Aalto University
School of Science

PHYS-E0421 Solid State Physics Period V, spring 2019

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Dielectric Properties of Solids
Magnetism

Lecture 14, Monday 20.5.2019

Magnetic properties

- Response of materials to an external magnetic field
  - Magnetic quantities, magnetism is quantum mechanics (home work)
  - Quantum mechanical description
  - Atomic diamagnetism, paramagnetism (lecture work)
  - Response of free electron gas

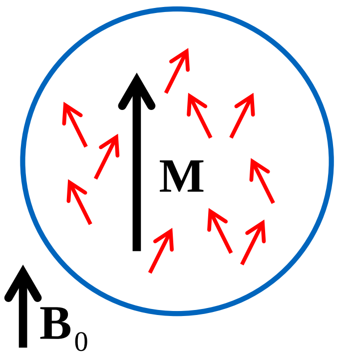
- Spontaneous magnetism (Ferromagnetism and antiferromagnetism)
  - Exchange interaction, H_2 molecule, Heisenberg spin Hamiltonian
  - Mean-field approximation for ferromagnetism of magnetic moments
  - Spin waves (low-energy excitations)
  - Free electron gas
  - Stoner model for ferromagnetism of itinerant electrons
  - Antiferromagnetism
  - Domain structure

The last lecture TODAY

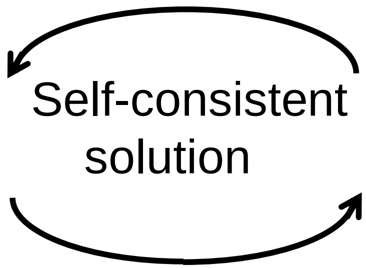
Ferromagnetism of Localized Moments, Summary

Mean-Field Theory

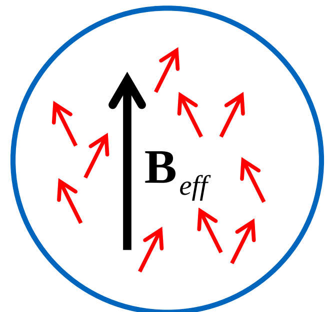
Ordered system of paramagnetic ions with magnetization **M** (?)

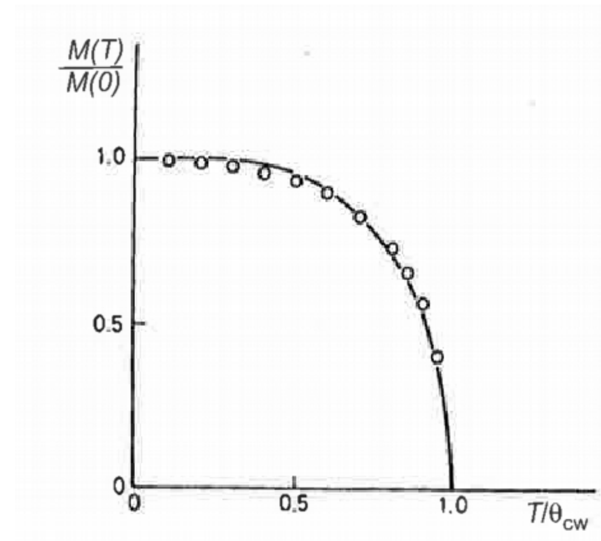


$$\mathbf{M} = \mathbf{M}_0(\mathbf{B}_{eff}, T)$$



Noninteracting gas of paramagnetic ions in field $\mathbf{B}_{eff}$





Exchange interaction

$$\mathbf{B}_{eff} = \underbrace{\frac{\nu J}{(g_J \mu_B)^2 n}}\mathbf{M} + \mathbf{B}_0$$

External field

$\theta_{CW} = \nu J / 4k_B$

Curie - Weiss temperature

$B_0 = 0$:

$T < \theta_{CW} \Rightarrow$ Ferromagnetism, $M > 0$

$T > \theta_{CW} \Rightarrow$ Paramagnetism, $M = 0$

M in different temperature regions:

$T << \theta_{CW}$: $M / M_{max} \approx 1 - 2\exp(-2\theta_{CW} / T)$

$T \approx< \theta_{CW}$: $M / M_{max} \approx \sqrt{3}(1 - T/\theta_{CW})^{1/2}$

$T > \theta_{CW}$: $\chi = \dfrac{C}{T - \theta_{CW}}$ Curie - Weiss law

Ferromagnetism of Localized Moments, Summary

Beyond the Mean-Field Theory, magnons

Mean field theory:

Excitations over the Stoner gap

$$\Rightarrow M / M_{\max} \approx 1 - 2\exp\left(-2\theta_{CW} / T\right)$$

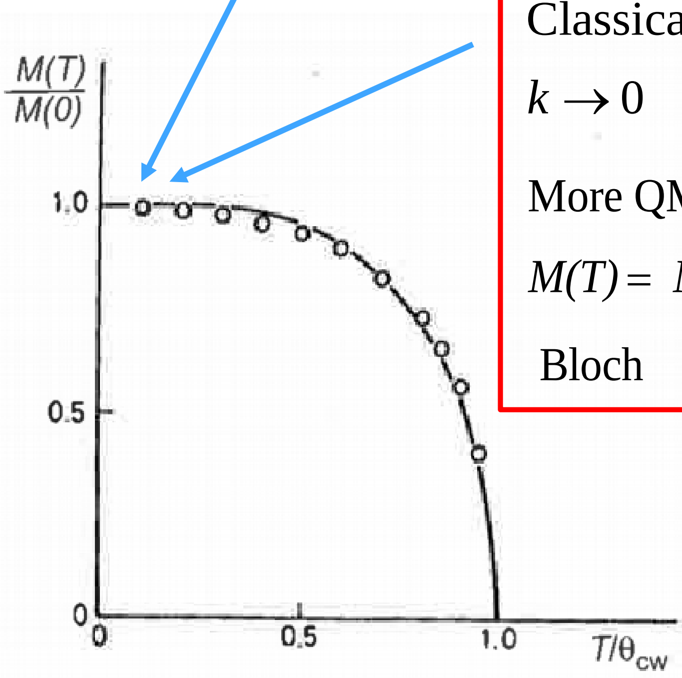
Classical & QM: Spin waves

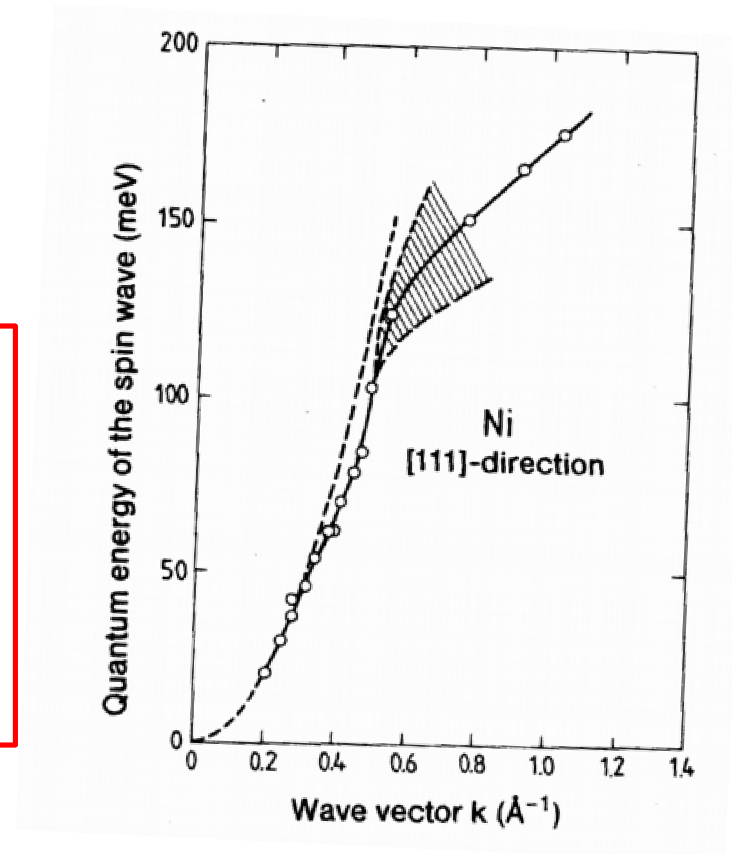
$$k \to 0 \quad \Rightarrow \quad \omega \propto k^2, \text{ no gap!}$$

More QM: B-E statistics

$$M(T) = M(0)\left(1 - \text{constant} \times T^{3/2}\right)$$

Bloch $T^{3/2}$-law, i.e., Experiment



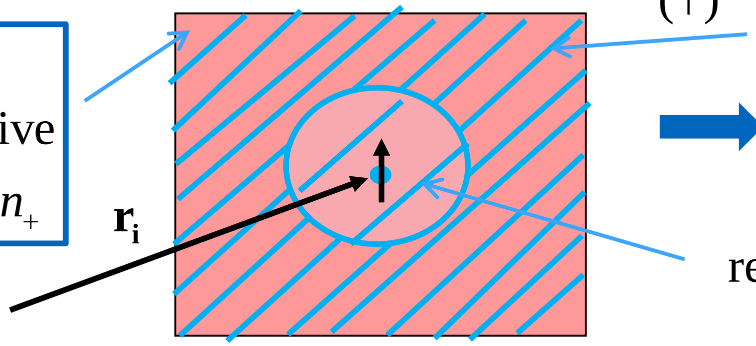


Ferromagnetism of Free Electron Gas

(Elliott pp. 607-608)

➔ Applying quantitative band theory

Ions $\rightarrow$ rigid homogeneous positive background charge n_+



(Infinite system)

➔ $J > 0 \Leftrightarrow$ Ferromagnetic coupling between electron spins

Spin triplet, antisymm. orbital w.f.

$$\Phi_T(1,2) = \phi_B(1)\phi_A(2) - \phi_A(1)\phi_B(2)$$

Cf. H_2

"Proof"

$$V(\mathbf{r}) \equiv 0, \text{ Plane waves } \varphi_i = \frac{1}{\sqrt{V}} \exp(i\mathbf{k}_i \bullet \mathbf{r}_i)$$

[E(7.211)]

$$\text{For a } \uparrow\uparrow\text{–system: } \Phi(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{\sqrt{2V}}\left[\exp(i\mathbf{k}_j \bullet \mathbf{r}_i)\exp(i\mathbf{k}_i \bullet \mathbf{r}_j) - \exp(i\mathbf{k}_i \bullet \mathbf{r}_i)\exp(i\mathbf{k}_j \bullet \mathbf{r}_j)\right]$$

$$\text{Probability density: } |\Phi|^2 d\mathbf{r}_i d\mathbf{r}_j = \frac{1}{V}\{1 - \cos[(\mathbf{k}_i - \mathbf{k}_j)\bullet(\mathbf{r}_i - \mathbf{r}_j)]\} d\mathbf{r}_i d\mathbf{r}_j \rightarrow 0, \text{ when } \mathbf{r}_i \rightarrow \mathbf{r}_j$$

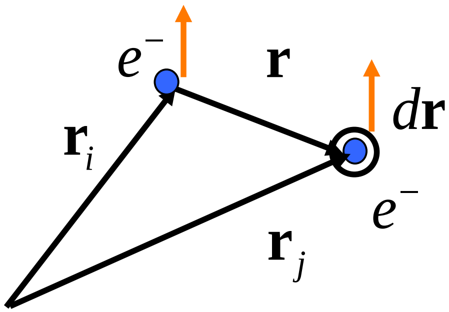
[E(7.212)]

➔ Non-perfect screening of pos. background charge n_+ around a $\uparrow$ electron ➔ Attractive electron - n_+ interaction favouring spin alignment ➔ $J > 0$

q.e.d.

Exchange Hole

Central quantity in electron structure theories



A pair of electrons → Total electron density around a given electron *i*

Fix the origin at the electron at $\mathbf{r}_i$

Probability for another spin-up electron inside *d***r** at **r**

$$P_{\uparrow\uparrow}(r)d\mathbf{r} \propto n_\uparrow d\mathbf{r}\left\{1-\cos\left[\left(\mathbf{k}_i-\mathbf{k}_j\right)\bullet\mathbf{r}\right]\right\}_{\text{ave}}$$

[~E(7.213)]

Insert

$$\left(\frac{3}{4\pi k_F^3}\right)^2\int d\mathbf{k}_i\int d\mathbf{k}_j$$

← Average over $\mathbf{k}_i$ and $\mathbf{k}_j$ inside Fermi spheres

Average densities

$$n_\uparrow=\frac{N_\uparrow}{V}\quad(\text{constant})$$

$$n=n_\uparrow+n_\downarrow$$

Total (spin up + spin down) electron charge density

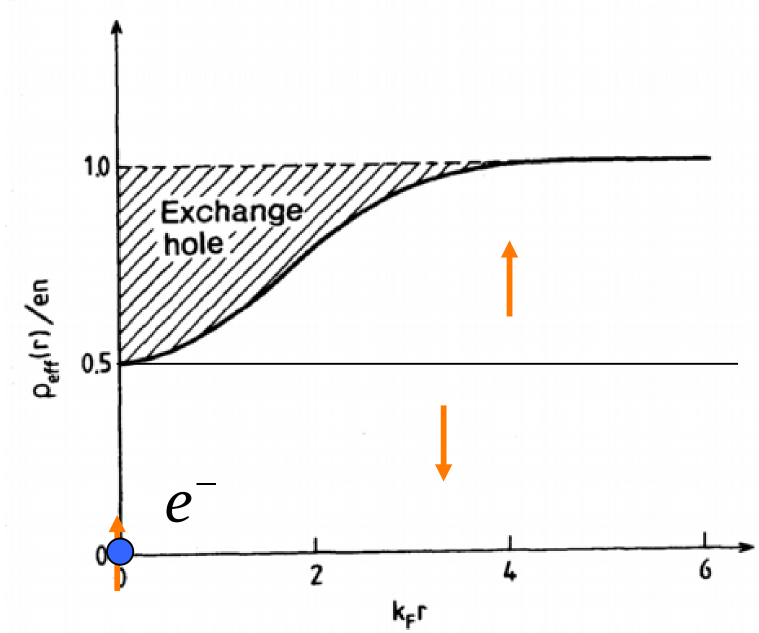
$$\rho_{eff}(r)=en\left[1-\frac{9}{2}\frac{\left[\sin(k_Fr)-k_Fr\cos(k_Fr)\right]^2}{(k_Fr)^6}\right]$$

[E(7.216)]

Oscillations

Fast decay

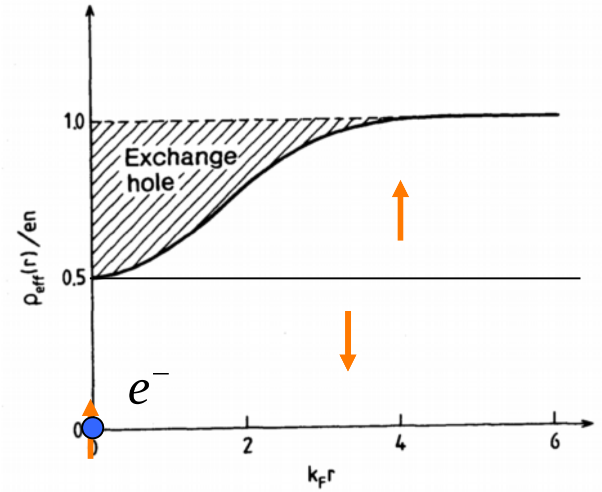
Electron density → length scale



Exchange Hole

Total (spin up + spin down) electron charge density

$$\rho_{eff}(r) = en\left[1 - \frac{9}{2}\frac{[\sin(k_F r) - k_F r\cos(k_F r)]^2}{(k_F r)^6}\right]$$ [E(7.216)]



Sum rule

$$\int d\mathbf{r}(en - \rho_{eff}(r)) = 1e$$

Exchange energy

$e^-(\mathbf{r}=0)$ – exchange-hole interaction

$$= -\frac{1}{4\pi\varepsilon_0}\int d\mathbf{r}\frac{e}{r}(en - \rho_{eff}(r)) < 0$$

Homogeneous electron gas

Hartree-Fock approximation:
Total energy = kinetic(+) + exchange(-) energies

See, Ashcroft-Mermin, Chapter 17 (HF fails for EG)

e^- - e^- repulsion more accurately → Additional correlation energy(-)

Quantum Monte Carlo

Atomistic systems

Density-functional theory (DFT)
Exchange-correlation functionals

→ First-principles electronic structure modeling

Ferromagnetism due to itinerant electrons
(Elliott 7.2.5.3)

➔ $J(\uparrow\uparrow)$ strong enough $\Rightarrow$ Ferromagnetism ?

Exchange interaction ➔ Heisenberg Hamiltonian

$$\hat{H} = \sum_{ij} (-J)\hat{\mathbf{S}}_i \bullet \hat{\mathbf{S}}_j$$

nearest neighbors

➔ Modeling magnetic *4f* and *3d* impurities

Free electrons
J > 0 (Ferromagnetic) ➔ STONER BAND MODEL ➔ Ferromagnetism of, e.g., bulk Fe, Co, and Ni

Stoner model

Exchange energy $E_x(n_\uparrow, n_\downarrow)$
added to $\uparrow$ and $\downarrow$ bands $E(\mathbf{k}_\uparrow)$, $E(\mathbf{k}_\downarrow)$

➔ Densities of states

$g_\uparrow(E)$, $g_\downarrow(E)$

➔ Spin-up and spin-down densities

$$n_\uparrow = \int_{-\infty}^{E_F} g_\uparrow(E)dE\ , \qquad n_\downarrow = \int_{-\infty}^{E_F} g_\downarrow(E)dE$$

➔ $E_x(n_\uparrow, n_\downarrow)$

➔ Self-consistent solution

Strong "Pauli paramagnetism" with an internal $\mathbf{B}_{eff}$

Stoner Band Model of Ferromagnetism

(Elliott 7.2.5.3)

Spin flips → Kinetic energy increases

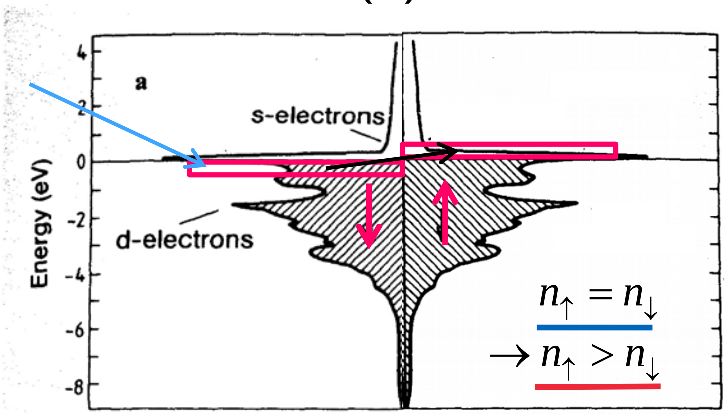
Flat d bands → High DOS(E_F) → Small energy increase for a large number of flips

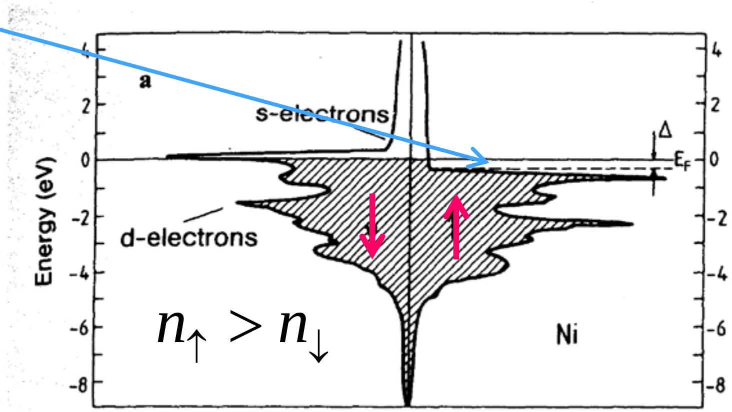
Exchange interaction lowers the energy levels of spin-up electrons

→ Stabilization of magnetic moment

$$n_\uparrow - n_\downarrow = \int_{-\infty}^{E_F} \left[g_\uparrow(E) - g_\downarrow(E) \right] dE$$

DOS(E), Ni





Magnetic moments / atom

→ Ni: $\mu_m = 0.56\ \mu_B$
Fe: $\mu_m = 2.2\ \mu_B$

- Itinerant electrons "decoupled" from ions → $\mu_m \neq$ integer x μ_B
- Quantitative materials parameters directly related to electron bands

Ferromagnetic materials

Table 1 Ferromagnetic crystals

Substance	Magnetization M_s, in gauss: Room temperature	0 K	μ_m n_B(0 K), per formula unit	Curie temperature, in K
Fe	1707	1740	2.22	1043
Co	1400	1446	1.72	1388
Ni	485	510	0.606	627
Gd	—	2060	7.63	292
Dy	—	2920	10.2	88
MnAs	670	870	3.4	318
MnBi	620	680	3.52	630
MnSb	710	—	3.5	587
CrO_2	515	—	2.03	386
$MnOFe_2O_3$	410	—	5.0	573
$FeOFe_2O_3$	480	—	4.1	858
$NiOFe_2O_3$	270	—	2.4	(858)
$CuOFe_2O_3$	135	—	1.3	728
$MgOFe_2O_3$	110	—	1.1	713
EuO	—	1920	6.8	69
$Y_3Fe_5O_{12}$	130	200	5.0	560

Kittel

Stoner Band Model of Ferromagnetism

➔ Quantitative criterion for existence of ferromagnetism

Exchange interaction ➡ Lowering of bands is the stronger, the more there are electrons with the same spin

k-independent shifts for bands

➡
$$E_\uparrow(\mathbf{k}) = E(\mathbf{k}) - I_S n_\uparrow$$
$$E_\downarrow(\mathbf{k}) = E(\mathbf{k}) - I_S n_\downarrow$$

[E(7.239)]

$n_\uparrow$ = # of $\uparrow$-electrons/atom

$n_\downarrow$ = # of $\downarrow$-electrons/atom

Stoner parameter (I_S)
← Strength of exchange interaction

Excess of $\uparrow$ -electrons/atom: $\Delta n = n_\uparrow - n_\downarrow$

Common energy reference

Splitting of bands $= I_S \Delta n$

➡
$$\begin{cases} E_\uparrow(\mathbf{k}) = \overbrace{E(\mathbf{k}) - I_S\left(n_\uparrow + n_\downarrow\right)/2}^{\tilde{E}(\mathbf{k})} + \overbrace{I_S\left(n_\uparrow + n_\downarrow\right)/2 - I_S n_\uparrow}^{-I_S \Delta n/2} = \tilde{E}(\mathbf{k}) - I_S \Delta n/2 \\ E_\downarrow(\mathbf{k}) = \tilde{E}(\mathbf{k}) + I_S \Delta n/2 \end{cases}$$

[~E(7.240)]

Stoner criterion of ferromagnetism

Fermi-Dirac statistics ➔ Occupation of spin-up and spin-down bands ➔ Δn

Total spin-degenerate DOS

(c.f. Theory of Pauli paramagnetism)

$$\Delta n = \frac{V}{N}\int_{-\infty}^{\infty} d\tilde{E}\,\frac{1}{2}g(\tilde{E})\left[f\left(\tilde{E}-\frac{I_S\Delta n}{2}\right)-f\left(\tilde{E}+\frac{I_S\Delta n}{2}\right)\right] \approx \frac{V}{N}\int d\tilde{E}\,\frac{1}{2}g(\tilde{E})\left[-\underbrace{\frac{df}{d\tilde{E}}}_{\sim -\delta(\tilde{E}-E_F)} I_S\Delta n - \frac{1}{24}\underbrace{\frac{d^3 f}{d\tilde{E}^3}}_{>0}(I_S\Delta n)^3\right]$$

spin-up spin-down

$T \to 0$:

$$1 = \frac{I_S V}{2N} g(E_F) - \frac{V}{24N}(\Delta n)^2 I_S^3 \overbrace{\int d\tilde{E}\,\frac{1}{2}g(\tilde{E})\frac{d^3 f}{d\tilde{E}^3}}^{>0}$$

[~E(7.243, 245)]

Spin-compensated calculation

$$\bar{g}(E_F) = \frac{\#\text{ of states at } E_F \text{ (excluding spin degen.)}}{dE\ \ \text{atom}}$$

Ferromagnetic (real) $\Delta n \neq 0$ solution, if $\underbrace{I_S \frac{V}{2N} g(E_F)}$ $-1 > 0$

Stoner criterion

$$I_S\bar{g}(E_F) > 1 \quad \Rightarrow \quad \text{Ferromagnetism}$$

[E(7.246)]

Δn is not calculated!
The criterion tells, is the spin-compensated solution stable!

Stoner Criterion

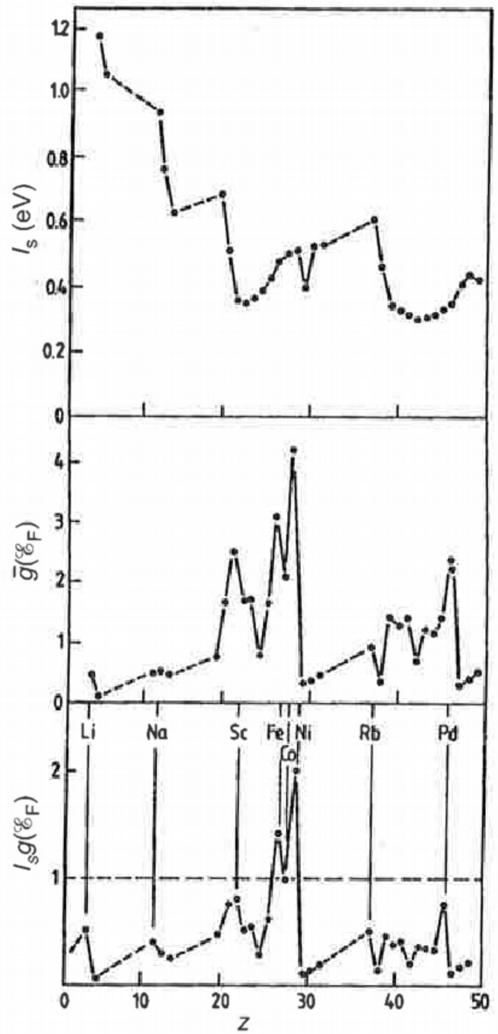
$$I_S \bar{g}(E_F) > 1 \;\Rightarrow\; \text{Ferromagnetism}$$

Obtained from spin-compensated band structure calculation

Obtained from atomic orbitals

High $\bar{g}(E_F)$ for Fe, Co, Ni
(open 3d-band,
BCC, HCP, FCC)

➡ Ferromagnetism



SUMMARY :
spin flips
$\Rightarrow$ 1) kinetic (band) energy $\uparrow$,
but only little for flat bands,
i.e., when $\bar{g}(E_F)$ is large!
2) exchange energy $\downarrow$

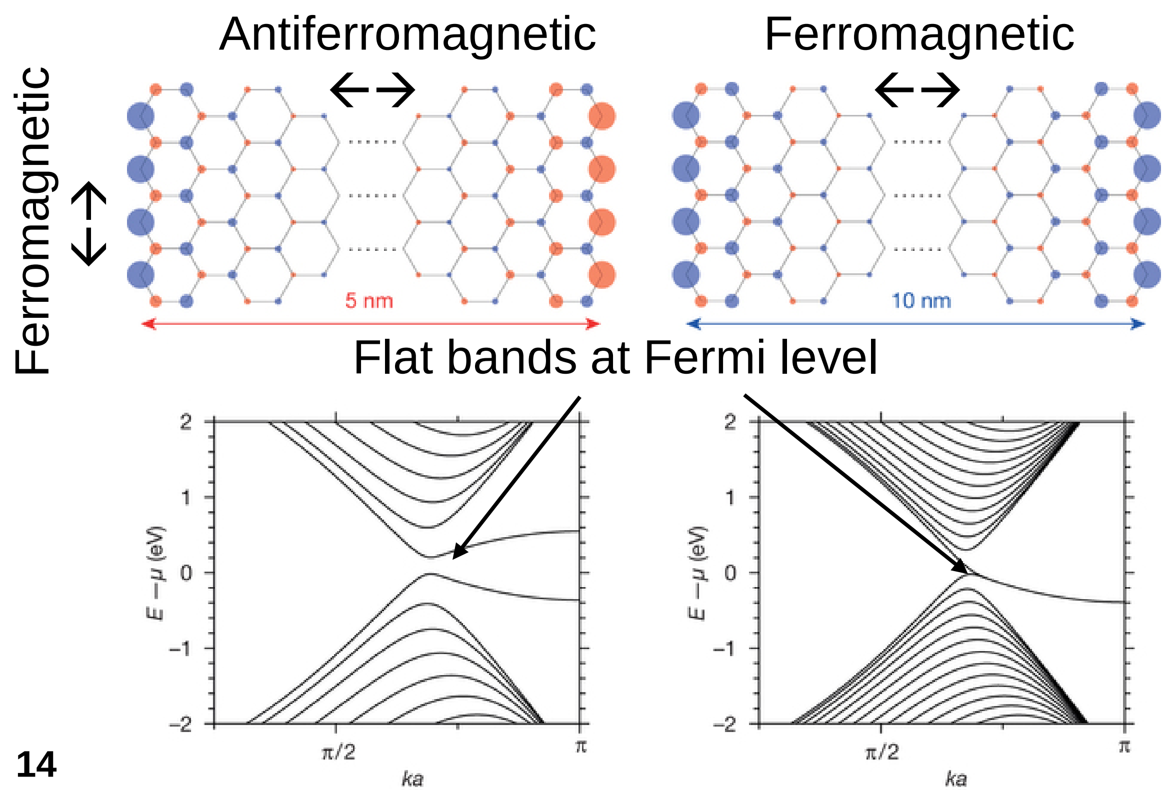
Stoner criterion fulfilled due to electron confinement

$$I_S \bar{g}(E_F) > 1 \;\Rightarrow\; \text{Ferromagnetism}$$

Electron confinement → Flat $E(\mathbf{k})$ bands, Large DOS(E_F) → Magnetism

Examples

1) Pd surfaces (2D)
2) Atomic chains (1D)
3) Zigzag graphene nanoribbons (Nature **514**, 608 (2014))



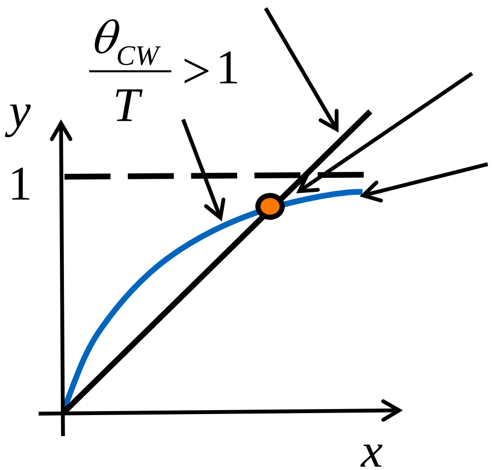
Stoner Model, Temperature Dependence of Magnetization

Mean field theory, $B_0 = 0$

$$\underbrace{\frac{M}{M_{max}}}_{x} = \tanh\left(\frac{\theta_{CW}}{T}\underbrace{\frac{M}{M_{max}}}_{x}\right) = y(x)$$

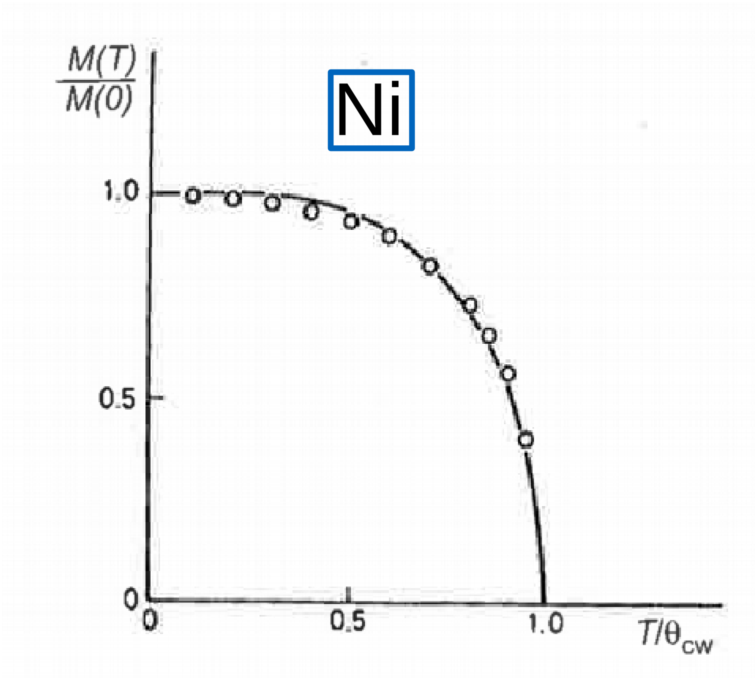
$y = x$

$\frac{\theta_{CW}}{T} > 1$



Spontaneous magnetization $M \neq 0$

$$y = \tanh\left(\frac{\theta_{CW}}{T}x\right)$$



Are mean field theory and Stoner model related? Can we find the same equation to be solved self-consistently?

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Stoner Model, Temperature Dependence of Magnetization

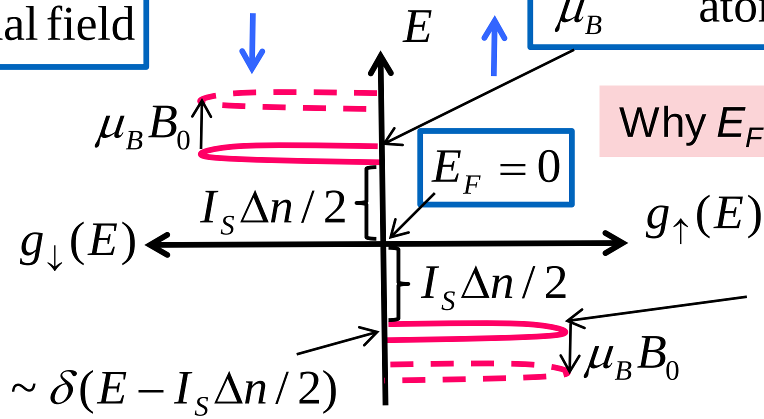
(Elliott pp. 618-619)

Simplified picture around E_F

States furher below E_F in balance

B_0 = external field

$\frac{\mu_B^{eff}}{\mu_B}\ \frac{e^-\ \text{states}}{\text{atom}}$, empty at $T=0$



Why E_F=0?

μ_B^{eff} = max. magnetic moment / atom

$\frac{\mu_B^{eff}}{\mu_B}\ \frac{e^-\ \text{states}}{\text{atom}}$, occupied at $T=0$

Two-level model in FD-statistics ($E_F = 0$), $T > 0$

Why still E_F=0?

[E(7.249)]

$$\Delta n = n_\uparrow - n_\downarrow = \frac{\mu_B^{eff}}{\mu_B}\left[\frac{1}{\exp[(-\mu_B B_0 - I_S\Delta n/2)/k_BT]+1} - \frac{1}{\exp[(\mu_B B_0 + I_S\Delta n/2)/k_BT]+1}\right]$$

$B_0 = 0$ $\quad M = \mu_B \Delta n N/V \quad M_{max} = \mu_B^{eff} N/V$

$$\frac{1}{\exp(-x)+1} - \frac{1}{\exp(x)+1} = \tanh(x/2)$$

$$M = M_{max}\tanh\left(\frac{I_S\Delta n}{4k_BT}\right) = M_{max}\tanh\left(\frac{I_S\mu_B^{eff}}{4k_B\mu_B}\frac{1}{T}\frac{\mu_B\Delta n N/V}{\mu_B^{eff}N/V}\right)$$

$$\frac{I_S\mu_B^{eff}}{4k_B\mu_B} = \theta_{CW}$$

$$M = M_{max}\tanh\left(\frac{\theta_{CW}}{T}\frac{M}{M_{max}}\right)$$

[E(7.250)]

Stoner Model, Temperature Dependence of Magnetization

$B_0 = 0$

$$M = M_{max} \tanh\left(\frac{\theta_{CW}}{T}\frac{M}{M_{max}}\right)$$

As in the mean-field model, but
Mf-model: total S of an ion ➔ M
Stoner model: Δn/atom ➔ M

$T < \theta_{CW}$

$M(T) \neq 0$

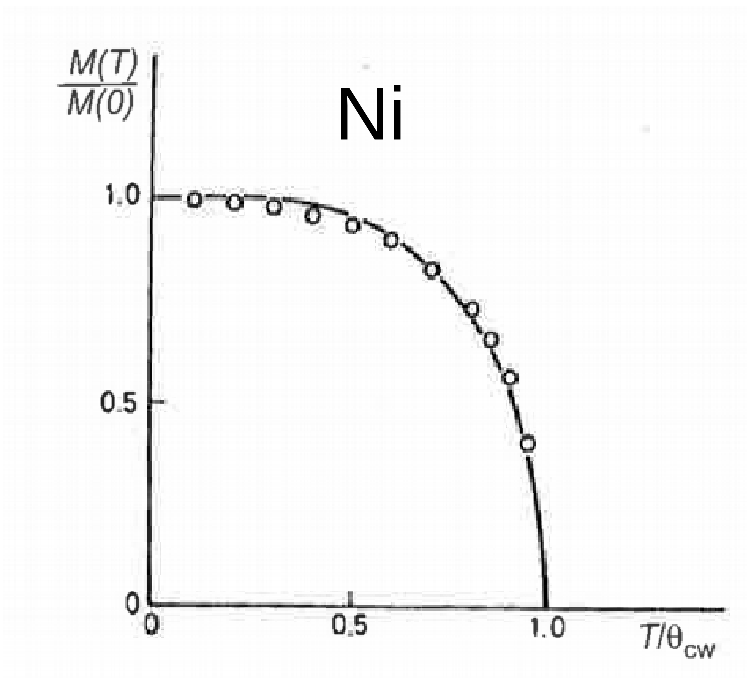
$T << \theta_{CW}$ and $T \approx \theta_{CW}$ limits

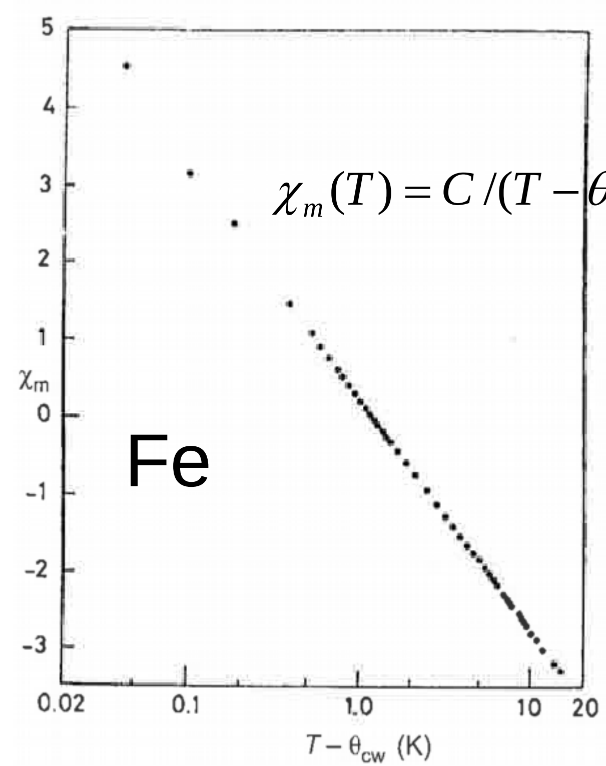
$T > \theta_{CW}$

$\mathbf{B_0} = 0 \rightarrow M = 0$

$\mathbf{B_0} \neq 0 \rightarrow M \neq 0, \quad \chi_m(T) = C/(T - \theta_{CW})$

Comparison with experiments:





$$\chi_m(T) = C/(T - \theta_{CW})^{1.33}$$

Antiferromagnetism and ferrimagnetism

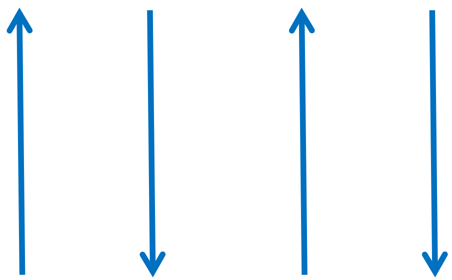
(Elliott 7.2.5.6)

➔ Microscopic origin

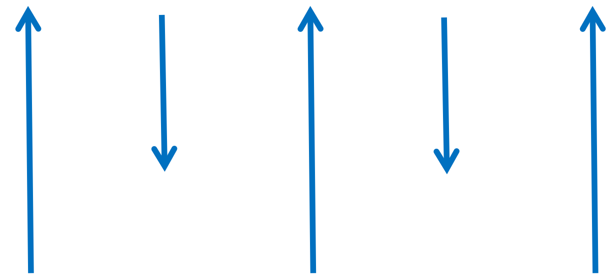
E.g. superexchange →

Exchange parameter $J_{ij} < 0$

Antiferromagnetism $\mathbf{M} = 0$



Ferrimagnetism $\mathbf{M} \neq 0$



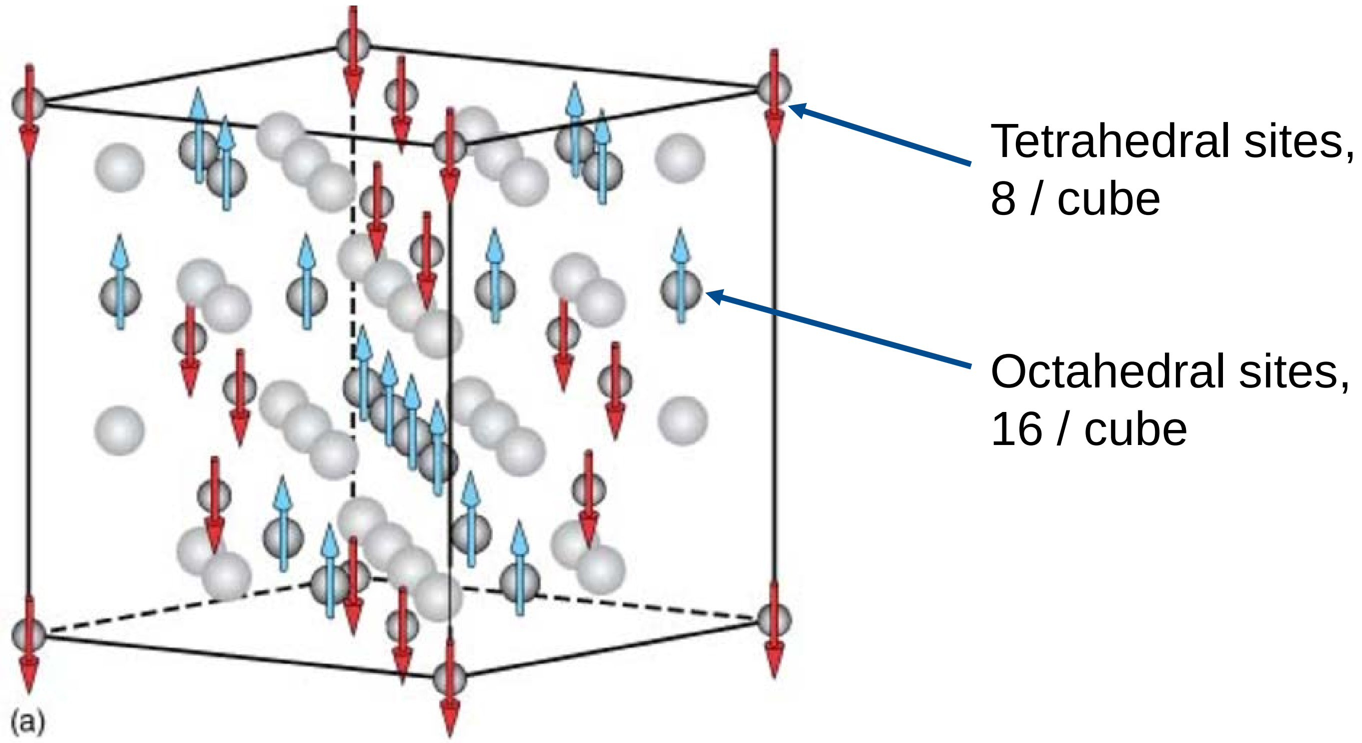
Examples, Mn, Fe, Co, and Ni –oxides
- band model → metals
- electron-electron correlations (Hubbard model) → insulator, antiferromagnet

Examples, Ferrites (metal oxides)
Intertwined ionic and electronic structures:
- Cubic unit cell with metal atoms in 8 tetrahedral (A) and 16 octahedral (B) sites
- E.g., Magnetite (lodestone) $FeO\ Fe_2O_3$ mixed valence system (Fe^{2+}, Fe^{3+})

Ferrimagnetism and antiferromagnetism

➔ Microscopic origin

Example: Ferrimagnetic magnetite (lodestone) FeO Fe_2O_3



https://www.researchgate.net/publication/227992376_Spin_Structures_and_Spin_Wave_Excitations

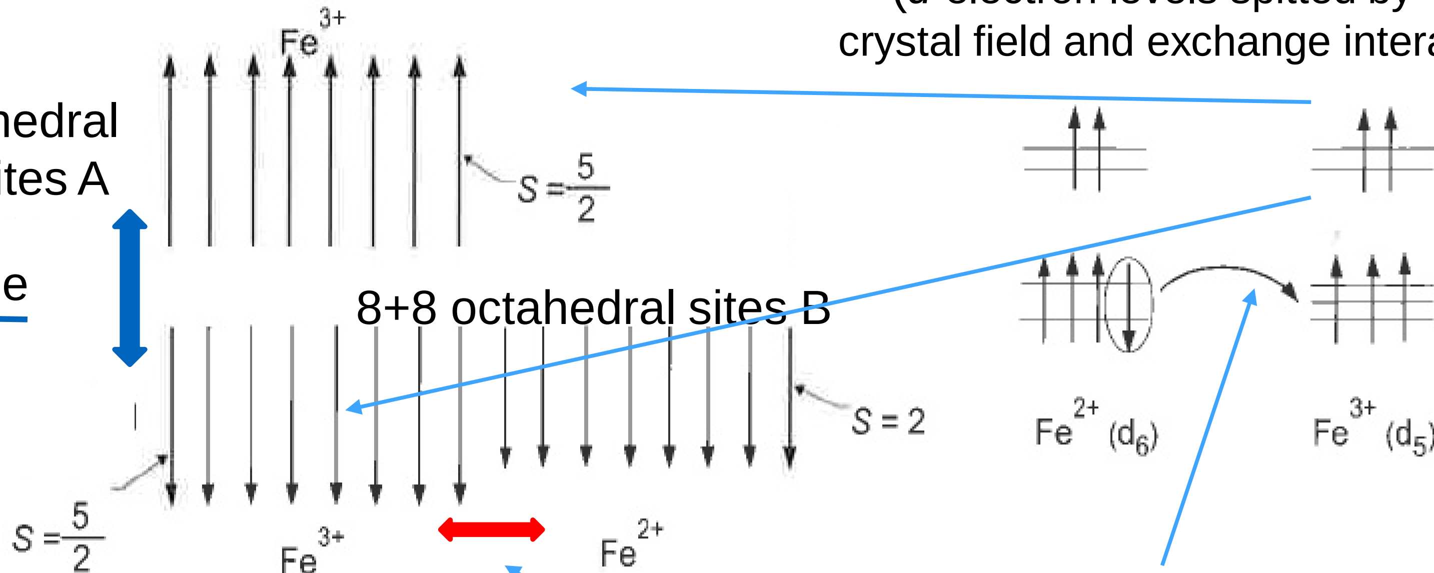
Ferrimagnetism and antiferromagnetism

➔ Microscopic origin

Example: Ferrimagnetic magnetite (lodestone) $FeO\ Fe_2O_3$

(*d*-electron levels spitted by crystal field and exchange interaction)

8 tetrahedral sites A



8+8 octahedral sites B

Superexchange via O-ions
→Antiferro-magnetism

Double Exchange:
Electron transfer and Pauli principle
→ Ferromagnetism

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Antiferromagnetism

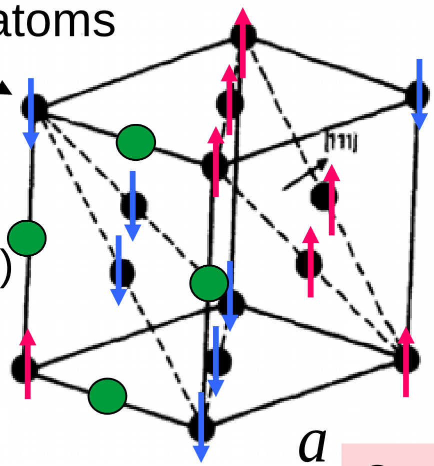
Example: (Hubbard) insulators Mn, Fe, Co, and Ni –oxides
NaCl –structure, two interpenetrating FCC’s

➔”Frustration”, neutron diffraction

Metal atoms

O atoms

(fill in more)



Magnetic structure

Adjacent (111) planes with opposite spins

Frustration

↑↑ and ↑↓ nearest-neighbor interactions

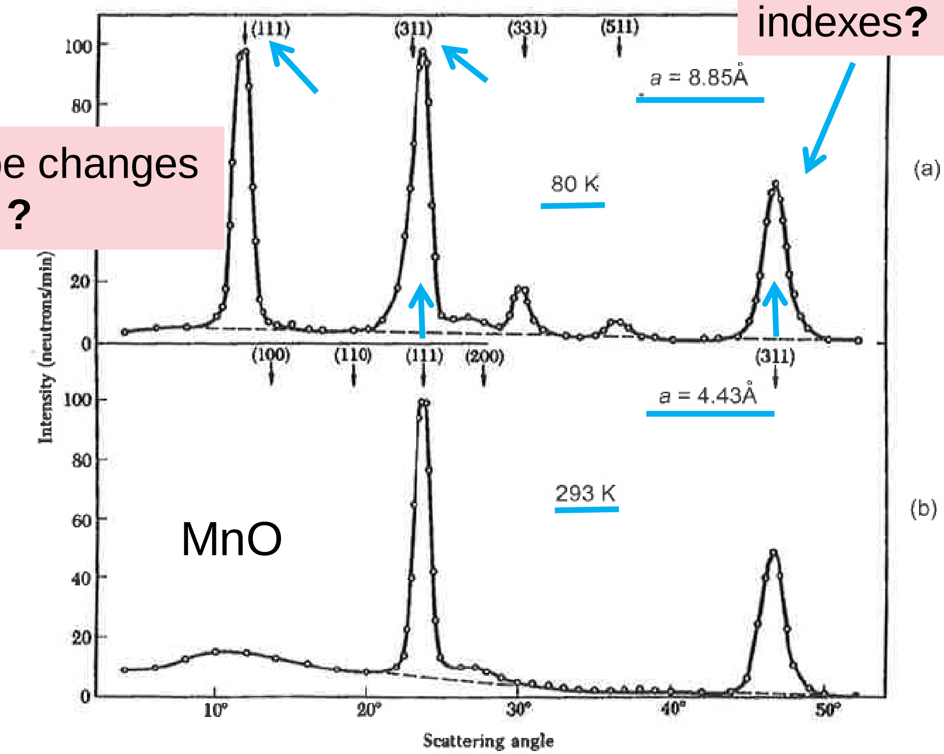
Lattice constant = $2a$

Neutron diffraction

"Extra" peaks

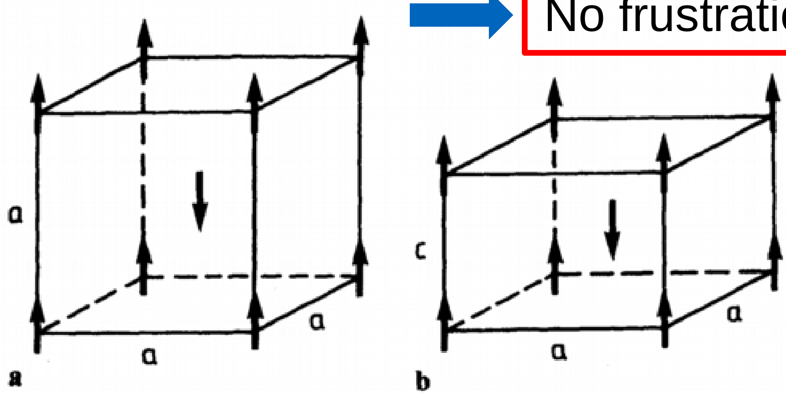
indexes?

Compare peak shape changes at ~23º and ~47º ➔ ?



Monatomic BCC, SC structures

No frustration



Antiferromagnetism

➔ Susceptibility above and below critical temperature, Mean field theory

Two sublattices A (↑) and B (↓)

$$\mathbf{B}_{eff}^{A} = \mathbf{B}_0 - \mu_0 \lambda_N \mathbf{M}_B$$
$$\mathbf{B}_{eff}^{B} = \mathbf{B}_0 - \mu_0 \lambda_N \mathbf{M}_A$$

$\lambda_N \propto J_{ij},\ \nu$

[E(7.279)]

$\mathbf{B}_0 = 0,\ T < \theta_N$ Néel temperature

$$\mathbf{M}_A \neq 0$$
$$\mathbf{M}_B \neq 0, \quad \mathbf{M} = \mathbf{M}_A + \mathbf{M}_B = 0$$

Susceptibility

$$\chi_m(T) = \mu_0 \frac{dM}{dB_0}$$

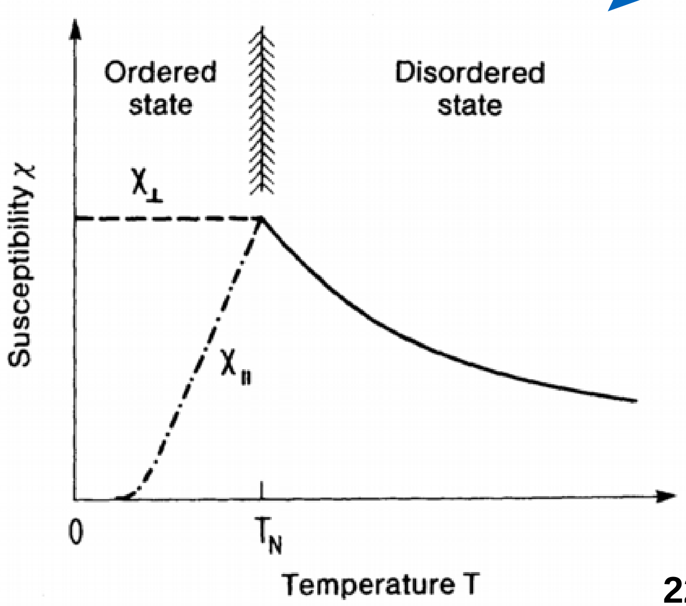
$$\mathbf{M} = \mathbf{M}_A + \mathbf{M}_B$$

$T > \theta_N$

$$\chi_m(T) = \frac{C}{T + \theta_N}$$

No divergence

[E(7.284)]



$T < \theta_N, \quad \mathbf{B}_0 \perp \boldsymbol{\mu}_i$

Easy to cant slightly $\boldsymbol{\mu}_i$'s ➔ $\chi_\perp \approx \text{constant}$

$T < \theta_N, \quad \mathbf{B}_0 \parallel \boldsymbol{\mu}_i$

A spin has to flip, excitation over a gap ➔ $\chi_\parallel \propto \exp(-2\theta_N / T)$

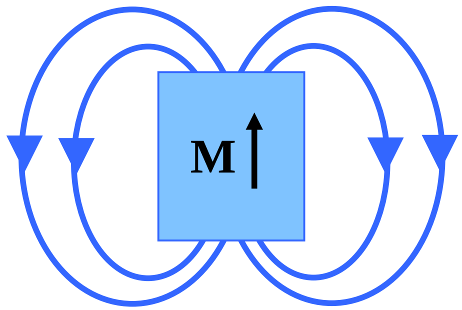
Ferromagnetic Domains, why do they exist?

(Elliott 7.2.5.5)

Macroscopic ferromagnetic samples at $T < T_c$ often "nonmagnetic" $\mathbf{M} = 0$ ← Domain structure

No domains

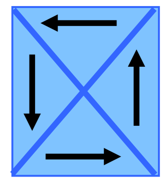
B



Energy density of magnetic field

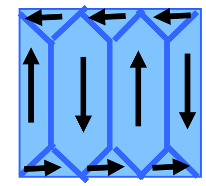
$$U_M = \frac{B^2}{2\mu_0}$$

$U_M \neq 0$ also outside a single domain



Outside

$\mathbf{B} = 0$ → $U_M \to 0$



Small → and ← domains

→ Small elastic energy

Magnetostriction

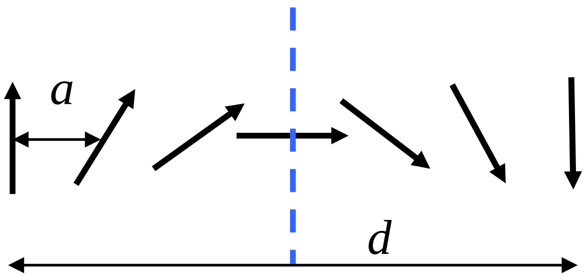
Expansion/contraction || $\mathbf{M}$

Large domains

→ Increase of elastic strain energy

Ferromagnetic Domains, Domain Walls

Magnetic moments misaligned over domain interfaces → Exchange energy ↑



180° Bloch walls between domains

Gradual canting of magnetic moments → Exchange energy ↓

cf. spin waves

Bloch wall thickness *d*= ?

Magnetocrystalline anisotropy

Existence of easy-magnetization directions ← Nonspherical components of electron density around nuclei

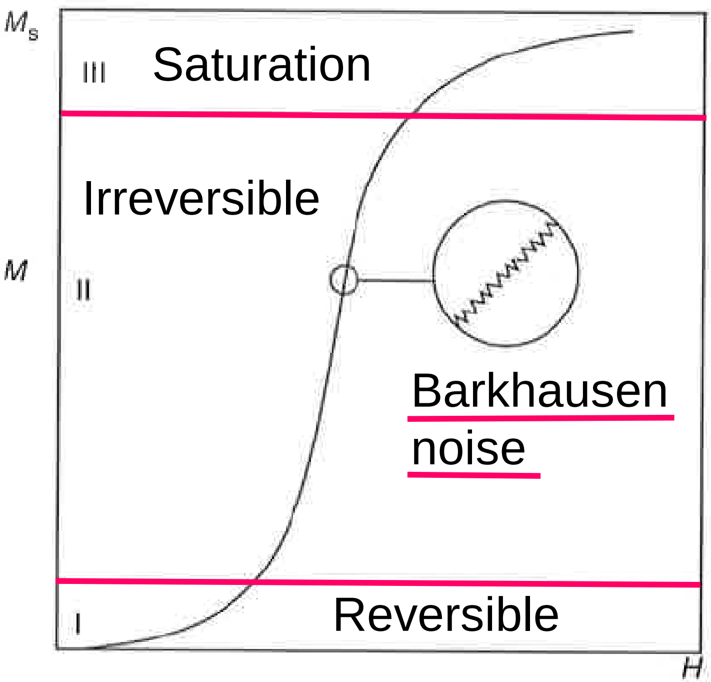
E.g. <100> in bcc-Fe, c-axis in hcp-Co, and <111> in fcc-Ni

→ $E_{anisotropy}$ ↑ when d ↑

$E_x + E_{anisotropy}$ minimized → Finite $d \approx 100\ a$

Ferromagnet in an External Field H, $T < \theta_{CW}$

Initial magnetization curve



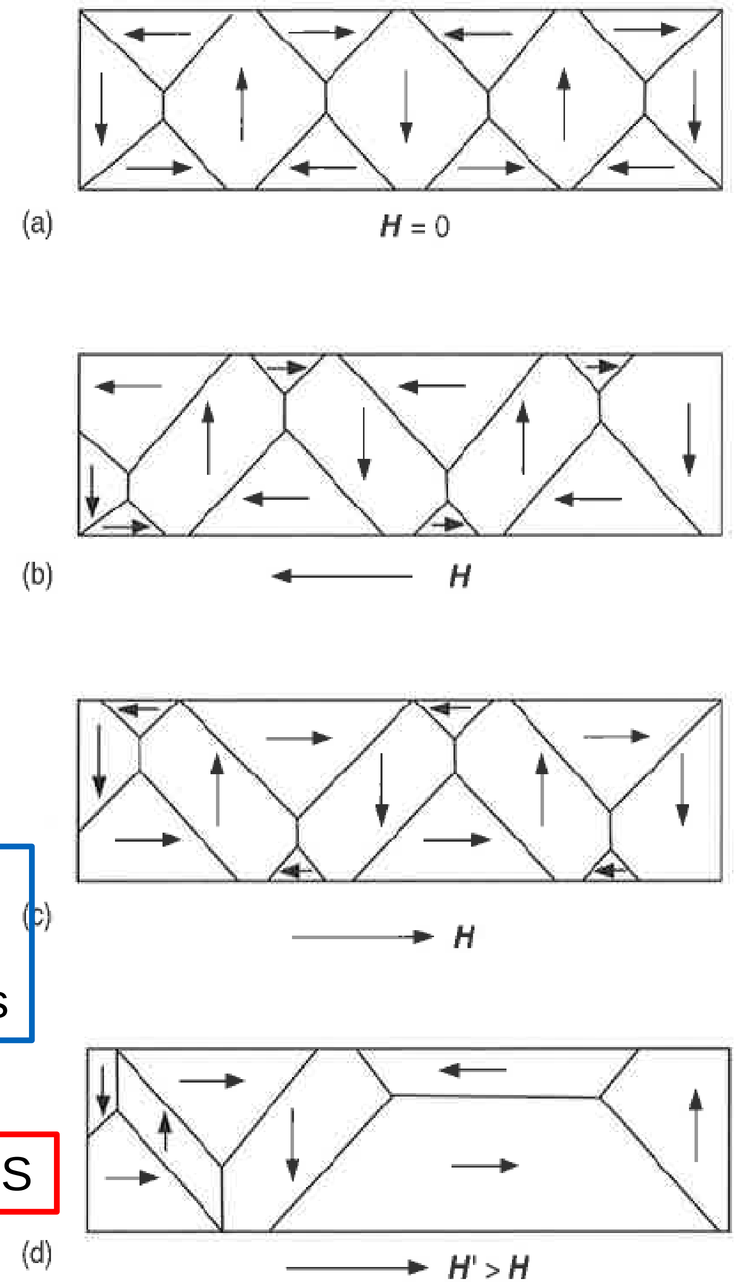
Bloch walls sticked when crossing material inhomogenities

→ Barkhausen jumps

M || **H** ∦ easy direction

→ Resistance of saturation

Reversible movement of domain walls



Irreversible disappearence of domain walls

→ HYSTERESIS

Ferromagnet in an External Field H, $T < \theta_{CW}$, Hysteresis

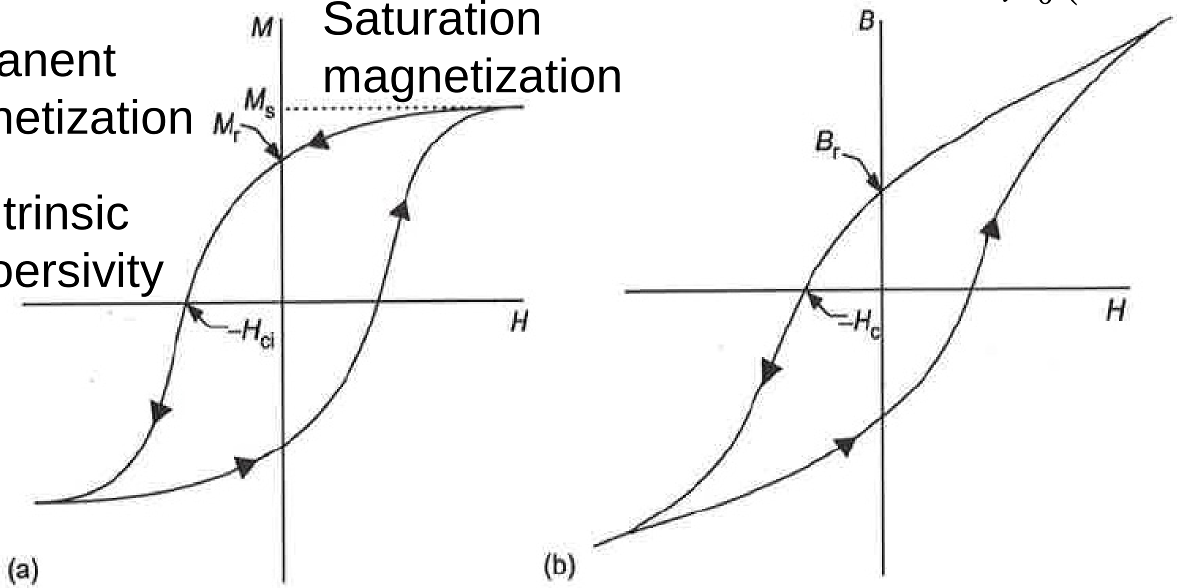
← Irreversible processes

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M})$$

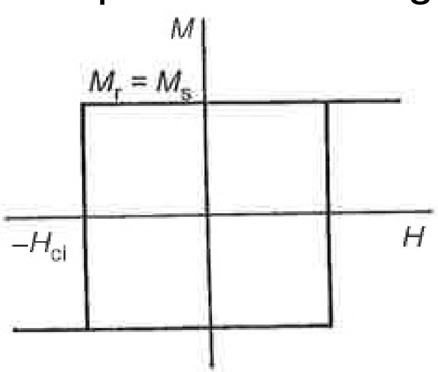
Remanent magnetization

Saturation magnetization

Intrinsic coersivity



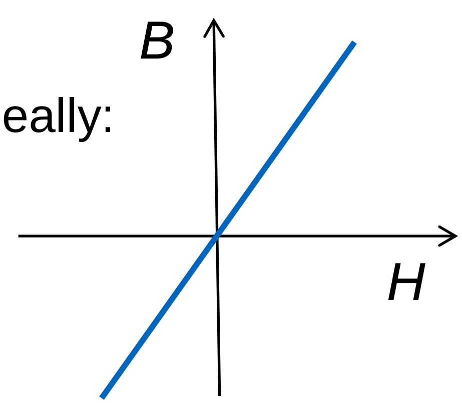
Ideal permanent magnet



Inhomogeneous material
➔ Pinning of domain walls

Transformer cores

Ideally:



Homogeneous materials
➔ Freely moving domain walls

Lamellar structure, high resistivity
➔ Eddy current losses ↓

Magnetic properties

- Response of materials to an external magnetic field
  - Magnetic quantities, magnetism is quantum mechanics (home work)
  - Quantum mechanical description
  - Atomic diamagnetism, paramagnetism (lecture work)
  - Response of free electron gas

- Spontaneous magnetism (Ferromagnetism and antiferromagnetism)
  - Exchange interaction, H_2 molecule
  - Mean-field approximation for ferromagnetism of magnetic moments
  - Spin waves (low-energy excitations)
  - Free electron gas
  - Stoner model for ferromagnetism of itinerant electrons
  - Antiferromagnetism
  - Domain structure