Materials Science/Engineering
Magnetic materials

1/3

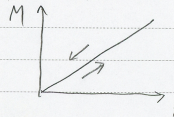
The origin is electron-spin.
Unpaired electron, odd-electron,

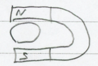
Radicals
ラジカル, NO, NO_x,
Cu^{2+} (d^9)

Degenerate
AO/MO
orbitals

O_2 ↑ ↑
Mn^{2+} ↑ ↑ ↑ ↑ ↑
Gd^{3+} ↑ ↑ ↑ ↑ ↑ ↑ ↑

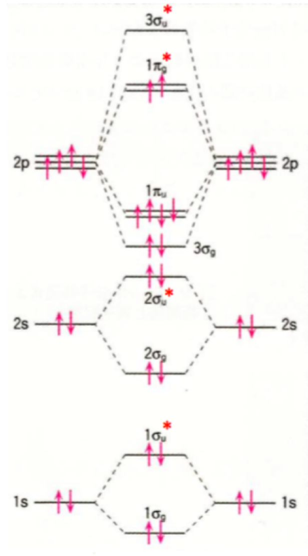
Isolated (magnetically isolated or far from each other)
unpaired electrons behaves as a “paramagnet”「常磁性体」.





Magnetized only when a magnetic field applied.
Magnetic susceptibility (d*M*/d*H*) is positive and very small.
「磁化率」

Oxygen molecule O_2



O atom O_2 molecule O atom

Explanation of paramagnetic oxygen is
a milestone of LCAO-MO method.

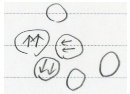
youtube: yamajun88413

youtube: NGK science site

Magnetic Coupling   Exchange interaction (, dipolar interaction, …)

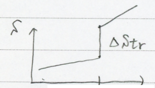
Ferromagnetic interaction: only nearest-neighbor
(強磁性的相互作用)   including intramolecular “Hund’s rule.”

Ferromagnet is defined in a bulk (long-range; macroscopic) materials.
(強磁性体)
“ferromagnet” and “ferromagnetic” are completely different words.

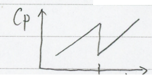


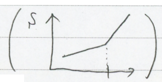
Ferromagnetic interaction does not always give a ferromagnet.

(Ferro)magnet is present below T_C as an ordered state.
Order state / disorder state are separated with as a phase boundary.
ice / water : first-order phase transition - - - exo/endothermic （発熱･吸熱）
ferromagnet / paramagnet: second-order phase transition
- - - No transition latent heat（転移潜熱は無い）



ice / water





ferromag. / paramag.

$S = -\left(\frac{\partial G}{\partial T}\right)_p$

$C_p = \left(\frac{d'q}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$

A gap appears in the first derivative of *G*.

A gap appears in the second derivative of *G*.

Competition between internal interaction with thermal excitation.

ordered phase
(low-temp. phase)

disordered phase
(high-temp. phase)

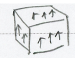
Tc

stronger internal interaction.
Materials essential character is evident.

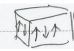
stronger thermal energy.
Particles, molecules, electron spins, etc. are thermally activated or agitated. Materials character is buried by Brownian motion.

Below the transition temperature;

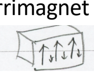
ferromagnet (強磁性体)



antiferromagnet (反強磁性体)



ferrimagnet (フェリ磁性体)



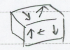
ferri

long-range-ordered state
(or simply ordered state)

Ordered state;
No spontaneous magnetization

Ordered state;
Incomplete cancellation gives *Ms*.

disordered phase



paramagnet 常磁性 (small positive susceptibility)

no spin

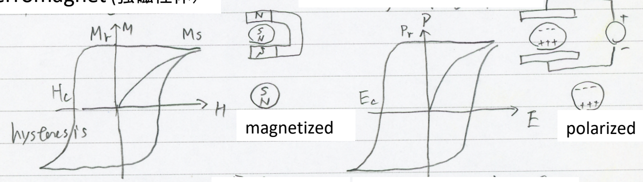
diamagnet 反磁性 (tiny negative susceptibility)

Caution: Order takes place without applying a magnetic field.

ordered phase

Ferromagnet (強磁性体)

Ferroelectric（強誘電体）



magnetized

polarized

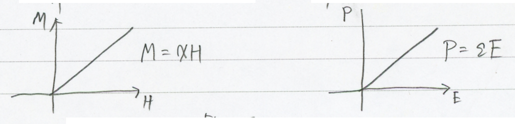
Hc (Ec) coercive field (coercive force)

large : “hard”
small : “soft”

disordered phase

Paramagnet（常磁性体）

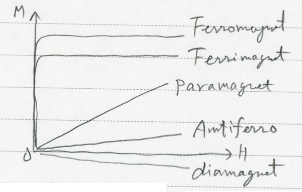
Paraelectric（常誘電体）



Small slope, but saturated somewhere at $H(E) \to \infty$.

磁化曲線、M-H 曲線

Classification from $M(H)$ profiles



molecular-field approximation 分子場近似

net outer internal

$H_i = H_o + H_E$

$= H + \alpha M$　　$H_E = \alpha M$ とする

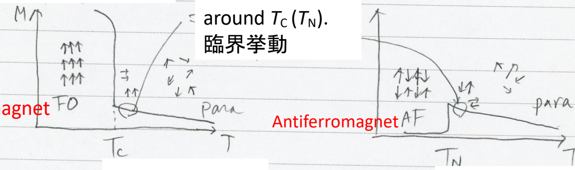
$\frac{H_i}{M} = \frac{H+\alpha M}{M} = \frac{H}{M} + \alpha$

$\frac{H_i}{M} = \frac{T}{C}$ より　$\frac{H}{M} = \frac{T}{C} - \alpha$

$\therefore \frac{M}{H} = \chi = \frac{C}{T - \alpha C}$

$M(T)$ profiles

Critical behavior around T_C (T_N). 臨界挙動



Ferromagnet

Antiferromagnet

Curie temp.

Neél temp.

Paramagnetic region: $M \propto \frac{1}{T}$

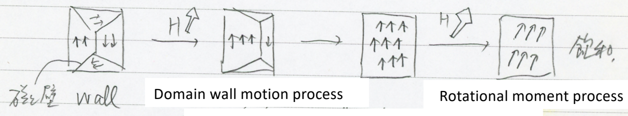
Curie’s law $\chi = \frac{C}{T}$

thermal agitation: **1/*T* effect**

Curie-Weiss’ law $\chi = \frac{C}{T-\theta}$　$\left(\chi \fallingdotseq \frac{C}{T-T_C},\ \chi \fallingdotseq \frac{C}{T+T_N}\right)$

C : Curie constant
θ : Weiss constant (Weiss temperature)

“Domain model” (磁区)



Domain wall motion process

Rotational moment process

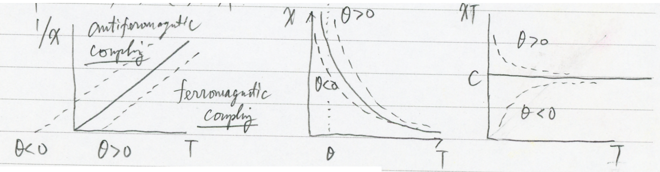
These processes requires activation energy.

Magnetic hysteresis appears due to metastability.

活性化エネルギーの存在が磁気ヒステリシスの源

“Curie-Weiss plot” （キュリー・ワイス　プロット）

To clarify the character of magnetic coupling in a paramagnetic phase.

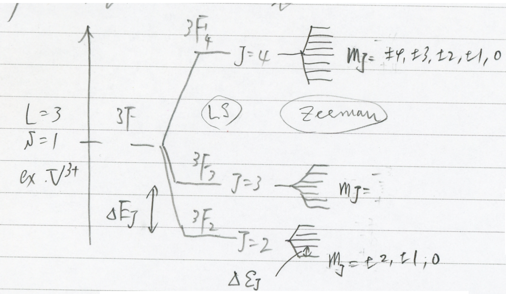


Ferromagnetic coupling favors
nearest-neighbor parallel spin structure (↑↑).

Antiferromagnetic coupling favors
nearest-neighbor antiparallel spin structure (↑↓).

Upward/downward deviations are easy to see!

Let’s derivate “Brillouin function ($M(H)$ curve)” and “Curie law ($\chi(T)$ curve)”!



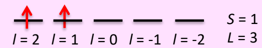
Multiplet splitting and Zeeman splitting

Zeeman splitting gap $E_J = g \mu_B H_0$

Landé g factor is a function of $J = L + S$.　g 因子 : ca. 2

Hund’s rule: (1) For spin configuration,
a state having max S is the most stable.
(2) For multiplicity,
a state having max L is the most stable.

Case study V^{3+} ($3d^2$)



LS coupling (when less than half)
$J = L - S = 2$, thus $^3F_2$ is ground.

Term symbol: $^{2S+1}L_J$ where L symbols = S,P,D,F,G,H... for L = 0,1,2,3,4,5..., respectively.

項記号

How to put electrons to orbitals:

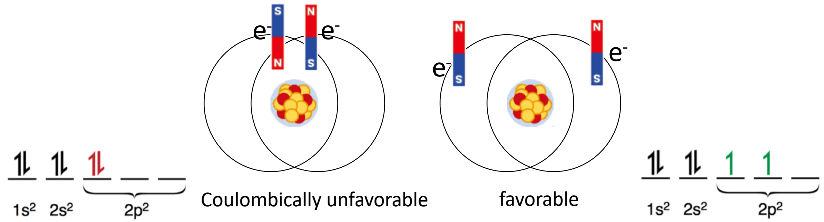
The same logic holds for AO and MO.

参考：1年化学概論第一、
2年無機化学、3年量子化学他

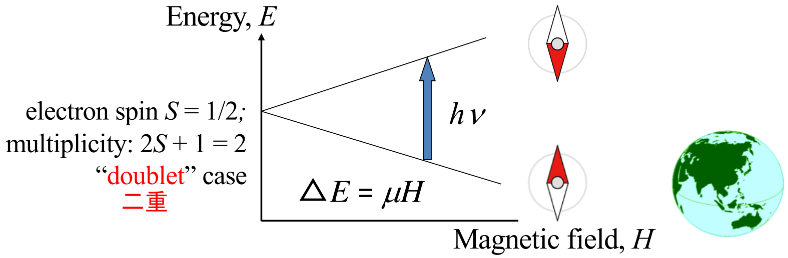
[1] Building-up Principle (Aufbau Principle) 構成原理
Fill from the bottom up.

[2] Pauli Exclusion Principle パウリの排他原理
No two electrons in an atom can have the same four quantum numbers.

[3] Hund's Rule フント則
If multiple orbitals have the same energy, one electron goes into each of them before they start to double up.

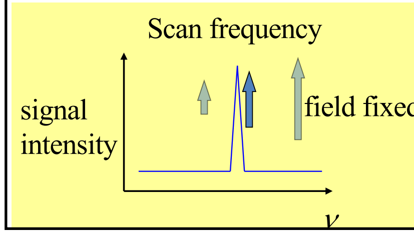


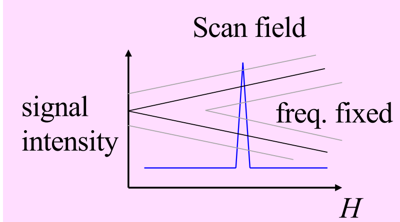
To study the Zeeman effect: Magnetic resonance theory as a familiar case



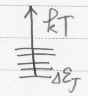
Resonance Condition: $h\nu = \mu H$

Two measurement modes:





$\Delta E_J \gg kT$ and $\Delta \varepsilon_J \lesssim kT$



This holds for systems at room temp.

to states:

$$\varepsilon_{m_J} = -g m_J \mu_B H_0$$

Boltzmann distribution rule is applied.

$$N_i = N \frac{\exp(-\varepsilon_i/kT)}{\sum \exp(-\varepsilon_i/kT)}, \quad \therefore N(m_J) = \frac{N \exp(g m_J \mu_B H_0/kT)}{\sum_{m_J=-J}^{+J} \exp(g m_J \mu_B H_0/kT)}$$

N: total number of particles
M: total magnetization

$$M = \sum_{m_J=-J}^{+J} \left(N(m_J)\, g m_J \mu_B\right) = N g \mu_B \frac{\sum m_J \exp(g m_J \mu_B H_0/kT)}{\sum \exp(g m_J \mu_B H_0/kT)}$$

number of particles at each state

moment of a particle at each state

$\Delta \varepsilon_J \gtrsim kT$ (at low temperature)

$$\frac{M}{N g \mu_B} = \frac{\sum m_J \exp(g m_J \mu_B H_0/kT)}{\sum \exp(g m_J \mu_B H_0/kT)}$$

It can be solved. Somewhat laborious but solvable.

上式を $\dfrac{\sum_{m_J=-J}^{J} m_J e^{-a m_J}}{\sum_{m_J=-J}^{J} e^{-a m_J}} = \dfrac{S_2}{S_1}$ とおく $\left(a = \dfrac{-g \mu_B H_0}{kT}\right)$

hyperbolic trigonometric functions

$$\left(\begin{aligned} \sinh x &= \tfrac{1}{2}(e^{x} - e^{-x}) \\ \cosh x &= \tfrac{1}{2}(e^{x} + e^{-x}) \end{aligned}\right)$$

denominator S_1

分母 初項 e^{aJ}, 公比 e^{-a}, 項数 $2J+1$ 個

sum of the geometric sequence

$$S_1 = \frac{e^{Ja}\left(1 - e^{-(2J+1)a}\right)}{1 - e^{-a}}$$

$$= \frac{e^{Ja} - e^{-(J+1)a}}{1 - e^{-a}} \cdot \frac{e^{\frac{a}{2}}}{e^{\frac{a}{2}}} = \frac{e^{(J+\frac{1}{2})a} - e^{-(J+\frac{1}{2})a}}{e^{\frac{a}{2}} - e^{-\frac{a}{2}}} \left(= \frac{\sinh (J+\frac{1}{2})a}{\sinh \frac{a}{2}}\right)$$

numerator S_2

分子 (tricky solution!)

$$S_2 = -J e^{-(-J)a} + (-J+1) e^{-(-J+1)a} + (-J+2) e^{-(-J+2)a} + \cdots + J e^{-Ja}$$

$$e^{-a} S_2 = -J e^{-(-J+1)a} + (-J+1) e^{-(-J+2)a} + \cdots + J e^{-(J+1)a}$$

$$\therefore (1 - e^{-a}) S_2 = -J e^{+Ja} + \underbrace{e^{-(-J+1)a} + e^{-(-J+2)a} + \cdots + e^{-aJ}}_{\text{初項 } e^{-(-J+1)a},\ \text{公比 } e^{-a},\ \text{項数 } 2J \text{個}} - J e^{-(J+1)a}$$

sum of the geometric sequence

$$\therefore (1-e^{-a})S_2 = -J(e^{Ja}+e^{-(J+1)a}) + \frac{e^{-(-J+1)a}(1-e^{-2Ja})}{1-e^{-a}}$$

$$S_2 = -J\frac{e^{Ja}+e^{-(J+1)a}}{1-e^{-a}} + \frac{e^{(J-1)a}-e^{-(J+1)a}}{(1-e^{-a})^2}$$

$$\therefore \frac{S_2}{S_1} = \left(-J\frac{e^{Ja}+e^{-(J+1)a}}{1-e^{-a}} + \frac{e^{(J-1)a}-e^{-(J+1)a}}{(1-e^{-a})^2}\right)\left(\frac{1-e^{-a}}{e^{Ja}-e^{-(J+1)a}}\right)$$

$$= -J\frac{e^{Ja}+e^{-(J+1)a}}{e^{Ja}-e^{-(J+1)a}} + \frac{1}{1-e^{-a}}\frac{e^{(J-1)a}-e^{-(J+1)a}}{e^{Ja}-e^{-(J+1)a}}$$

$$= -J\frac{e^{Ja}+e^{-(J+1)a}}{e^{Ja}-e^{-(J+1)a}}\cdot\frac{e^{\frac{1}{2}a}}{e^{\frac{1}{2}a}} + \frac{e^{-a}}{1-e^{-a}}\cdot\frac{e^{Ja}-e^{-Ja}}{e^{Ja}-e^{-(J+1)a}}$$

$$= -J\coth\left(J+\tfrac{1}{2}\right)a + A$$

As for a part of A, (tricky solution again!)

$$e^{Ja}-e^{-Ja} = \frac{1}{2}\left\{\left(e^{(J+1)a}+e^{Ja}-e^{-Ja}-e^{-(J+1)a}\right)-\left(e^{(J+1)a}-e^{Ja}+e^{-Ja}-e^{-(J+1)a}\right)\right\}$$

$$= \frac{1}{2}\left\{\left(e^{(J+\frac{1}{2})a}-e^{-(J+\frac{1}{2})a}\right)\left(e^{\frac{a}{2}}+e^{-\frac{a}{2}}\right)-\left(e^{(J+\frac{1}{2})a}+e^{-(J+\frac{1}{2})a}\right)\left(e^{\frac{a}{2}}-e^{-\frac{a}{2}}\right)\right\}$$

Accordingly,

factorization (因数分解)

$$A = \frac{e^{-a}}{1-e^{-a}}\frac{e^{\frac{1}{2}a}}{e^{\frac{1}{2}a}}\frac{e^{Ja}-e^{-Ja}}{e^{Ja}-e^{-(J+1)a}}\frac{e^{\frac{1}{2}a}}{e^{\frac{1}{2}a}}$$

$$= \frac{1}{e^{\frac{1}{2}a}-e^{-\frac{1}{2}a}}\frac{(e^{Ja}-e^{-Ja})}{e^{(J+\frac{1}{2})a}-e^{-(J+\frac{1}{2})a}}$$

$$= \frac{1}{2}\cdot\left\{\frac{e^{\frac{a}{2}}+e^{-\frac{a}{2}}}{e^{\frac{1}{2}a}-e^{-\frac{1}{2}a}} - \frac{e^{(J+\frac{1}{2})a}+e^{-(J+\frac{1}{2})a}}{e^{(J+\frac{1}{2})a}-e^{-(J+\frac{1}{2})a}}\right\}$$

$$= \frac{1}{2}\coth\frac{a}{2} - \frac{1}{2}\coth\left(J+\tfrac{1}{2}\right)a$$

$$\therefore \frac{S_2}{S_1} = -J\coth\left(J+\tfrac{1}{2}\right)a + \left(\frac{1}{2}\coth\frac{a}{2} - \frac{1}{2}\coth\left(J+\tfrac{1}{2}\right)a\right)$$

$$= \frac{1}{2}\coth\frac{a}{2} - \frac{2J+1}{2}\coth\left(\frac{2J+1}{2}a\right)$$

to the beginning,

$$a = -\frac{g\mu_B H_0}{kT}$$

$$\frac{M}{Ng\mu_B} = \frac{2J+1}{2}\coth\left(\frac{2J+1}{2J}\frac{g\mu_B H_0}{kT}J\right) - \frac{1}{2}\coth\left(\frac{1}{2J}\frac{g\mu_B H_0 J}{kT}\right)$$

$$\therefore M = NgJ\mu_B\left[\frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right)\right]$$

where $x = \frac{gJ\mu_B H_0}{kT}$ (end of derivation)

[ ] = $B_J(x)$
Brillouin function

At the next stage, the Curie law is proven, when $\frac{H_0}{T}\to 0\ (x\to 0)$ キュリー則の導出

$$B_J(x) = \frac{2J+1}{2J}\coth\frac{2J+1}{2J}x - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right)$$

$$= \frac{a(e^{ax}+e^{-ax})}{e^{ax}-e^{-ax}} - \frac{b(e^{bx}+e^{-bx})}{e^{bx}-e^{-bx}} \quad \left(a=\frac{2J+1}{2J},\ b=\frac{1}{2J}\right)$$

Maclaurin expansion of the e^x function
指数関数の展開

factorial n : nの階乗

$$= \frac{a\left\{1+\frac{(ax)^2}{2!}+\frac{(ax)^4}{4!}+\cdots\right\}}{\left\{ax+\frac{(ax)^3}{3!}+\cancel{\frac{(ax)^5}{5!}}+\cdots\right\}} - \frac{b\left\{1+\frac{(bx)^2}{2!}+\frac{(bx)^4}{4!}+\cdots\right\}}{\left\{bx+\frac{(bx)^3}{3!}+\cancel{\frac{(bx)^5}{5!}}+\cdots\right\}} \quad ax\ll 1,\ bx\ll 1$$

$$\fallingdotseq a\left(\frac{1}{ax}+\frac{ax}{2}-\frac{ax}{6}-\frac{(ax)^3}{12}\right) - b\left(\frac{1}{bx}+\frac{bx}{2}-\frac{bx}{6}-\frac{(bx)^3}{12}\right)$$

$$\fallingdotseq \frac{1}{x}+\frac{a^2x}{3}-\frac{1}{x}+\frac{b^2x}{3}$$

$$= \frac{1}{3}(a^2-b^2)x$$

$$= \frac{J+1}{3J}x$$

$$M = Ng\mu_B J\frac{J+1}{3J}\frac{gJ\mu_B H_0}{kT} = \frac{Ng^2\mu_B^2 J(J+1)}{3kT}H_0$$

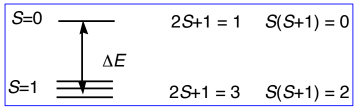
$\frac{H_0}{T}\to 0$ ならば $\chi = \frac{M}{H} = \frac{Ng^2\mu_B^2 J(J+1)}{3kT}$ (Q.E.D)

Curie's law
$1/T$ effect

Quiz (homework; upload to GClassroom in a week)

[1] A magnetized iron(0) block attracts steal nails and clips. After heated over 770 ° C (T_C) in a flame and then cooled to room temperature, it does not attract nails or clips anymore. As for the samples before and after such annealing, which is a stable phase or metastable phase? Why does a ferromagnet (an ordered state below T_C) not behave as a "magnet"?

[2] In a general biradical, the singlet and triplet states are thermally equilibrated (see Figure).



Derive the following Bleaney-Bowers equation.

$$\boxed{\chi_{\mathrm{mol}} = \frac{2Ng^2\mu_B^2}{kT}\frac{1}{3+\exp(-\Delta E/kT)}}$$

A critical hint:
Based on the Boltzmann distribution law, the molar magnetic susceptibility χ_{mol} is described with the van Vleck equation:

$$\chi_{\mathrm{mol}} = \frac{Ng^2\mu_B^2}{3kT}\frac{\sum(2S_i+1)S_i(S_i+1)\exp(-E_i/kT)}{\sum(2S_i+1)\exp(-E_i/kT)}$$