Magnetism and Magnetic Materials

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1. 1. Magnetism of free atoms and ions

History of magnetism

Three forces in natural world: Universal gravitation, Nuclear force, Magnetic force
(万有引力) (核力) (磁気力)

Magnetic force is one of the oldest physical phenomena that human knows.

The origin of the word " Magnet"

Magnetic ores (Magnetite, Fe_3O_4) were found in Magnesia, the name of a region of the ancient Middle East, in what in now Turkey.

The "Magnet" was also found in China in BC 7. Magnet = "慈石", In Japanese, 磁石.
慈石 = loving stone, 慈＝love, treat tenderly, Attraction or friendship, similar to magnet

History on magnetism

1. Discovery of functionality of the magnet
   Loadstone compass : China (BC 3)
2. Discovery of electromagnetic field
   Oersted (Denmark, 1820): Current gives a force on a loadstone compass
   → Establishment of Electromagnetism
   → Maxwell's equations
3. Relation between the substance and magnetism
   Ampere : Magnetism is based on the special molecular field (1821)
   Langivin : Angular momentum by electron orbital motion (1905)
   Dirac : Discovery of spin angular momentum (1928)
   Heisenberg: The origin of ferromagnetism is in the exchange interaction (1933)

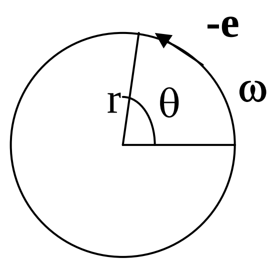
Origin of Atomic Moment

What is the microscopic origin of magnetism in materials ?

Magnetic moment of a free electron

Consider an electron which rounds an atomic nucleus with a radius r and an angular velocity ω :

Magnetic moment by orbital motion, μ_l is defined as



$A = \pi r^2$

$$\mu_l = \mu_0 A \cdot \boldsymbol{i} \qquad (1.1)$$

$A = \pi r^2$

$\mu_0 = 4\pi \times 10^{-7}$ [H/m] : Permeability in vacuum

$$\boldsymbol{i} = -e\,f = -e\,\omega / 2\pi \quad \text{: Current} \qquad (1.2)$$

By inserting $A = \pi r^2$ and $i = -e\,\omega/2\pi$ to (1.1), we obtain

$$\mu_l = \mu_0 \pi r^2 \,(-e\,\omega / 2\pi)$$
$$= -e\mu_0 \omega \mathbf{r}^2/2 \qquad (1.3)$$

While, angular momentum of an electron is given by

$$\mathbf{P}_l = m\,r^2 \omega \qquad (1.4)$$

Thus, magnetic moment by an electron orbital motion

$$\mu_l = -(\mu_0 e / 2\,m)\,\mathbf{P}_l \qquad (1.5)$$

According to the quantum mechanics electron orbital motion around an atomic nucleus is **quantized**.
So, orbital angular momentum is given by using the orbital angular momentum number **l**

$$\mathbf{P}_l = \hbar\,\mathbf{l} \qquad (1.6)$$

$$\hbar = h/2\pi = 1.055 \times 10^{-34} \quad [\mathrm{J \cdot s}]$$

Thus, magnetic moment due to the orbital motion of an electron is

$$\mu_l = \mu_0(-e\hbar/2m)\,\mathbf{l}$$
$$= -\mu_B\,\mathbf{l} \qquad (1.7)$$

$$\mu_B = \mu_0 e\hbar/2m = 0.927 \times 10^{-23}\,[\mathrm{A\,m^2}]$$
$$= 1.165 \times 10^{-29}\,[\mathrm{Wb \cdot m}]$$: **Bohr magneton**

On the other hand, magnetic moment by **electron spin** is given using spin angular momentum number **s** from the Dirack equation

$$\mu_s = -(\mu_0 e/m)\,\mathbf{P}_s = -(\mu_0 e/m)\,\hbar\,\mathbf{s} \qquad (1.8)$$
$$= -2\,\mu_B\,\mathbf{s}$$

where $\mathbf{P}_s = \hbar\,\mathbf{s}$, $\quad \mathbf{s} = \pm 1/2$.

Thus, the total magnetic moment by an electron is

$$\mu = \mu_l + \mu_s = -(\mathbf{l} + 2\,\mathbf{s})\,\mu_B = -g\,\mathbf{j}\,\mu_B \qquad (1.9)$$

$\mathbf{j} = \mathbf{l} + \mathbf{s}$: total angular momentum

g: g factor $\quad g = 2$ for $\mathbf{l} = 0$

Magnetic moment of an atom with multi-electrons

1) Pauli principle

Only two electrons can occupy one energy state including spin

2) Hund rule : Rule for electron occupancy

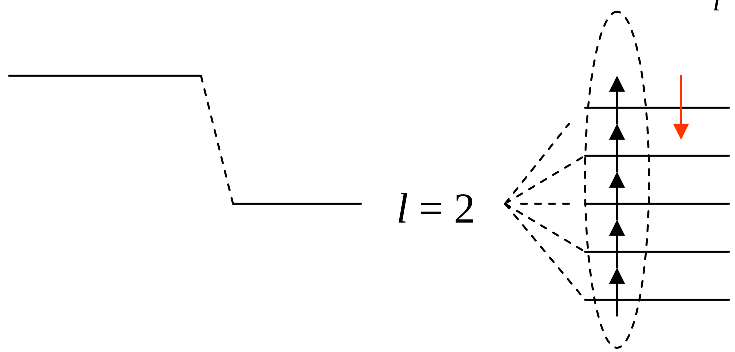
① Total S is maximum

② Total L is maximum

Principal quantum number n
Orbital angular momentum quantum number l
Magnetic quantum number m_l
Spin quantum number m_s

$l = 0, 1, 2 \ldots\ldots n-1$
$m_l = -1, -l + 1, -l + 2, \ldots, l$
$m_s = +1/2, -1/2$

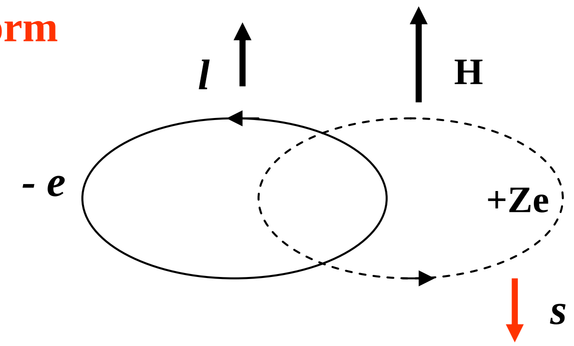
Ex) 3d^6 : Fe^{2+} ion



Total L = 2, S = 2

3) Russel-Sanders coupling

How do the spin and orbital angular momenta combine to form the total angular momentum of an atom ?



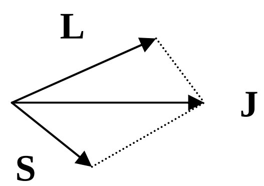
s* is antiparallel to *l

Spin-orbit interaction:

$$H_{ls} = \Sigma\, \zeta\, \boldsymbol{l}_j \cdot \boldsymbol{s}_j = \lambda\, \mathbf{L} \cdot \mathbf{S} \qquad (1.10)$$

$$\mathbf{S} = \Sigma\, \boldsymbol{s}_j \qquad \mathbf{L} = \Sigma\, \boldsymbol{l}_j$$

If spin-spin and orbit-orbit couplings are strongest and spin-orbit interaction is not so strong,



$\mathbf{J} = \mathbf{L} + \mathbf{S} = \Sigma\, \boldsymbol{l}_j + \Sigma\, \boldsymbol{s}_j$: **Russel-Sanders coupling**

$J = (L + S), (L + S - 1), (L + S - 2), \ldots\ldots |L - S|$

$\lambda > 0$: **L** is antiparallel to **S** for less than half electrons

$\lambda < 0$: **L** is parallel to **S** for more than half electrons

Magnetic moment μ

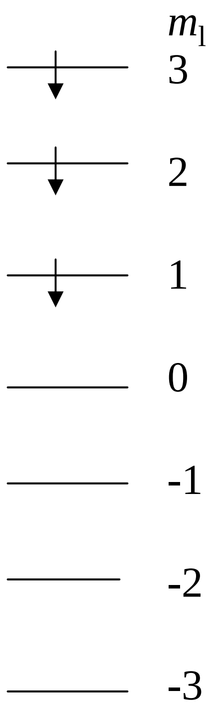
$$\mu = -\mu_B\,(\mathbf{L} + 2\,\mathbf{S}) = -g\,\mu_B\,\mathbf{J}$$

$$g = [3J(J+1) + S(S+1) - L(L+1)] \,/\, [2J(J+1)]$$: **Lande's g factor** (1.11)

Effective magnetic moment $\mu_{eff} = g\,\mu_B\,\sqrt{J(J+1)}$ (1.12)

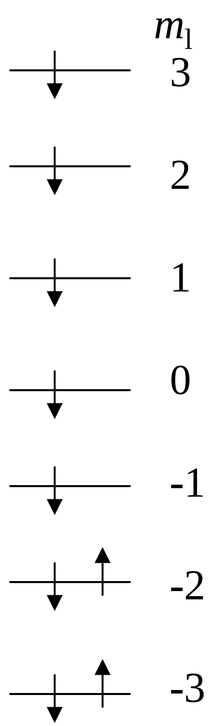
Practice problems

[1] Nd^{3+} : $4f^3 5s^2 5p^6$



L = 6, S = 3/2
J = L – S = 9/2
g = 8/11
μ_{eff} = 3.62 μ_B

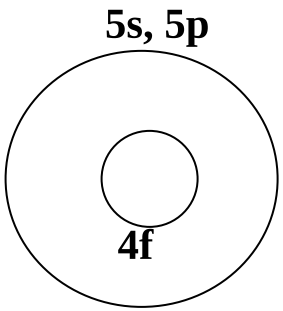
[2] Tb^{3+} : $4f^9 5s^2 5p^6$



L = 5, S = 5/2
J = L + S = 15/2
g = 4/3
μ_{eff} = 10.65 μ_B

Effective magnetic moment:
theory and experiment

$$\mu_{eff} = g\,\mu_B \sqrt{J(J+1)}$$

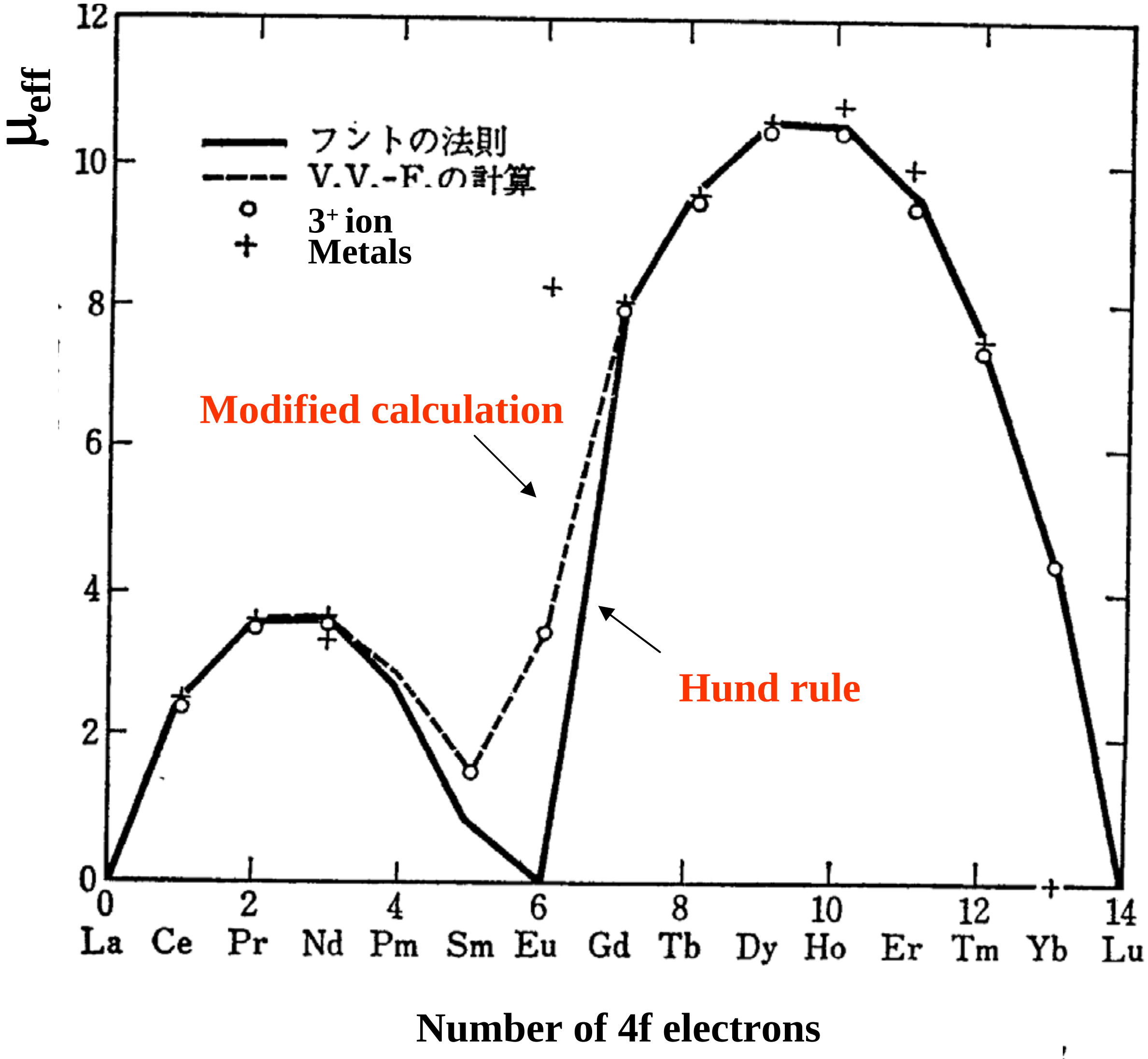


Rare earth metals follow the **Russel-Sanders coupling**

<u>J is a good quntum number.</u>

Ferromagnetic 3d metals

	Fe	Co	Ni
g	2.10	2.21	2.21



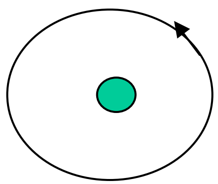
Quenching of the orbital angular momentum

In 3d series of elements **J** = **S** has been found experimentally as shown in the table.

Table 10.1 Magnetic moments of isolated ions of the 3d transition metal series

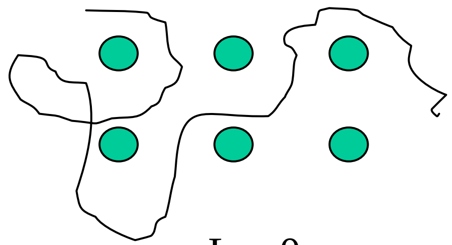
Ion	*Configuration*	*Calculated moment* $g\sqrt{[J(J+1)]}$	$g\sqrt{[S(S+1)]}$	*Measured moment*
Ti^{3+}, V^{4+}	$3d^1$	1.55	1.73	1.8
V^{3+}	$3d^2$	1.63	2.83	2.8
Cr^{3+}, V^{3+}	$3d^3$	0.77	3.87	3.8
Mn^{3+}, Cr^{3+}	$3d^4$	0	4.90	4.9
Fe^{3+}, Mn^{2+}	$3d^5$	5.92	5.92	5.9
Fe^{2+}	$3d^6$	6.70	4.90	5.4
Co^{2+}	$3d^7$	6.63	3.87	4.8
Ni^{2+}	$3d^8$	5.59	2.83	3.2
Cu^{2+}	$3d^9$	3.55	1.73	1.9

Electrons in such as 3d series cannot draw a definite orbit due to the interactions between electrons. This leads to the negligible orbital contribution to the magnetic moment.



$L \neq 0$

Isolated atom



$L = 0$

Solid

<u>Thus, the magnetic moment in 3d magnetic materials is mainly caused by electron spin.</u>

j-j coupling

There is other way of coupling to form the total angular momentum of an atom.

j-j coupling

The orbital and spin angular momenta are dependent on each other. It assumes there is a strong spin - orbit (**l** - **s**) coupling for each electron and that this coupling is stronger than the **l** - **l** or **s** - **s** coupling between electrons.

$$\mathbf{J} = \Sigma\, \mathbf{j}_i = \Sigma\, (\mathbf{l}_i + \mathbf{s}_i) \qquad (1.13)$$

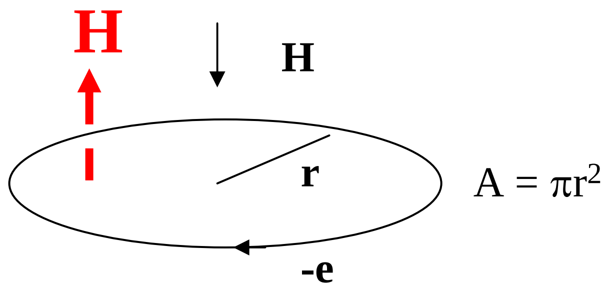
This form of coupling is more **applicable to very heavy atoms**.

2. Magnetism in materials

The various different types of magnetic materials are traditionally classified according to their bulk susceptibility χ.

2.1 Diamagnetism

Closed shell of electrons: S = 0
Weak magnetism
Negative magnetic susceptivility : $\chi = I/H \sim -10^{-5}$



Electric field is induced

$\mathbf{E} = -\,d\Phi/dt = A d\mathbf{B}/dt$
$\quad = -\,\mu_0 A \mathbf{H}/dt$
Φ: magnetic flux
B: Flux density

<u>Lenz law</u>
Changing magnetic field H induces an electric field whose current generates a magnetic field that opposes the change in the first H field.

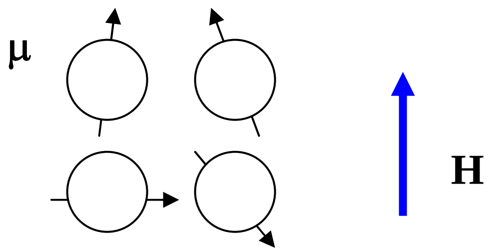
This field induces the magnetization I

Current
$i = E / R$
induces opposite magnetic field

	χ
Cu	-9.7×10^{-6}
Ag	-25
Al_2O_3	-18
C (graphite)	-14

$\chi = -1$: Perfect diamagnetism
= Superconductor

2.2 Paramagnetim: Localized model



Random orientation of moment

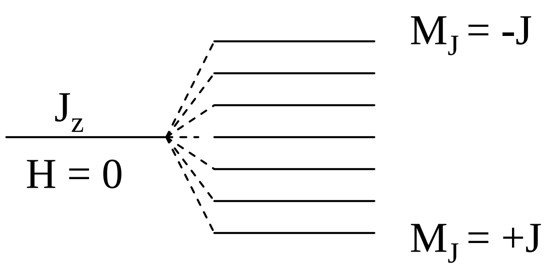
χ is small and positive, typically $\chi \sim 10^{-3} – 10^{-5}$

Atomic magnetic moment μ = - (L + 2S) μ_B
No interaction between atomic moments

Zeeman energy:

$$E = -\mu \cdot H = -\mu_B (L + 2S) H = -g \mu_B J \cdot H \qquad (2.1)$$

For H // z , $E = g \mu_B J_z \cdot H = g \mu_B M_J \cdot H = E_M$ (2.2)
where M_J is the eigen value of J_z



Probability for occupying energy E_M is determined

by **Boltzmann** statictics

$$P(M_J) = \exp(-E_M/k_BT) / \Sigma \exp(-E_M/k_BT) \qquad (2.3)$$

Magnetization (Magnetic moment μ per unit cell)

$$I = N\mu = Ng\mu_B \Sigma P(M_J)M_J$$
$$= Ng\mu_B J B_J(x) \qquad (2.4)$$

$B_J(x) = [(2J + 1)/2J] \coth [(2J + 1) /2J] x – (1/2J) \coth (x/2J)$: **Brillouin function**
$x = gJ\mu_B H/k_BT$ (2.5)

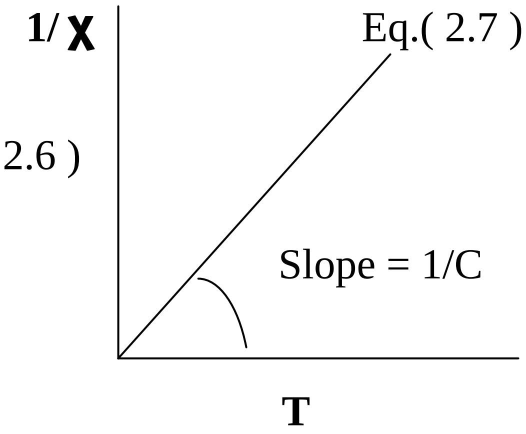
High temperature limit

$$B_J(x) = [(J+1)/3J]\, x$$

$$\xrightarrow{\lim_{x\to 0}} \quad I = Ng^2\mu_B{}^2 J(J+1)/3\,k_BT = [\,N\mu_{eff}{}^2/3k_BT\,]\,H \qquad (2.6)$$

$\chi = I/H = C/T$: **Curie law**

$C = N\mu_{eff}{}^2/3k_B$ (2.7)

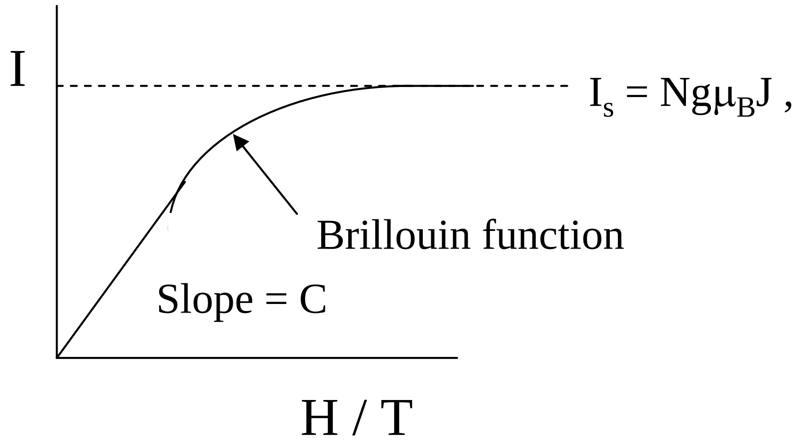


High field limit

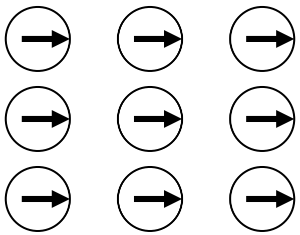
$B_J(x) = 1 \qquad (H \to \infty)$

$$\xrightarrow{\lim_{x\to \infty}} \quad \left.\begin{aligned} I_s &= N\,\mu_s \\ \mu_s &= g\mu_B J \end{aligned}\right\} \qquad (2.8)$$

N: Number of atoms per unit volume



Saturation



$I_s = N\,\mu_s$
$\mu_s = g\mu_B J$

$\longrightarrow$ **H**

Experiments obey
The Brillouin function

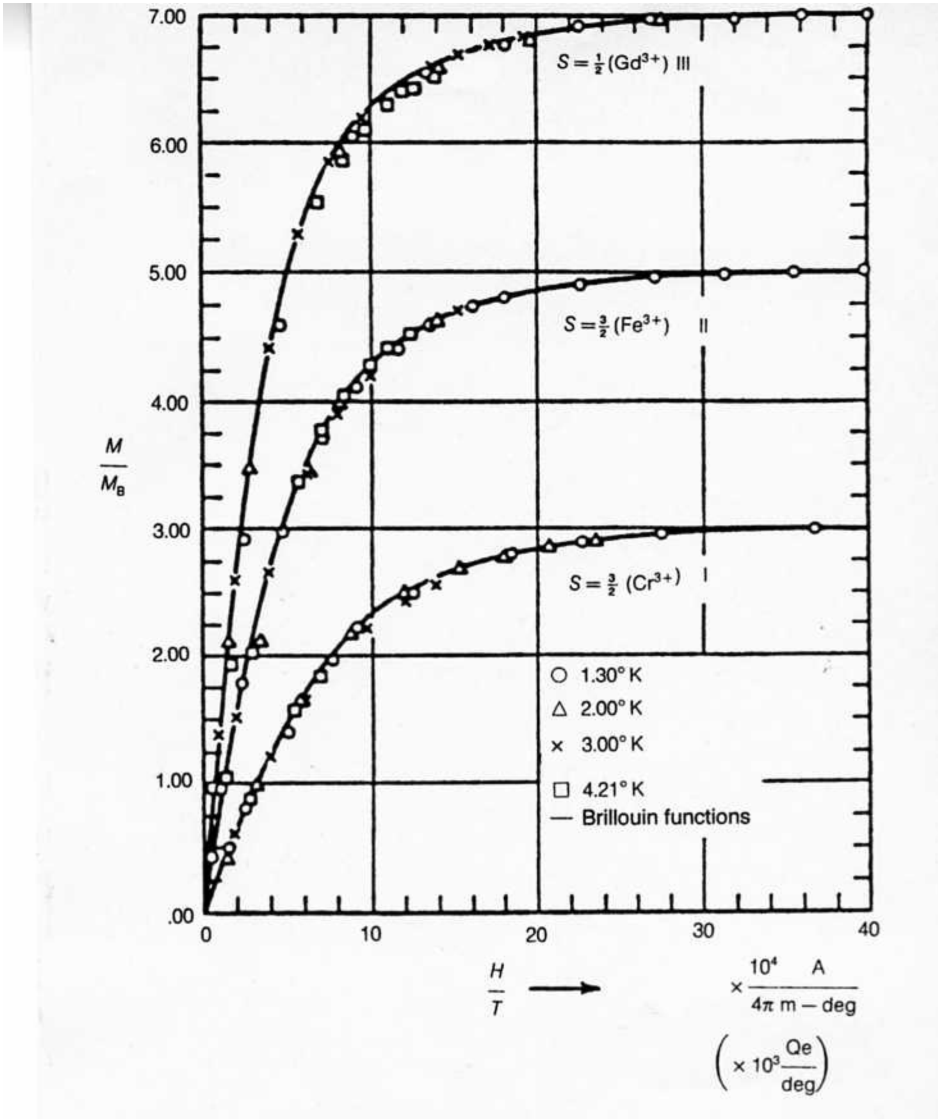
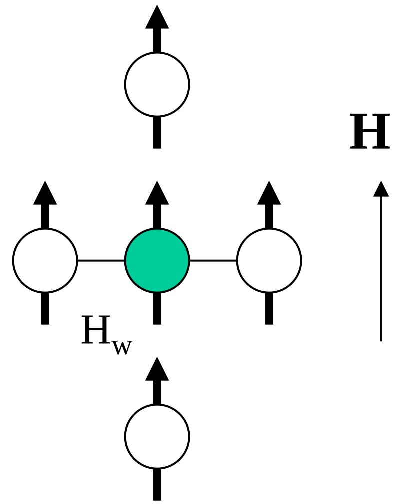


Fig. 11.6 Comparison of theory and experiment for the magnetization curves of thre paramagnetic salts containing Gd^{3+}, Fe^{3+} and Cr^{3+} ions, respectively, after Henry [20] These salts are potassium chromium alum, ferric ammonium alum and gadolinium sulfat octahydrate.

2.3 Ferromagnetism: Localized model



Weiss theory

Molecular field $\mathbf{H}_w = w\,\mathbf{I}$ (2.8)

Total magnetic field

$\mathbf{H_T} = \mathbf{H} + w\,\mathbf{I}$

$E = -\,g\mu_B M_J (H + w I)$

$I = N\mu = Ng\mu_B \Sigma\, P(M_J)M_J$

$= Ng\mu_B J\, B_J(x)$

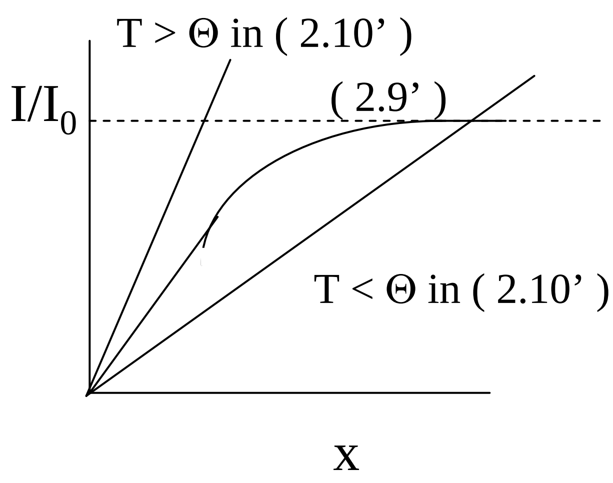
$= I_0\, B_J(x)$ (2.9)

$\left.\begin{array}{l} I_0 = Ng\mu_B J \\ x = gJ\mu_B (H + w I) / k_B T \end{array}\right\}$ (2.10)

When H = 0

$I / I_0 = kTx / N(g\mu_B J)^2 w$ (2.10')

$I/I_0 = B_J(x)$ (2.9')



High temperature limit; x << 1

$B_J(x) = (J + 1)\, x / 3J$

$\longrightarrow$ $k_B T / N(g\mu_B J)^2 w = (J + 1)/3J$, $T = N(g\mu_B)^2 J (J + 1) w / 3k_B = C\,w = \Theta$ (2.11)

Θ: Paramagnetic Curie temperature $C = N\mu_{eff}^2/3k_B$,

$\Theta = N\mu_{eff}^2 w/3k_B$ (2.12)

Temperature dependence of spontaneous magnetization

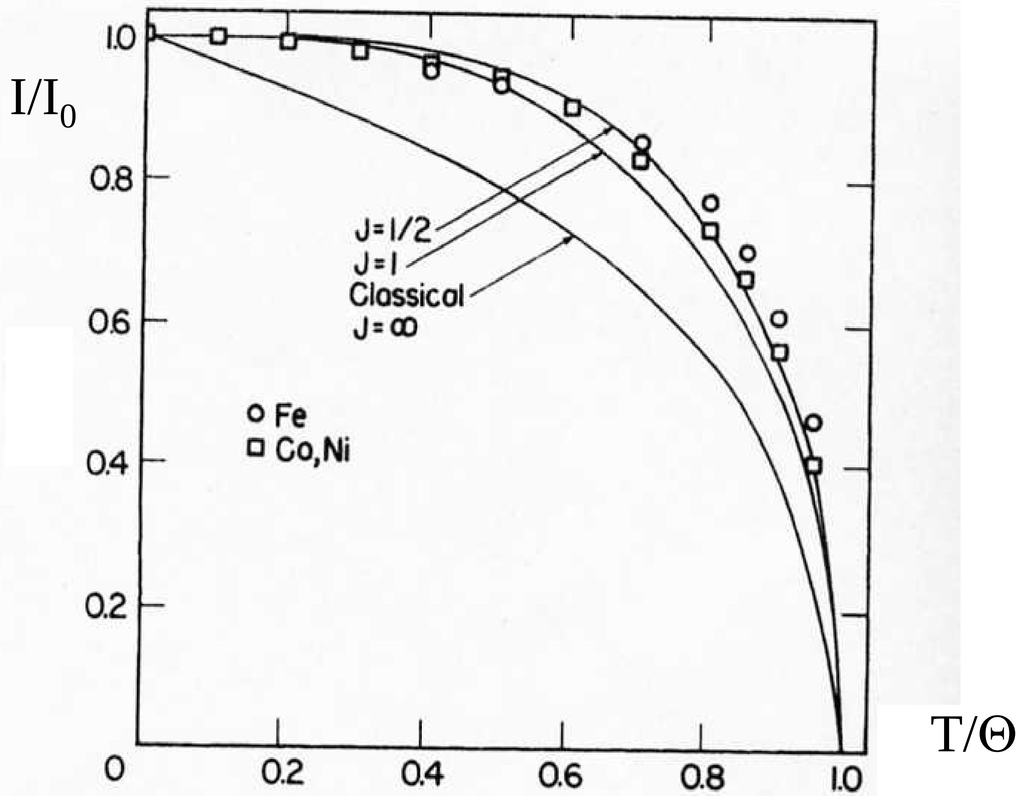


Fig. 11.7 Temperature dependence of the spontaneous magnetization within a domain for i
cobalt and nickel, compared with calculations based on the ferromagnetic Brillouin functi

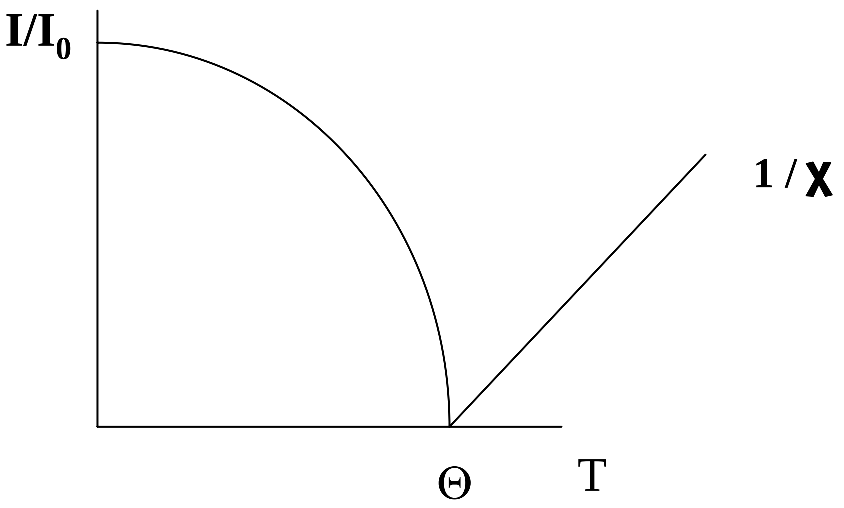
T > Curie temperature (Θ)

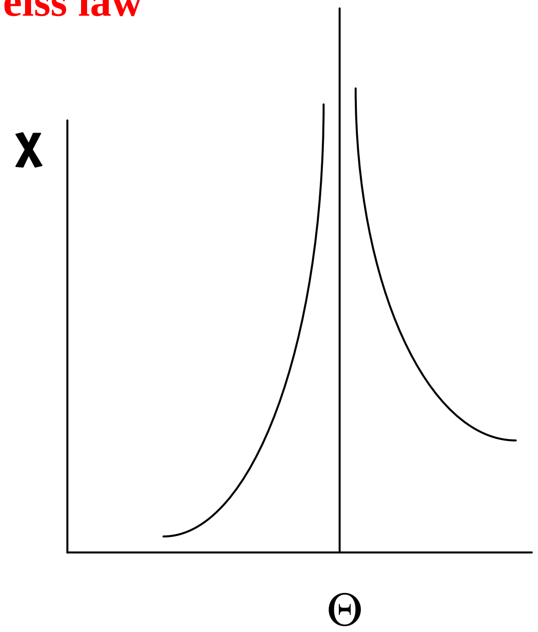
For x << 1, $B_J(x) = (J + 1)\, x / 3J$

$(2.9) \rightarrow I = Ng\mu_B J (J + 1)\, x / 3 = (C/T)(H + wI)$

$I = CH / (T - Cw)$

$\chi = I / H = C / (T - \Theta), \Theta = Cw$ Curie-Weiss law





Molecular field approximation

Estimation of w

Ex) Fe

Θ= 1063 K, μ = 2.2 μ_B, N = 8.54 × 10^{28}/m^3

J = 1 → w = 3kΘJ/(J + 1) N μ^2 = 3.9 × 10^8 [A m / Wb]

Molecular field H_m = w I = wNμ = 0.85 × 10^9 [A/m]
= 1.1 × 10^7 Oe = 11 [MOe]

This is quite large.

The w is based on the quantum mechanical exchange interaction

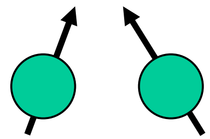
$$- J \, \mathbf{S}_1 \, \mathbf{S}_2$$

J **is exchange integral**

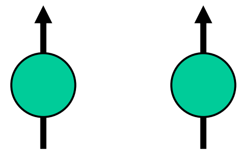
Summary: Types of Magnetism

Diamagnetism $\mathbf{S} = 0$, Orbital magnetic moment only

Paramagnetism $\mathbf{S} \neq 0$ and no atomic interaction



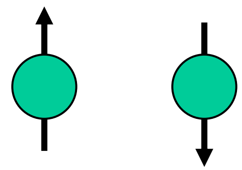
Ferromagnetism $S \neq 0$ and parallel coupling



$$-J\,\mathbf{S_1}\,\mathbf{S_2} \quad , \quad J > \mathbf{0}$$

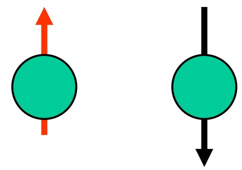
J**:Exchange Integral**

Antiferromagnetism $S \neq 0$ and antiparallel coupling



$$-J\,\mathbf{S_1}\,\mathbf{S_2} \quad , \quad J < \mathbf{0}$$

Ferrimagnetism $S \neq 0$, antiparallel coupling
and different atomic moments



$$-J\,\mathbf{S_1}\,\mathbf{S_2} \quad , \quad J < \mathbf{0}$$

$$\mathbf{S_1} \neq \mathbf{S_2}$$