FERRIMAGNETS

- Show spontaneous magnetization below some critical temperature, $T_c$ (like ferromagnets) BUT

\[ M \quad \text{Fe} \quad \text{Typical ferrimagnet} \quad \text{Typical ferrimagnet} \quad \frac{1}{X} \]

\[ T_c \quad T \]

Néel\(^*\) explained the $T$-dependence of $M + X$ using the Weiss theory + assuming \textit{antiparallel} coupling between magnetic moments of different magnitude.

\[ \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \]

**Molecular Field Theory**

- Works well (ionic compounds)

**Simplest Case:**

\[
\begin{align*}
(A - A) \\ (B - B) \\ (A - B)
\end{align*}
\]

\(\{\text{interactions}\}\)

\(n\) magnetic ions per unit volume

\(\alpha = \text{fraction of} \ A\)

\(\beta = \text{fraction of} \ B\) \((= 1 - \alpha)\)

\(M_A = \text{moment of one} \ A\) atom \(\uparrow\) in direction of field @ temp. \(T\).

\(M_B = \text{moment of one} \ B\) atom \(\uparrow\) below \(T_c\).

**Then:**

Magnetization of \(A\) sublattice = \(M_A = \alpha n M_A\)

Magnetization of \(B\) sublattice = \(M_B = \beta n M_B\)

Total magnetization, \(M = M_A + M_B = \alpha n M_A + \beta n M_B\)

**Molecular field on \(A\) sublattice is**

\[
H_{\text{WA}} = -\gamma_{AB} M_B + \gamma_{AA} M_A
\]

**Molecular field on \(B\) sublattice is**

\[
H_{\text{WB}} = -\gamma_{AB} M_A + \gamma_{BB} M_B
\]

Assuming:

\[
\begin{align*}
\uparrow & \uparrow \uparrow \uparrow \\
A & A & B & B & A & B
\end{align*}
\]
Above \( T_c \) - as for AFMs, assume Curie law behavior for each sublattice

\[ \chi = \frac{M}{H} = \frac{C}{T} \Rightarrow M = \frac{HC}{T} \]

so \[ M_A = \frac{C}{T} (H + Hw^A) \]
\[ M_B = \frac{C}{T} (H + Hw^B) \]

solve for \( M = M_A + M_B \) and take \( \chi = \frac{M}{H} \)

\[ \frac{1}{\chi} = \frac{T + \frac{C}{\chi_0}}{C} - \frac{b}{T - \Theta} \]

\[ \frac{1}{\chi_0} = \gamma_{AB} \left( 2 \lambda \beta - \frac{\gamma_{AA} \chi^2}{\gamma_{AB}} - \frac{\gamma_{BB} \beta^2}{\gamma_{AB}} \right) \]
\[ b = \gamma_{AB}^2 C \lambda \beta \left[ \chi \left( 1 + \frac{\gamma_{AA}}{\gamma_{AB}} \right) - \beta \left( 1 + \frac{\gamma_{BB}}{\gamma_{AB}} \right) \right]^2 \]
\[ \Theta = \gamma_{AB} C \lambda \beta \left( 2 + \frac{\gamma_{AA}}{\gamma_{AB}} + \frac{\gamma_{BB}}{\gamma_{AB}} \right) \]

What does this look like?
\[ \frac{1}{\chi} = \frac{T + \frac{c}{\chi_0}}{C} - \frac{b}{T - \Theta} \]  

Fig. 6.6 Theoretical variation of the reciprocal susceptibility with temperature for a ferrimagnetic above the Curie point.

Equation (6.23) represents a hyperbola, and the physically meaningful part of it is plotted in Fig. 6.6. It cuts the temperature axis at \( \theta_p \), called the paramagnetic Curie point. At high temperatures the last term of Eq. (6.23) becomes negligible, and the equation reduces to a Curie-Weiss law:

\[ \chi = \frac{C}{T + (C/\chi_0)} \]

This is the equation of a straight line, shown dashed in Fig. 6.6, to which the \((1/\chi)\), T curve becomes asymptotic at high temperatures.
Real data:

Fig. 6.7 Reciprocal susceptibility of Mg ferrite. (Here $\chi_m$ refers to a half molecule of the ferrite, i.e. to one mol of Fe$^{2+}$.) Experimental data by Serres [6.6]; curve from constants given by Néel [6.1].

A. Serres "Recherches sur les moments atomiques," Annales de Physique 17, 5 (1932)

- Good agreement except near Curie point
- $O_f =$ ferrimagnetic Curie point, where $X \rightarrow \infty$
  + Spontaneous magnetization appears
- $O_f \neq O_p$ because of short range magnetic order which persist for a few degrees above $T_c$
Below Tc

- Each sublattice spontaneously magnetized.
- Net observable magnetization,
  \[ M = |M_A| - |M_B| \]
- Each sublattice has the Brillouin function magnetization curve (just like a FM), with \( H \) the molecular field acting on the sublattice.

\[ M_A^s = N m B(J, \frac{m H_{wA}}{kT}) \]
\[ M_B^s = N m B(J, \frac{m H_{wB}}{kT}) \]

Substituting for \( H_{wA} \) and \( H_{wB} \) gives

\[ M_A^s = N m B(J, \frac{m \left[ g_A M_A - g_B M_B \right]}{kT}) \]
\[ M_B^s = N m B(J, \frac{m \left[ g_B M_B - g_A M_A \right]}{kT}) \]

\( \to \) NOT INDEPENDENT \( \Rightarrow \) can't do single graphical solution.

- Magnetization of A sublattice depends on magnetization of B sublattice \( \& \) vice versa.
Typical solution:

![Diagram](image)

Fig. 6.8 Spontaneous magnetizations of the A and B sublattices, and the resultant $M_e$ (schematic).

Both sublattices must have the same Curie point, otherwise at some temperature one of the lattices would have zero moment, $\mathbf{M}$ would not be able to align the moments on the other sublattice.

Shape of curves depend on $T_{AA}$, $T_{BB}$, $T_{AB}$, on distribution of ions - can be quite unusual!
Some Unusual Ferrimagnetic Magnetization Curves

- $M_s$ increases with $T$, and goes through a maximum before falling to zero.
- $|M_{0^A}|$ decreases less rapidly with increasing temperature than $|M_0^0|$.
- e.g. NiO, Cr$_2$O$_3$

- $M_s$ decreases to zero below $T_c$, then the material develops a $M_s$ in the opposite direction.
- The two sublattices are exactly balanced at the compensation point.
- e.g. Li$_{0.5}$Fe$_{1.25}$Cr$_{1.25}$O$_4$
FIG. 1. Schematic illustration of mixed ferroferrimagnets composed of \((\text{Ni}^{II}_6\text{Mn}^{II}_6\text{Fe}^{II}_c)_{1.5}[\text{Cr}^{III}(\text{CN})_6] \cdot 2\text{H}_2\text{O}\). Zeolitic water molecules in the unit cell are omitted for clarity. The ferromagnetic \((J_{\text{NiCr}} > 0\) and \(J_{\text{FeCr}} > 0\)) and antiferromagnetic \((J_{\text{MnCr}} < 0\) superexchange interactions can coexist without spin frustration, because the \(A^{II}\) \((A = \text{Ni, Mn, or Fe})\) \((\circ)\) and \(\text{Cr}^{III}\) \((\bullet)\) ions of the Prussian blue structure are linked in an alternating fashion.
FIG. 2. Calculated temperature dependence curves for each sublattice and total magnetization for $(\text{Ni}^{11}_0\text{Mn}^{11}_0\text{Fe}^{11}_0)_1.5[\text{Cr}^{11}(\text{CN})_6] \cdot n\text{H}_2\text{O}$, based on molecular field theory, with four sublattice sites (Ni, Mn, Fe, Cr), with $J$ coefficients $J_{\text{NiCr}} = +5.6 \text{ cm}^{-1}$, $J_{\text{FeCr}} = +0.9 \text{ cm}^{-1}$, and $J_{\text{MnCr}} = -2.5 \text{ cm}^{-1}$: (a) sublattice magnetization ($M_{\text{Mn}}$, $M_{\text{Ni}}$, $M_{\text{Fe}}$, $M_{\text{Cr}}$); and (b) total magnetization ($M_{\text{total}}$).
FIG. 3. Experimental magnetization vs temperature curves for \((\text{Ni}^{\text{II}}_{0.22}\text{Mn}^{\text{II}}_{0.60}\text{Fe}^{\text{II}}_{0.18})_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6]\cdot 7.6\text{H}_2\text{O}\): (■) field-cooled magnetization obtained with decreasing temperature (80 K → 2 K) in an external magnetic field of 10 G; (○) remanent magnetization obtained with increasing temperature (2 K → 80 K) after the temperature was first lowered in the applied magnetic field of 10 G.
An Example - the cubic ferrites

\[ \text{Mn}_2 \text{O}_3 \]

- a divalent ion, eg. Mn\(^{2+}\), Ni\(^{2+}\), Fe\(^{2+}\), Co\(^{2+}\), Mg\(^{2+}\)
- most are magnetically soft
- lodestone contains magnetite,
  \[ \text{Fe}_3\text{O}_4 = \text{FeO} \cdot \text{Fe}_2\text{O}_3 \]
- manufactured using ceramic techniques
  eg. powdered NiO and Fe\(_2\)O\(_3\) are mixed, pressed into shape, then heated
- insulators: ac field does not induce eddy currents \(\rightarrow\) high frequency application
- spinel structure (named after \(\text{MgO} \cdot \text{Al}_2\text{O}_3\))
  oxygen anions packed in fcc arrangement
cations occupy spaces

\(2\) kinds of "spaces" \(\rightarrow\) A \(\oplus\) B sublattices

(not all the spaces are occupied)
Fig. 9-3.1. The unit cell of the spinel lattice. The large spheres represent oxygen ions, the small light spheres in tetrahedral ($A$) sites and the small dark spheres in octahedral ($B$) sites. For only two octants are the positions of all the ions shown. The other octants have one or the other of these two structures and are arranged so that no two adjacent octants have the same configuration. [Adapted from E. W. Gorter, *Philips Res. Rept.* 9, 295 (1954).]

Only the inverse spinels are ferrimagnetic:

Normal Spinel: $\text{M}^{2+}$ in $A$ sites ([4]) is a non-magnetic ion, $\text{Fe}^{3+}$ in $B$ sites ([6]) equal $\uparrow + \downarrow \Rightarrow$ no net moment

- eg. $\text{ZnO. Fe}_2\text{O}_3$
- $\text{CdO. Fe}_2\text{O}_3$ \[ \text{paramagnetic} \]

Inverse Spinel: $\text{M}^{2+}$ on $B$ sites ([6]) $\uparrow + \uparrow + \downarrow$

- $\text{Fe}$, $\text{Co}$ or $\text{Ni}$ ferrite
- all ferrimagnetic.
Fig. 6.11 Saturation magnetization of some cubic ferrites as a function of temperature, after Smit and Wijn [G.10].

**Mixed Ferrites**

Solid solutions of spins can be formed readily, and used to tune properties such as saturation magnetization and Curie temperature.

Also Important - hexagonal ferrites (magnetically hard)
A History Lesson - Ferrite Core Memories

- more than 15 billion ferrite cores were produced in 1968

- store information by having two stable magnetic states, + Br and - Br (the remanent flux densities)

- to "switch" a core at a particular intersection requires the coincidence of two currents, either of which is insufficient to exceed the threshold of the core's hysteresis loop.
Desirable Characteristics

- "square" hysteresis loop

\[ B \]

+ Br \quad Hc

- Br

\[ H \]

then H slightly greater than Hc will switch the magnetization from its remnant value Br (\approx Bsat) to - Br.

- fast switching times

- no temperature variation \iff high Tc.

- mechanical strength (small cores)

- low magnetostriiction

Typical Material \( \text{Mg}_0.45 \text{Mn}^{2+}_{0.55} \text{Mn}^{3+}_{0.23} \text{Fe}_{1.77} \text{O}_4 \)

\[ H_c = 72 \text{A/m} \]

switching constant \( 5 \times 10^{-3} \mu \text{V/A} \cdot \text{m} \)

\[ B_r = 0.22 \text{ Wb/m}^2 \]

\[ B_s = 0.36 \text{ Wb/m}^2 \]

\[ T_c \approx 300^\circ \text{C} \]