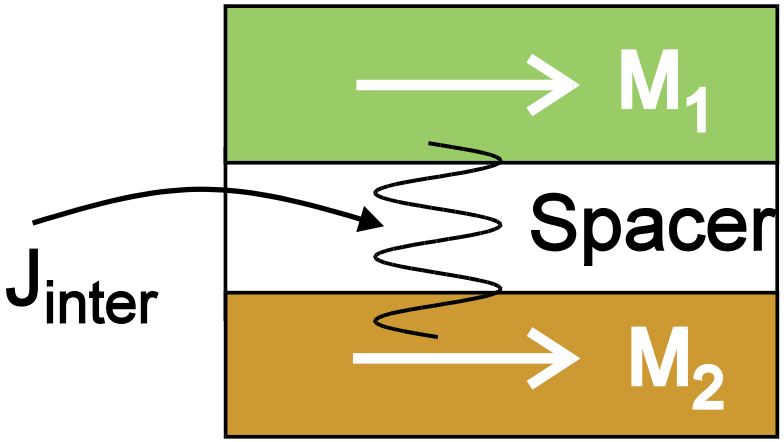
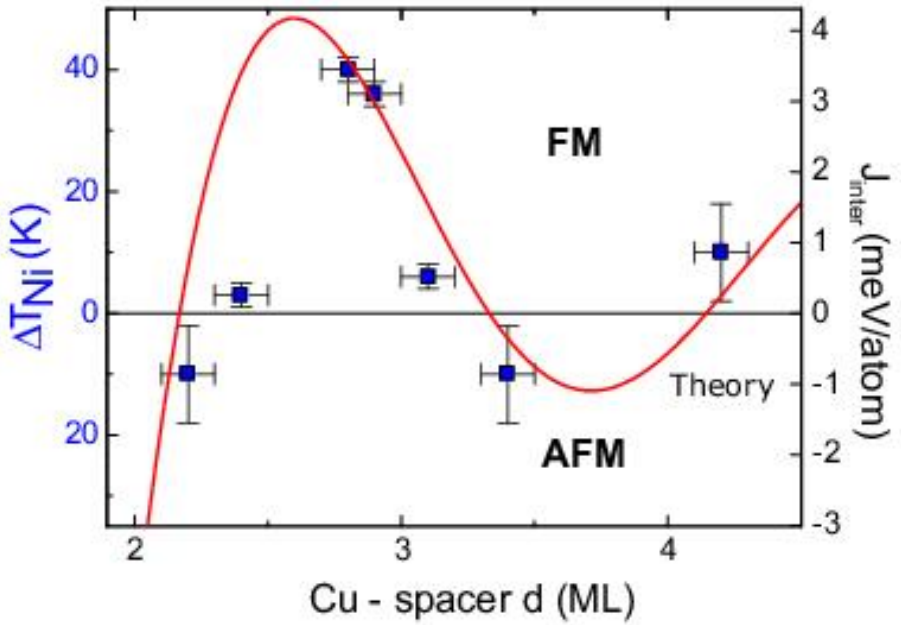
Μαγνητισμός στα Μέταλλα – Μαγνητικοί Ημιαγωγοί

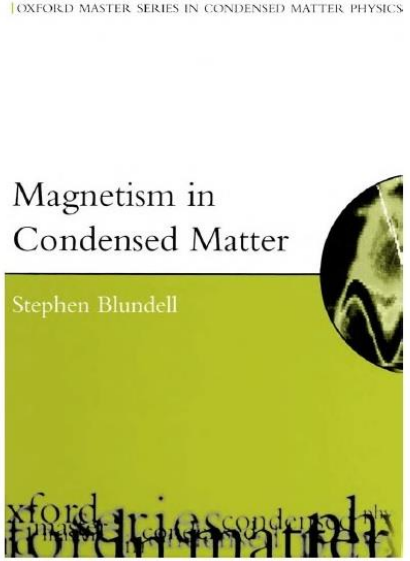
P. Poulopoulos, 3 July 2020, Patra

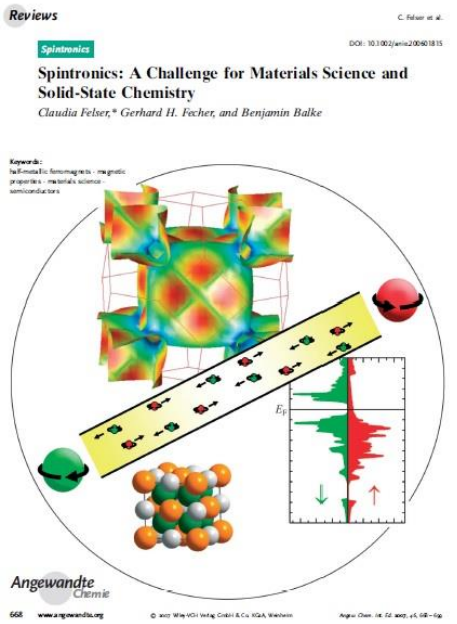


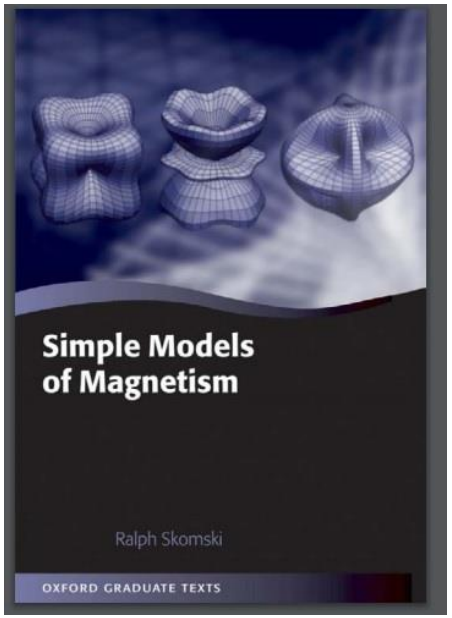


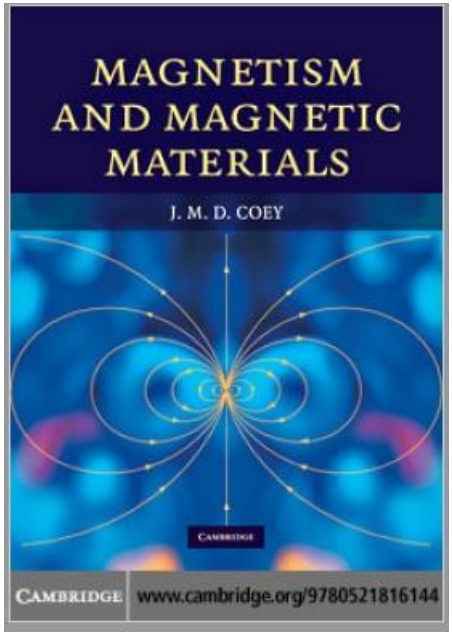
Η διάλεξη αυτή γίνεται διαδικτυακά στα πλαίσια των προβλημάτων του Covid-19. Είναι μόνο για διευκόλυνση των φοιτητών για το εξ αποστάσεως μάθημα και δεν έχει κανένα στόχο εμπορικής εκμετάλλευσης. Επίσης παρακαλώ τους φοιτητές να τις κρατήσουν μόνο για τους εαυτούς τους και τις εξετάσεις τους

Βιβλιογραφία









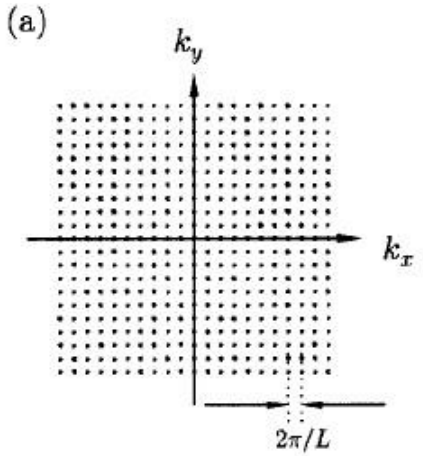
A correct theory of magnetism in metals has to involve bands as the electrons are not localized to atoms. However, most of the electrons (especially in 3*d* metals, which are elemental magnets) are rather localized and the 'free' electrons (4*s*) do not contribute to the ferromagnetic behavior. *Truly speaking the 3d electrons in transition metals are neither fully localized nor fully free.*

Band theory is able to explain the non-integral values of magnetic moment per atom; though, the values may often not match exactly.

$\mu_{Ni} = 0.6\ \mu_B/at$, $\mu_{Co} = 1.7\ \mu_B/at$, $\mu_{Fe} = 2.2\ \mu_B/at$

The Free Electron Model

Eigenstates



$$\psi(x,y,z) = \psi_o \sin\left(\frac{\pi n_x x}{L}\right)\sin\left(\frac{\pi n_y y}{L}\right)\sin\left(\frac{\pi n_z z}{L}\right)$$

and the energy levels

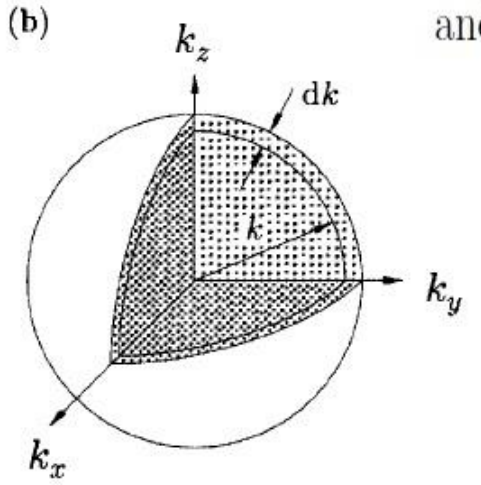


Fig. 7.1 (a) Electron states are separated by $2\pi/L$. Each state can be doubly occupied and occupies a volume $(2\pi/L)^3$. (b) The density of states can be calculated by considering the volume in k-space between states with wave vector k and states with wave vector $k + dk$, namely $4\pi k^2\, dk$.

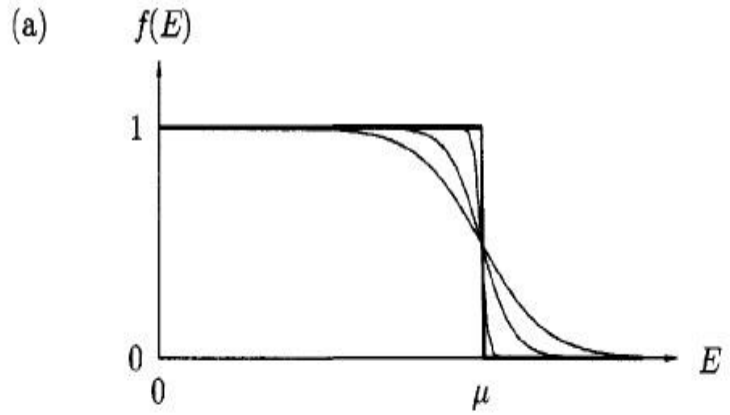
$$E(n_x, n_y, n_k) = \frac{\pi^2\hbar^2}{2m_e L^2}(n_x^2 + n_y^2 + n_z^2)$$

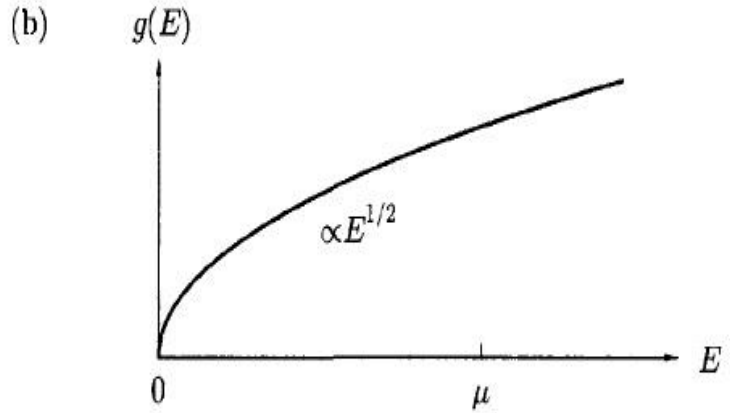
Density of states

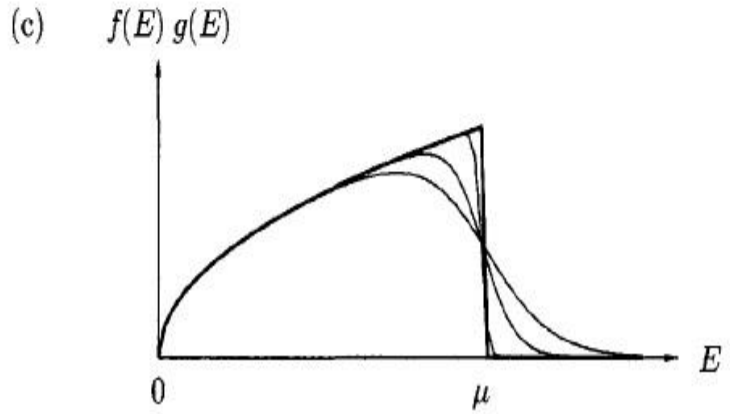
$V = L^3$

$g(k)dk = [2/(2\pi/L^3)]x4\pi k^2 dk \Rightarrow$

$g(k)dk = = Vk^2dk/\pi^2$







The Free Electron Model

if n = N/V (electrons per volume unit)

$g(E) = dn/dE \propto \sqrt{E}$

$E = (h/2\pi)^2 k^2/2m_e$

$E_F = (h/2\pi)^2 k_F^2/2m_e$

$g(E_F) = (3/2)n/E_F$

$g(E_F) = 4m_e k_F/h$

Fermi-Dirac

$f(E) = 1/[e^{(E-\mu)/k_B T} + 1]$,

μ εδώ είναι το χημικό δυναμικό ~ E_F

Pauli Paramagnetism

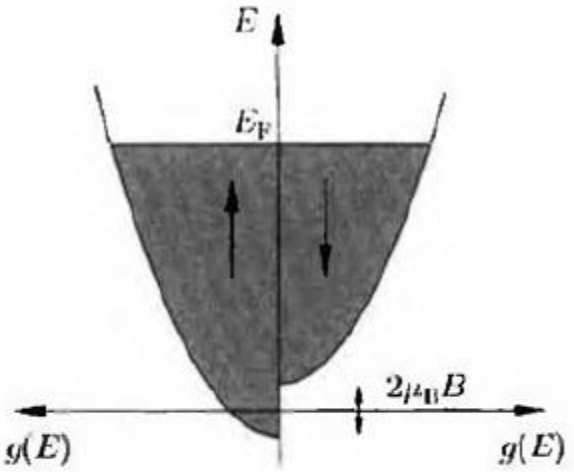


Fig. 7.4 Density of states showing splitting of energy bands in a field B. The splitting is shown greatly exaggerated.

We take only spin contribution.

Inside a field B the electron band is spin-split:

$$g\mu_B B = 2\mu_B B$$

Excess $n\uparrow = (1/2)g(E_F)\mu_B B$ and

Lack $n\downarrow = (1/2)g(E_F)\mu_B B$

$$M = \mu_B(n\uparrow - n\downarrow) = g(E_F)\mu_B^2 B$$

T-independent Susceptibility

$$\chi_P = M/H = \mu_0 M/B = \mu_0\mu_B^2 g(E_F) =$$

$$3n\mu_0\mu_B^2/2E_F$$

Spontaneous Spin-Split Bands

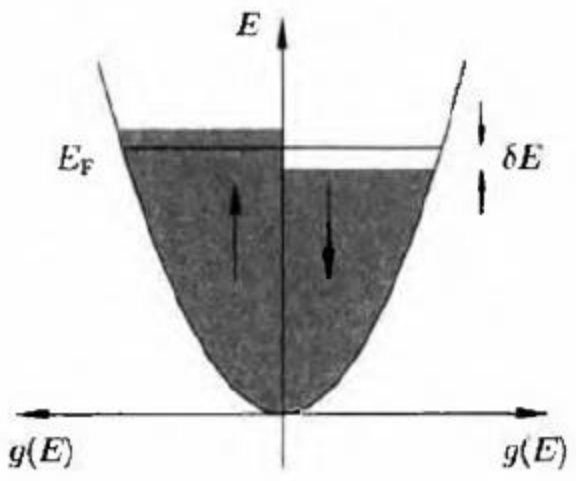


Fig. 7.5 Density of states showing spontaneous splitting of energy bands without an applied magnetic field.

Cost: $\Delta E_{KE} = g(E_F)\delta E/2 \times \delta E$

$\Delta E_{KE} = \frac{1}{2}\, g(E_F)\delta E^2$

Gain:

$n\uparrow\downarrow = \frac{1}{2}(n \pm g(E_F)\delta E)$

Magnetization: $M = \mu_B(n\uparrow - n\downarrow)$

$\Delta E_{MF} = -1/2\mu_0\mu_B^2\lambda(n\uparrow - n\downarrow)^2$

$\Delta E_{MF} = -1/2U(g(E_F)\delta E)^2$

$\Delta E = \Delta E_{KE} + \Delta E_{MF} =$

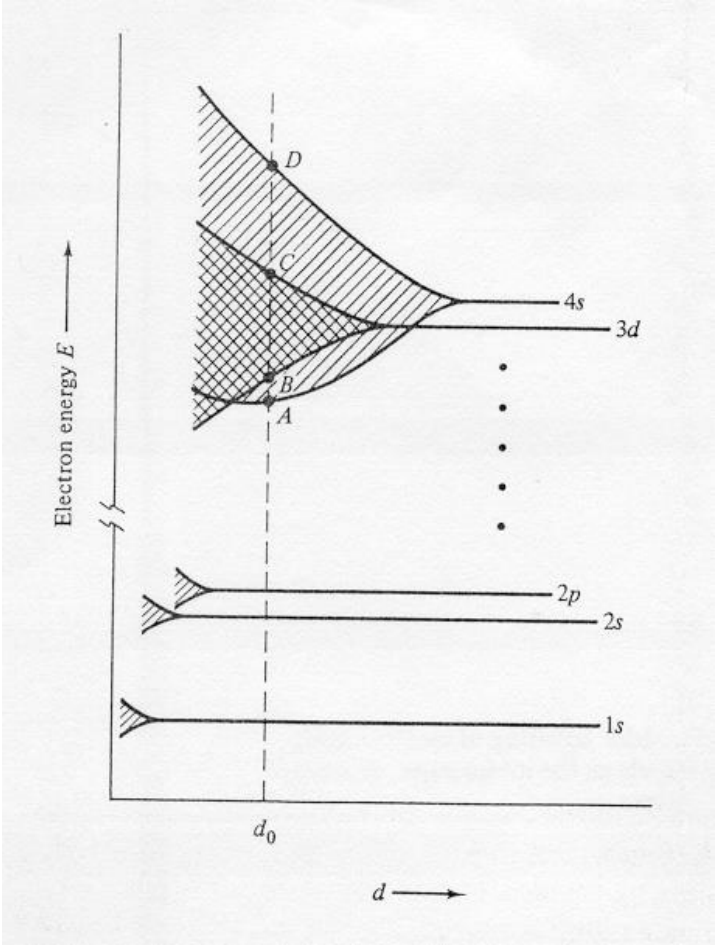
$= 1/2g(E_F)\delta E^2(1-Ug(E_F))$

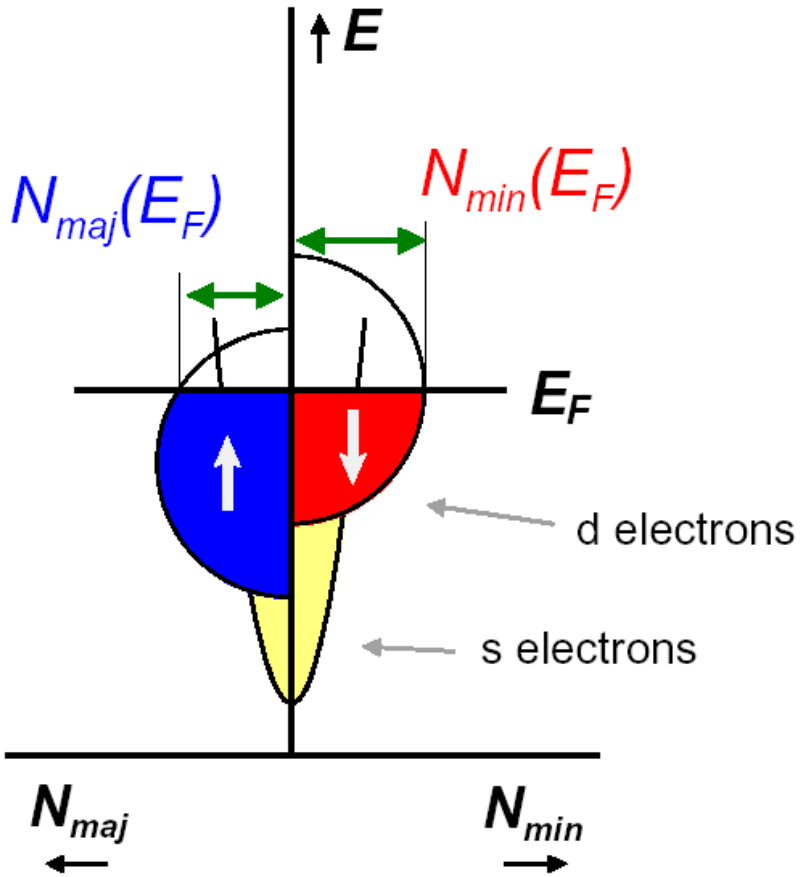
Spontaneous Ferromagnetism if

$1 \leq Ug(E_F)$ **Stoner Criterion**

Susceptibility $X = \chi_P/(1-Ug(E_F))$

Band Structure

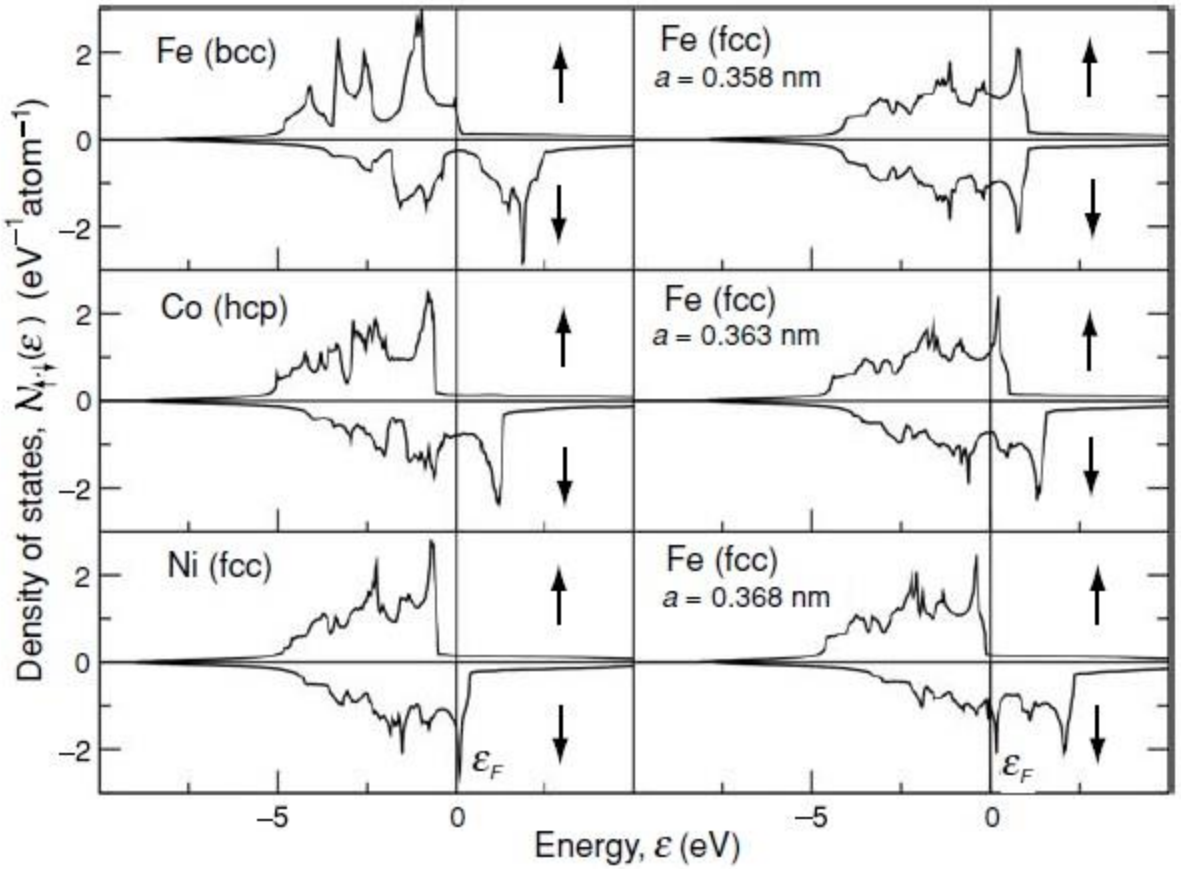




Band Structure

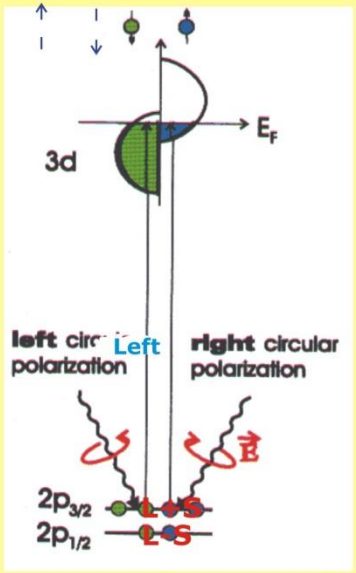
Figure 5.15

Densities of states for some elements in the ferromagnetic state. Fe is a weak ferromagnet, Co and Ni are strong. Results for γFe with different lattice parameters illustrate the sensitivity of the Fe moment to lattice parameter in a dense-packed structure. (Calculations courtesy of Ivan Rungger.)



XMCD - magnetometry

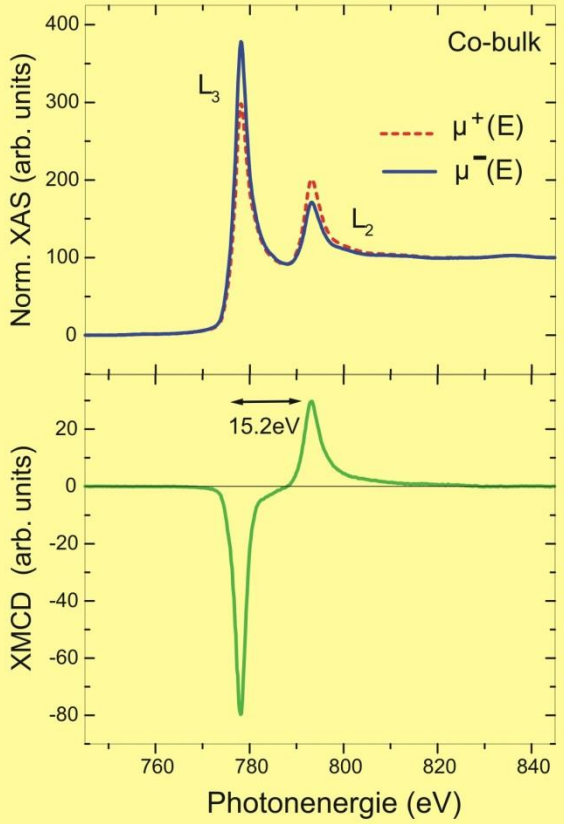
X-ray Magnetic Circular Dichroism



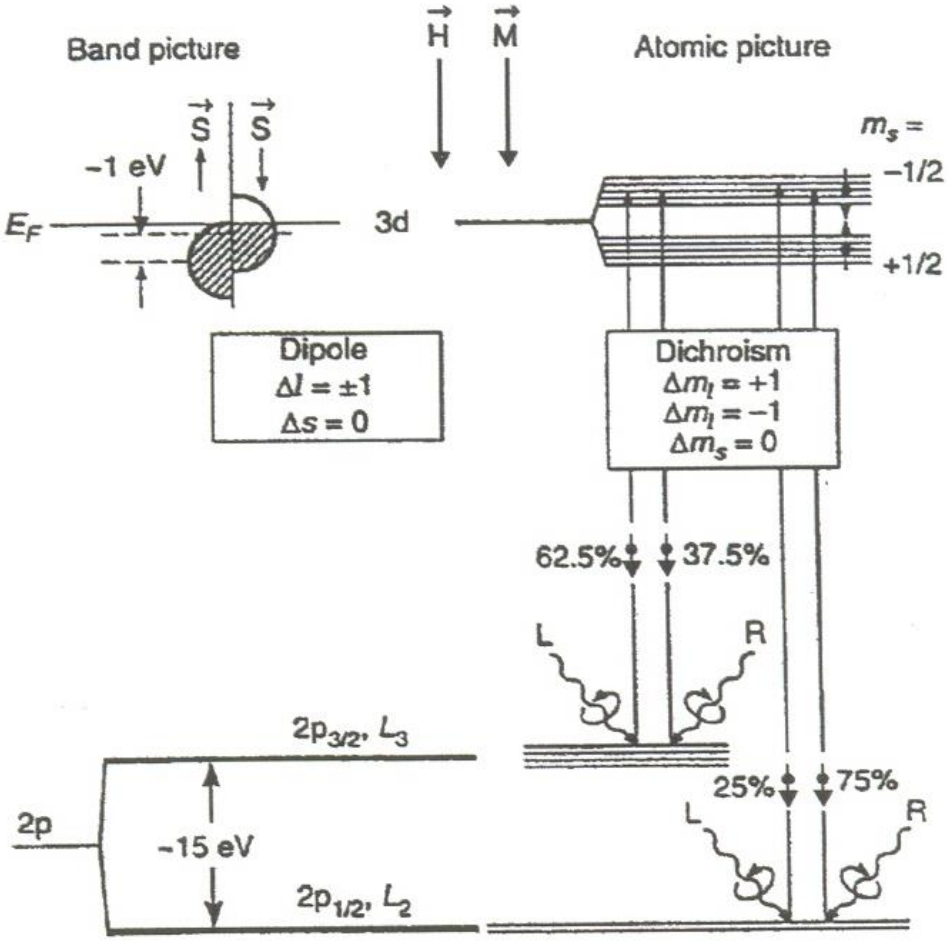
$$XMCD := \mu^{+}(E) - \mu^{-}(E)$$

ΣΠΟΥΔΑΙΟΤΗΤΑ:

Στοιχειακη Διακριτικη Ικανοτητα



XMCD – two step model



The useful end-equations

$$m_l/m_s = (2/3)\,[(R+1)/(R-2)]$$

accuracy 5%

$$R = \Delta A_3/\Delta A_2, \text{ usually } \Delta A_3 < 0, \Delta A_2 > 0$$

$$m_s = (-2n_h/P_C\cos\theta).\,[(\Delta A_3 - 2\Delta A_2)/2(A_3+A_2)]$$

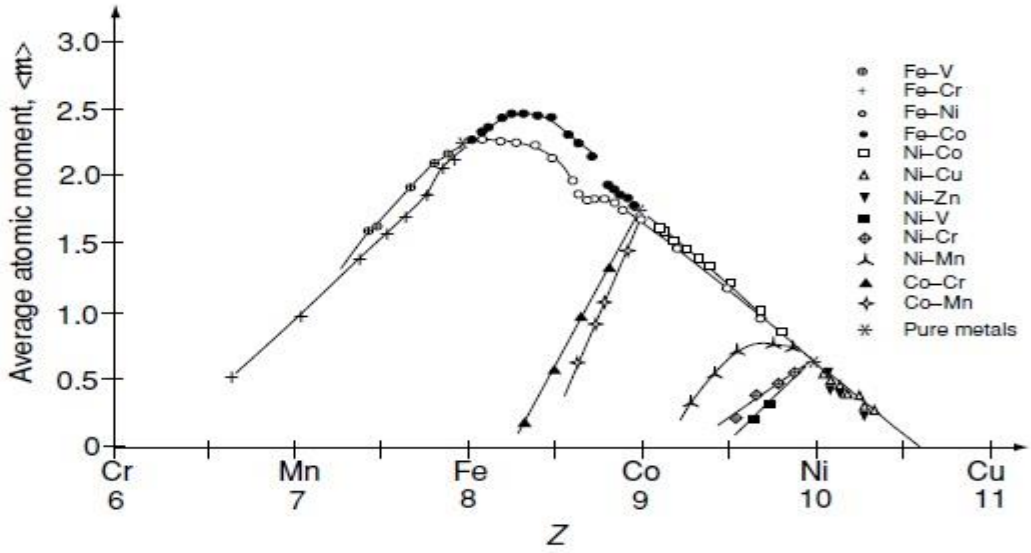
$$m_l = (-4n_h/3P_C\cos\theta).\,[(\Delta A_3 + \Delta A_2)/2(A_3+A_2)]$$

accuracy 10-20%

The Slater - Pauling curve

Figure 5.17

The Slater–Pauling curve. The average atomic moment is plotted against the number of valence $(3d + 4s)$ electrons.



$\mu = [10 - (n - x)]\mu_B$, x number of 4*s*, n number of 3*d*+4*s*

Table 5.4. Intrinsic properties of the ferromagnetic 3d elements at room temperature

	T_C (K)	d (kg m^{-3})	σ_s (A m^2 kg^{-1})	M_s (kA m^{-1})	J_s (T)	m (spin/orbit) (μ_B)	$\mathcal{N}_{\uparrow,\downarrow}(\varepsilon_F)$ (eV^{-1})	$\mathcal{I}$ (eV)	K_1 (J m^{-3})	λ_s (10^{-6})	g	D_{sw} (10^{-40} J m^2)
Fe	1044	7874	217	1710	2.15	2.17 (2.09/0.08)	1.54	0.93	48	−7	2.08	4.5
Co	1360(ε)	8920	162(ε)	1440	1.81	1.71 (1.57/0.14)	1.72	0.99	410	−60	2.17	8.0
Ni	628	8902	54.8	488	0.61	0.58 (0.53/0.05)	2.02	1.01	−5	−35	2.18	6.3

The Bethe – Slater curve

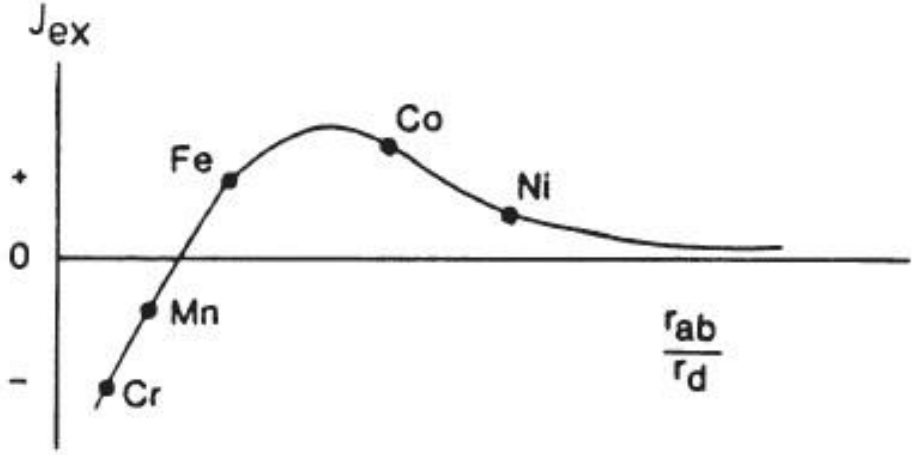
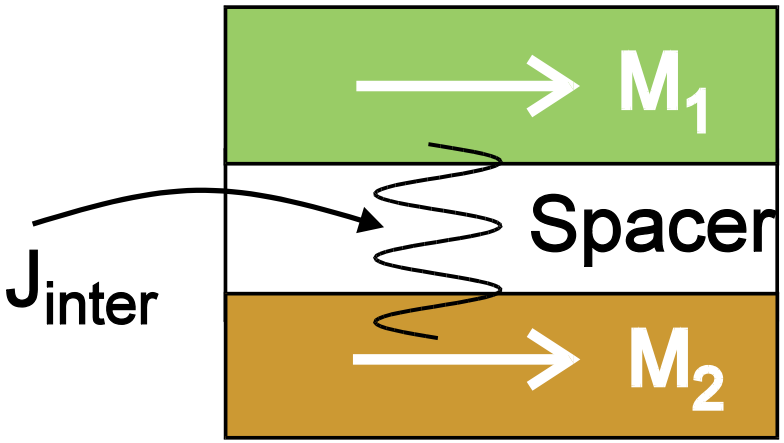


Fig. 11.2 The Bethe–Slater curve representing the variation of the exchange integral J with interatomic spacing r_{ab} and radius of unfilled d shell r_d. The positions of various magnetic elements on this curve are indicated. The rare earth elements lie to the right of nickel on the curve.

$$J = \int\int \psi_a^*(r_1)\psi_b^*(r_2)\left[\frac{1}{r_{ab}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{21}}\right]\psi_b(r_1)\psi_a(r_2)\mathrm{d}\tau,$$

Coupled Layers – Interlayer Exchange Coupling

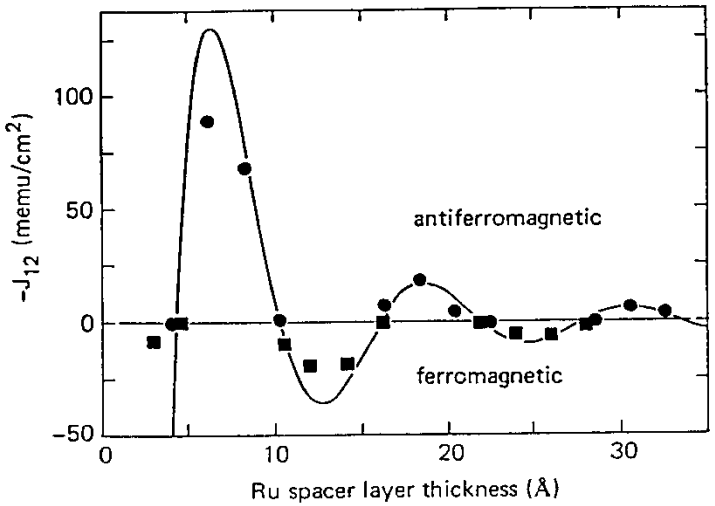


$E_{12} = -J_{inter}\cos(\theta_1-\theta_2)$:

$J_{inter}>0$ ↑↑

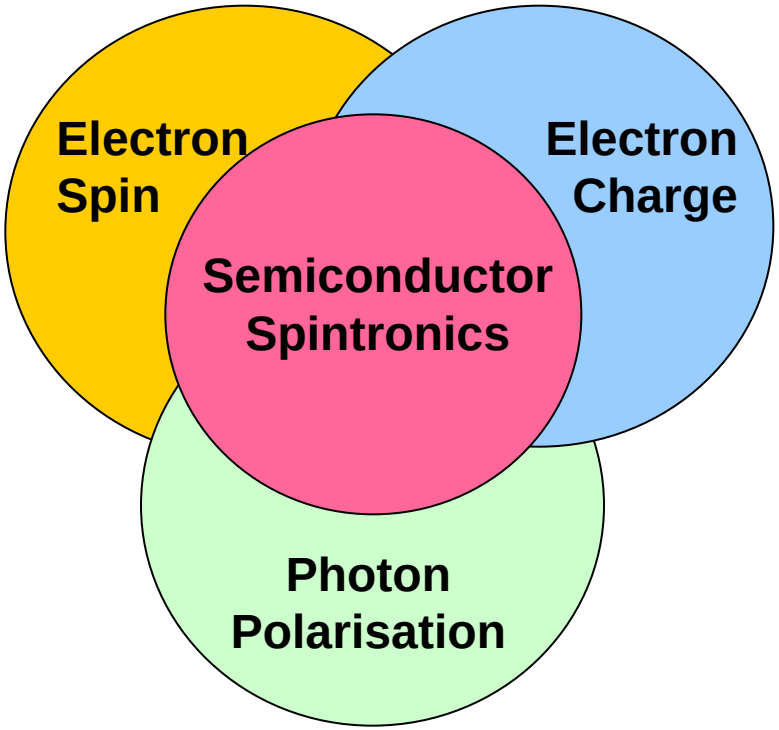
$J_{inter}<0$ ↑↓

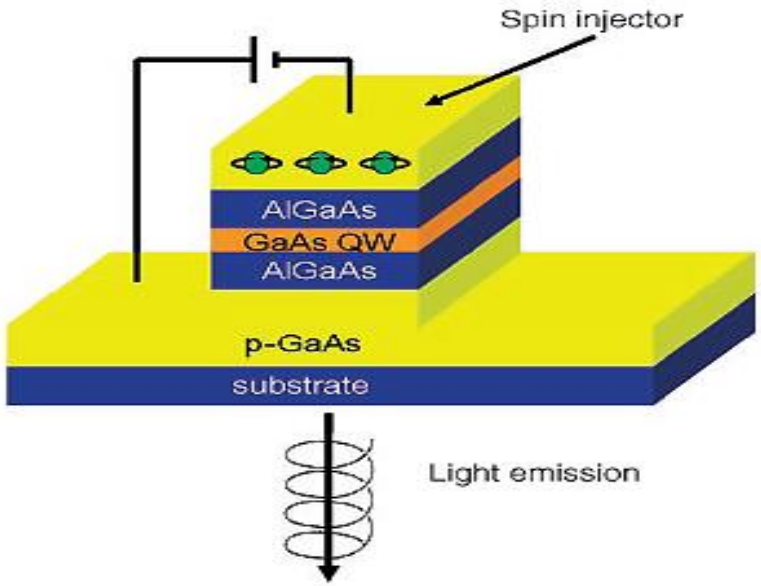
Oscillation of J_{inter} with the spacer thickness d



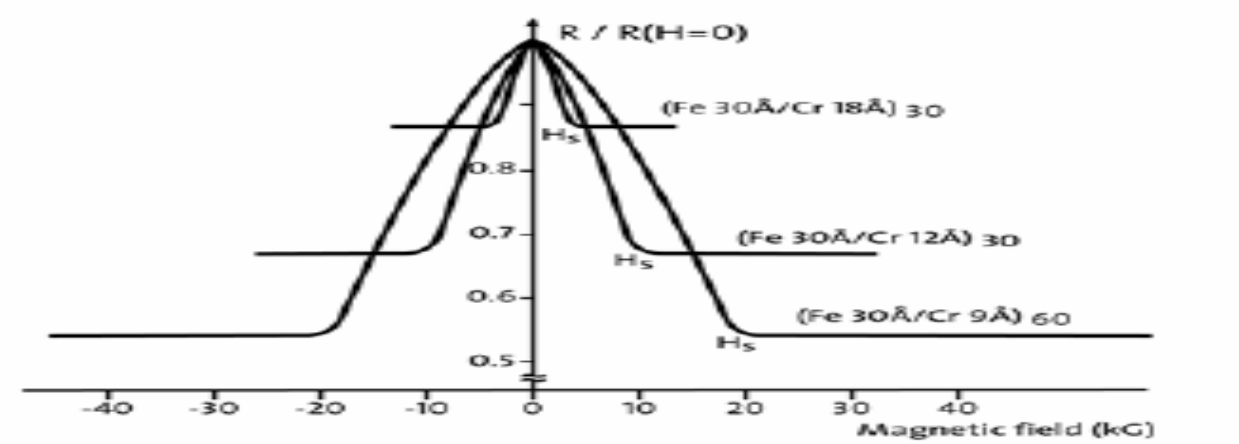
S.S.P. Parkin et al.,
APL 68, 686 (1991)

Μαγνητικοί Ημιαγωγοί





Giant Magnetoresistance: The start of Spintronics period

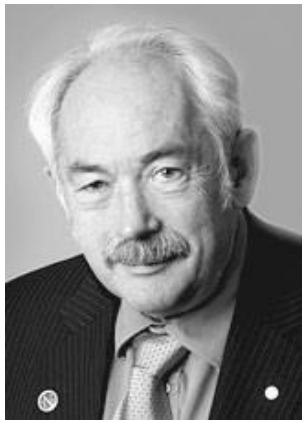


M.N. Baibich et al., PRL 61, 2472 (1988)

$$MR = R_0/R_H$$

Nobel Prize in Physics 2007

Albert Fert, France



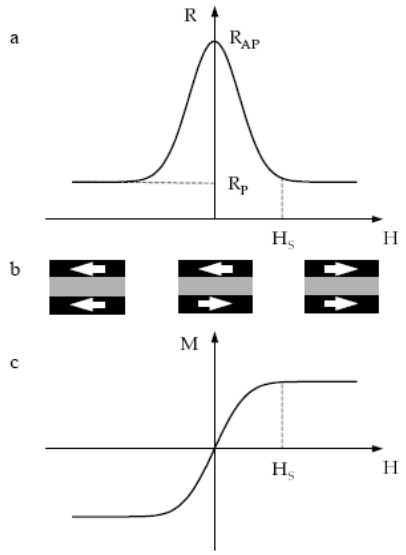
Peter Gruenberg, Germany

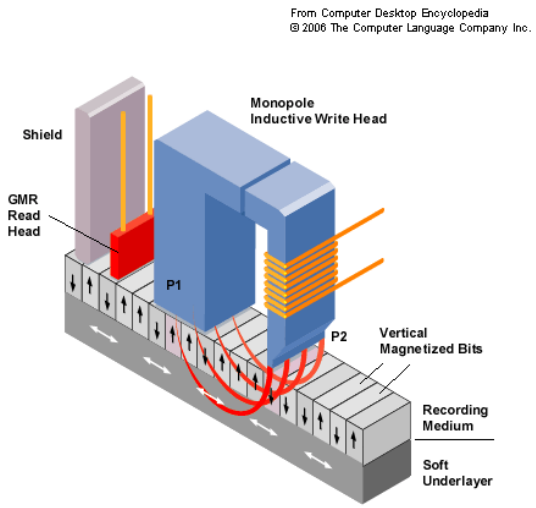
GMR and devices

$$GMR(\%) = (R^{AP}-R^{P})/R^{P}$$

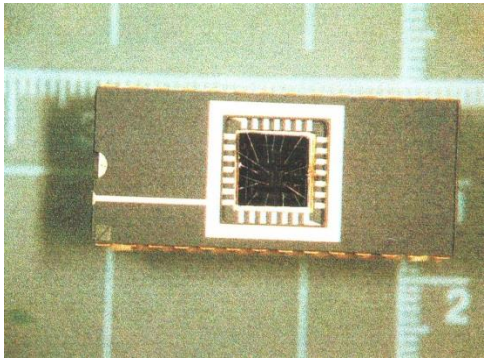
R^{AP}: Resistance in the antiparallel configuration

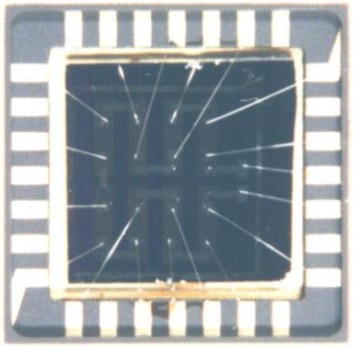
R^{P} : Resistance in the parallel configuration





Miniature Read Heads for Tbits/sq.inch, see e.g. Hitachi, BHMA-Science, November 2007





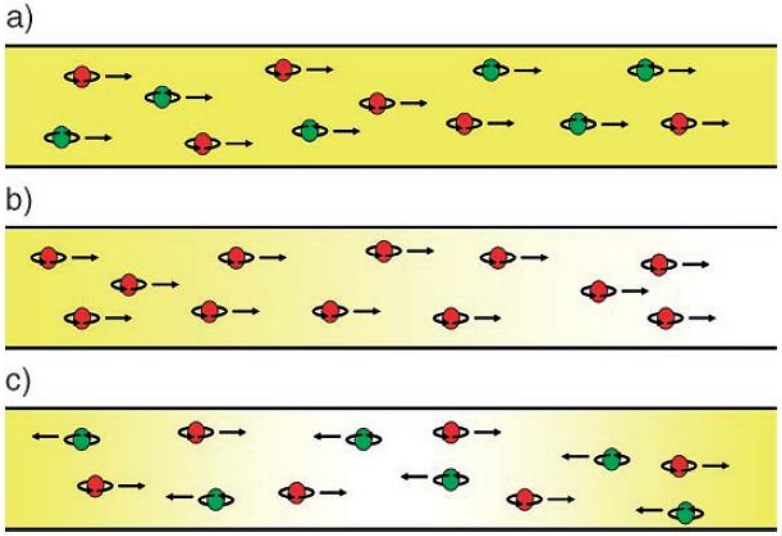
First efforts in Greece

M. Angelakeris, P. Poulopoulos et al., JMMM 165, 334 (1997)

M. Angelakeris, P. Poulopoulos et al., Sensors and Actuators A91, 180 (2001)

Magnetoelectronics-Spintronics

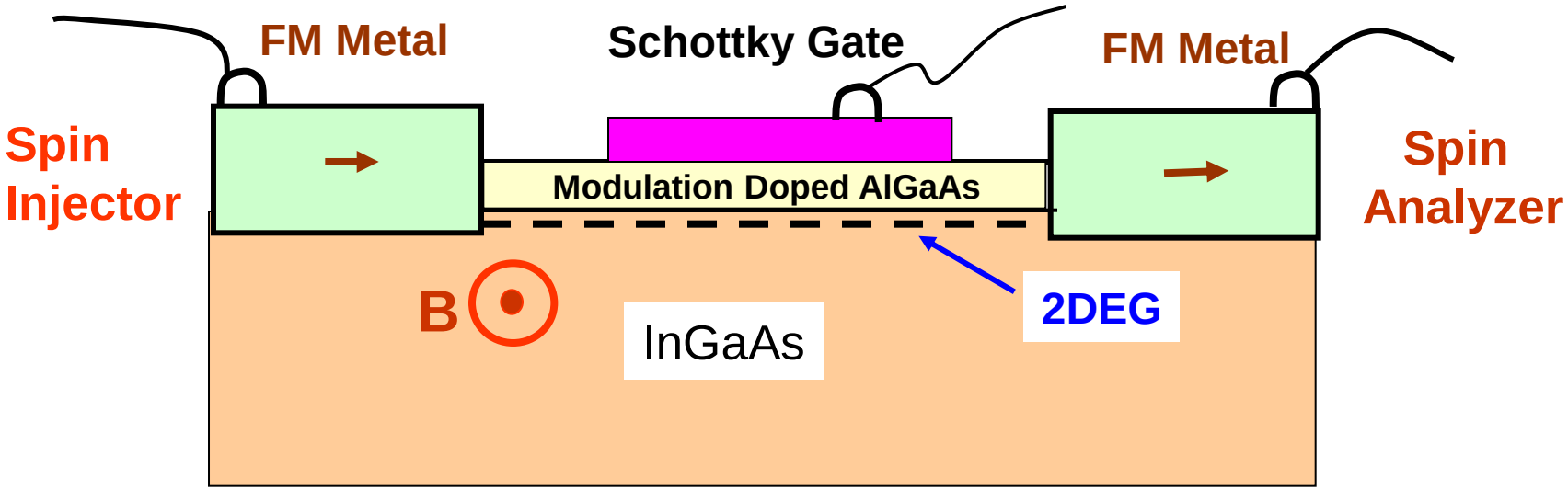
Spintronics: manipulate electron spin (or resulting magnetism) to achieve new/improved functionalities -- spin transistors, memories, higher speed, lower power, tunable detectors and lasers, bits (Q-bits) for quantum computing. Just as conventional electronic devices require charge currents, spin-based electronic (spintronic) devices require spin currents.



a) A regular charge current, b) a spin and charge current, and c) a pure spin current through a wire. The spin (red or green) and direction of movement of the electrons are indicated. These states, spin up or spin down, can be used to represent '1' and '0' in binary logic. In certain **spintronic materials**, spin orientation can be used as ***spintronic memory*** as these orientation do not change when system is switched off.

Spin Injection and Devices

When electrons from a ferromagnet are injected into a nonmagnetic material, they can retain their spin polarization over a certain distance. The prerequisites for this retention of spin polarization are successful spin injection, spin transport within the semiconductor with a spin diffusion length of several microns, spin lifetimes greater than 100 ns, and finally, successful spin detection.



C. Felser et al., Angew. Chemie 46, 668 (2007)

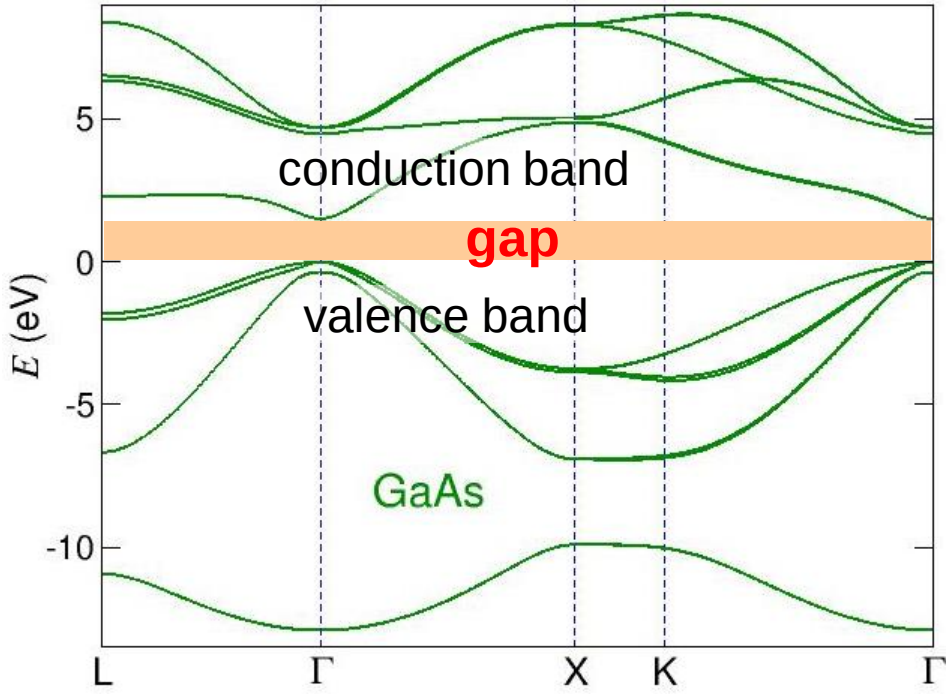
Advantages of Spintronics

- **Low power consumption.**
- **Less heat dissipation.**
- **Spintronic memory is non-volatile.**
- **One does not need extra hard disks with sizeable mechanical parts.**
- **Takes up lesser space on chip, thus more compact.**
- **Spin manipulation is faster , so greater read & write speed.**
- **Spintronics does not require unique and specialized semiconductors.**

Basics of semiconductor physics

Undoped (intrinsic) semiconductors:

Band structure has energy gap E_g at the Fermi energy



Conduction only if electrons are excited (e.g., thermally, optically) over the gap

Same density of electrons in conduction band and holes in valence band:

$$n_e = n_h \sim e^{-E_g/2k_BT}$$

Non-degenerate electron/hole gas in bands (i.e., no Fermi sea), transport similar to classical charged gas

Doping: Introduce charged impurities

Example: replace Ga by Si in GaAs

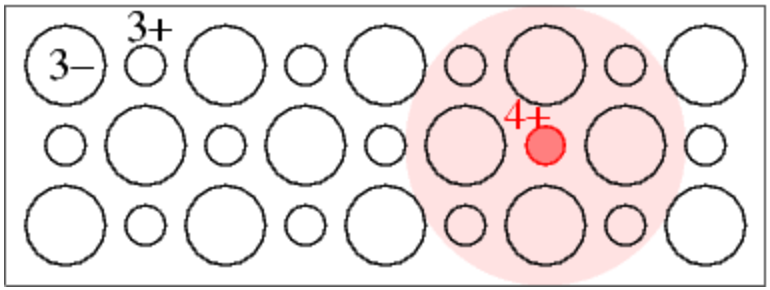
Si has one valence electron *more*
→ introduces extra electron: donor

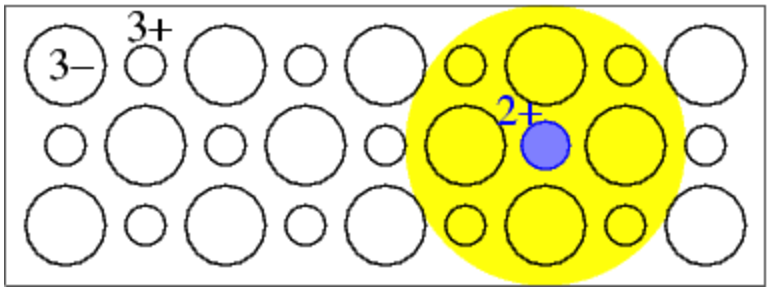
Si^{4+} weakly binds the electron:
hydrogenic (shallow) donor state

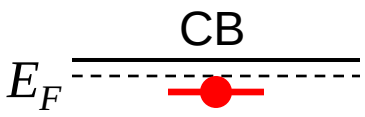
Example: replace Ga by Zn in GaAs

Zn has one valence electron *less*
→ introduces extra hole: acceptor

Zn^{2+} weakly binds the hole:
hydrogenic (shallow) acceptor state

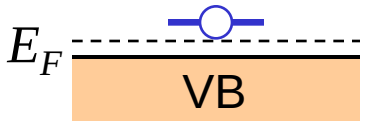






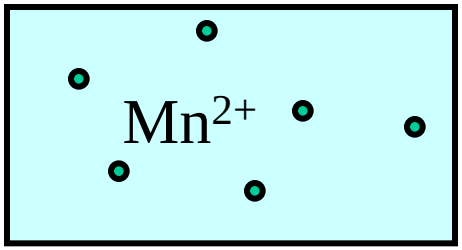
excitation energy is
strongly reduced

conduction at lower
temperatures

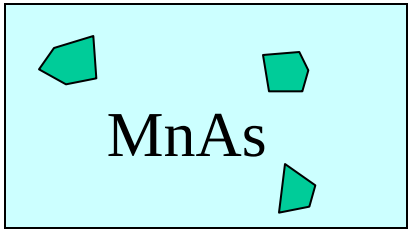


Ferromagnetic Semiconductors

The best-suited material would be a ferromagnetic semiconductor with a Curie temperature far above room temperature. Semiconductors doped with small amounts of ferromagnetic impurities, such as Co or Mn, exhibit room-temperature ferromagnetism and are called diluted magnetic semiconductors (DSMs).



$T_{growth} < 300^{o}C$



$T_{growth} > 300^{o}C$

However, element-specific techniques like X-ray magnetic circular dichroism show actually paramagnetic or superparamagnetic states of impurities and absence of real ferromagnetism at room temperature.

A. Ney et al., Phys. Rev. Lett. 100, 157201 (2008)
V. Ney et al., J. Nanosci. Nanotechnol. 10, 5958 (2010)
V.N. Antonov et al., J. Appl. Phys. 111, 073702 (2012)

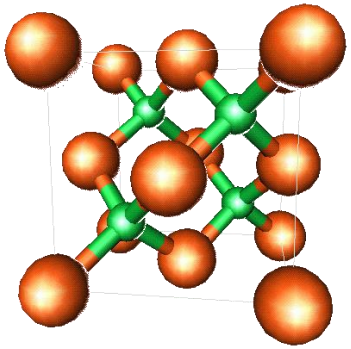
Diluted magnetic semiconductors (DMS):

Magnetic ions are introduced into a non-magnetic semiconductor host

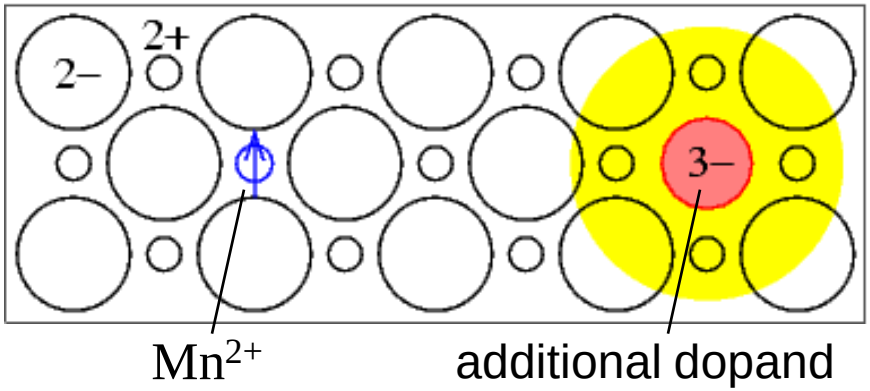
Typically substitute for the cation as 2+-ions, e.g. Mn^{2+} (high spin, $S = 5/2$)

- II-VI semiconductors (excluding oxides)
  (Cd,Mn)Te, (Zn,Mn)Se, (Be,Mn)Te… zinc-blende structure
  studied extensively in 70's, 80's

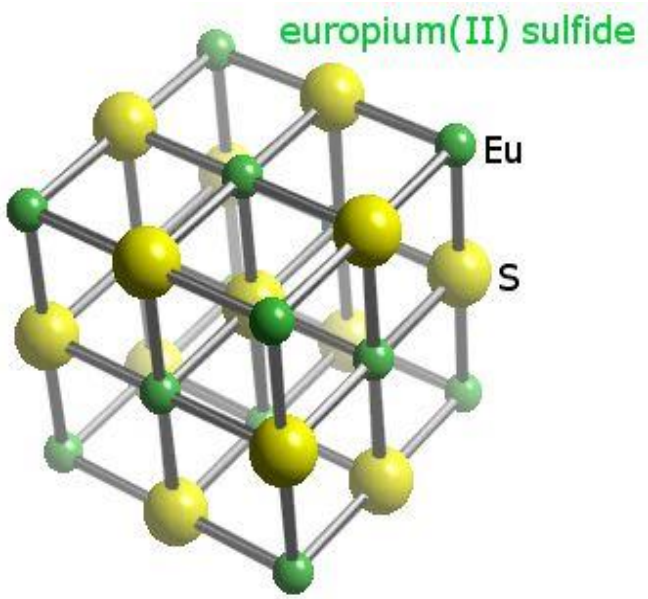
  Mn^{2+} is isovalent → low carrier concentration



  - usually paramagnetic or spin-glass (antiferromagnetic superexchange)
  - ferromagnetism hard to achieve by additional homogeneous doping
  - ferromagnetic at $T < 4$ K employing modulation p-doping (acceptors and Mn in different layers):
    Haury *et al.*, PRL **79**, 511 (1997)



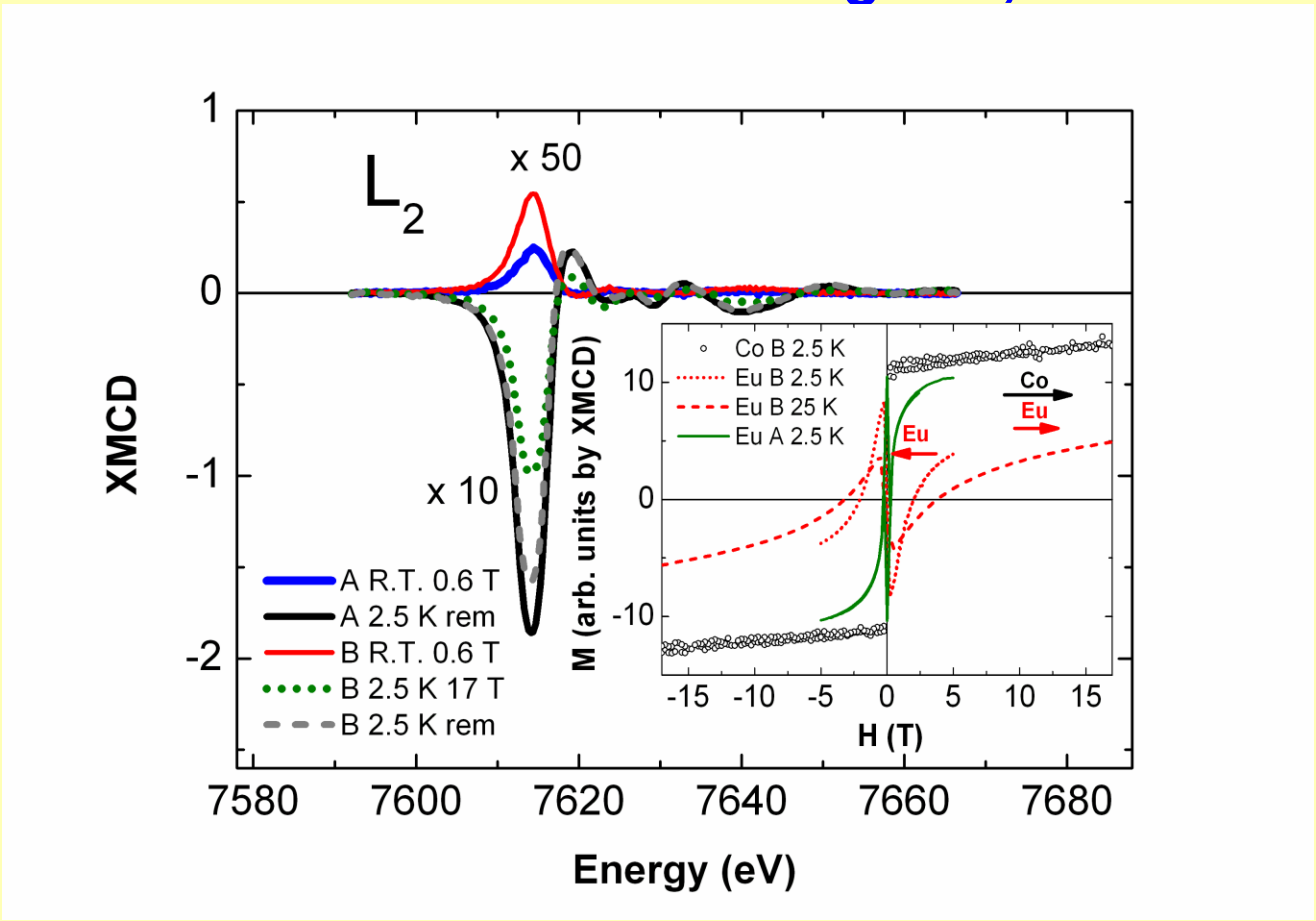
The EuS intrinsic magnetic semiconductor



Europium sulfide (EuS) is a natural ideal Heisenberg ferromagnetic semiconductor with *very large magneto-optical response*. As compared to layered systems ferromagnet/semiconductor, it presents the advantage that the spin-polarized electrons are created within the semiconductor itself. The main disadvantage of it is a low T_C of only ~ 16.6 K. In 1998, Fumagalli *et al.* reported that EuS nanospheres with a diameter of about 10 nm become ferromagnetic at about 160 K when placed in a Co matrix. Since then, a strong effort has been put on making EuS ferromagnetic at R.T. by formation of EuS/Co trilayers with EuS layers thicker than 3.5 nm, but no promising direct evidence was provided.

P. Fumagalli et al., Phys. Rev. B 57, 14294 (1998)

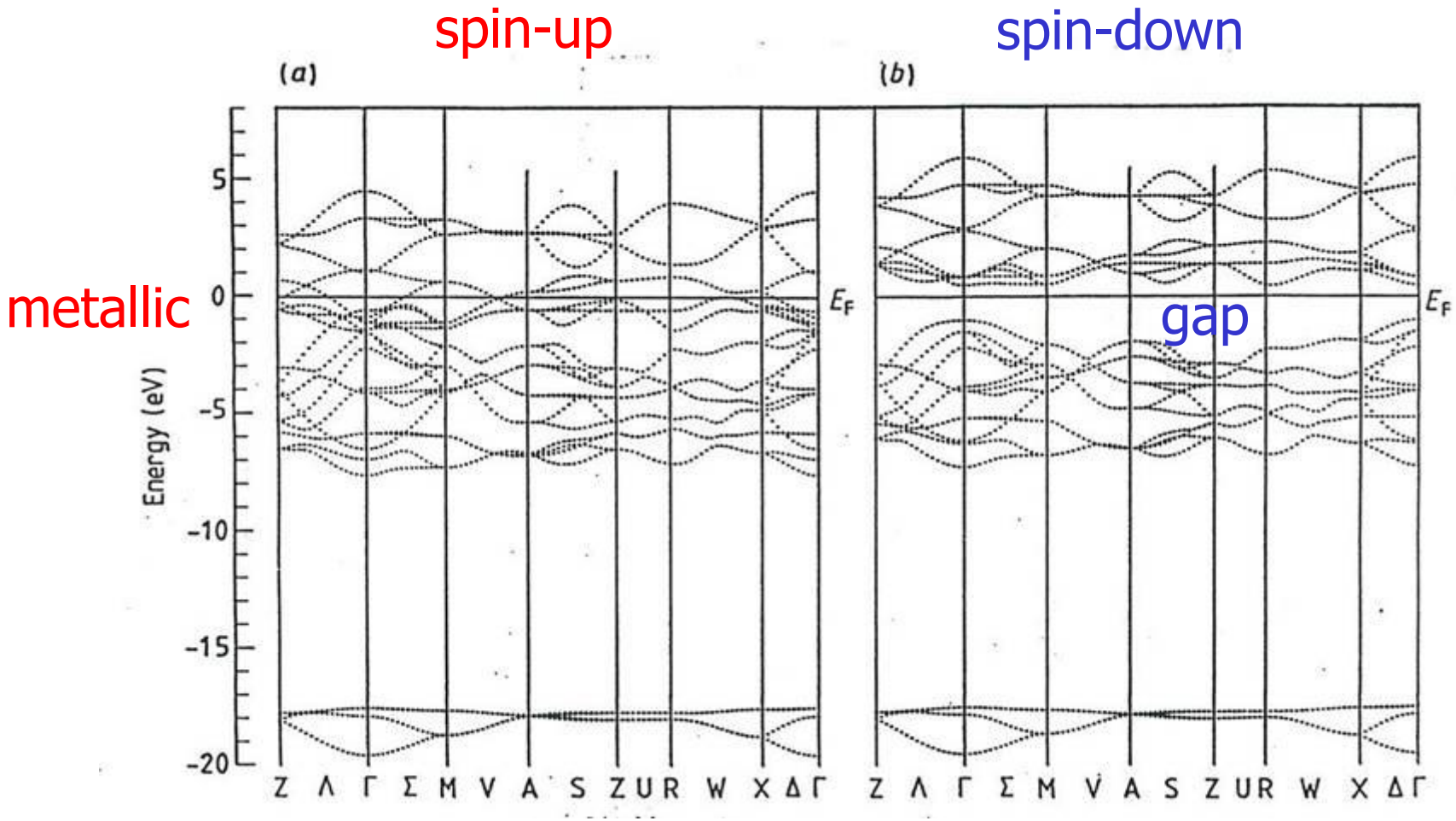
EuS Magnetic Semiconductor at Room Temperature:
Element-Specific Magnetization Curves
ESRF ID12 beam line A. Rogalev, F. Wilhelm



S. D. Pappas, P. Poulopoulos et al. Nature Scientific Reports 3, 1333 (2013)
Also Editors choice in Nature Materials April 2013
And currently ESRF Highlights 2013 and spotlight at the ESRF web site www.esrf.eu

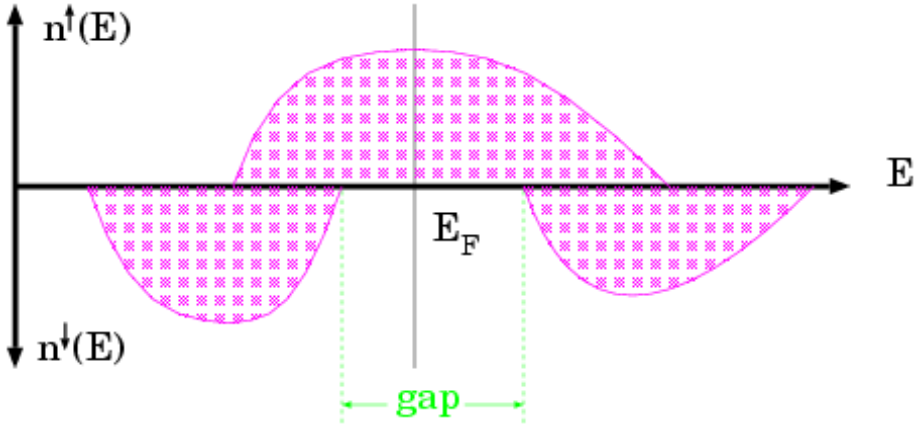
Half-metallic ferromagnet

- CrO_2 (rutile structure)



Introduction: Definition & properties (Ph. Mavropoulos)

What is a half-metallic ferromagnet?



Spin-polarised material showing

100% polarisation at E_F

Examples:

- **Heusler alloys (NiMnSb etc)**

  (de Groot et al, PRL 1983)
- **Diluted Magnetic Semiconductors**
- **Zinc-blende pnictides and chalcogenides (CrAs etc)**
- **Some manganites (eg LSMO)**

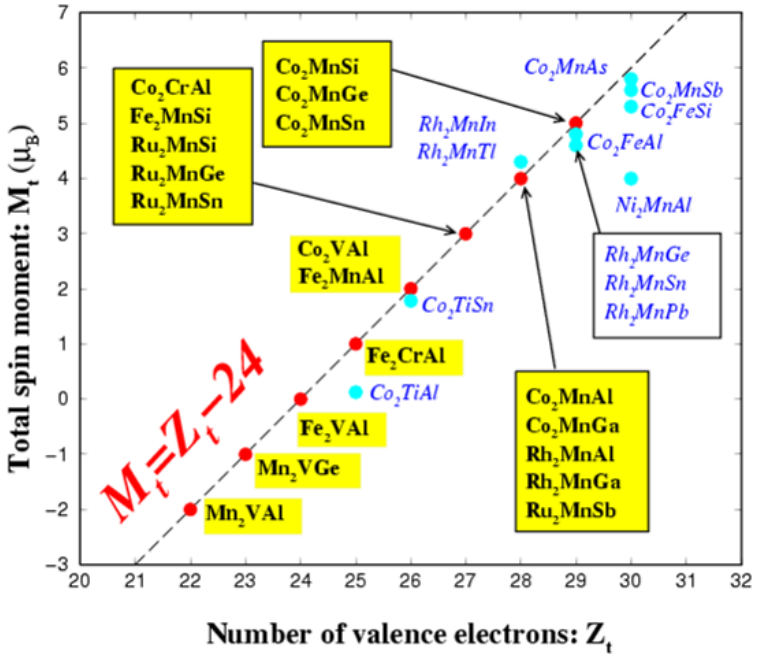
Relevance to spintronics:

- **Conductance through only one spin channel**
- **Possibility for 100% spin-polarised current, 100% spin injection etc.**

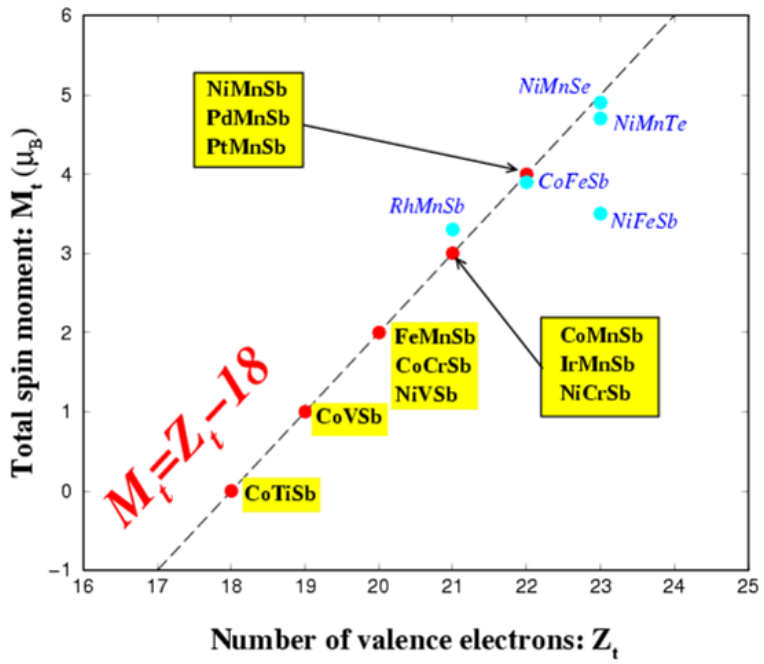
Example: Heusler alloys

Slater-Pauling behaviour in Heusler alloys *(I. Galanakis, P.H. Dederichs)*

Full Heusler



Half Heusler



•Total magn. Moment per unit cell is integer in half-metallic systems.

Παλαιότερη Έρευνα στο Π.Π.

Acta Cryst. (1971). B27, 1864

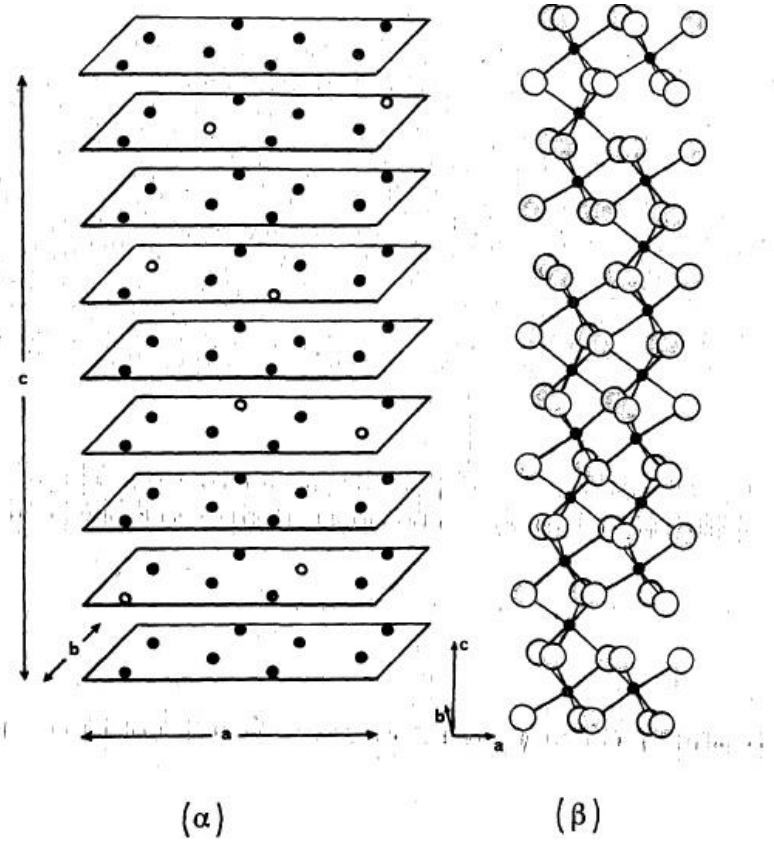
The Crystal Structure of a Pyrrhotite (Fe_7S_8)

BY M. E. FLEET

Department of Geology, University of Western Ontario, London, Ontario, Canada

(*Received* 30 *November* 1970)

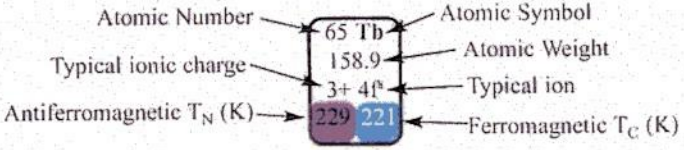
The structure of a pyrrhotite exhibiting a hexagonal ($a=2A$, $c=3C$) supercell has been determin analysis of three-dimensional single-crystal intensity data. The symmetry of the structure is space group $P3_1$; the hexagonal symmetry shown by single crystals possibly results from twi which platy domains stacked normal to **c** are related by 180° rotations about **c**. The structure posed of 12 subcell units stacked in three layers of four. The vacancies in the Fe sites are ordered, to alternate layers of Fe atoms normal to **c**. The distortions observed in the structure are anal those in the structure of troilite. Three Fe atoms in each Fe layer are displaced toward an enlarg hedral site; the displacements from the ideal positions are 0·22 Å in both the vacancy layers an Fe layers.



This material has strong magnetic anisotropy. It is an antiferromagnet. Below T_N it is semicoductor. Above T_N becomes a metal. Interestingly, when it is antiferromagnetic, it presents also ferromagnetic areas (ferrons), which result in a complicate magneto-electric behavior. It is among the first magnetic semiconductors ever studied.

•Ε. Βιτωράτος, διδακτορική διατριβή

Magnetic Periodic Table



1 H 1.00																	2 He 4.00
3 Li 6.94 $1+\ 2s^0$	4 Be 9.01 $2+\ 2s^0$											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00 24	9 F 19.00	10 Ne 20.18
11 Na 22.99 $1+\ 3s^0$	12 Mg 24.21 $2+\ 3s^0$											13 Al 26.98 $3+\ 2p^6$	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10 $1+\ 4s^0$	20 Ca 40.08 $2+\ 4s^0$	21 Sc 44.96 $3+\ 3d^0$	22 Ti 47.88 $4+\ 3d^0$	23 V 50.94 $4+\ 3d^1$	24 Cr 52.00 $3+\ 3d^3$ 312	25 Mn 54.94 $2+\ 3d^5$ 96	26 Fe 55.85 $3+\ 3d^5$ 1043	27 Co 58.93 $2+\ 3d^7$ 1390	28 Ni 58.69 $2+\ 3d^8$ 629	29 Cu 63.55 $2+\ 3d^9$	30 Zn 65.39 $2+\ 3d^{10}$	31 Ga 69.72 $3+\ 3d^{10}$	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47 $1+\ 5s^0$	38 Sr 87.62 $2+\ 5s^0$	39 Y 88.91 $3+\ 4d^0$	40 Zr 91.22 $4+\ 4d^0$	41 Nb 92.91 $5+\ 4d^0$	42 Mo 95.94 $3+\ 4d^3$	43 Tc 97.9	44 Ru 101.1 $3+\ 4d^5$	45 Rh 102.9 $3+\ 4d^6$	46 Pd 106.4 $2+\ 4d^8$	47 Ag 107.9 $1+\ 4d^{10}$	48 Cd 112.4 $2+\ 4d^{10}$	49 In 114.8 $3+\ 4d^{10}$	50 Sn 118.7 $4+\ 4d^{10}$	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.6
55 Cs 132.9 $1+\ 6s^0$	56 Ba 137.3 $2+\ 6s^0$	57 La 138.9 $3+\ 4f^0$	72 Hf 178.5 $4+\ 5d^0$	73 Ta 180.9 $5+\ 5d^0$	74 W 183.8 $6+\ 5d^0$	75 Re 186.2 $4+\ 5d^3$	76 Os 190.2 $3+\ 5d^5$	77 Ir 192.2 $4+\ 5d^5$	78 Pt 195.1 $2+\ 5d^8$	79 Au 197.0 $1+\ 5d^{10}$	80 Hg 200.6 $2+\ 5d^{10}$	81 Tl 204.4 $3+\ 5d^{10}$	82 Pb 207.2 $4+\ 5d^{10}$	83 Bi 209.0	84 Po 209	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226.0 $2+\ 7s^0$	89 Ac 227.0 $3+\ 5f^0$															

58 Ce 140.1 $3+\ 4f^1$ 13	59 Pr 140.9 $3+\ 4f^2$	60 Nd 144.2 $3+\ 4f^3$ 19	61 Pm 145	62 Sm 150.4 $3+\ 4f^5$ 105	63 Eu 152.0 $2+\ 4f^7$ 90	64 Gd 157.3 $3+\ 4f^7$ 293	65 Tb 158.9 $3+\ 4f^8$ 229 221	66 Dy 162.5 $3+\ 4f^9$ 179 89	67 Ho 164.9 $3+\ 4f^{10}$ 132 20	68 Er 167.3 $3+\ 4f^{11}$ 85 20	69 Tm 168.9 $3+\ 4f^{12}$ 56	70 Yb 173.0 $3+\ 4f^{13}$	71 Lu 175.0 $3+\ 4f^{14}$
90 Th 232.0 $4+\ 5f^0$	91 Pa 231.0 $5+\ 5f^0$	92 U 238.0 $4+\ 5f^2$	93 Np 237.0 $5+\ 5f^3$	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

Ferromagnetic with T_C>290 K

Antiferromagnetic with T_N>290 K

Antiferromagnetic with T_N<290 K

Elements with ferromagnetic and antiferromagnetic transitions

Metals

Radioactive elements