Half-metals, semimetals and magnetic carbon

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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+ $5f^2$	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

Key: 65 Tb / 158.9 / 3+ $4f^8$ / 229 221

Atomic Number; Atomic Symbol; Typical ionic charge; Atomic Weight; Typical ion; Antiferromagnetic T_N (K); Ferromagnetic T_C (K)

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

Spin Electronics

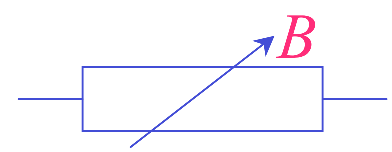
Conventional electronics has ignored the spin in the electron:

- Code information into the ↑ and ↓ channels
- Manipulate the ↑ and ↓ electrons independently
- Exploit magnetic and electric fields

$e = 1.6\ 10^{-19}$ C

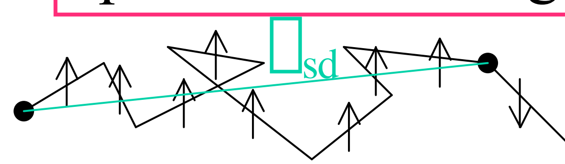
$m = e\hbar/2m = 1\mu_B$

TWO-TERMINAL DEVICES; Magnetoresistors



Source of spin-polarized electrons → Medium with long spin-diffusion length → spin-sensitive detector

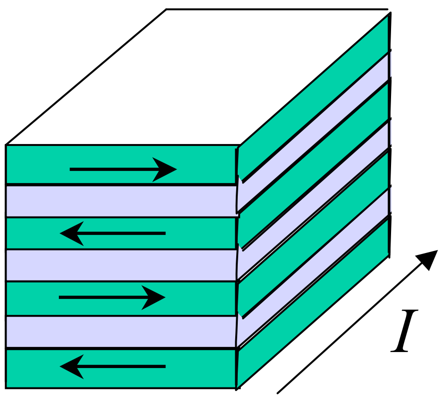
Ferromagnetic metal; NiFe, CoFe



Normal metal; Cu

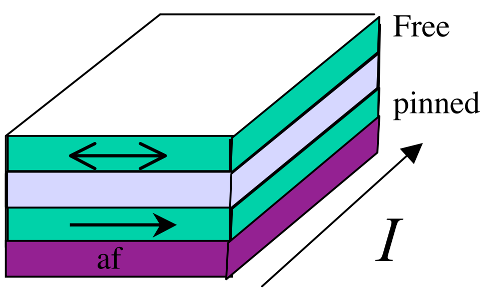
Ferromagnetic metal NiFe, CoFe

Magnetoresistance

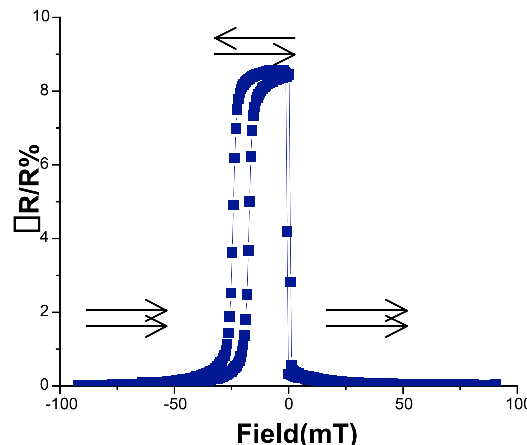


Giant magnetoresistance

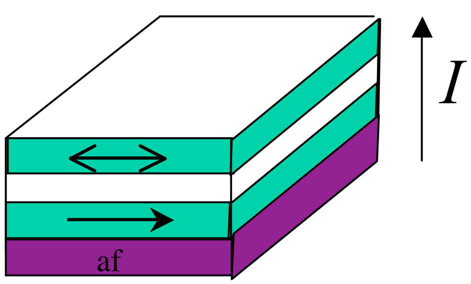
Fert et al 1988



Spin valve

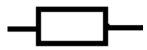
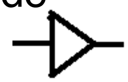
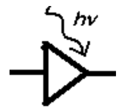
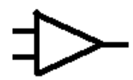
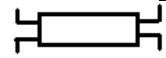
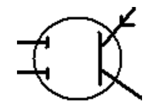
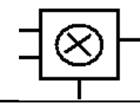
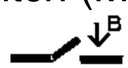
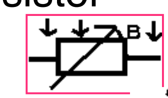
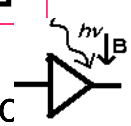
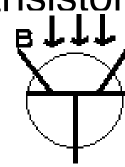
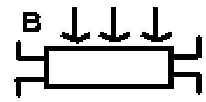
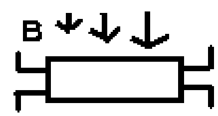


10^8 sensors / year — read heads



Magnetic tunnel junction

(10^{16} / year MRAM)

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

1. Half Metals

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

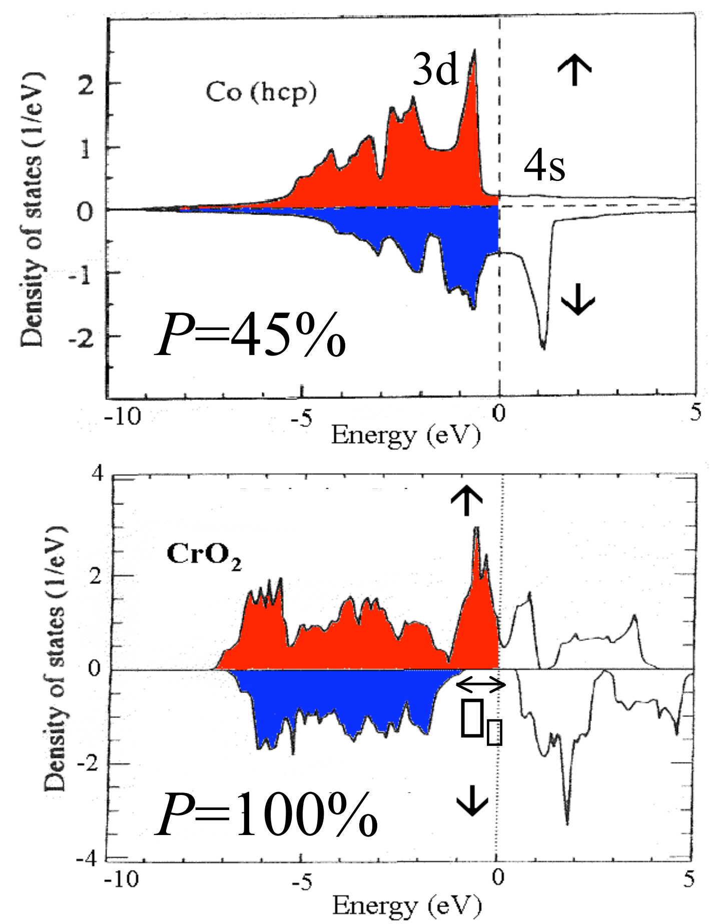
  $P = (N^{\uparrow} - N^{\square})/(N^{\uparrow} + N^{\square})$

- Metallic for ↑ electrons but semiconducting for □ electrons. Spin gap $\square_{\uparrow}$ or $\square_{\square}$

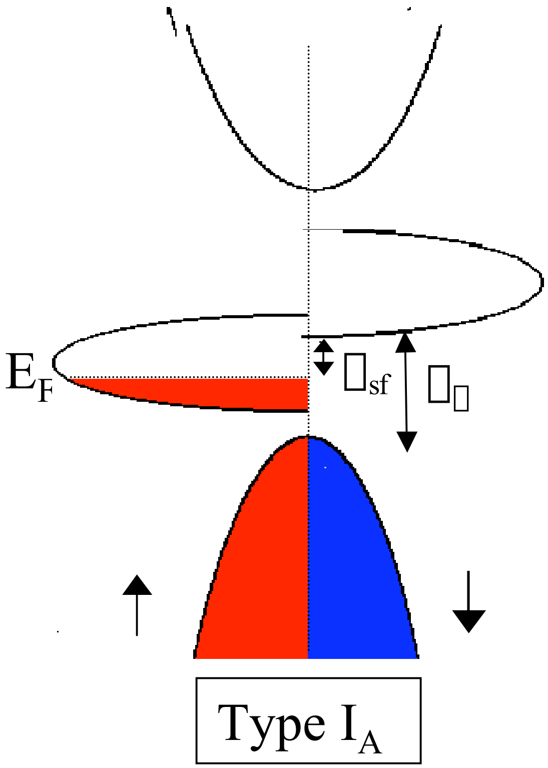
- Integral spin moment $n\,\square_{\square}$

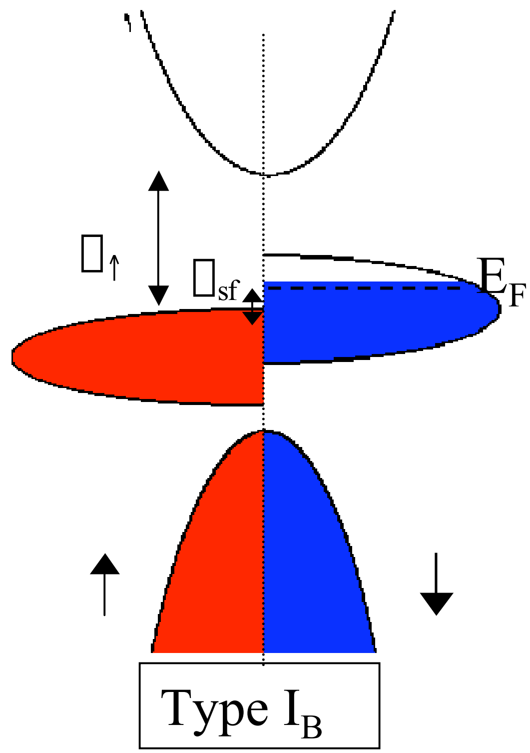
- Mostly oxides, Heusler alloys

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



Type I half metals





Examples: CrO_2; NiMnSb
$(Co_{1-x}Fe_x)S_2$
$(La_{0.7}Sr_{0.3})\ O_3$

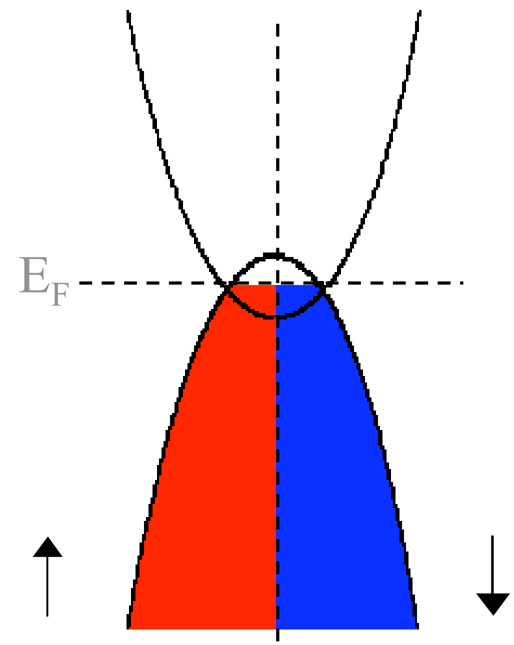
Fe_3O_4, Sr_2FeMoO_6;
Mn_2VAl

2. Semimetals

— A metal with very slight overlap of valence and conduction bands

— Equal numbers of electrons and holes

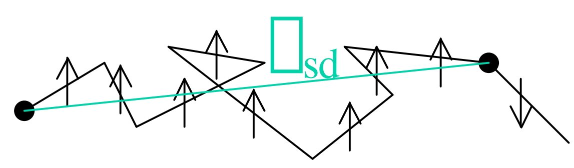
— Examples: graphite, Bi, As



Semimetal

Spin diffusion lengths (nm)

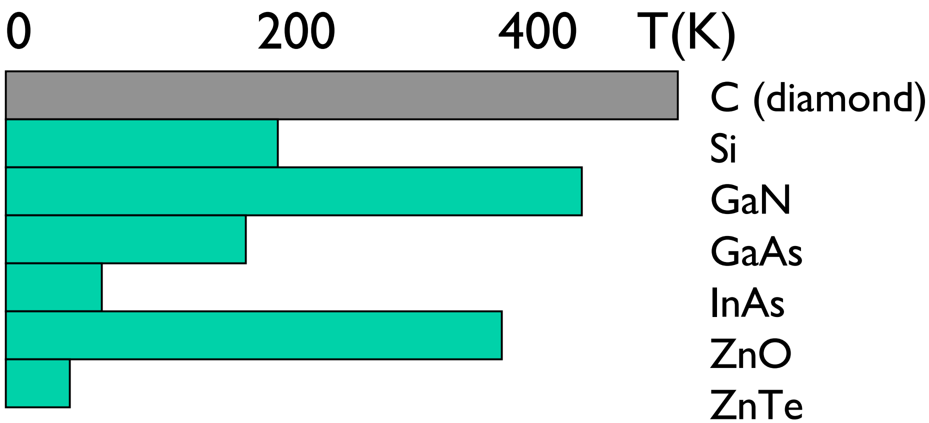
	□$_\uparrow$ □$_□$	□$_{sd}$
semiconductors	200	2000
semimetals	>50	>500
s-band metals	30	300
d-band metals	5.0 0.9	30

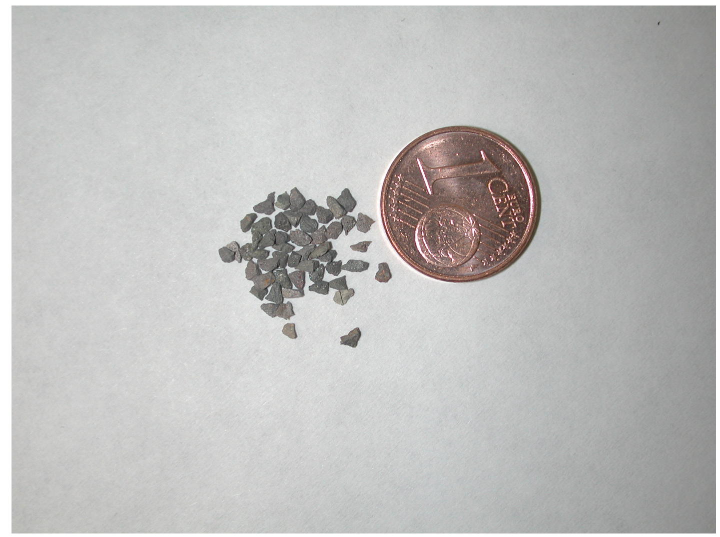


Mobility of semiconductors, semimetals and metals

		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

Magnetic semiconductors





Curie temperatures of semiconductors with 5 at% Mn

Dietl et al 2001

Carbonado diamonds (meteoritic origin?) are strongly magnetic

But the magnetism is due to metallic iron inclusions !

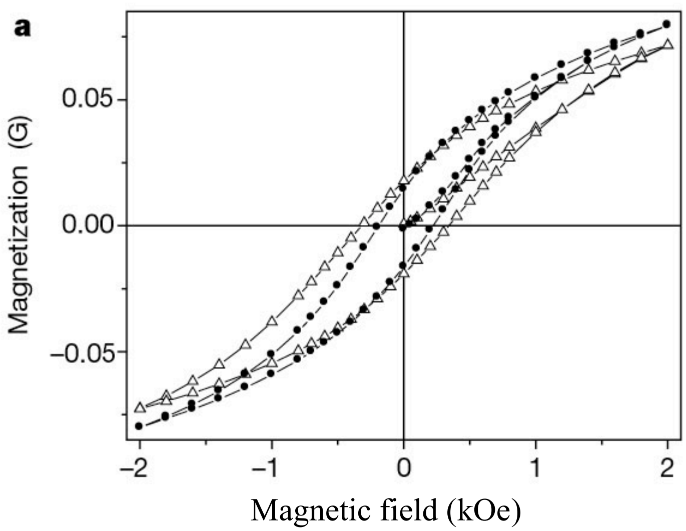
Ferromagnetic carbon ?

- **Rhombohedral C_{60}**

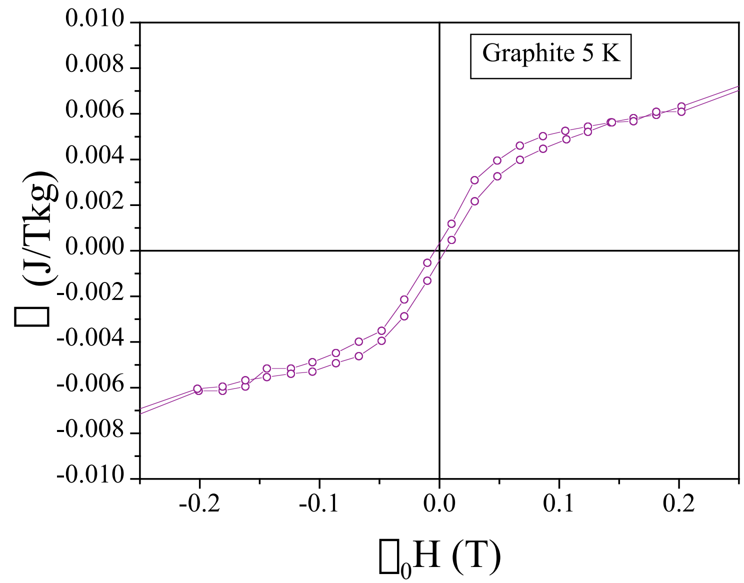
Makarova T. L. *et al*, Magnetic Carbon, *Nature* **413** 716 – 718 (2001)

□$_s$ = 0.09 Am^2kg^{-1} or 0.0002 □$_B$/C

T_c ~ 500 K



- **Rock graphite**

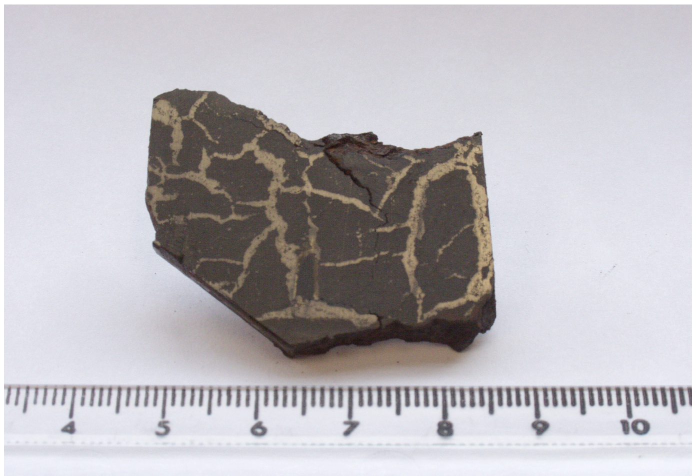


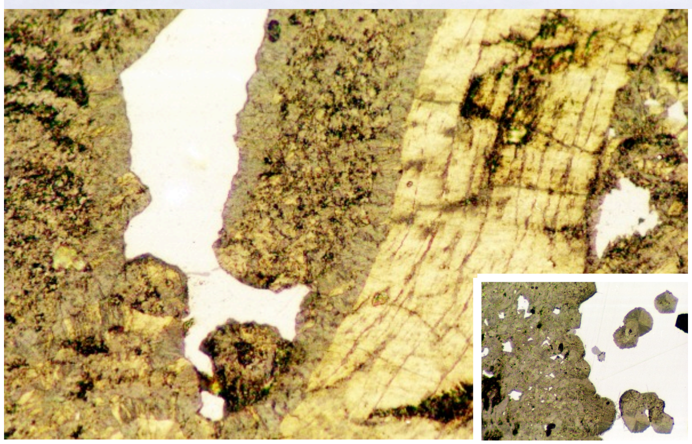
□$_s$ = 0.005 Am^2kg^{-1} or 0.00001 □$_B$/C

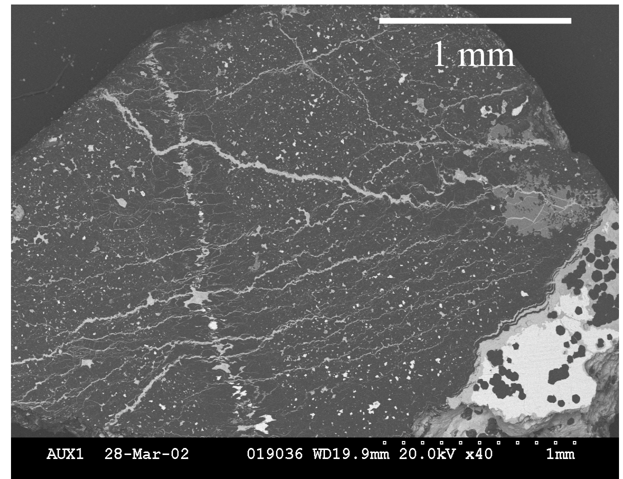
The Canyon Diablo Meteorite

- A type IAB iron meteorite
- Origin: Impact of an asteroid with carbonaceous chondritic composition with another asteroid having a molten iron-nickel core
- Mass ~ 50,000 t
- Impact in the Arizona desert ~ 50,000 years ago
- Peculiar feature; rounded graphite-rich nodules

Graphite nodules







Graphite nodules: Magnetization

Each part of every powder is strongly ferromagnetic

- Ten samples: 0.1 – 0.5 g

  σ_s = 21 – 70 Am^2kg^{-1}

  average 41.4 Am^2kg^{-1}

  $\mu_0 H_c$ = 6 – 8 mT

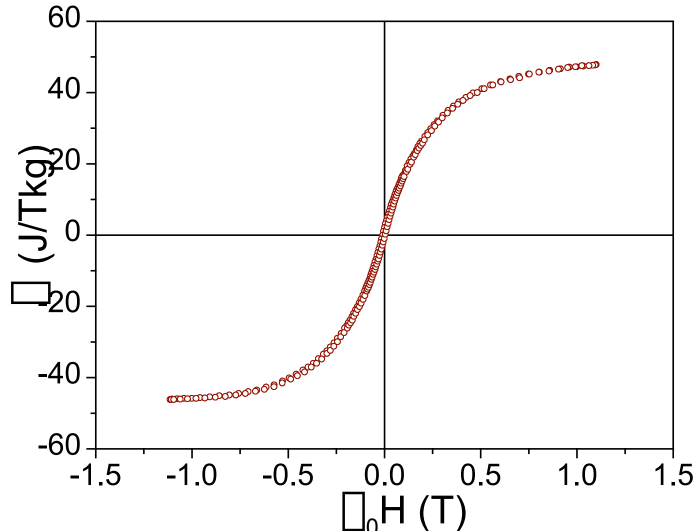
- Milligram pieces:

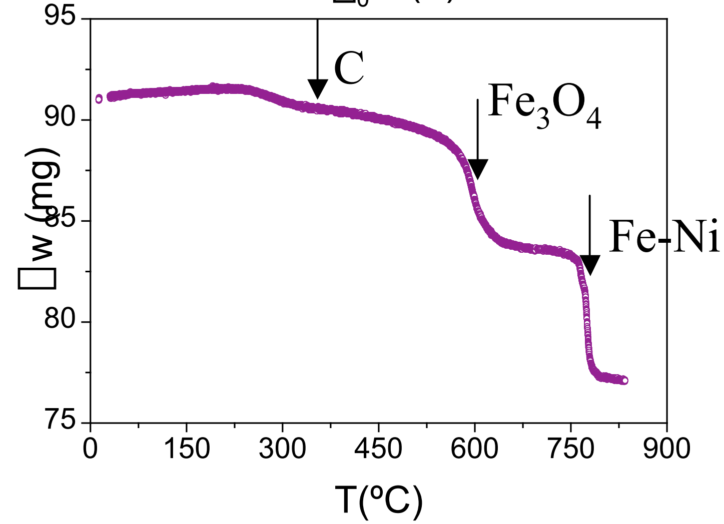
  σ_s = 6 – 185 Am^2kg^{-1}

cf Magnetite σ_s ~ 80 Am^2kg^{-1}

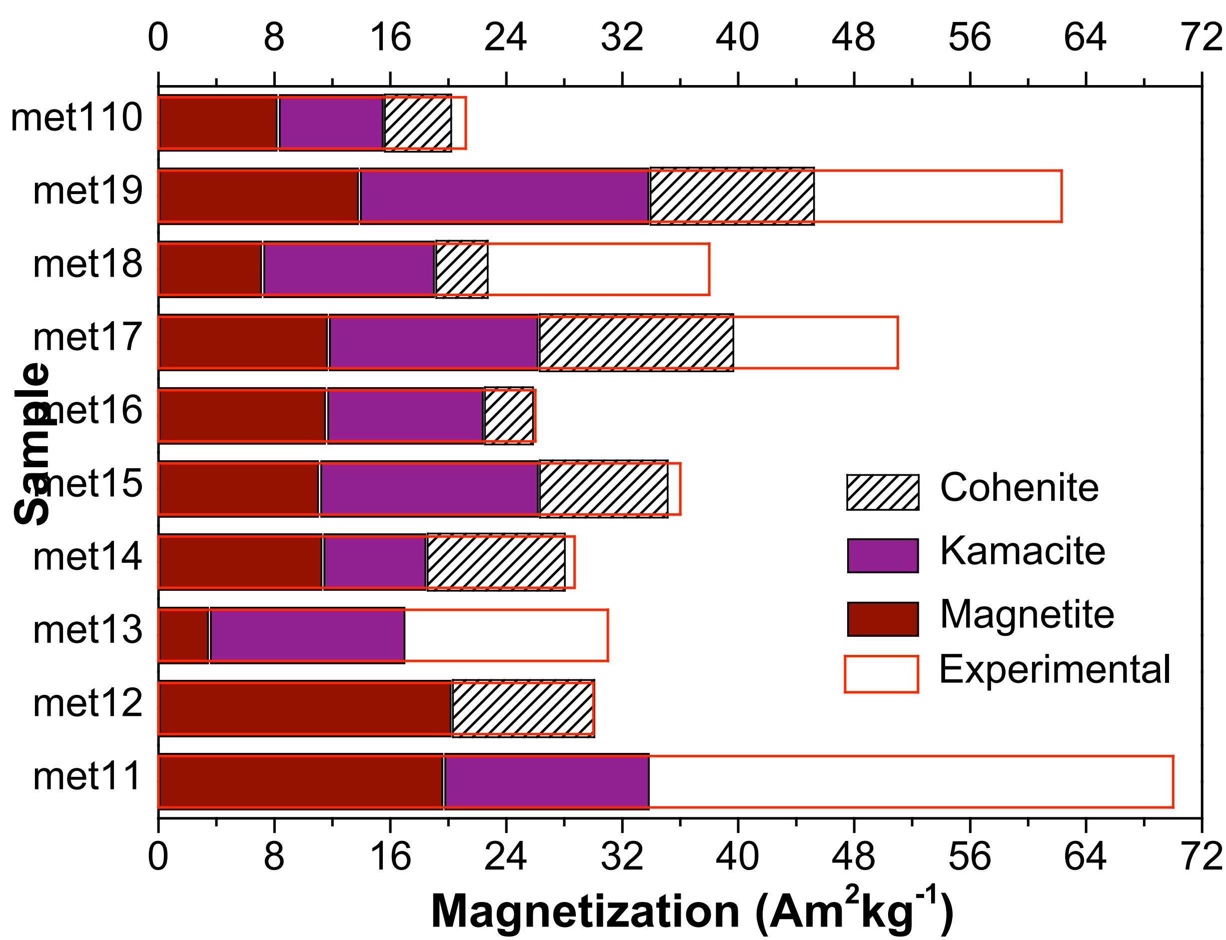
Kamacite σ_s ~ 216 Am^2kg^{-1}

Schreibersite σ_s ~ 146 Am^2kg^{-1}





Graphite nodules: Magnetic phases



Magnetism of meteoritic graphite

There is a significant residue unaccounted for by known ferromagnetic phases; it is associated with graphite.

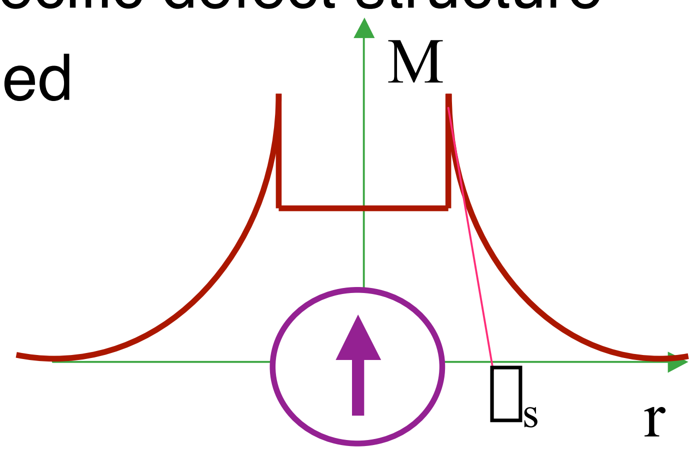
$\square_g = 24\ \mathrm{Am^2kg^{-1}}$ or $0.05\ \square_B$/carbon

Explanations?

•Intrinsic moment due to a specific defect structure

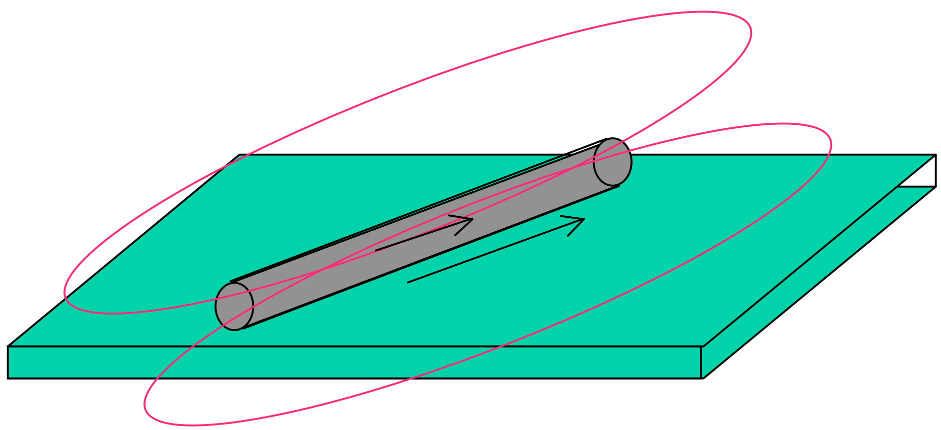
•Moment induced by embedded ferromagnetic particles

Magnetic proximity effect.



Magnetic Proximity Effect

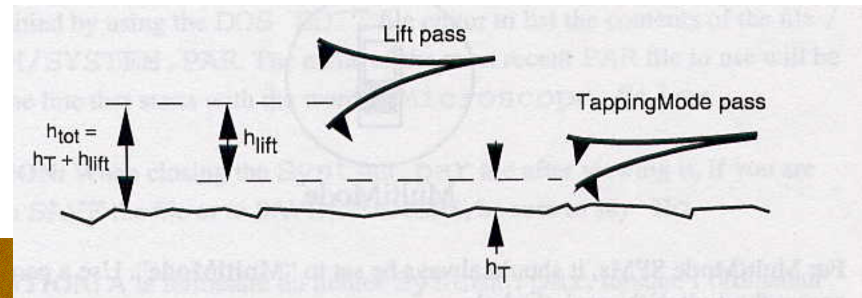
How could we detect a small induced moment in graphite ?

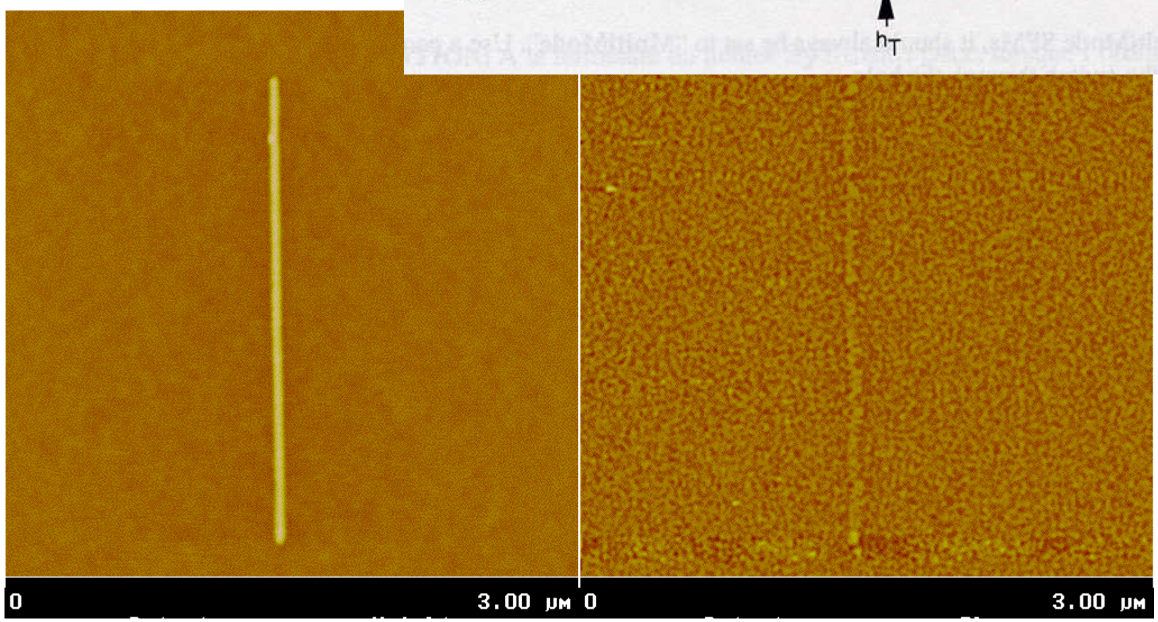


A uniformly-magnetized ferromagnetic thin film produces no stray field, *whatever* the direction of magnetization.

The stray field of the graphite tube could be detected by magnetic force microscopy

MFM on Cu

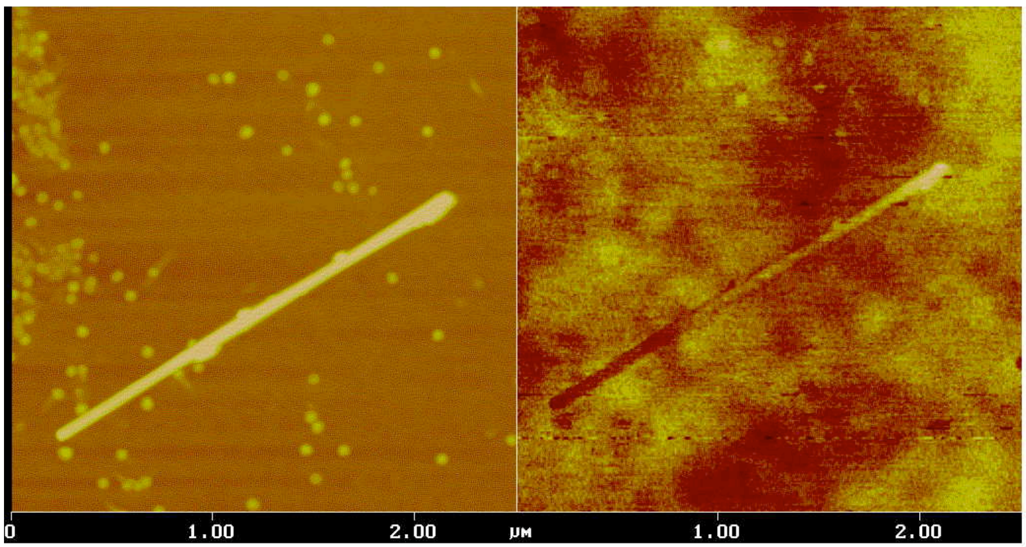


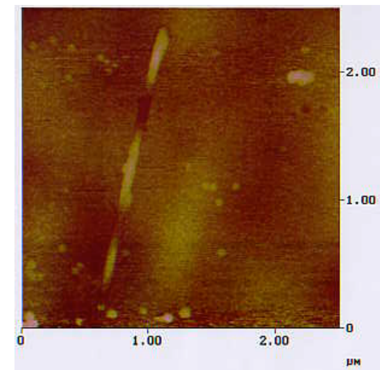


Topographic AFM image Magnetic MFM image

Multiwalled carbon nanotube shows no magnetic contrast on Cu

MFM on magnetite





Topographic AFM image   Magnetic MFM image

Magnetite is a half-metal; charge transfer at the contact is 100 % spin polarized.

This level of stray field implies $M \approx 10$ kA m^{-1}, $m \approx 0.01\ \mu_B$/C

Conclusions

- Spin control will add a new dimension to electronics
- Ferromagnetic semimetals or semiconductors are needed for new, laterally-patterned spin electronic devices
- Meteoritic graphite is ferromagnetic; $m \sim 0.05\ \mu_B$/carbon; $T_c \sim$ 600 K. Magnetism may be due to spin-polarised charge-transfer at interfaces with magnetite or kamacite
- Evidence for contact-induced ferromagnetism for nanotubes on magnetite or cobalt, $m \sim 0.01\ \mu_B$/carbon.
- New field of carbon-based spin electronics ?

Thanks to the group www.tcd.ie/Physics/Magnetism and SFI