MTLE-6120: Advanced Electronic Properties of Materials

Magnetic properties of materials

Reading:

- Kasap: 8.1 - 8.8

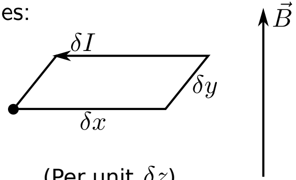
Materials in magnetic fields

- Charges circulate around magnetic field due to force $q\vec{v} \times \vec{B}$
- Magnetic dipole moment of infinitesimal current loop (per unit δz)

$$\begin{aligned}\delta\vec{\mu} &= \frac{1}{2}\oint \vec{r} \times \vec{\mathrm{d}l}\,\delta I \\ &= \frac{1}{2}\left(0 + \delta x \delta y \hat{z} \delta I + \delta y \delta x \hat{z} \delta I + 0\right) \\ &= \delta x \delta y \hat{z} \delta I\end{aligned}$$

- Magnetization is density of induced magnetic dipoles:

$$\vec{M} = \frac{\delta \mu}{\delta x \delta y} = \hat{z} \delta I$$



(Per unit δz)

Angular momentum and magnetic moments

- Classical charges circulating in magnetic fields
- Angular momentum $L = mvr$
- Current $I = \frac{qv}{2\pi r}$
- Magnetic moment $\mu = \frac{1}{2}\oint \vec{r} \times \mathrm{d}\vec{l} I = qvr/2$
- Classical particle $\mu = \frac{q}{2m} L$
- Exactly true for orbital angular momentum

  $$\mu_z = \frac{-e}{2m} m_l \hbar = -m_l \mu_B$$

  where $\mu_B \equiv \frac{e\hbar}{2m}$ is the Bohr magneton
- Similarly for spin:

  $$\mu_z = -g_e m_s \mu_B$$

  where $g_e \approx 2.0023 = 2 + \frac{e^2}{4\pi\epsilon_0 hc} + \cdots$ is called the gyromagnetic ratio
- Both components produce and interact with magnetic fields the same way
- $\vec{M}$ is the total density of orbital and spin magnetic moments

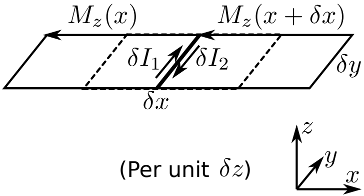
Bound current density due to magnetization

- Current within dotted element (per unit δz)

$$\delta I_y = \delta I_1 - \delta I_2$$

- Corresponding current density:

$$j_y = \frac{I_y}{\delta x} = \frac{\delta I_1 - \delta I_2}{\delta x} = \frac{M_z(x) - M_z(x+\delta x)}{\delta x} = -\frac{\partial M_z}{\partial x}$$



- Generalizing to all directions:

$$\vec{j}_b = \nabla \times \vec{M}$$

Constitutive relations

- Material determines how $\vec{P}$ (and hence $\vec{D}$) depends on $\vec{E}$
- Material determines how $\vec{M}$ (and hence $\vec{H}$) depends on $\vec{B}$
- Simplest case: linear isotropic dielectric

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} \qquad \vec{H} = \frac{\vec{B}}{\mu_0} - \vec{M}$$

$$\vec{P} = \chi_e \epsilon_0 \vec{E} \qquad \vec{M} = \chi_m \vec{H}$$

$$\vec{D} = (1 + \chi_e)\epsilon_0 \vec{E} \qquad \vec{B} = (1 + \chi_m)\mu_0 \vec{H}$$

$$\epsilon = (1 + \chi_e)\epsilon_0 \qquad \mu = (1 + \chi_m)\mu_0$$

- Anisotropic magnetism: $\vec{M} = \bar{\chi}_m \cdot \vec{H}$ (magnetic susceptibility tensor)
- Nonlinear magnetism: $\vec{M} = \chi_m(H)\vec{H}$ (field-dependent susceptibility)
- Hysterisis: $\vec{M} = \chi_m(\{H(t)\})\vec{H}$ (history-dependent susceptibility)

Types of magnetic materials

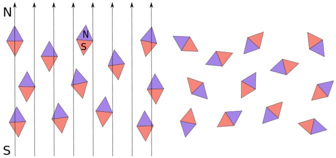
- Distinguish based on magnetic susceptibility χ_m and zero-field magnetization $\vec{M}_0$
  - Diamagnetic: $\chi_m < 0$ and small, $\vec{M}_0 = 0$ (closed shell, insulators)
  - Paramagnetic: $\chi_m > 0$ and small, $\vec{M}_0 = 0$ (open shell, metals)
  - Ferromagnetism: $\chi_m \gg 1$, $\vec{M}_0 \neq 0$ (certain metals)
  - Antiferromagnetism: $\chi_m > 0$ and small, $\vec{M}_0 = 0$ (insulators)
  - Ferrimagnetism: $\chi_m \gg 1$, $\vec{M}_0 \neq 0$ (insulators)
- Bohr-van Leeuwen theorem:
  Classical statistical mechanics of charged particles $\Rightarrow \vec{M} = 0$
- *All* magnetism is quantum mechanical despite our picture of current loops
- In fact, can mostly ignore orbital component; it's all spin!

Diamagnetism

$\chi_m < 0, |\chi_m| \ll 1$

- Magnetic moment in field: torque $\vec{T} = \vec{\mu} \times \vec{B}$
- Angular momentum $\vec{L} = \vec{\mu}\frac{2m}{gq}$
- But $\vec{T} = \mathrm{d}\vec{L}/\mathrm{d}t \Rightarrow$ rotation with $\omega = \frac{gqB}{2m}$ (Larmor precession)
- Corresponding current $\delta I = \frac{q\omega}{2\pi} = \frac{gq^2}{4\pi m}B$
- Induced magnetic moment $\delta\mu = \delta I \cdot \pi r^2 = \frac{gq^2 r^2}{4m}B$ (loop radius r)
- Therefore, $\chi_m = -\mu_0 n \frac{gq^2 r^2}{12m}$ (direction opposite to B, average over x, y, z)
- Typical values $n \sim 0.1$Å^{-3}, $r \sim 1$Å $\Rightarrow \chi_m \sim -6 \times 10^{-6}$
- Example: for Si, $\chi_m = -5.2 \times 10^{-6}$
- Temperature-independent diamagnetic response present in all materials!

Paramagnetism: gases and liquids



$\chi_m > 0, |\chi_m| \ll 1$

- Closed-shell molecule: every orbital has $\uparrow\downarrow$; no net spin, $\mu = 0$
- Open-shell molecule: some unpaired $\uparrow$ / $\downarrow$; can have net spin, $\mu \neq 0$
- With no applied field, $\vec{\mu}$ in random directions $\Rightarrow M = 0$
- With field, energy of one magnetic dipole is $-\mu \cdot \vec{B}$
- Therefore, magnetic susceptibility is:

$$\chi_m = \mu_0 N \frac{\mu^2}{k_B T} \frac{x \coth x - 1}{x^2} \qquad \text{where } x \equiv \frac{\mu B}{k_B T}$$

- $\mu B \ll k_B T$ for practical magnetic fields, so $\chi_m = \frac{\mu_0 N \mu^2}{3 k_B T}$
- Typical values $N \sim 0.01\text{Å}^{-3}$, $\mu \sim \mu_B \sim 10^{-23}$ J/T $\Rightarrow \chi_m \sim +10^{-4}$
- Unpaired spins $\Rightarrow$ paramagnetism typically dominates over diamagnetism
- Paramagnetic response (Type B) decreases with increasing temperature

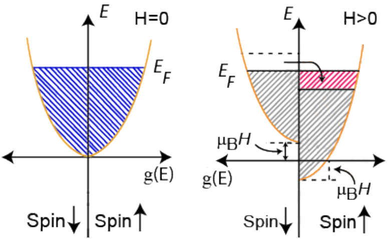
Paramagnetism: metals

$$\chi_m > 0, |\chi_m| \ll 1$$

- Magnetic field changes energy of $\uparrow$ vs $\downarrow$ by $2\frac{g\mu_B}{2}B \approx 2\mu_B B$
- Fermi level same for both spins (equilibrium)
- Spin imbalance $n_\uparrow - n_\downarrow = \frac{g(E_F)}{2} \cdot 2\mu_B B$
- Magnetization $M = (n_\uparrow - n_\downarrow)\frac{g\mu_B}{2} = \mu_B^2 g(E_F)B$
- Therefore susceptibility

$$\chi_m = \mu_0 \mu_B^2 g(E_F)$$

- Typical value eg. in Al, $\chi_m \approx 2 \times 10^{-5}$
- Temperature independent (Type A)
- For Cu, Ag, Au, $\chi_m < 0$: why?



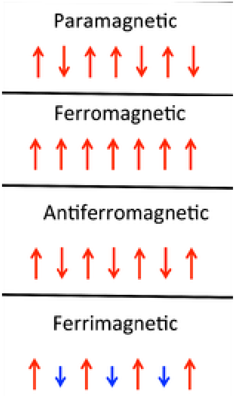
Hund's rule and exchange interaction

- So far, treated spins independently. How would spins interact?
- Due to their magnetic field i.e. dipole-dipole: typically weak
- Consider filling up electrons in degenerate p_x, p_y, p_z orbitals
- One electron: $\uparrow, 0, 0$
- Two electrons: $\uparrow, \uparrow, 0$ or $\uparrow\downarrow, 0, 0$?
- Two electrons in p_x repel more than p_x with p_y
- Hund's rule of maximum multiplicity: prefer parallel spins
- Exchange interaction between spins $-2J\vec{S_1} \cdot \vec{S_2}$
- Very sensitive to distance and can flip sign! (Kasap Figure 8.20)
- Next: materials with strong exchange interactions between adjacent atoms
- If N spins response to magnetic field together, then $\chi_m \propto \mu_B g(E_F)$ increases by N (because effective $\mu \propto N$ and effective $g \propto 1/N$)
- Other possibility: symmetry breaking and phase transitions!

Ferro-, antiferro- and ferri-magnetism

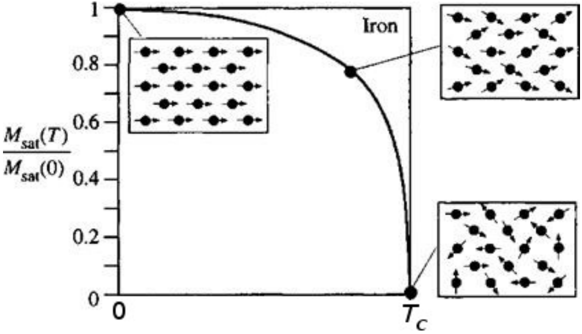
- J wants to align (or anti-align) neighbouring spins
- Entropy (T) wants to randomize them
- $T > T_c$: entropy wins, paramagnet with $\chi_m \propto \frac{\mu^2}{T}$
- $T < T_c$: J wins, three ordering possibilities:

1. $J > 0$: parallel spins $\Rightarrow M \neq 0$, ferromagnet (eg. Fe, Co, Ni)
2. $J < 0$: anti-parallel spins $\Rightarrow M = 0$, antiferromagnet (many oxides)
3. $J < 0$: anti-parallel dissimilar spins $\Rightarrow M \neq 0$, ferrimagnet (eg. ferrite Fe_3O_4)



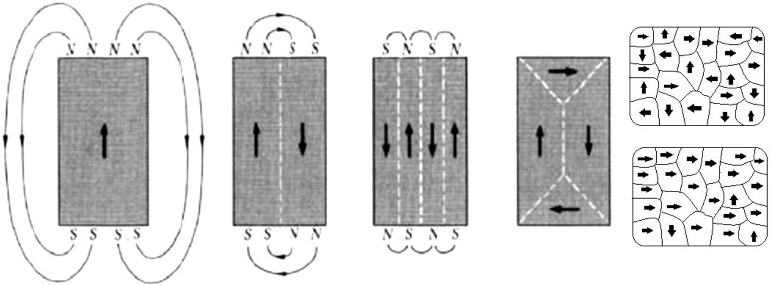
T_c = Curie temperature for ferromagnets and Neel temperature for antiferro/ferrimagnets

Saturation magnetization



- At $T = 0$, all spins aligned, maximum magnetization $M_{\text{sat}}(0)$
- Increasing T, spins randomized $\Rightarrow$ reduces $M_{\text{sat}}(T)$
- Spontaneous magnetization vanishes at $T = T_c$ $\Rightarrow$ paramagnet

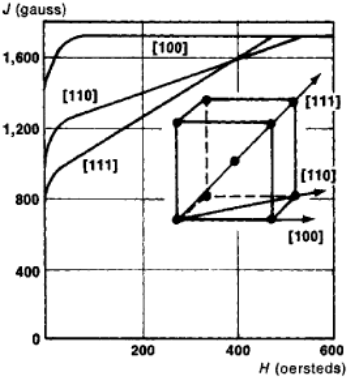
Magnetic domains



- Spins align locally in domains
- Spins misaligned along domain walls
- Energy cost (and entropy gain) per area of domain wall
- Gain: reduction in magnetic energy $\int \frac{B^2}{2\mu}$ reduced
- Random domains: unmagnetized state $(M = 0, B = 0)$
- Magnetized state: domains aligned which costs magentic energy
- Will magnetization disappear automatically?
- Not necessarily: barrier to domain rotation

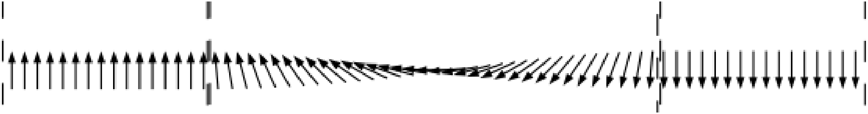
Rensselaer

Magneto-crystalline anisotropy



- Exchange interaction anisotropic, so M has preferred directions
- eg. In Fe, strong J along (100) directions: easy axis
- Weaker J along (111) directions: hard axis
- Domains tend to snap to easy axes, barrier to rotate through hard axes
- Difference in energies: magnetocrystalline anisotropy energy K

Domain walls



- Thick domain wall: slow change in spin
- Favorable for minimizing exchange interactions
- With thickness δ, energy cost $U_{\text{exchange}} \propto \delta^{-1}$ $(\approx \frac{\pi^2 E_{\text{ex}}}{2a\delta})$
- Thin domain wall: rapid change in spin
- Favorbale for minimizing magnetization along non-easy axes
- With thickness δ, energy cost $U_{\text{anisotropy}} \propto \delta$ $(\approx K\delta)$
- Total energy $U_{\text{wall}} = U_{\text{exchange}} + U_{\text{anisotropy}} \approx \frac{\pi^2 E_{\text{ex}}}{2a\delta} + K\delta$
- Energy minimized for optimal thickness $\delta = \sqrt{\frac{\pi^2 E_{\text{ex}}}{2aK}}$
- Corresponding minimum energy $U_{\text{wall}} = \sqrt{\frac{\pi^2 E_{\text{ex}} K}{2a}}$
- For iron, $E_{\text{ex}} = k_B T_c \approx 0.1$ eV, $a \approx 3$ Å and $K \approx 50$ kJ/m^3
  $\Rightarrow \delta \approx 70$ nm and $U_{\text{wall}} \approx 7 \times 10^{-3}$ J/m^2

Crystal grains vs magnetic domains

- Domain wall thickness sets typical magnetic domain size
- Therefore, two regimes in polycrystalline materials:

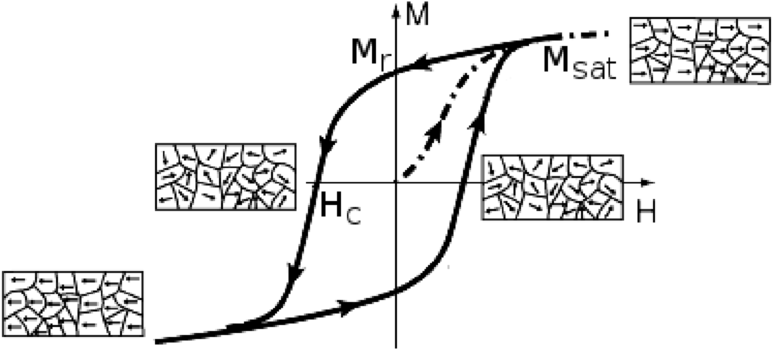
1. Grain size smaller than domain wall thickness
   - Single magnetic domain per grain
   - Adjacent domains have different easy / hard directions
2. Grain size larger than domain wall thickness
   - Many magnetic domains per grain
   - Adjacent domains within grain have same anisotropy
   - Anisotropy directions change along grain boundaries

- Grain-size distribution: combination of grains in both regimes

Magnetostriction

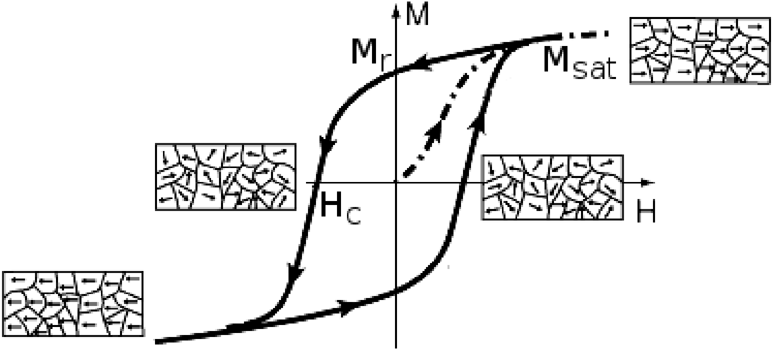
- Bond lengths along and perpendicular to spin differ
- Consequence: spin polarization produces anisotropic strain
- Magnetostrictive strain λ: value along magnetization
- Iron $\lambda > 0$ while nickel $\lambda < 0$
- Couples oscillating magnetic fields to mechanical oscillations $\Rightarrow$ losses
- Iron-nickel alloys reduce electrostriction with cancelling contributions
- Transverse strain typically opposite sign (volume conservation)
- High fields: overall compression (minimizes field energy)
- Analogous effect in dielectrics: electrostriction
- How is this different from piezo-electricity?

Magnetization to saturation



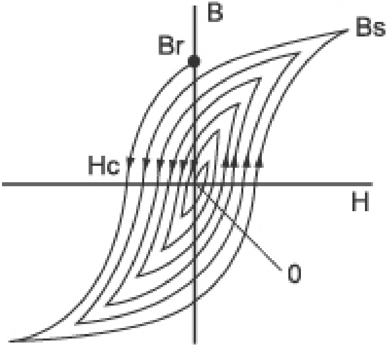
- Increase field: domains align to field
- Reversible: smooth domain wall motion within grains
- Irreversible: domain walls pinned by defects, and broken free
- Barkhausen effect / noise: magnetization increases in jumps (magnitude of jumps span several orders of magnitude $\Rightarrow$ noise)
- Domain wall motion till grains align along easy axis closest to field
- Beyond that, field overcomes K so as to align M to H in each grain $\Rightarrow M_{\mathrm{sat}}$ saturation magentization

Reversing magnetization



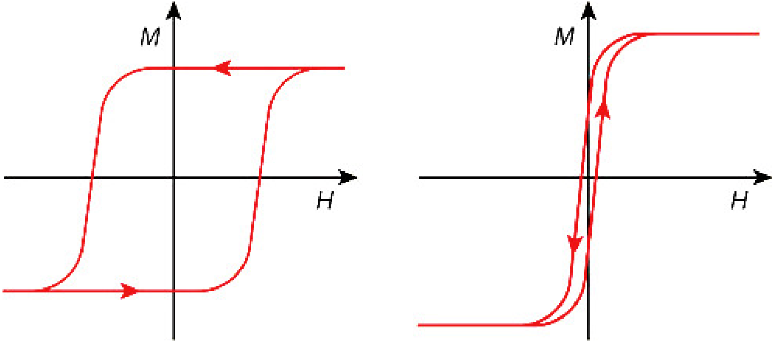
- Reduce field: domains return to easy axis
- But domains along easy axis closest to field direction
- Residual magnetization M_r at zero field
- Apply reverse magnetic field to randomize domains
- Coercive field strength H_c zeros magnetic field
- Subsequent cycles follow outer loop
- Energy loss per cycle = area inside M-H curve

Magentization patterns



- Smaller M-H (or B-H) loops for smaller driving fields
- Lower peak magnetization, but lower losses per cycle
- Arbitrary pattern of H: trajectory stays within full-saturation loop
- To restore M to zero, spiral in by reducing ocsillations of H

Hard vs. soft magnetic materials



- Hard materials: large H_c and M_r
- Useful for permanent magnets which need high M_r and B_r
- Metal alloys like alnico (0.9 T), SmCo (1.1 T) and NdFe (1.2 T)
- Soft materials: low H_c and M_r (still high μ)
- Can cycle magnetic field with lower energy loss
- Useful for transformers and electromagnets
- Pure metals, metallic glasses, certain alloys and ferrites