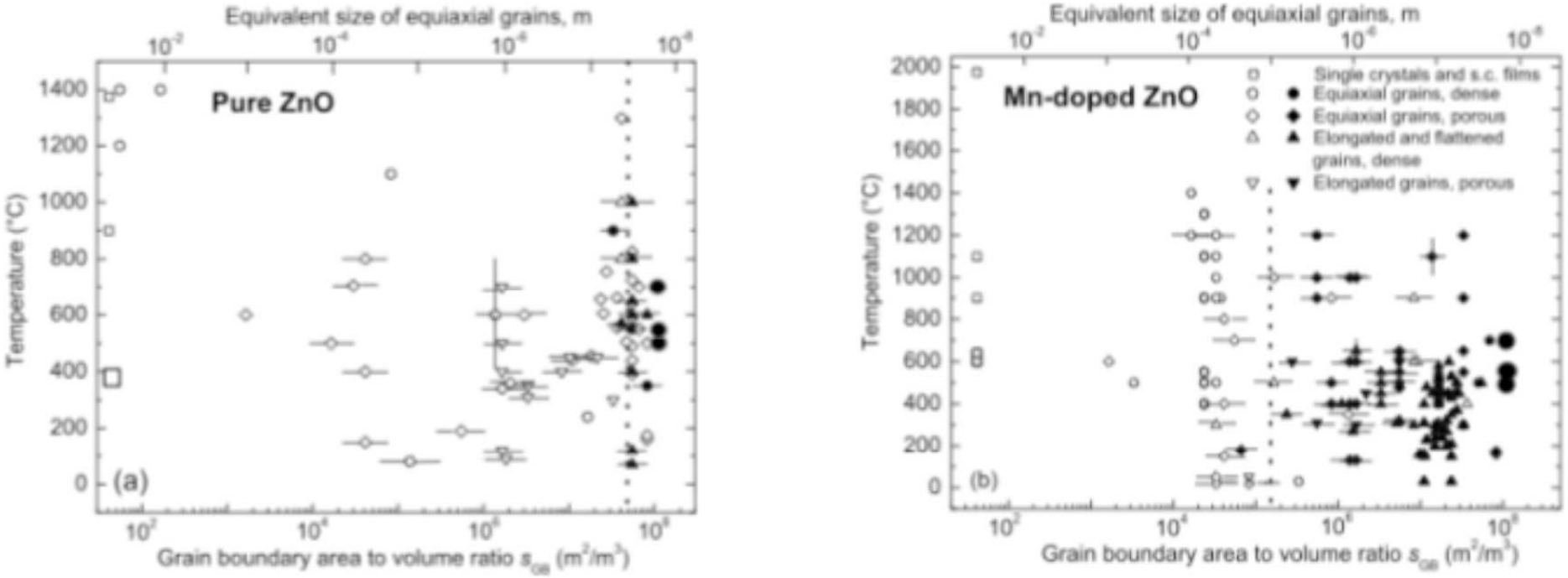
Recent results

Element-specific XMCD studies on ferromagnetic Co-doped ZnO films reveal:

- No ferromagnetic moment on the cobalt
- No ferromagnetic moment on the zinc
- No ferromagnetic moment on the oxygen

Conclusion. The moment must be somewhere else, maybe associated with electrons trapped in vacancies or other defects

Recent results



Plot of magnetic moment versus grain-boundary area for undoped and Mn-doped ZnO ceramics.

Straumal et al. Phys Rev B (2009)

Summary

I. The oxides are usually n-type. They may be partially compensated, semiconducting, insulating, or even metallic

II. The average moment per dopant cation mion approaches (or even exceeds) the spin-only value at low dopant levels x. It falls progressively as x increases. Moment per area is 200-300 m_B nm^{-2}

III. The ferromagnetism appears far below the percolation threshold x_p for nearest-neighbour cation coupling. T_C can be far above RT.

IV. The ferromagnetism is almost anhysteretic and temperature-independent below RT. Sometimes it is hugely anisotropic

V. Magnetism is found even in some samples of undoped oxides. The moment does not seem to come from the magnetically-ordered dopants, but from lattice defects

VI. The effect may be unstable in time, decaying over weeks or months.

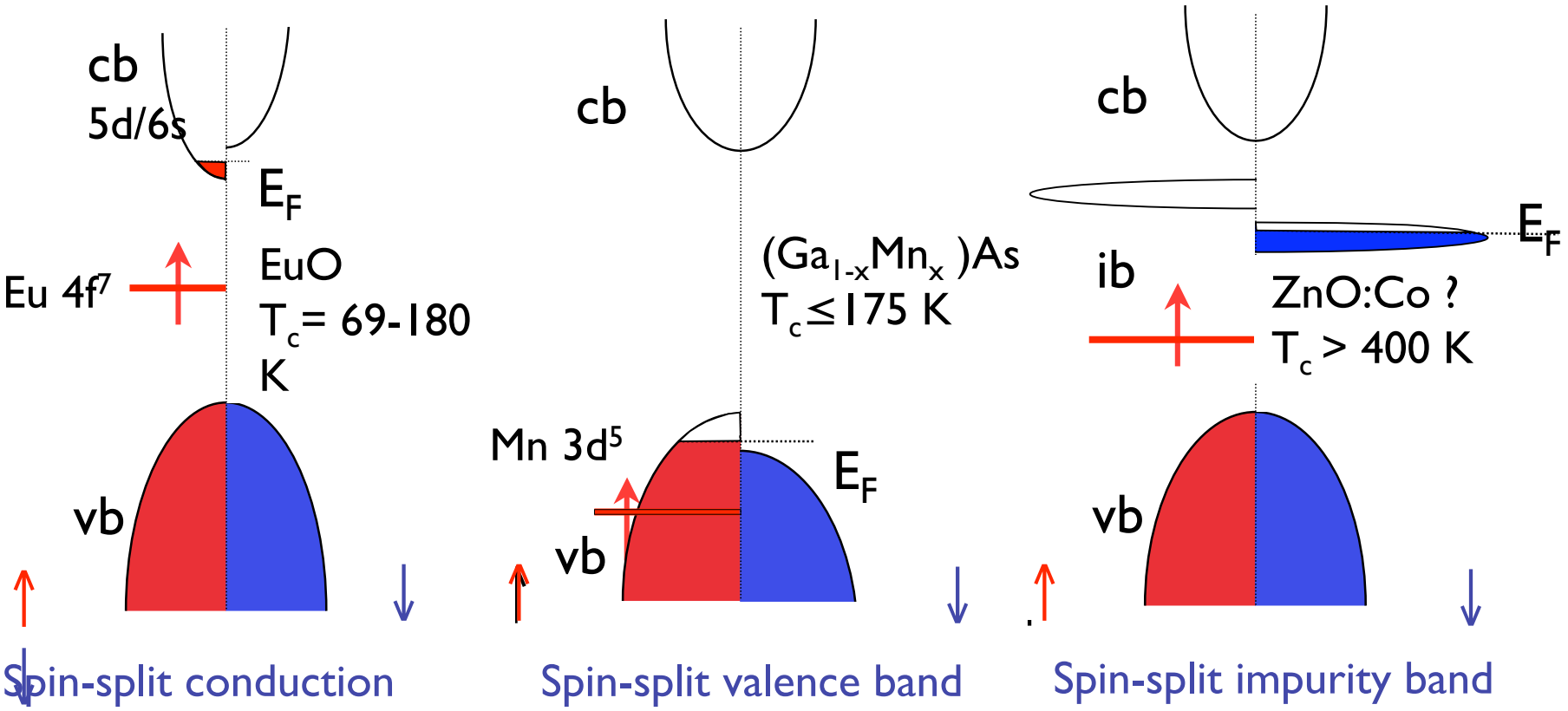
Fickle ferromagnetism

3. How can we explain the results?

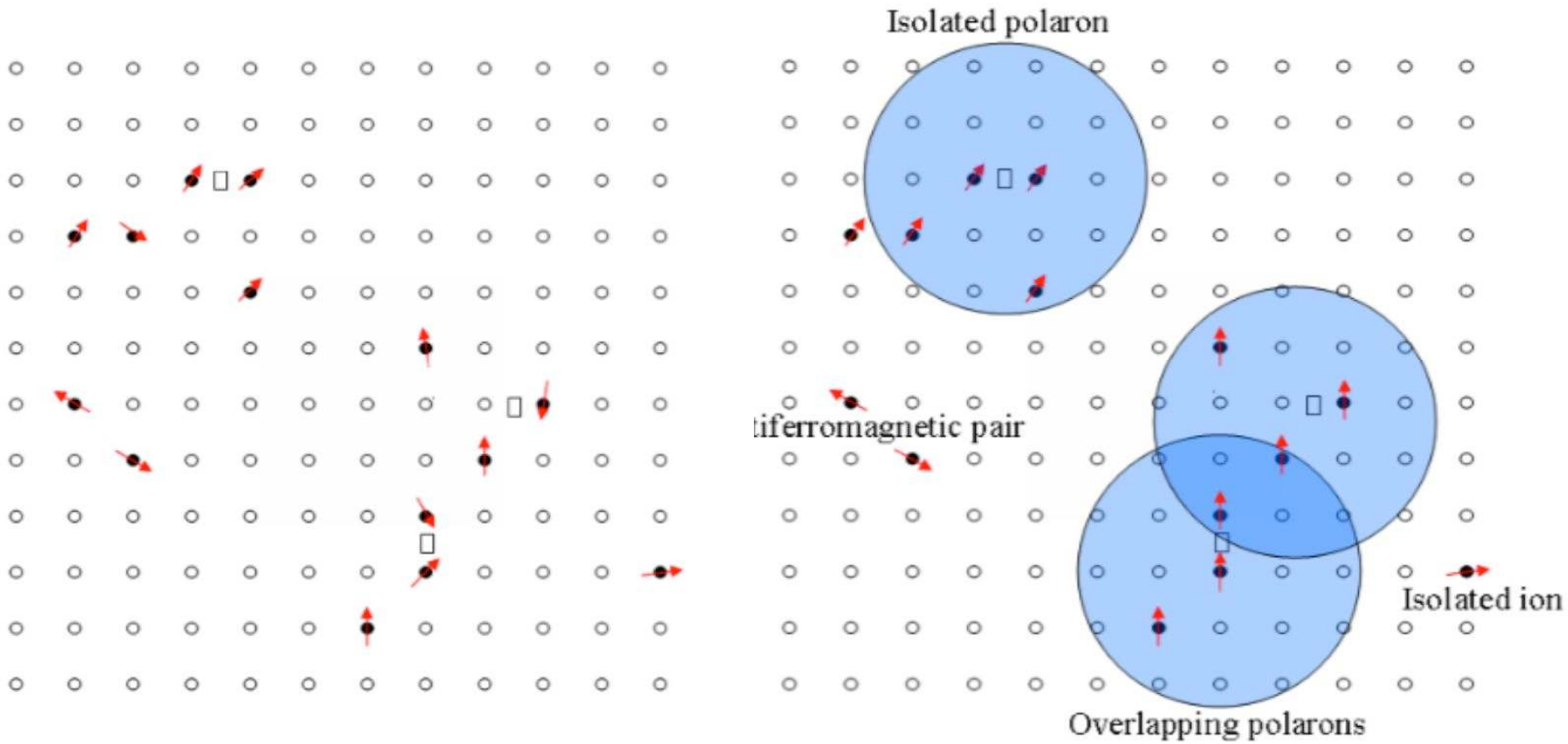
- Dilute magnetic semiconductor (DMS) Uniform magnetization due to 3*d* dopants, ferromagnetically coupled via valence band or conduction band electron
- Bound magnetic polaron model (BMP) Uniform magnetization of the 3*d* dopants, ferromagnetically coupled via electrons in a defect-related impurity band
- BMP' model; Defect-based moments coupled via electrons in a defect-based impurity band

All these are Heisenberg models; ***m*** - *J paradigm*

Magnetic Semiconductors



Coey et *al* Nat. Mater. **4** (2006))



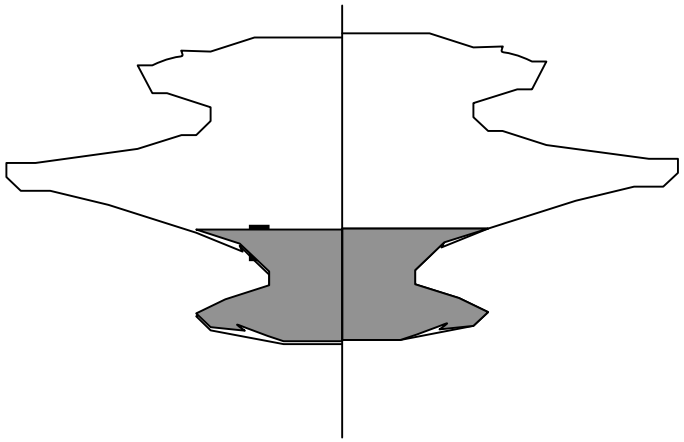
BMP model: Distribution of dopant ions in a dilute magnetic semiconductor. Donor defects which create magnetic polarons where the dopant ions are coupled ferromagnetically.

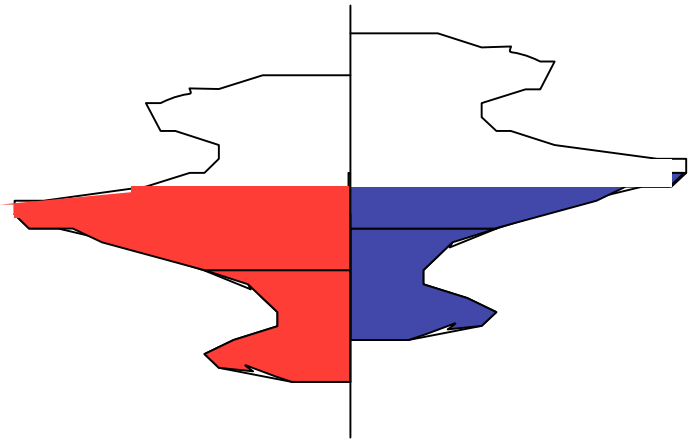
Problems with local-moment models

- Superexchange is usually antiferromagnetic
- No magnetic order is expected below the percolation threshold
- Even of there was an indirect interaction via mobile electrons, the Curie temperatures are 1 - 2 orders of magnitude too low
- There is little evidence that the dopant ions order magnetically; they are paramagnetic.

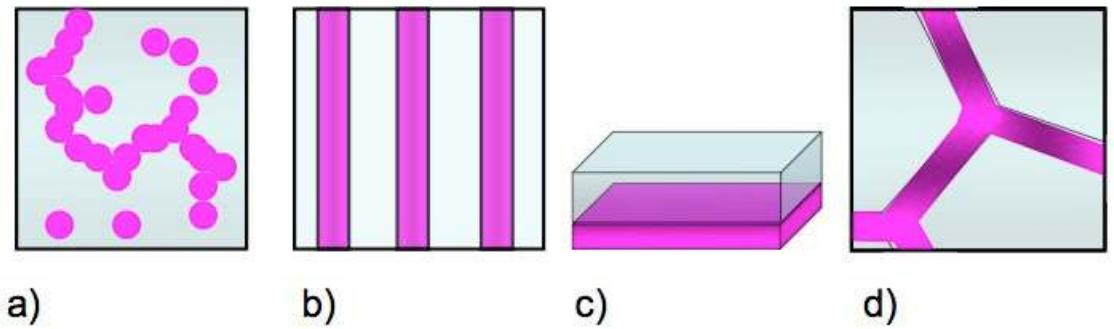
- Split impurity band model (SIB) A defect-related impurity band is spontaneously spin split. Edwards and Katsnelson J Phys CM (2006)
- The charge-transfer ferromagnetism model (CTF). A defect-related impurity band is coupled to a charge reservoir, which enables it to split Coey et al (2009)

These are Stoner models; The spin-split impurity band fills only a fraction of the sample.





Inhomogeneous distributions of defects



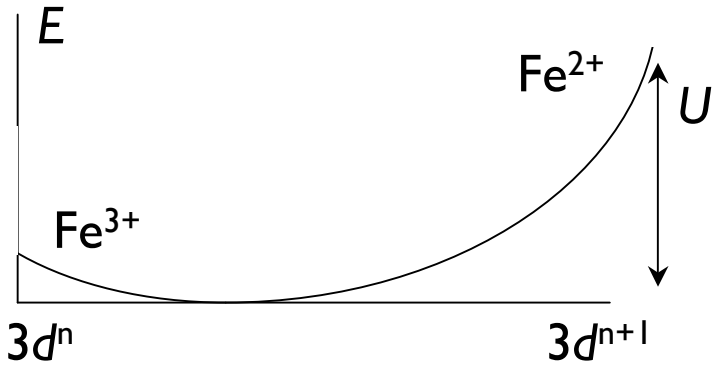
Inhomogeneous ferromagnetism in a dilute magnetic oxide. The ferromagnetic defect-related regions are distributed a) at random, b) in spinodally segregated regions, c) at the surface/interface of a film and d) at grain boundaries.

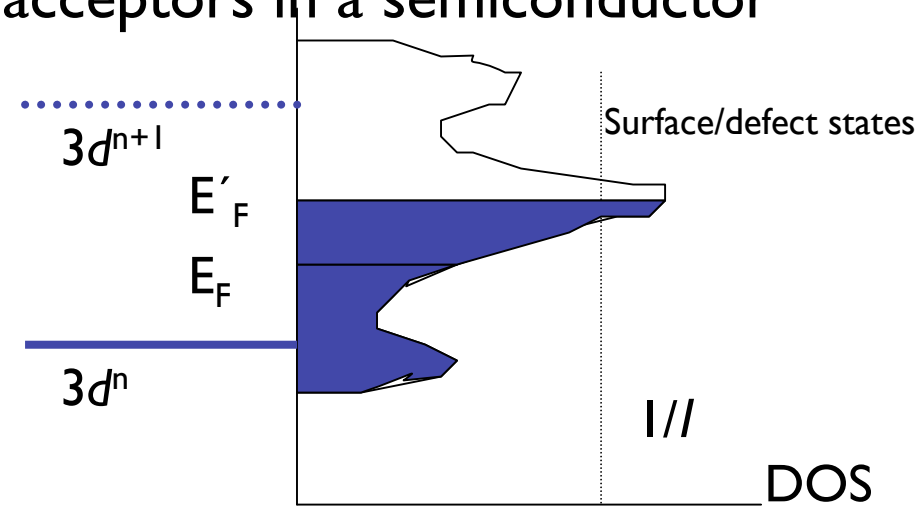
Charge-transfer ferromagnetism

If there is a nearby *resevoir* of electrons, the electrons can be transferred at little cost, and the system benefits from the Stoner splitting *I* of the surface/defect states.

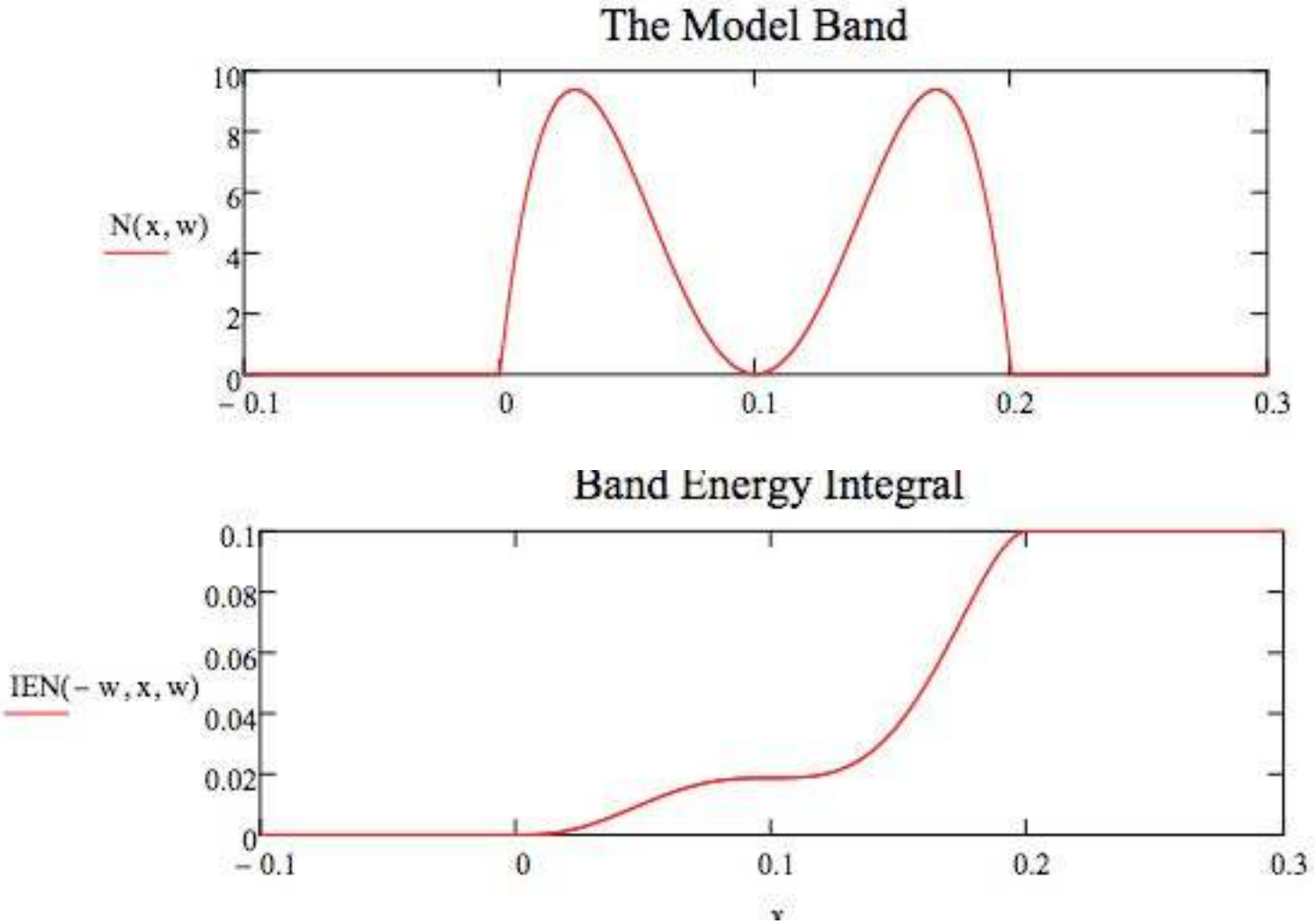
The resevoir may be

- 3*d* cations which coexist in different valence states (dilute magnetic oxides)
- A charge-transfer complex at the surface (Au-thiol)
- Charge due to ionized donors or acceptors in a semiconductor

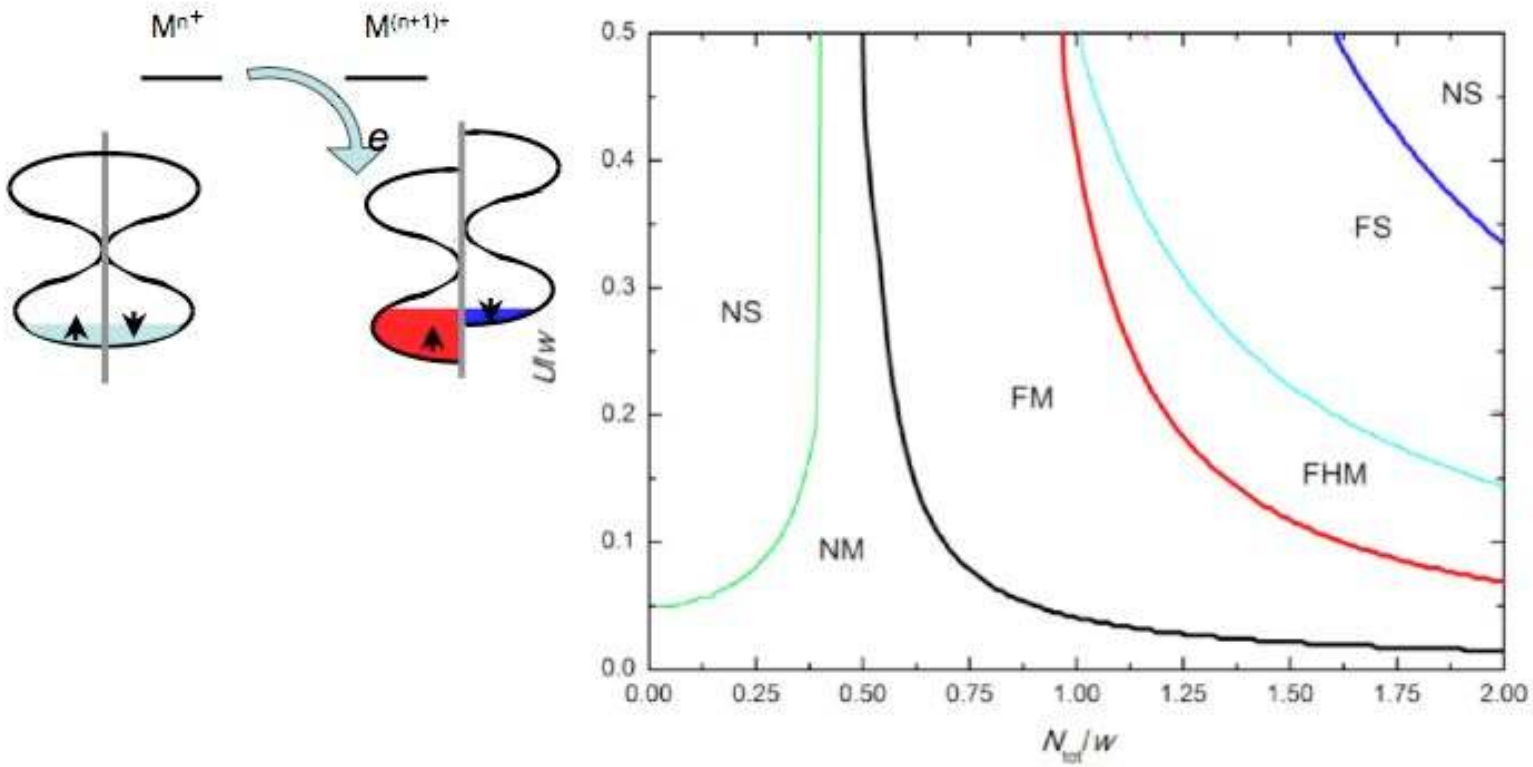




CTF Model calculations

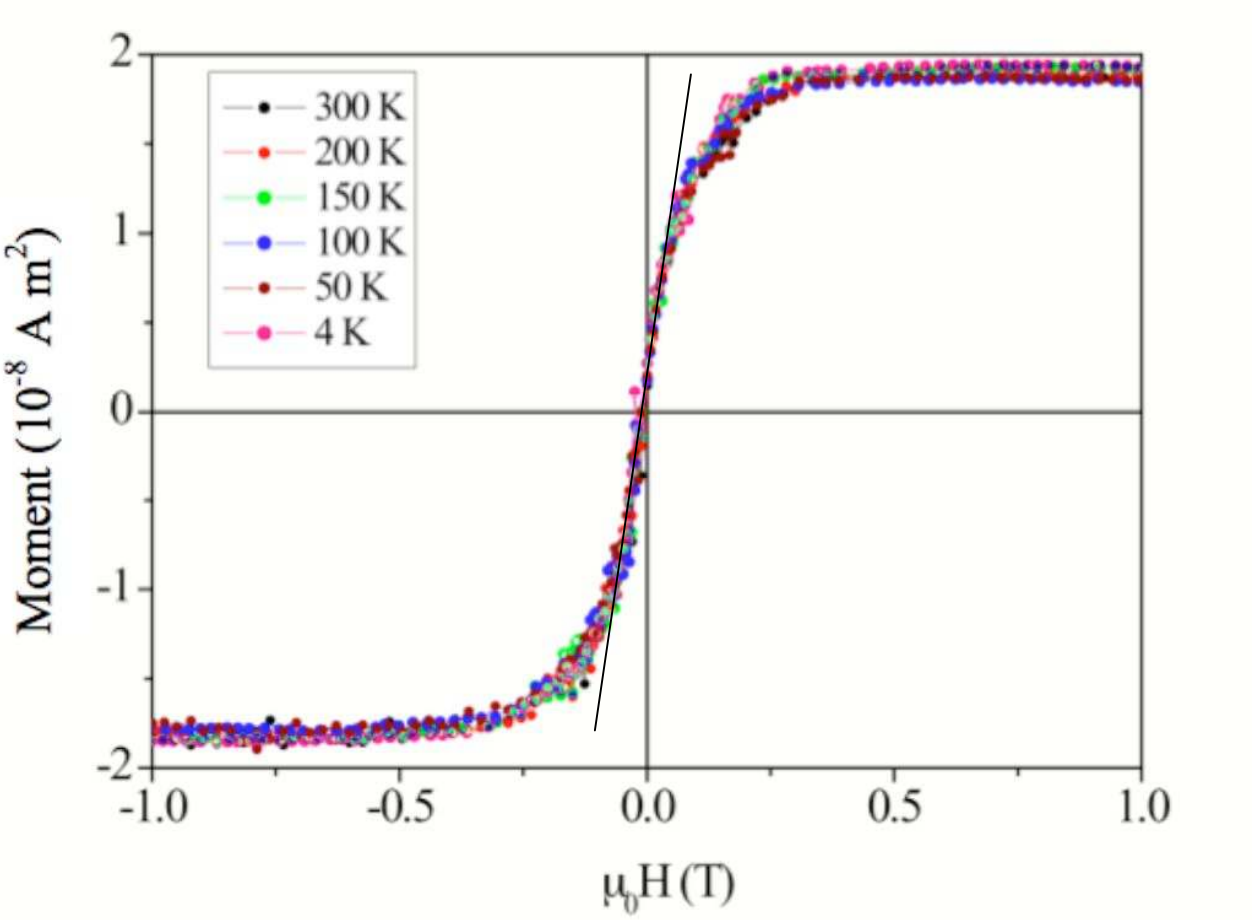


Charge-transfer ferromagnetism



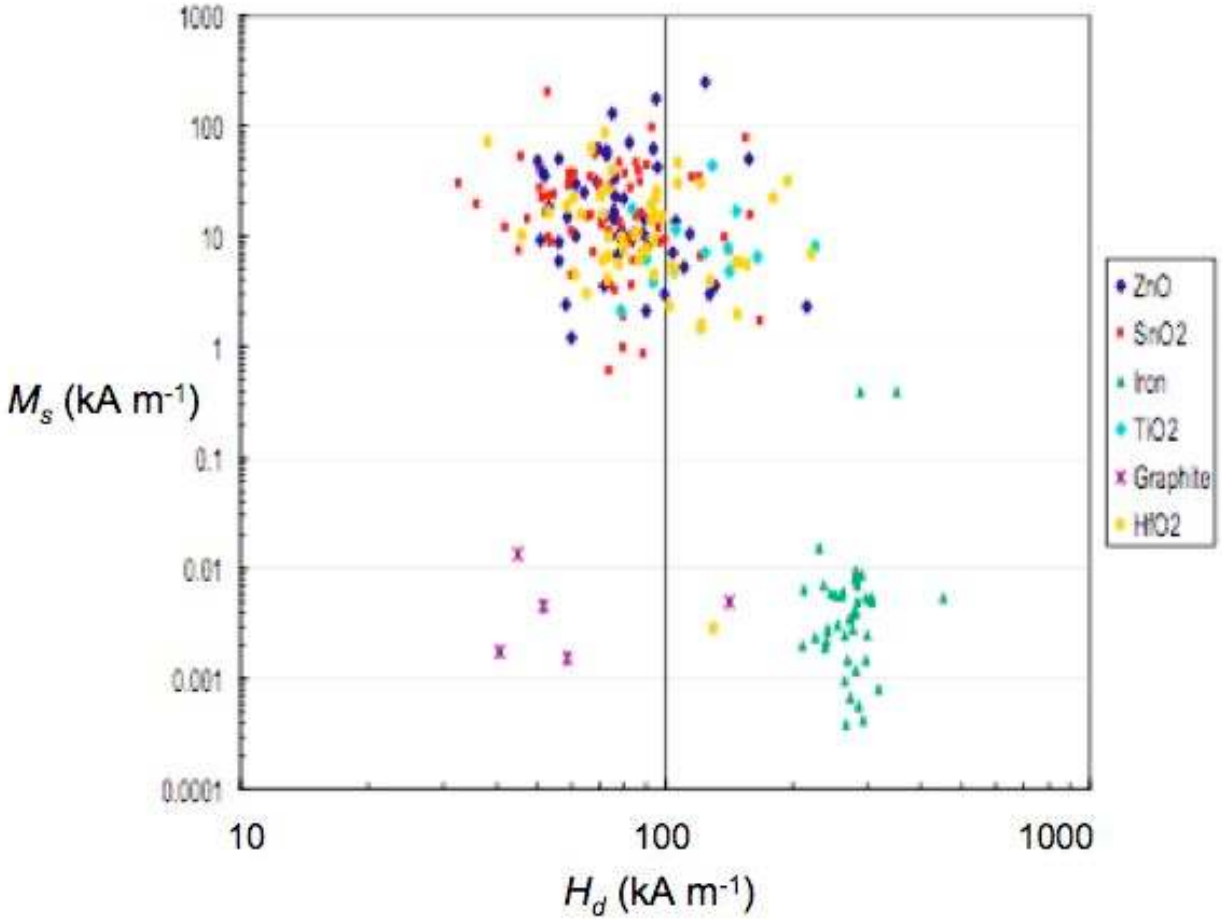
Phase diagram for the charge-transfer ferromagnetism (CTF) model. Electron transfer from the 3*d* charge reservoir into the defect-based impurity band, leading to spin splitting is shown on the left. The variables are the number of electrons in the system N_{tot} and the 3*d* coulomb energy U_d, each normalized by the impurity bandwidth W. The Stoner integral I is taken to be 0.6. The regions in the phase diagram are NS nonmagnetic semiconductor, NM nonmagnetic metal, FM ferromagnetic metal, FHM ferromagnetic

Magnetization process



The magnetization process in anhysteretic; It must be governed by *dipole interactions.*

A field of only ~ 100 mT is needed to approach saturation. $M \approx M_0 \tanh(H/H_0)$



$H_0 = 0.16\ M_0$

Local dipole field H_d

	H_d kA m^{-1}
TiO_2	125 (40)
SnO_2	79 (30)
HfO_2	94 (35)
ZnO	83 (30)
Graphite	68 (42)
Fe	275 (40)

Magnetization M_s vs internal field H_0 for thin films and nanoparticles of doped and undoped oxides. For thin films the magnetization M_s clusters around 10 kA m^{-1}, but H_0 is about 100 kA m^{-1}

It follows that the ferromagnetic volume fraction in the films is 1 - 2 %.

In nanoparticles the ferromagnetic volume fraction is 10 - 100 ppm

4. Conclusions

- The dilute magnetic oxides are not dilute magnetic semiconductors.
- The magnetism is essentially related to defects. The paramagnetic dopant ions do not necessarily order magnetically.
- A Stoner model based on a spin-split defect-related impurity band is the likely explanation of the high-temperature ferromagnetism
- The charge-transfer ferromagnetism (CTF) model is able to account for the observed features. The 3*d* dopants need to exhibit mixed valence
- Applications will depend on our ability to make materials with stable and controlled defect distributions