OXIDE and SEMICONDUCTOR MAGNETISM

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1. Single-ion effects
2. Collective Effects
3. Examples

www.tcd.ie/Physics/Magnetism

3. Examples - A visit to the Zoo

3.1 The ‘famous five’. Magnetite (Fe_3O_4); Hematite (□Fe_2O_3); Goethite (□FeOOH); Barium hexaferrite ($BaFe_{12}O_{19}$); YIG ($Y_3Fe_5O_{12}$).

3.2 The ‘special seven’ EuO, CrO_2, $SrRuO_3$, NiO, a-FeF_3, $(La_{0.7}Sr_{0.3})MnO_3$, Sr_2FeMoO_6.

3.3 Magnetic semiconductors

Some references:

Materials for spin electronics: J. M. D. Coey in Spin Electronics, M. Ziese amd M. J. Thornton, (editors) Springer 2001 p277-297

http://link.springer.de/series/lnpp/

2.1 The famous five.

These are the most common magnetic oxides, which occur naturally or are synthesised industrially.

- Magnetite Fe_3O_4
- Hematite □Fe_2O_3
- Goethite □FeOOH
- Barium hexaferrite $BaFe_{12}O_{19}$
- Yttrium iron garnet $Y_3Fe_5O_{12}$

Magnetite, Fe_3O_4

spinel; $a_0 = 0.\ 839$ nm

Most common magnetic mineral, source of rock magnetism, lodestones.. A ferrimagnet.

Fe^{2+} and Fe^{3+} are disordered on B-sites above the Verwey transition at 120 K, ordered below;

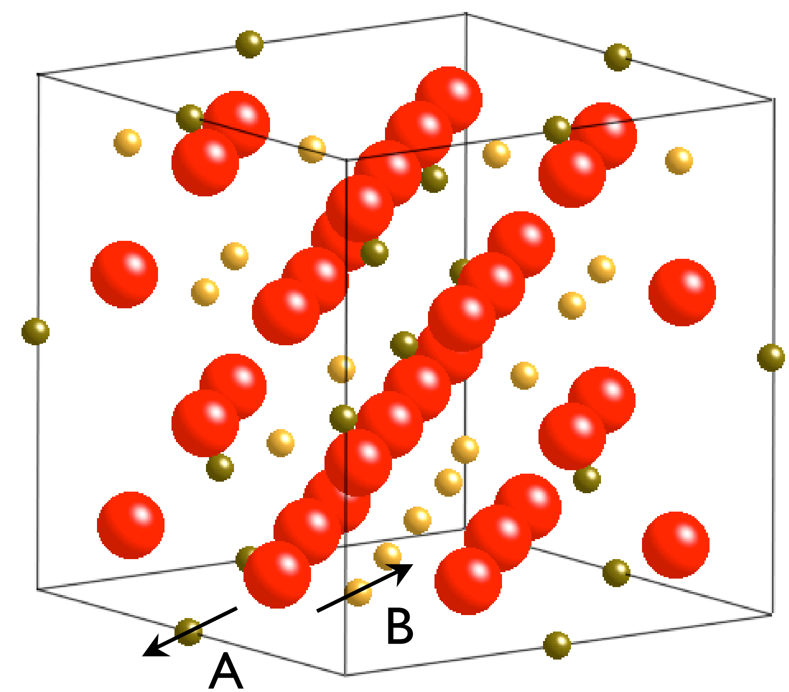
$[Fe^{3+}]_{oct}\ \{Fe^{2+}\ Fe^{3+}\}_{tet}\ O_4$

□ ↑ ↑

$-5\ \mu_B \quad +4\ \mu_B \quad +5\ \mu_B \ = \ 4\ \mu_B$

Type IIb half-metal. Fe(B) □ electrons hop in a t_{2g} band

Potential for spin electronics. Used as toner, and i ferrofluids.

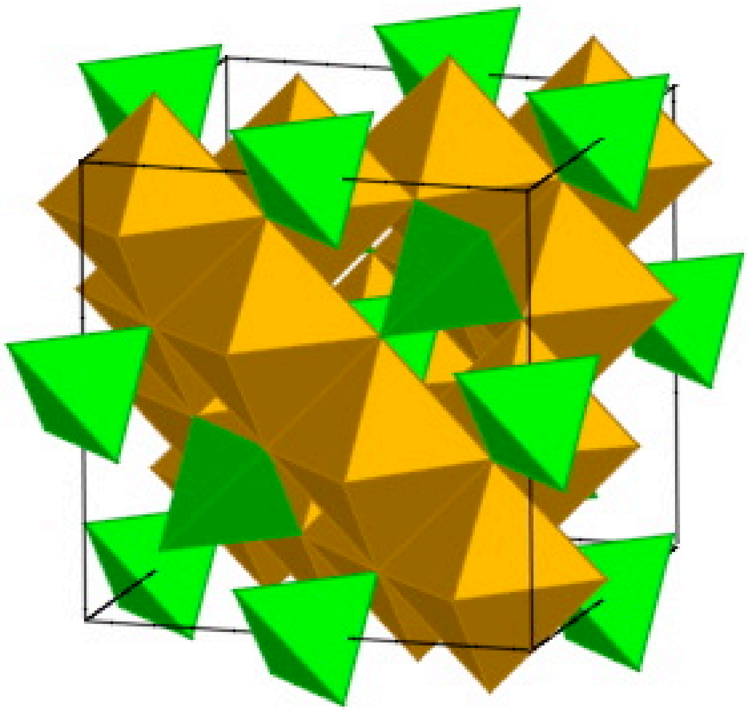


$[A]\{B_2\}O_4$

$J_s = 0.6$ T $\qquad m_0 = 4.0\ \mu_B$ / fu

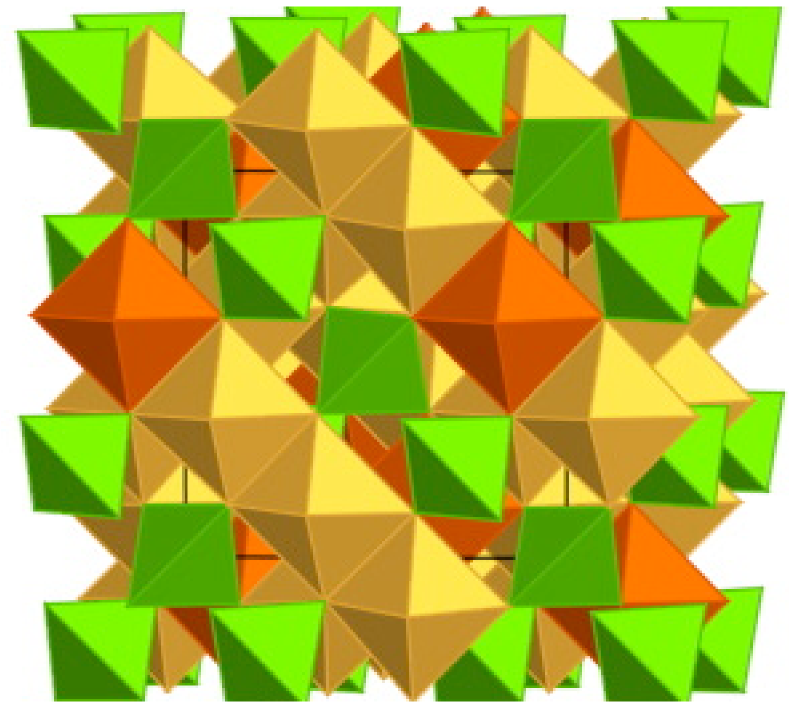
$K_1 = -13$ kJ m^{-3} $\qquad$ □$_s = 40\ 10^{-6}$

$T_C = 843$ K



Magnetite Fe_3O_4

$[Fe^{3+}]\{Fe^{2+}\ Fe^{3+}\}O_4$



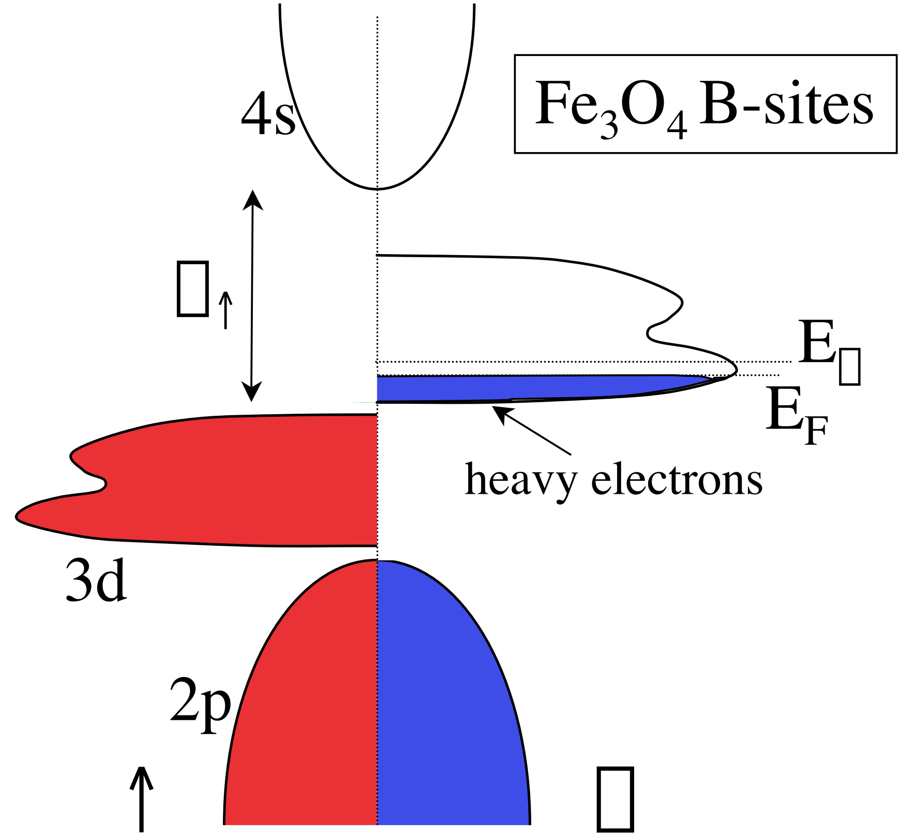
Maghemite □Fe_2O_3

$[Fe^{3+}]\{Fe^{3+}{}_{5/3}\quad {}_{1/3}\}O_4$

The B sites are populated by a mixture of $Fe^{3+}(3d^5)$ and $Fe^{2+}(3d^6)$ ions. At RT the t_{2g}□ electrons hop in a narrow polaron band. Resistivity is ≈ 50 μ□ m.

At the Verwey transition T_V = 119 K, the interatomic Coulomb interactions lead to charge ordering – ‘Wigner crystallization’ Resistivity increases by 100x. Symmetry is reduced to monoclinic; details of charge order are still controversial

J_{AB} = -28 K J_{AA} = -18 K J_{BB} = +3 K



Magnetite is the prototype for a family of spinel ferrites, which includes Ni-Zn ferrite for rf applications and □Fe_2O_3 i.e. $[Fe]\{Fe_{5/3}\ {}_{1/3}\}O_4$ for magnetic recording.

Related compounds: Spinel ferrites

		a_0 (pm)	T_C (K)	M_s (MA/m)	K_1 (kJ/m^3)	λ_s (10^{-6})	ρ (Ωm)
$MgFe_2O_4$	I	836	700	0.18	-3	-6	10^5
$ZnFe_2O_4$	N	844	T_N = 9	-	-	-	1
$MnFe_2O_4$	I	852	575	0.40	-3	-5	10^2
Fe_3O_4	I	840	860	0.50	-12	40	10^{-1}
$CoFe_2O_4$	I	839	790	0.45	180	-110	10^5
$NiFe_2O_4$	I	834	865	0.33	-7	-17	10^2
$Li_{0.5}Fe_{2.5}O_4$		829	943	0.33	-8	-8	1
γFe_2O_3		834	1020*	0.43			

Hematite, Fe_3O_4

corundum; a = 0. 5036, c = 1.375 nm

Most common iron oxide mineral. Antiferromagnetic hcp oxygen array with Fe^{3+} in 2/3 of octahedral interstices..

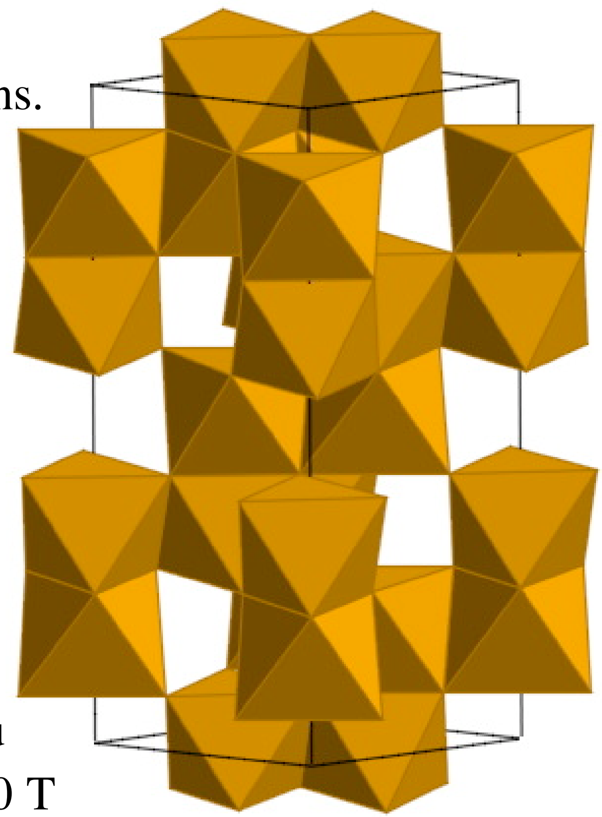
Red insulator with localized d electrons.
$3d^5$ $6A_1$ state.

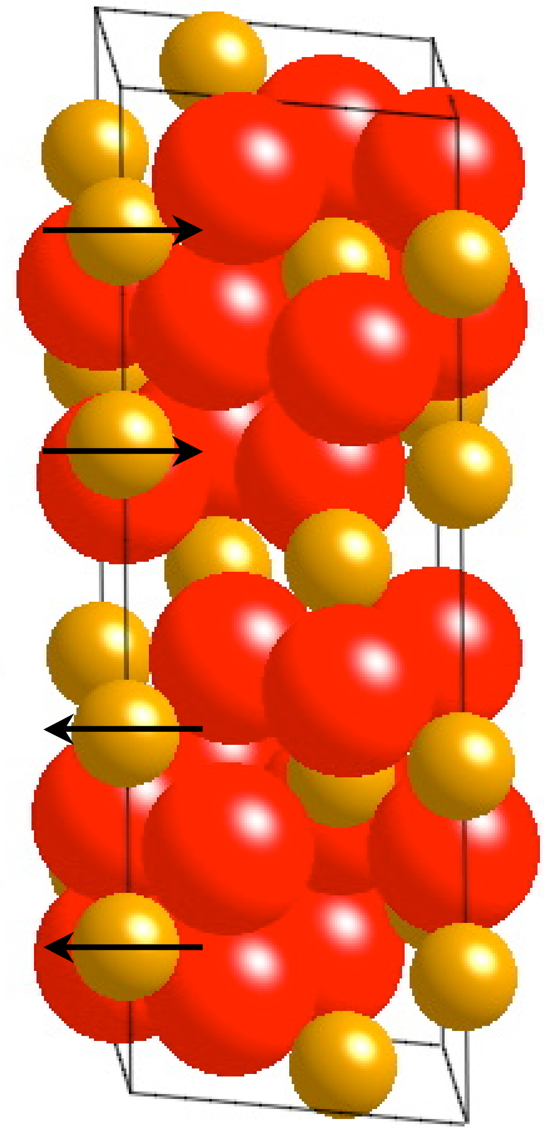
T_N = 960 K.
J_1 = 6.0 K, J_2 = 1.6K
J_3 = -29.7 K, J_4 = -23.2 K.

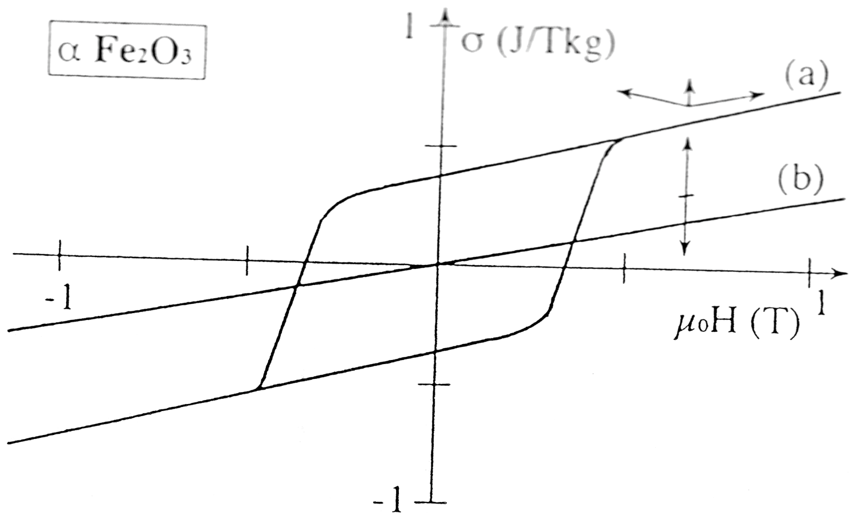
Af sublattices are slightly canted by D-M interaction

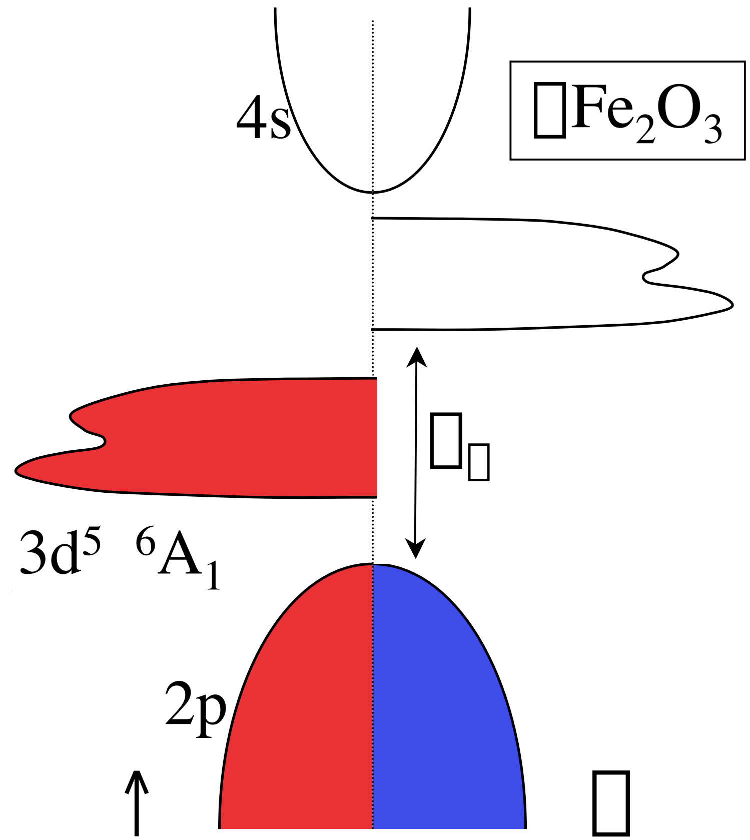
.

$J_s = 2.8\ 10^{-3}$ T $\quad$ $m_0 = 0.002\ \mu_B$ / fu
K_1 = 23 kJ m^{-3} $\quad$ $B_a = 2\mu_0 K_1/J_s$ = 20 T

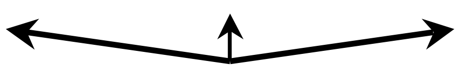








Ar room temperature there is a weak ferromagnetic moment caused by canting of the sublattice magnetizations by the D-M interaction.



Below 260 K there is a spin reorientation to the c-axis. ***D*** is then zero by symmetry, and the weak interaction disappears.

What causes the spin reorientation ?

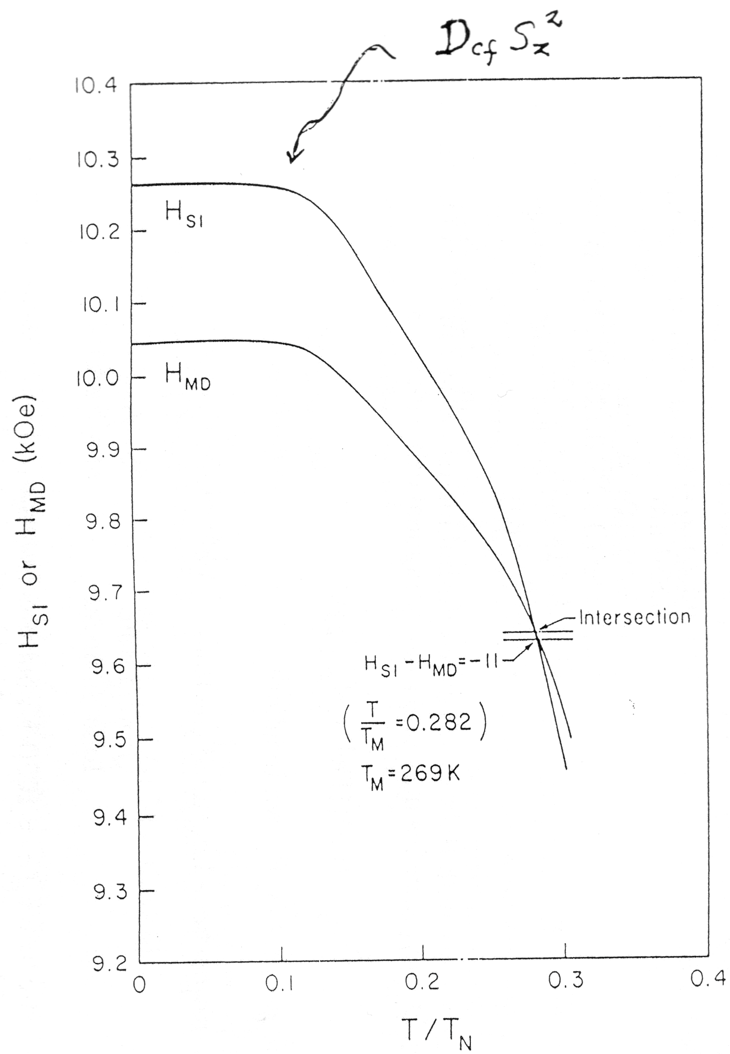


Figure 4.6: The temperature dependence of single-ion and magnetic-dipole fields to illustrate the prediction of the Morin temperature.

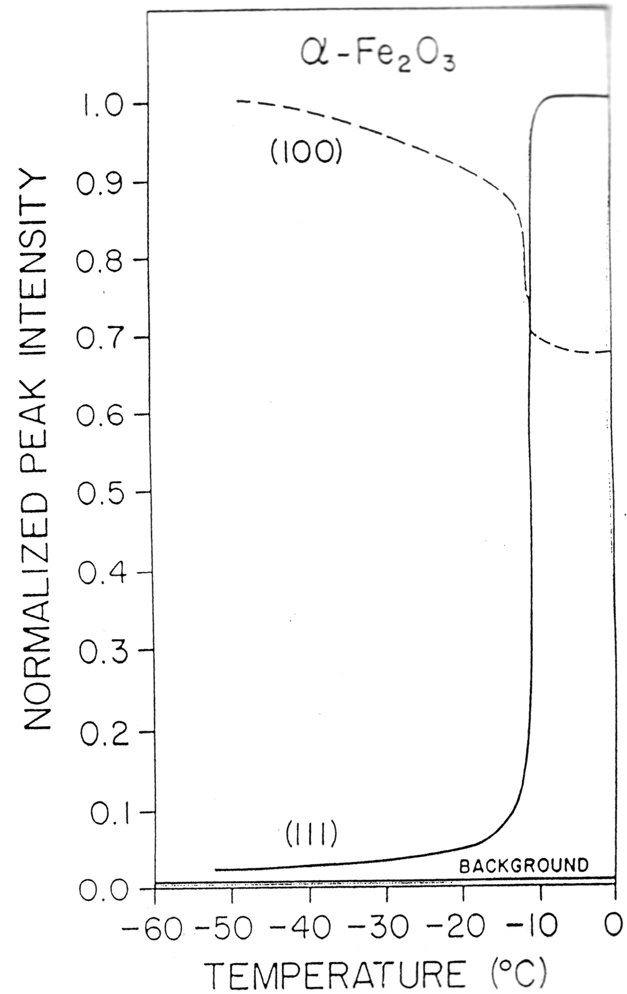


Figure 2.8: Neutron-diffraction intensities of the (111) and (100) lines as a funct of temperature. The background intensity is also shown.

The spin direction is set by competing cf and dipole dipole interactions, which vary as $\langle S_z^2\rangle$ and $\langle S_z\rangle^2$ respectively.

$$B_{dip} = \mu_0/4\pi[3(\boldsymbol{m}.\mathbf{r})\mathbf{r}/r^5 - \boldsymbol{m}/r^3]$$

□FeOOH *Goethite;* $a = 0.995$ nm, $b = 0.301$ nm $c = 0.462$ nm

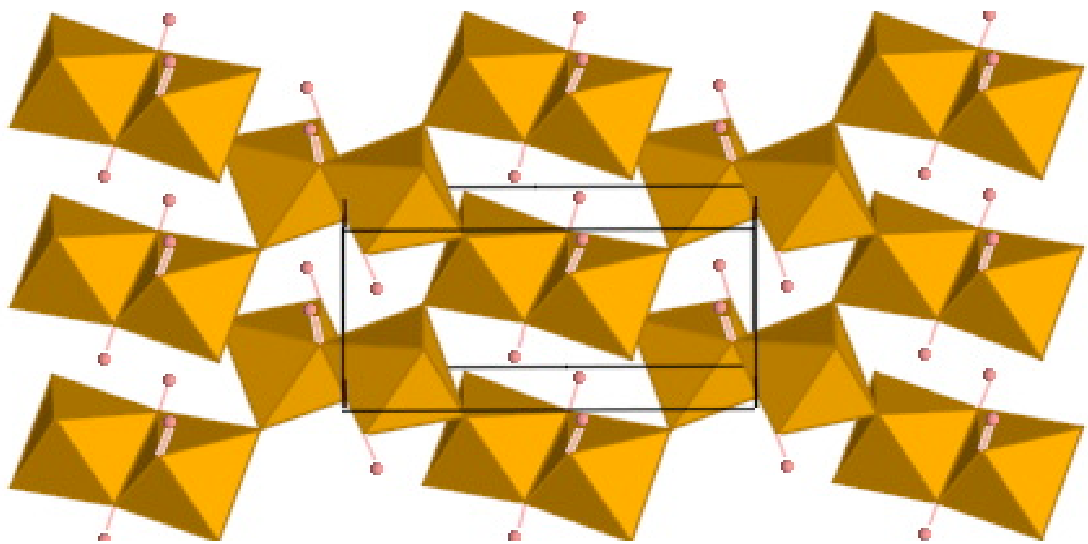
A brown antiferromagnetic insulator named for Goethe!

The magnetic structure consists of double zig-zag chains ordered antiferromagnetically

$T_N \approx 460$ K.

The main constituent of rust, also found in tropical soils.

Often superparamagnetic when well crystallized.

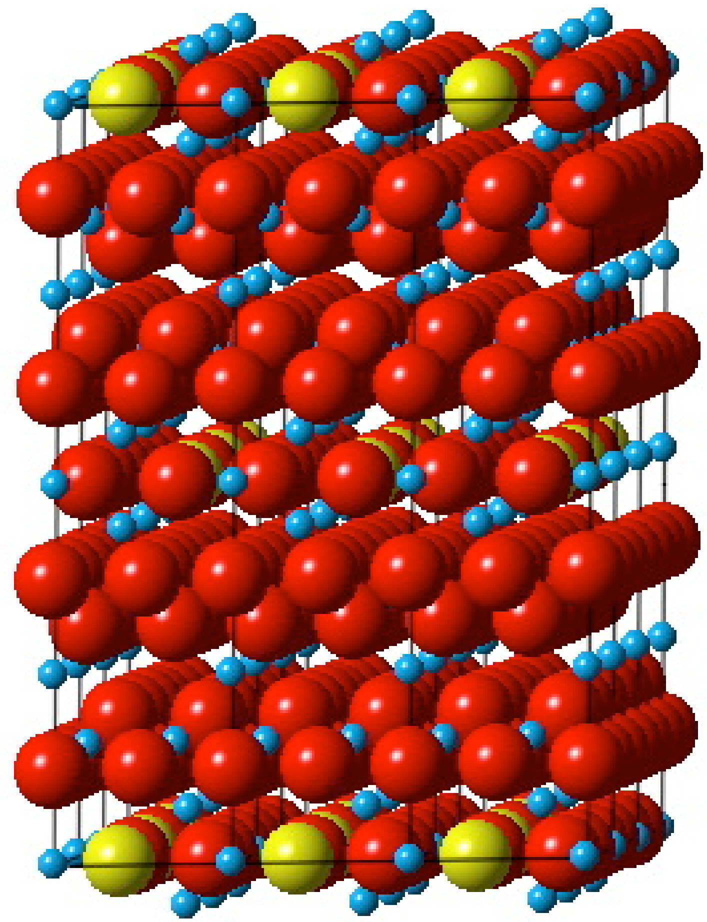


$BaFe_{12}O_{19}$ *hexagonal ferrite;* a = 0.589 nm, c = 2.319 nm

An hcp lattice of .oxygen and Ba, with iron in octahedral (12k, $4f_2$, 2a) tetrahedral ($4f_1$) and trigonal bipyramidal (2b) sites.

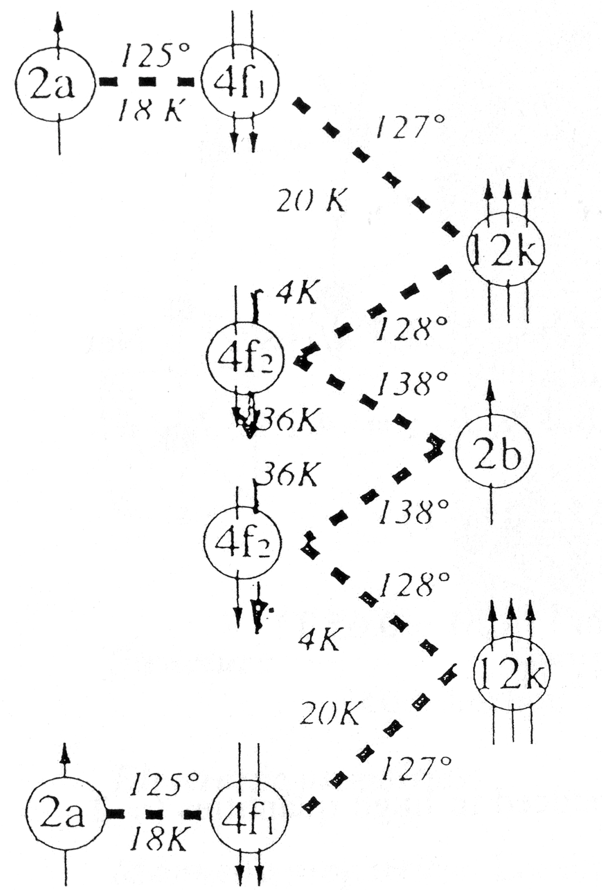
Brown ferrimagnetic insulator. All magnetic ions are Fe^{3+}. Structure is $12k\uparrow 2a\uparrow 2b\uparrow 4f_1$□$4f_2$□

T_C = 740 K.



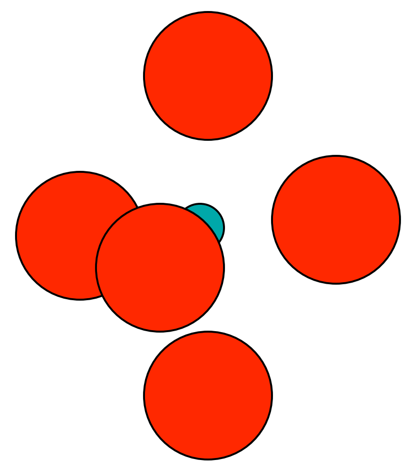
The first permanent magnet to break the 'shape barrier'. 98% of all permanent magnets by mass are Ba or Sr ferrite. Found on every fridge door and in innumerable dc motors. 50g manufactured per year for everyone on earth

J_s = 0.48 T . K_1 = 450 kJ m^{-3}. B_a = 1.7 T



What is the source of the anisotropy ?

Fe^{3+} is an S-state ion.



The 2b site has noncubic symmetry, and the cf mixes an excited term 4G (t_2^4e) into the ground state.

$H_{cf} = DS_z^2$

$Y_2Fe_5O_{12}$

YIG; $a_0 = 1.238$ nm,

A synthetic garnet, with iron in tetrahedral (24d) and octahedral (16a) sites. The Y and O form a ≈ close-packed array..

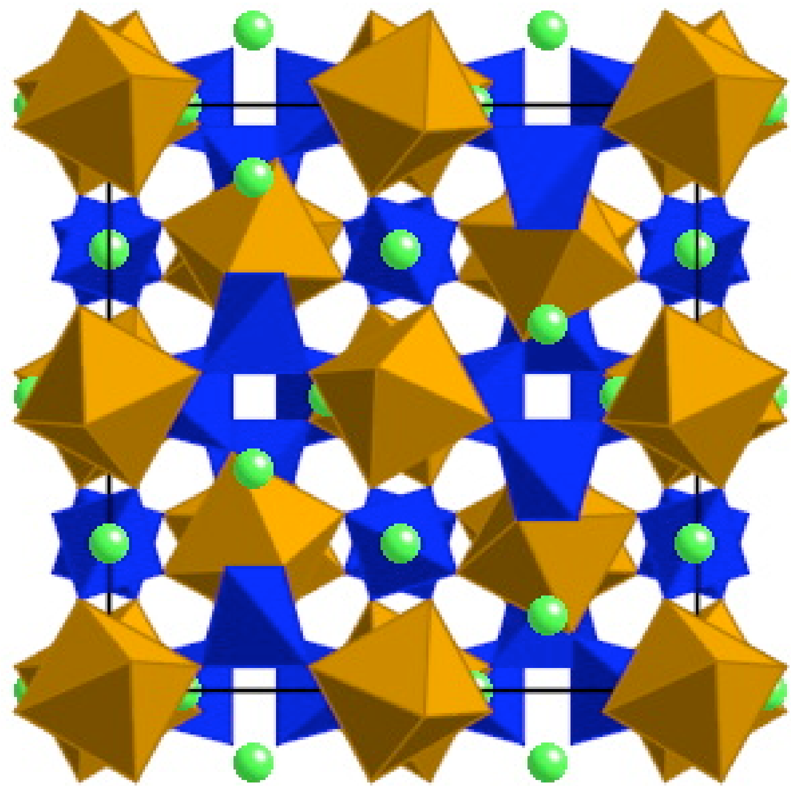
YIG – Yttrium iron garnet is a green ferrimagnetic insulator.

T_C =560 K

The magnetic structure is ferrimagnetic, with a magnetic structure 24d ↑, 16a

$J_s = 0.18$ T

$m_0 = 5.0\ \mu_B$/fu



YIG is an insulator with excellent high-frequency magnetic properties., and a very narrow ferromagnetic resonance linewidth. It is used for microwave components.

Also useful as a magneto-optic material when doped with Bi

2.1 The special seven.

These are oxides with some unusual feature which is of contemporary interest

- CrO_2
- EuO
- $SrRuO_3$
- NiO
- a-FeF_3
- $(La_{0.7}Sr_{0.3})MnO_3$
- Sr_2FeMoO_6

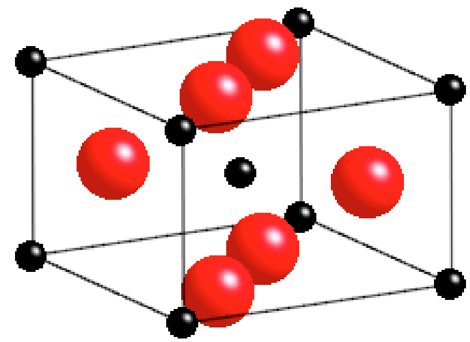
CrO_2

rutile; a = 0.442 nm, c = 0.292 nm

The only simple oxide that is a ferromagnetic metal, CrO_2 is a black type Ia half-metal with a spin gap of about 0.5 eV.

The compound is metastable, usually prepared by high-pressure synthesis

Acicular powder with 8:1 aspect ratio and $l \approx 300$ nm has $H_c \approx 50$ kA/m; it is used as a particulate medium for video recording



$J_s = 0.49$ T	$m_0 = 2.0\ \mu_B$/fu
$T_C = 396$ K	$K_1 = 30$ kJ m^{-3}
$\rho_0 \approx 3\ \mu\Omega$ cm	

Half metals - what are they ?

- Magnetically-ordered metals with fully spin-polarised conduction band

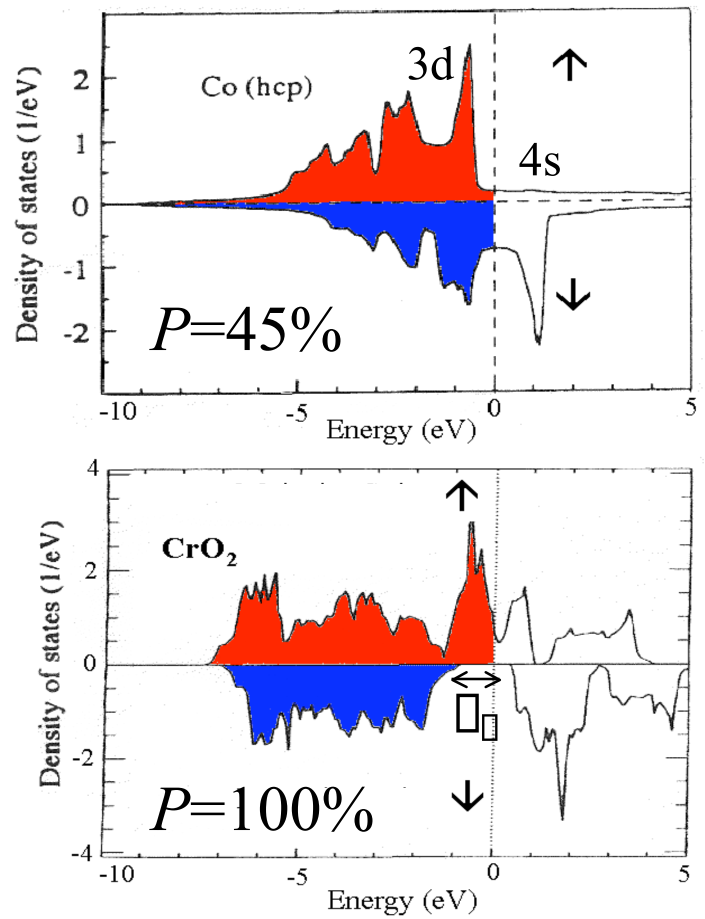
  $P = (N^{\uparrow} - N^{□})/(N^{\uparrow} + N^{□})$

- Metallic for ↑ electrons but semiconducting for □ electrons. Spin gap $□_{□}$ or $□_{\uparrow}$ for type A or B

- Integral spin moment n $□_{□}$

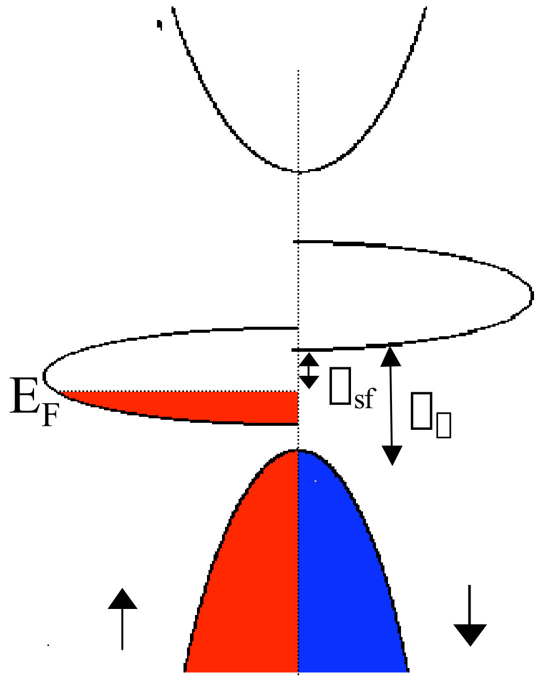
- Mostly oxides, Heusler alloys

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

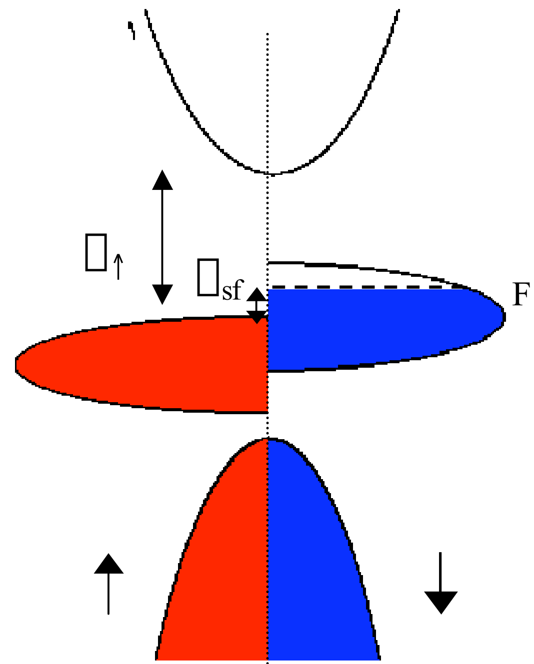


Co is not a half-metal, there are 4s electrons of both spins at E_F. CrO_2 is a Type Ia half metal.

Type I half metals



Type I_A



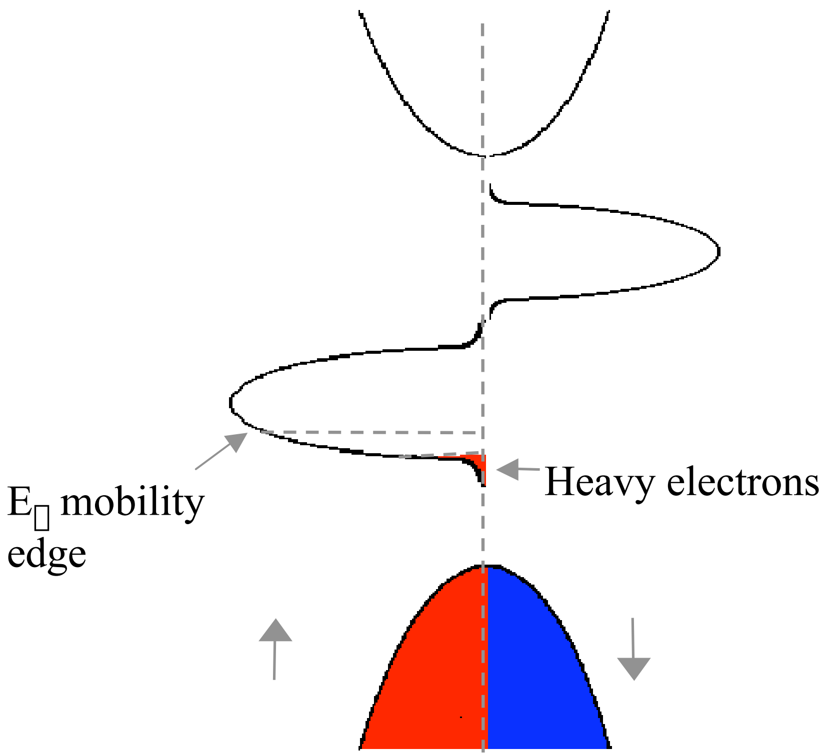
Type I_B

Examples: CrO_2; NiMnSb $(Co_{1-x}Fe_x)S_2$

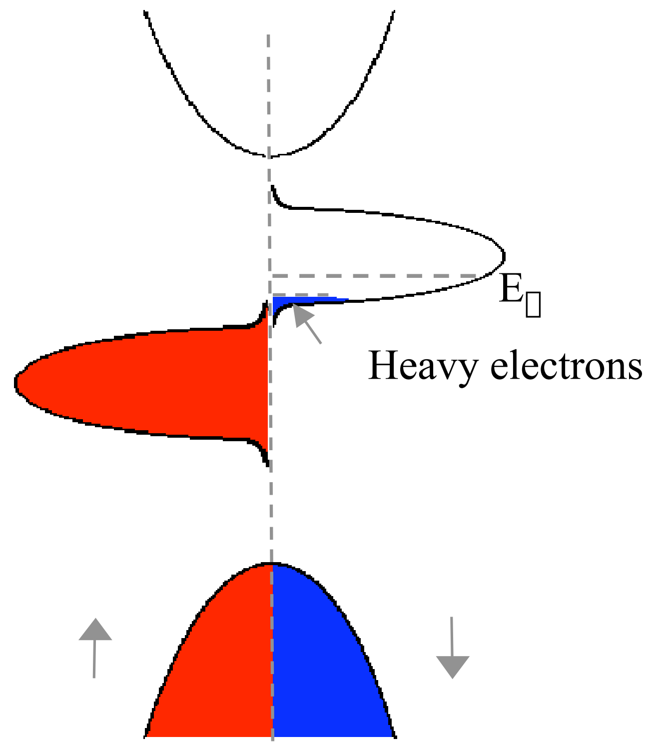
Sr_2FeMoO_6; Mn_2VAl

Type II half metals

Similar to type I except the bands are narrow, and the electrons form polarons.



Type II_A



Type II_B

Example: Fe_3O_4

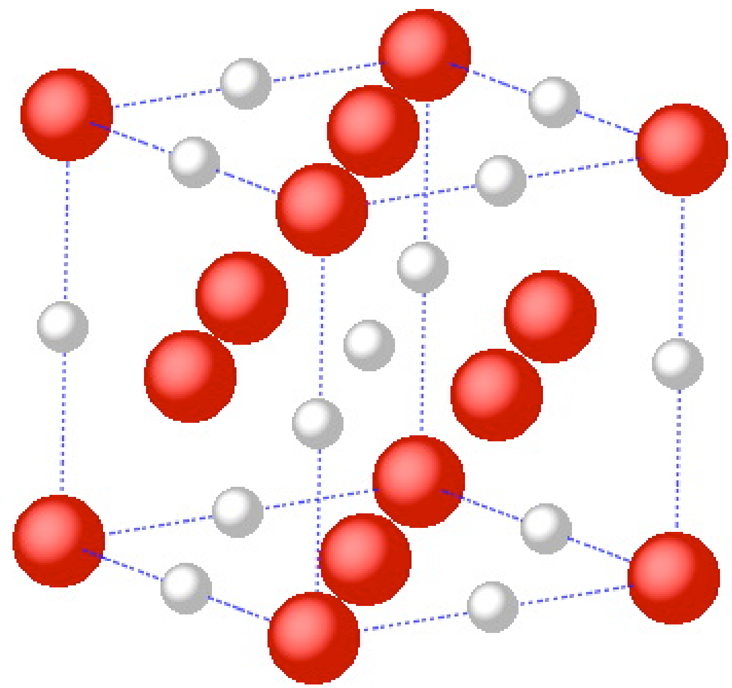
EuO

NaCl; $a_0 =$ 0.516 nm

A black ferromagnetic insulator when stoichiometric. The Eu^{2+} is $4f^7$ $J = S = 7/2$

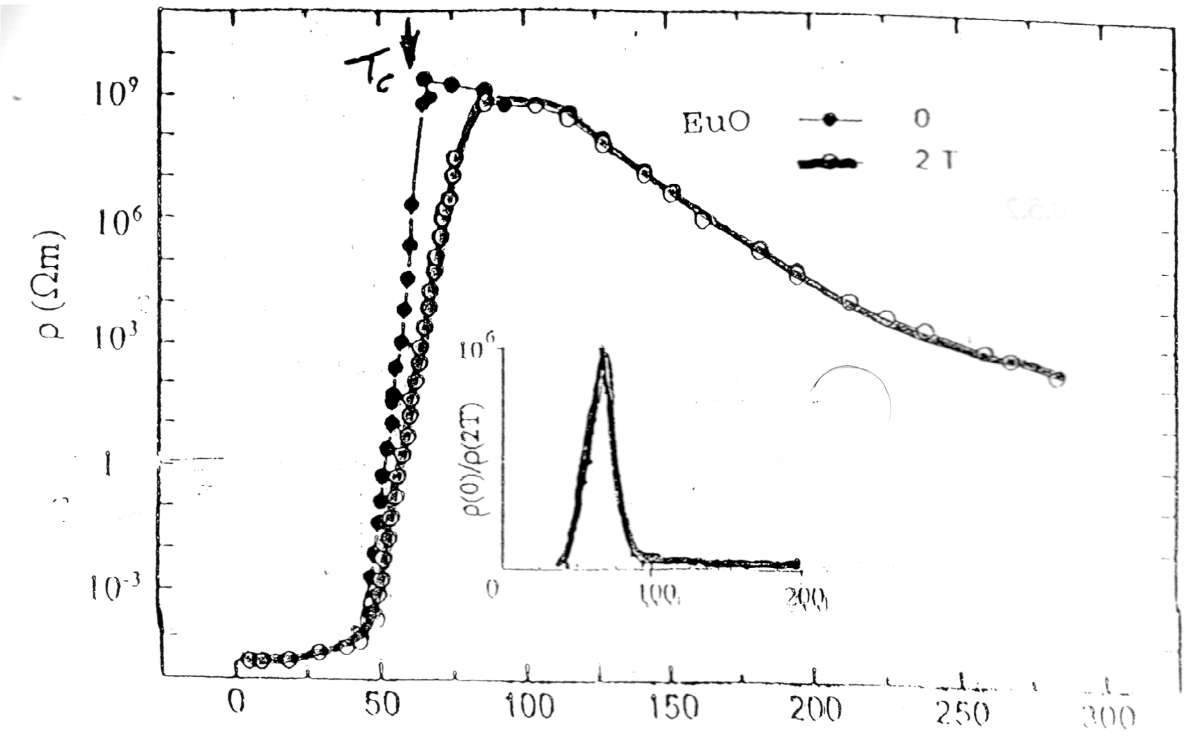
EuO is metallic below T_C when oxygen deficien and the resistivity increases by up ti 14 order of magnitude there. A colossal magnetoresistance is observed near T_C with effects of up to 10^6. Carriers in the paramagnetic state are magnetic polarons.

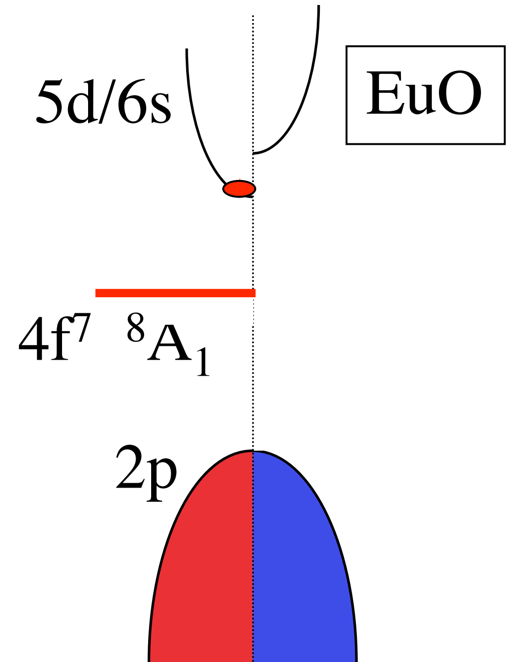
EuO is a magnetic model compound for Heisenberg exchange. The low T_C precludes uses as a magnetic semiconductor.



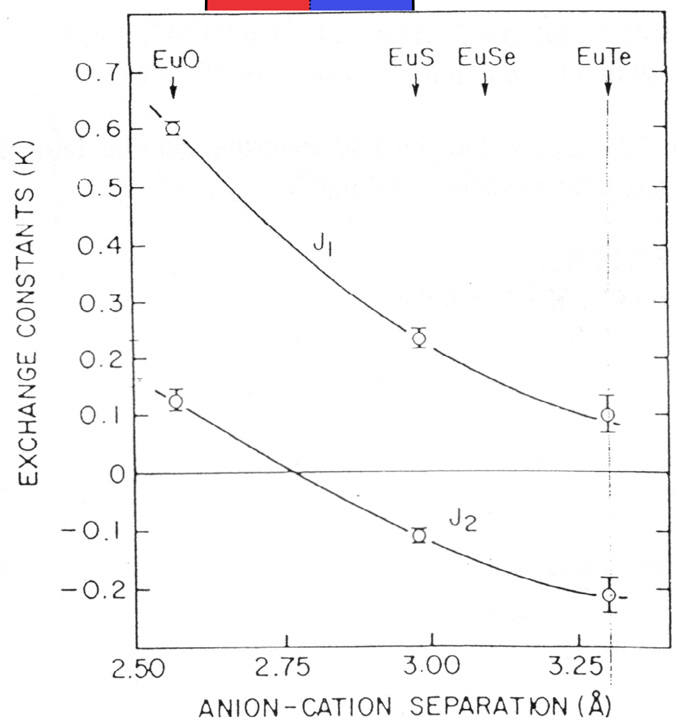
$J_s = 2{,}37$ T $\quad$ $m_0 = 7.0\ \mu_B$/fu

$T_C = 69$ K





	A_0 (pm)		T_C(K)	J_1(K)	J_2(K)
EuO	516	ferro	69.4	0.60	0.12
EuS	696	ferro	16.5	0.23	-0.11
EuSe	620	Ferro antifer	4.6 2.8	0.16	-0.16
EuTe	661	antifer	9.5	0.10	-0.21



NiO

NaCl; a_0 = 0.516 nm

A green insulator when stoichiometric (black conductor when cation deficient).

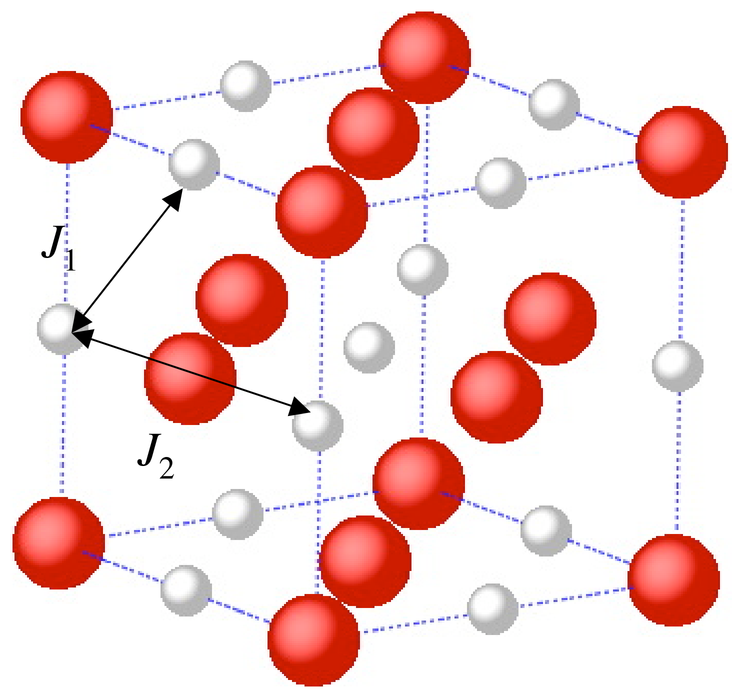
The Ni^{2+} is $3d^8$ $t_{2g}^6 e_g^2$ S = 1, $m = 2\mu_B$

T_N = 525 K

Ni^{2+} ions form an fcc lattice with partly-frustrat antiferromagnetic interactions. <111> is a hard direction, which produces a tiny rhombohedral distortion by magnetostrictior

J_1 = -50 K, J_2 = -85 K.

NiO was used as an exchange bias layer in early spin valves.



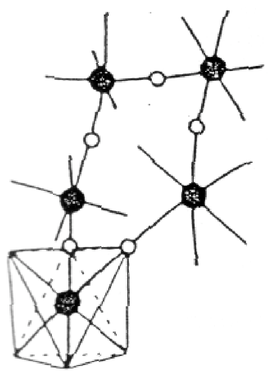
Amorphous FeF_3

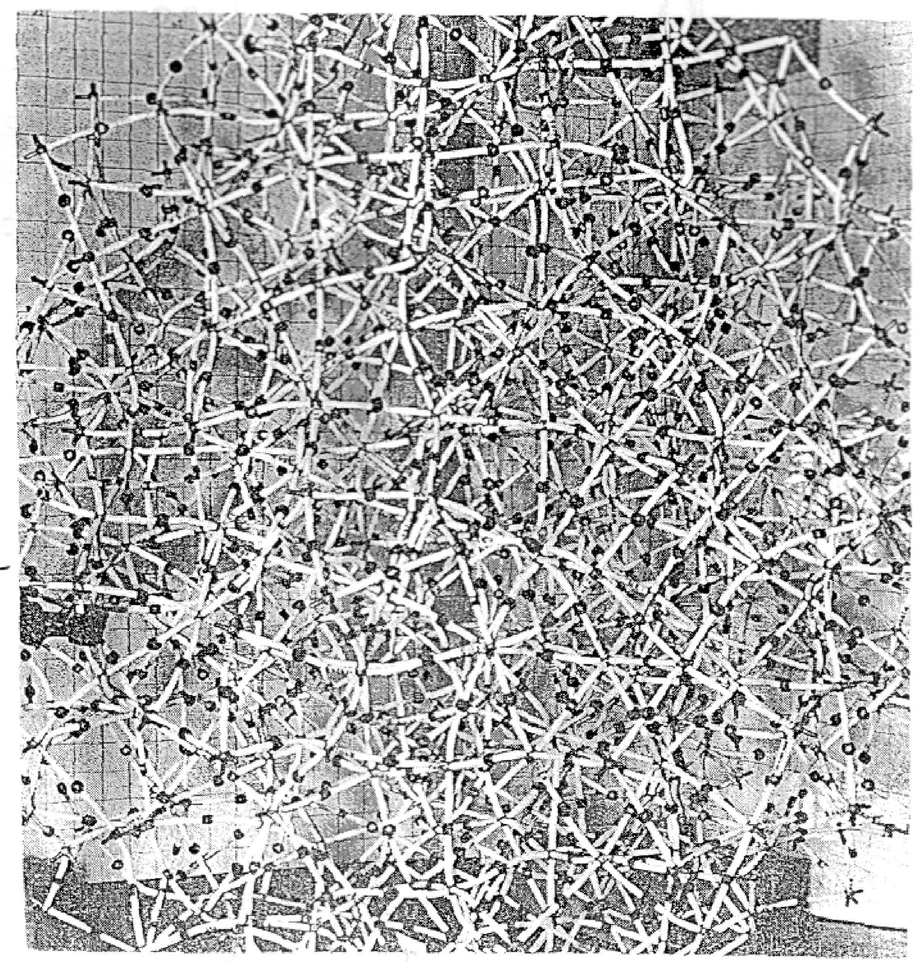
An amorphous insulator with a continuous random network of octahedra with 3- 4- and 5-membered rings - randomlv frustrated antiferromagnetic superexchange - speromagnetism

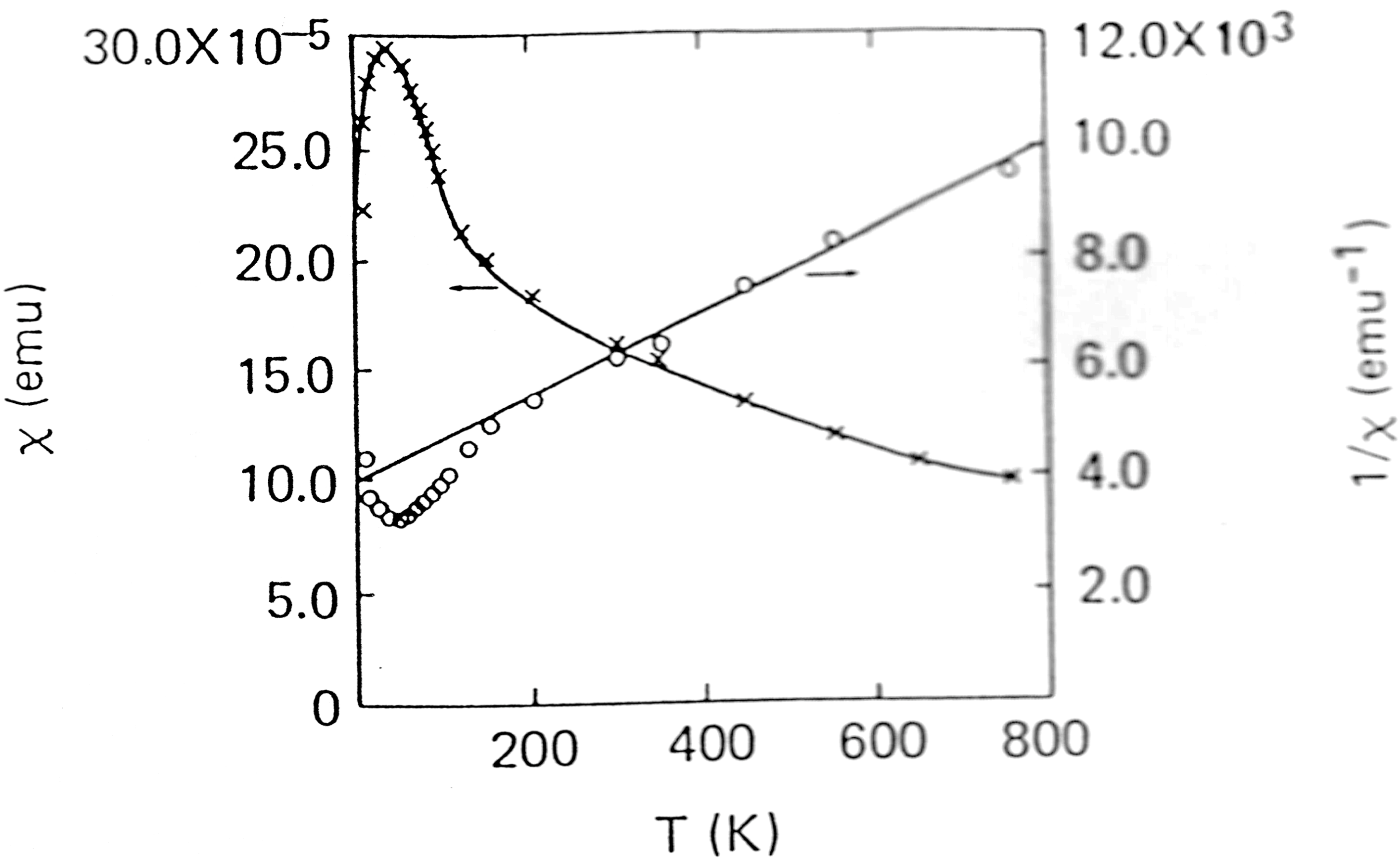
A brown insulator

Spins freeze at ≈ 29 K

Small remanence ≈ 0.1 μ_B/f







30.0X10^-5
25.0
20.0
15.0
10.0
5.0
0
χ (emu)
12.0X10^3
10.0
8.0
6.0
4.0
2.0
1/χ (emu^-1)
200
400
600
800
T (K)

$SrRuO_3$

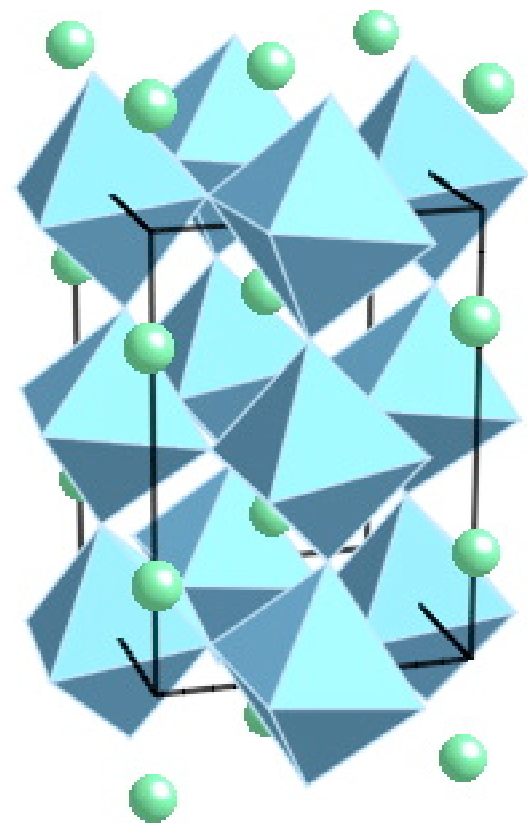
O-type perovskite; $a = 0.5573$ nm
$b = 0.5538$ c = 0.7856

A black metal with spin-split Ru 4d t_{2g} band of width ≈ 1 eV. A rare example of a ferromagnetic 4d metal

Low-spin Ru^{4+} (t_{2g}^{4})

The compound is ferromagnetic, with T_C = 165 K

$m_0 \approx 1\mu_B$/fu
□$_0$ ≈ 4 □ m



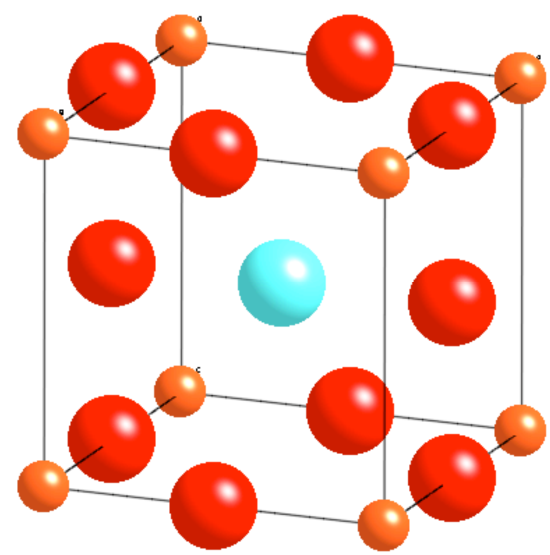
$(La_{0.7}Sr_{0.3})MnO_3$

Manganite; a = 0.584 nm

□ ≈ 60°

A type IIIa half-metal with both Mn↑(e_g) and Mn□(t_{2g}) electrons at E_F

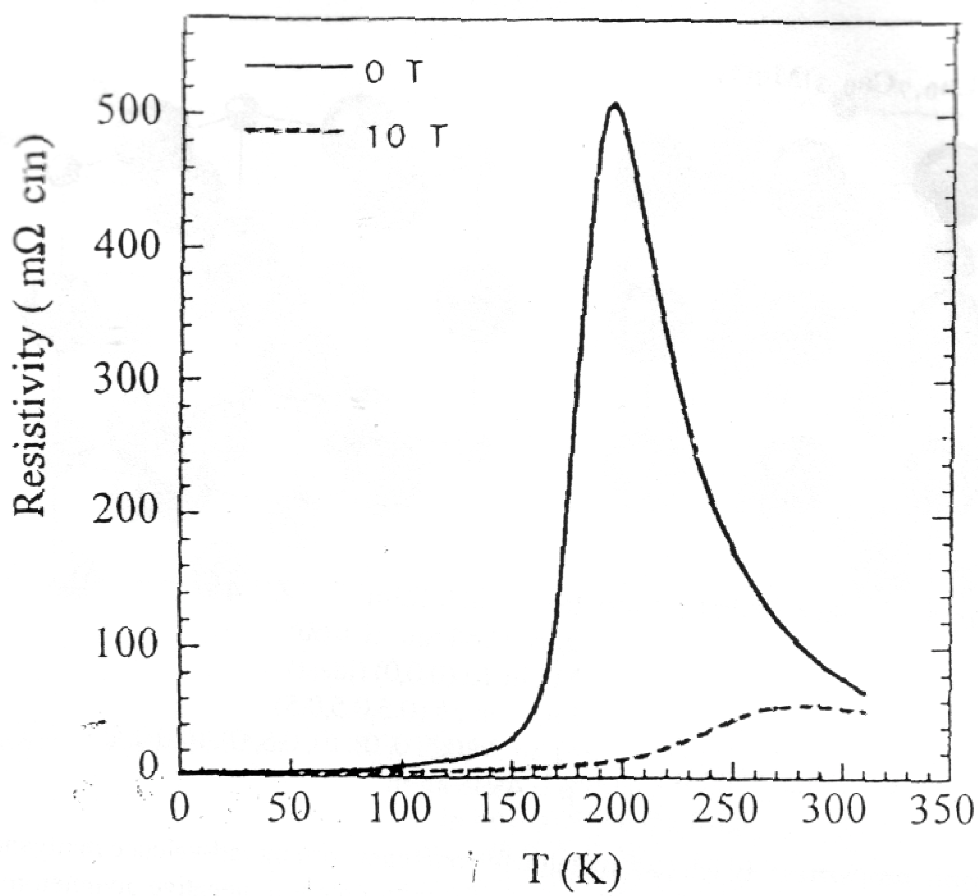
The compound is ferromagnetic, and shows CMR near T_C

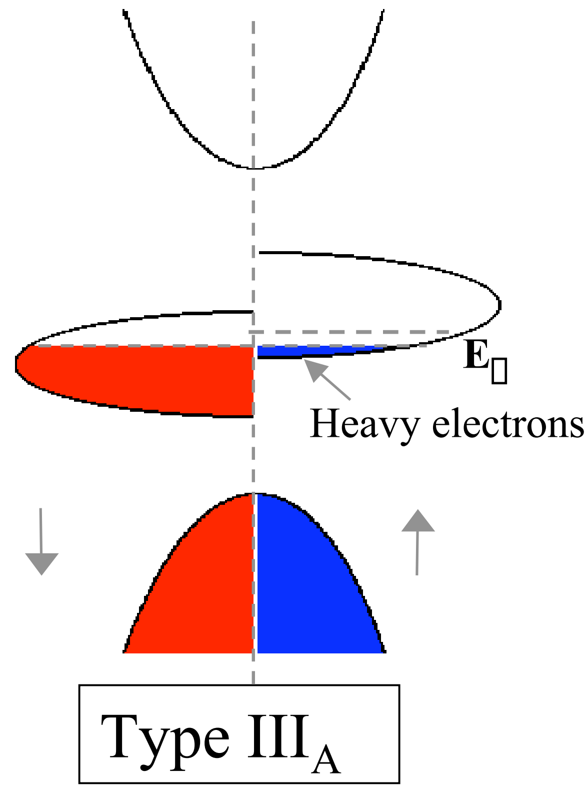


J_s = 0.32 T　　$m_0 = 3.6\ \mu_B$/fu

T_C = 370 K

□$_0$ ≈ 0.1 μ□ m


Resistivity (mΩ cm)
500
400
300
200
100
0
0 T
10 T
0
50
100
150
200
250
300
350
T (K)


E
Heavy electrons
Type III_A

Sr_2FeMoO_6 *Double perovskite;* $a = 0.557$ nm, c = 0.791 nm

A perovskite with an ordered NaCl-type superstructure of Fe and Mo, Sr_2FeMoO_6 is a type Ib half-metal with a spin gap of about 0.5 eV.

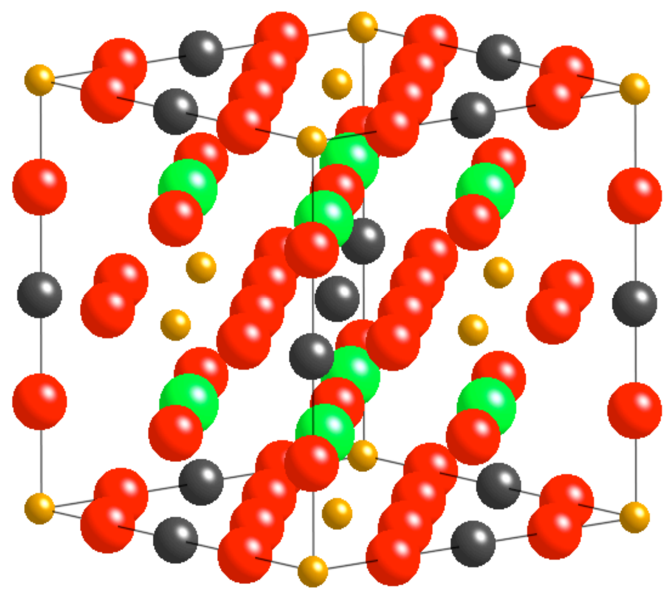
The magnetic structure is ferrimagnetic, with Fermi level in a □ band of mainly Mo(5d) character. These electrons couple the Fe(d^5) cores ferromagnetically

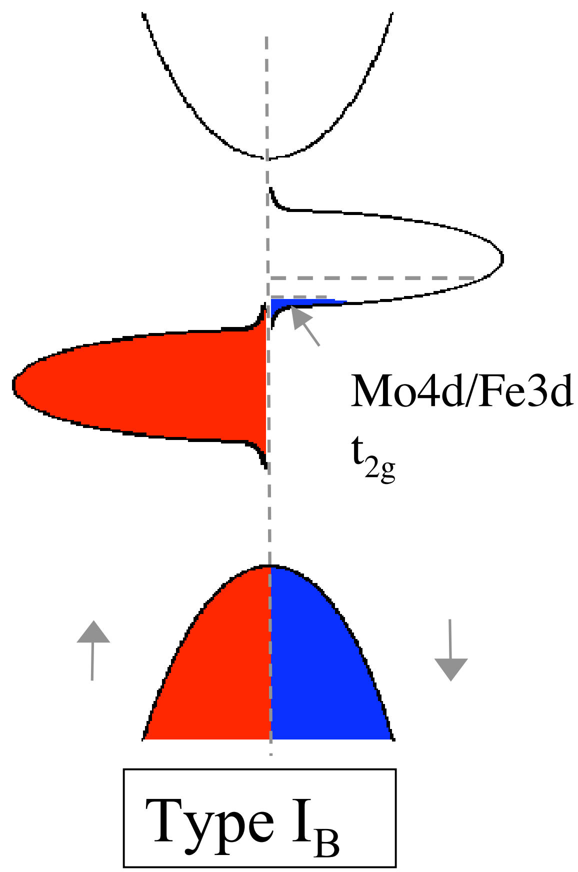
The compound usually includes some antisite disorder, which reduces m_0

$J_s = 0.20$ T $m_0 = 3.6\ \mu_B$/fu

$T_C = 420$ K

$\square_0 \approx 3\ \mu\square$ m

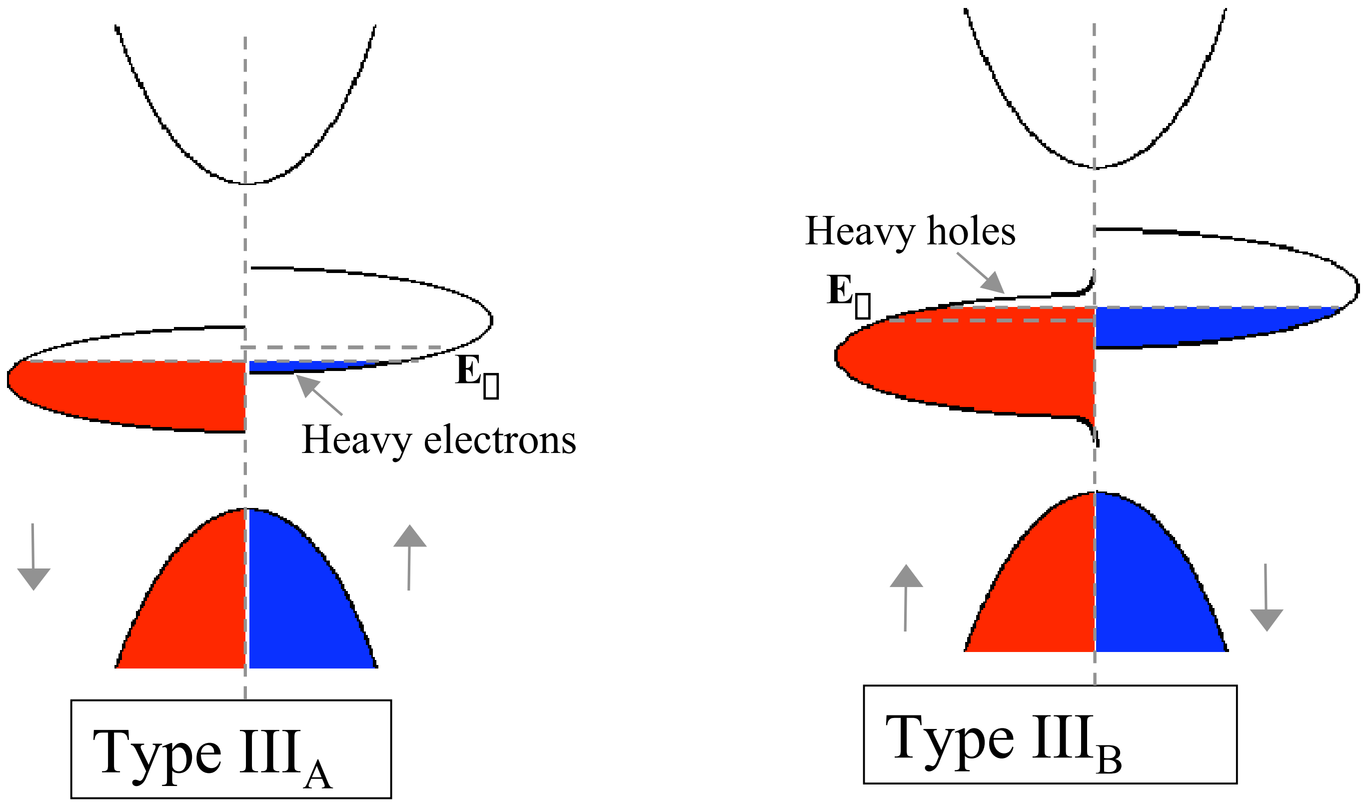




Mo4d/Fe3d
t_{2g}
Type I_B

Type III half metals (transport half metals)

Both ↑ and □ electrons are present at E_F, but one band is localised, the other delocalised.



Examples: $(La_{0.7}Sr_{0.3})MnO_3$
$(La_{0.7}Ca_{0.3})MnO_3$

2.3 Magnetic semiconductors.

Mobility of semiconductors, semimetals and metals

		Curie Point (K)	**Mobility ($cm^2V^{-1}s^{-1}$)**
Semiconductors	Si	-	1400
	InSb	-	30000
	GaAs	-	8000
	(GaMn)As	160	
Semimetals	Graphite	-	2000
	Bi	-	180000
Metals	Cu	-	44
	Au	-	48
	Fe	1044	20
	Co	1380	12
	Ni	628	16
Half Metals	CrO_2	392	1.4
	Fe_3O_4	860	0.2

Transition metal doped semiconductors

Compound	E_g (eV)	Doping	T_C (K)	Reference(s)
Ge	0.67	Mn – 3.5 %	116	Park et al Science, 295, 651 (2002)
GaAs	1.43	Mn – 5%	110	Ohno et al Science, 281, 951 (1998)
GaSb	0.70	Mn – 2.3%	25	Matsukura et al, JAP, 87, 6442 (2000).
GaN	3.50	Mn – 9%	940	S. Sonoda et al, J. Crys. Growth, 237 1358 (2002).
GaP	2.26	Mn – 3%	270	N. Theodoropoulou et al, PRL, 89, 107203 (2002)
InAs	0.36	Mn – 5%	30	Ohno et al, PRL, 68, 2664 (1992).
InSb	0.18	Mn – 2.8%	8.5	T. Wojtowicz, cond-mat/0303212 (2003).
TiO_2	3.20	Co – 1-2%	650-700	Shinde et al, PRB, 67, 115211 (2003).
SnO_2	3.50	Co – 5%	650	Ogale et al,cond-mat/0301456 (2003)
ZnO	3.30	Co – 5-15%	280-300	Ueda et al APL, 79, 988 (2001).
EuO	1.10	-	69.5	Nolting et al, Physica B, 321, 189 (2002)
Cu_2O	2.0	Co – 5% Al – 0.5%	> 300	Kale et al, APL, 82, 2100 (2003).

(GaMn)As

Zinc blende; a = 0. xxx nm

Ordered diamond structure

Mn^{2+} d^5 e^2t^3

T_C for 5% Mn is 160 K

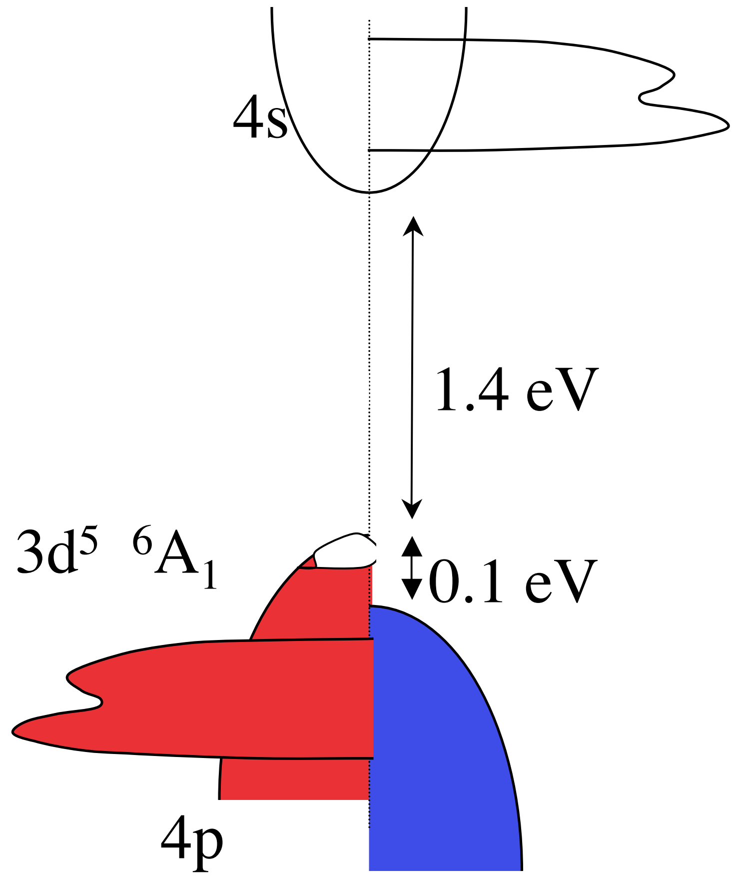
Moment is $4\mu_B$/Mn

$3d^5\uparrow$ + 4p hole

J_{sd} = 0.2 eV

J_{pd} = 2.0 eV

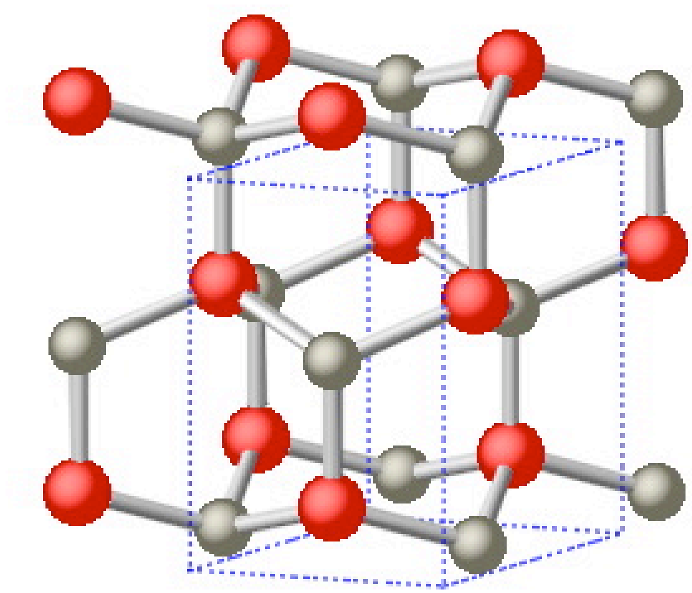
Antisite defects pin E_F



Zincite, ZnO

wurstite; *a* = 0. 335 nm, c = 0.523 nm

SG $P6_3mc$ O (1/3,2/3,3/8); Zn (1/3,2/3,0)



A structure of corner-sharing tetrahedra;
4 - 4 coordination..
Zn- O, 4 bonds, 0.204 nm
Zn-O-Zn 6 bonds 109°, 6 bonds 110°

Band gap 3.3 eV

Impurity configurations.

Mn^{2+} d^5 e^2t^3 Fe^{2+} d^6 e^3t^3 (J-T); Co^{2+} d^7 e^4t^3

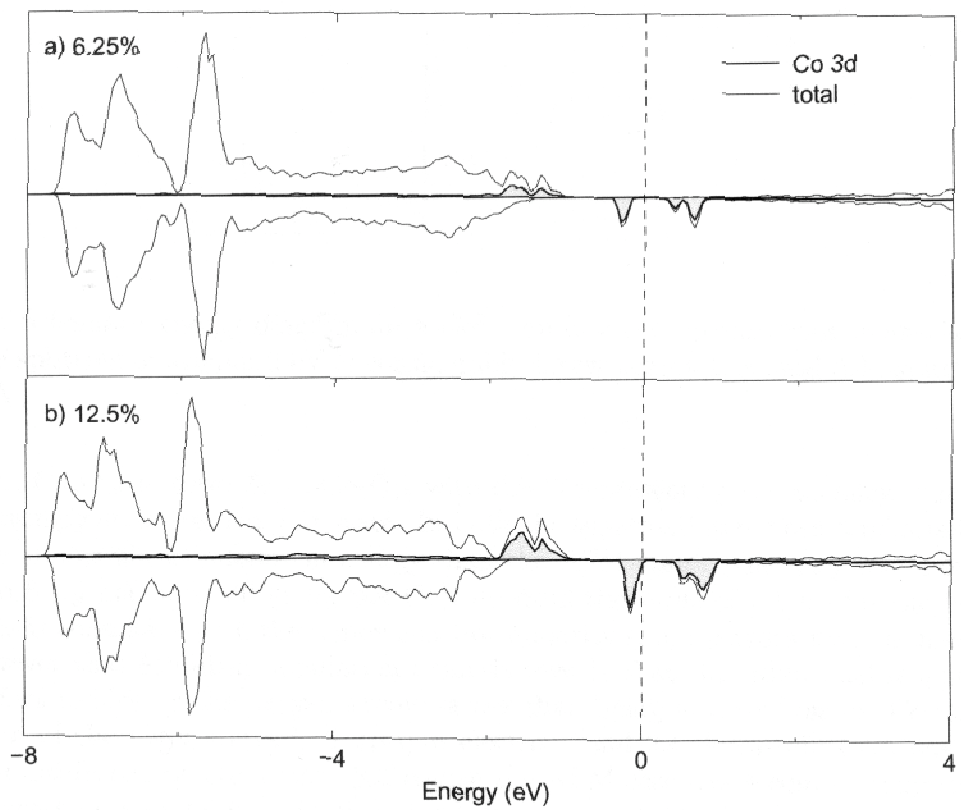


Figure 2: Calculated densities of states in ferromagnetic (Zn,Co)O with cobalt dopant concentrations of (a) 6.25 % and (b) 12.5 %. The thin solid lines show the (Zn,Co)O total densities of states and the thick solid lines with the gray shading indicate the contribution from the Co 3*d* orbitals. Majority spin states are plotted along the positive y axis, and minority spin along $-y$.

LSDA calculation for (ZnCo)O   Nicola Spaldin

Hole-doping is necessary for ferromagnetism

Anatase, TiO_2

tetragonal; a = 0. 379 nm, c = 0.951 nm

SG: 4_1/amd   O (0, 0, 0.2066); Ti (0, 0, 0)

A structure of edge-sharing octahedra;

6 - 5 coordination.

Ti - O, 4 bonds, 0.194 nm, 2 bonds 0.197 nm

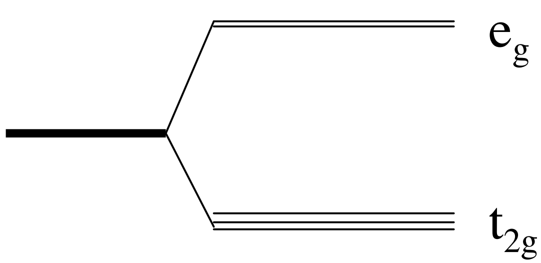
Zn-O-Zn8 bonds 102°, 4 bonds 155°

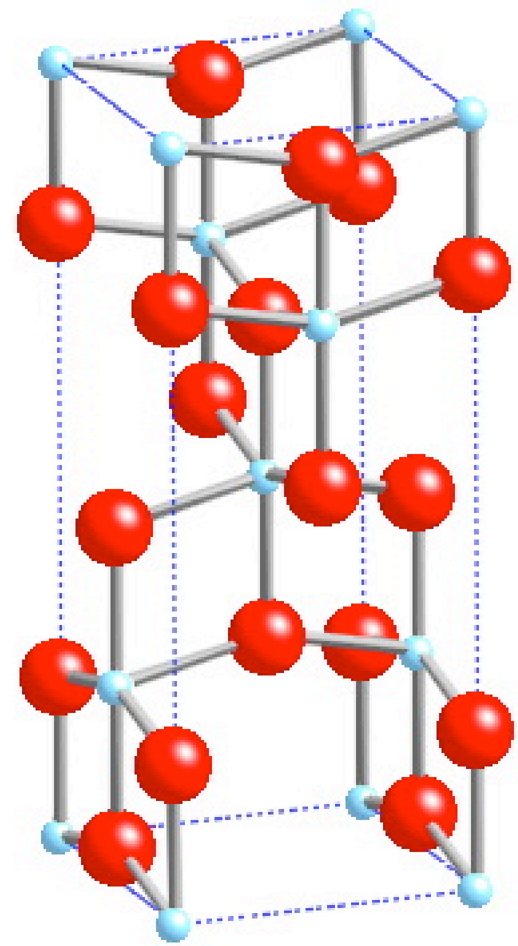
Band gap 3.2 eV

Impurity configurations.

Mn^{4+} d^3 $t_{2g}{}^3$ Fe^{3+} d^5 $t_{2g}{}^3$ $e_g{}^2$; Co^{3+} d^6 $t_{2g}{}^3$ $e_g{}^3$

J-T





Cassiterite, SnO_2

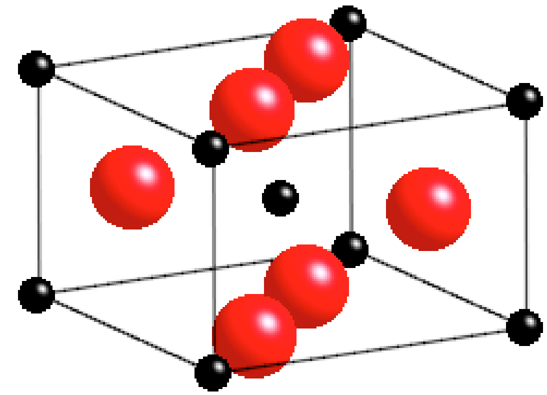
rutile; a = 0. 474 nm, c = 0.319 nm

SG: $P4_2/mnm$ O (0.307, 0.307, 0); Sn (0, 0, 0)

A structure of edge and corner-sharing octahedra; 6 - 3 coordination.

Sn - O, 4 bonds, 0.205 nm, 2 bonds 0.206 nm

Zn-O-Zn, 8 bonds 129°.

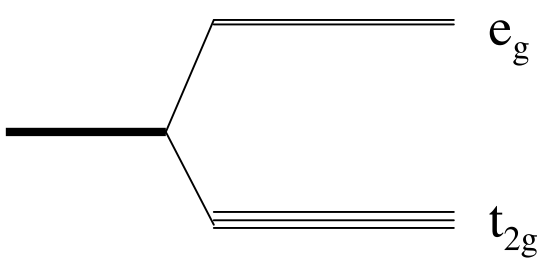


Band gap 3.6 eV

Impurity configurations.

Mn^{4+} $d^3t_{2g}{}^3$ Fe^{3+} d^5 $t_{2g}{}^3e_g{}^2$; Co^{3+} d^6 $t_{2g}{}^3e_g{}^3$

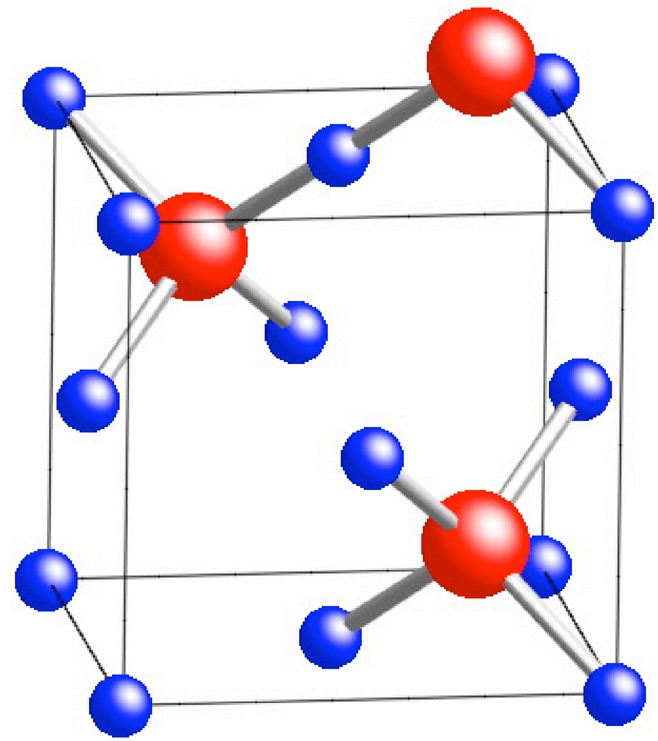
J-T



Cuprite, Cu_2O

cubic; $a = 0.427$ nm

SG: $Pn\bar{3}m$ O (1/4, 1/4, 1/4); Cu (0, 0, 0)



A structure with 2 - 4 coordination.

Cu - O, 2 bonds, 0.185 nm,

Cu-O-Cu, 6 bonds 109°.

Band gap 2.8 eV

Impurity configurations.

Mn^{2+} d^5 Fe^{2+} d^6 Co^{2+} d^7