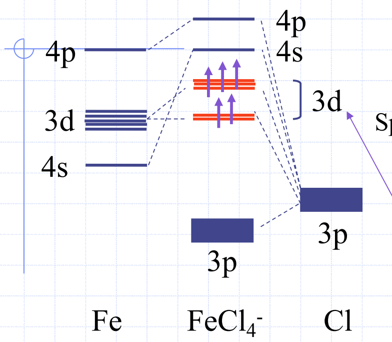
Magnetism

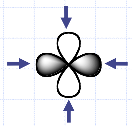
Molecular orbital of transition metal compounds



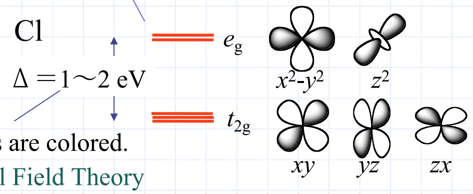
Ligand orbital: bonding
Transition metal d-orbitals: antibonding
s, p levels are further antibonding
All valence electron enters in the d levels

Splitting of the d levels (Coordination Splitting)

For octahedral



Two e_g orbitals directed to the ligands are lifted, and more antibonding.



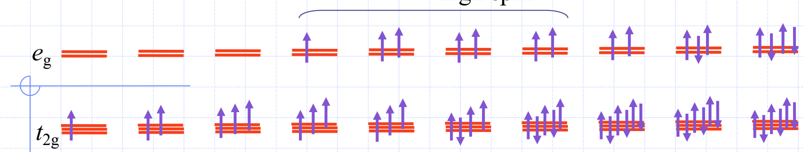
Absorb visible light
→Transition metal compounds are colored.

Ligand Field Theory or Crystal Field Theory

Molecular Field Theory of Transition Metal Compounds

Three t_{2g} orbitals have nodes in the direction of the ligands, and are nonbonding.

For octahedral

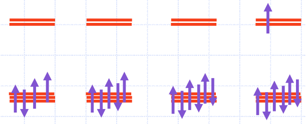


	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$S=$	1/2	1	3/2	2	5/2	2	3/2	1	1/2	0
	Ti^{3+}	Ti^{2+}	Cr^{3+}	Cr^{2+}	Fe^{3+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
	V^{4+}	V^{3+}	Mn^{4+}	Mn^{3+}	Mn^{2+}	Co^{3+}	Ni^{3+}			Cu^{+}
				Ti^0	V^0	Cr^0	Mn^0	Fe^0	Co^0	Ni^0
				4	5	6	7	8	9	10

For d = 4〜7, when crystal field > Hund rule, low spin state achieved

Transition from high spin to low spin by changing T

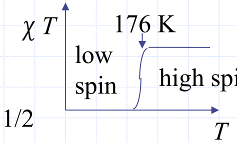
Spin crossover



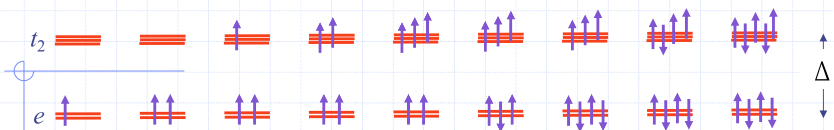
	d^4	d^5	d^6	d^7
$S=$	1	1/2	0	1/2

Low spin d^6 is nonmagnetic

$[Fe^{II}(phen)_2(NCS)_2]$

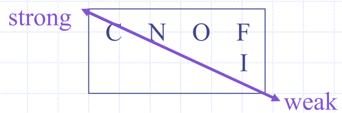


For tetrahedral：upside down. always high spin



	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
$S=$	1/2	1	3/2	2	5/2	2	3/2	1	1/2

Order of Δ： spectroscopic series
$I^- < Br^- < Cl^- < F^- < OH^- < H_2O$
$< NCS^- \sim NH_3 <$ en < phen $< CN^-$

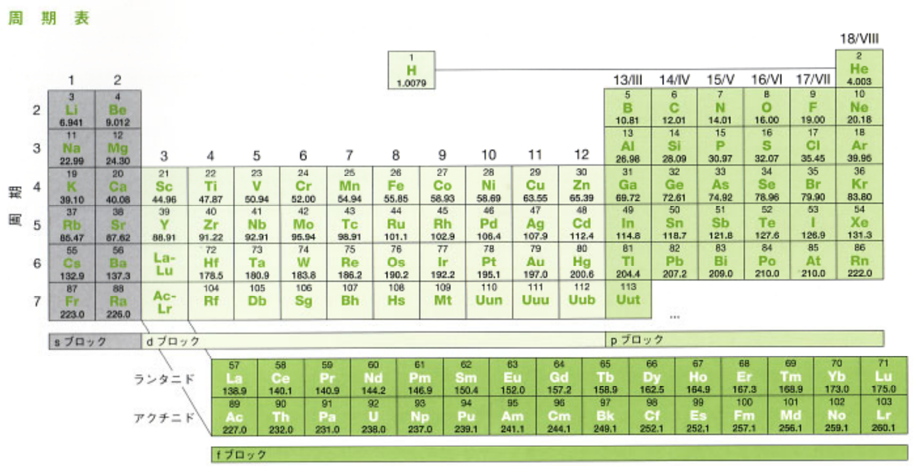


For example, $FeCl_4^-$ is Fe^{3+} so d^8 for Fe^0 minus 3 leads to d^5, so $S=5/2$

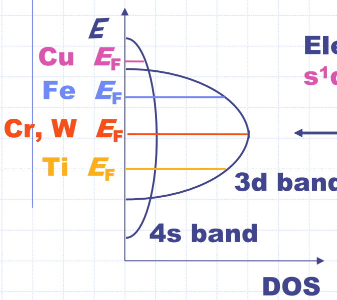
Exercise: Estimate spins of the following ions and compounds.

$MnCl_4^{2-}$ [ ] MnO_4^- [ ] $CuCl_4^{2-}$ [ ]

$CoCl_4^{2-}$ [ ] $NiCl_4^{2-}$ [ ] MnO_2 [ ]



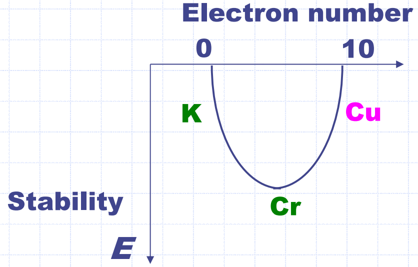
Density of states in transition metals



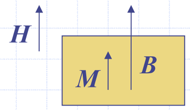
3d band is narrower than 4s band

Element metals are to be regarded as s^1d^{n-1}

W has the higherst mp (3380℃)
← strong bond



Magnetic Susceptibility



Application of $\boldsymbol{H}$ to materials gives rise to magnetization $\boldsymbol{M}$. $\boldsymbol{B}$ in the material is $\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M})$

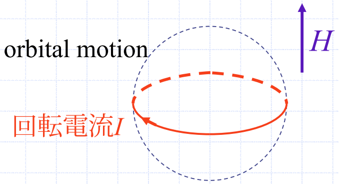
$\chi = M / H$ Magnetic Susceptibility

$\chi < 0$ $\quad B < \mu_0 H$ Diamagnetism: Materials without spins

$\chi > 0$ $\quad B > \mu_0 H$ Paramagnetism: Materials with unpaired spins

Diamagnetism of Atoms

Materials with unpaired spins → Atomic orbital motion



$$I = (-Ze)\left(\frac{1}{2\pi}\frac{eB}{m}\right)\frac{1}{2}$$

charge cyclotron frequency ω_c

(Mag. Moment) = I × (Circular Area)

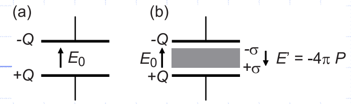
$$\mu = -\frac{Ze^2B}{4m}<x^2+y^2> = -\frac{Ze^2B}{6m}<r^2>$$

leads to $\frac{2}{3}<r^2>$

$$\chi = \frac{N\mu}{B} = -\frac{NZe^2}{6m}<r^2>$$ Diamagnetism inherent in the atoms $\chi < 0$

Sum of atomic diamagnetism gives the Pascal diamagnetism.

Dielectrics in a capacitor



Capacitors:

$Q = CV$ $\quad q = \varepsilon E$ $\quad E = V/d$

$C = \varepsilon S/d$ $\quad Q = qS$

ε_0 = 0.088 pF/cm

Insert dielectrics with keeping q

Actual field Original electric field

$E = E_0 - 4\pi P$ $\qquad \varepsilon_0 E = D - P$ $\qquad q' = q - \sigma$

→ $D = E + 4\pi P$ cgs $\qquad D = \varepsilon_0 E + P$ MKS

$D = \varepsilon E$ dielectric const. $\qquad D = \varepsilon_0\varepsilon_r E$ →

E* decreases 1/ε of *D **e.g. Si (ε = 11.9) → 1/11.9 water → 1/80**

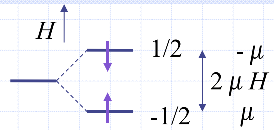
Insert dielectrics with keeping V → C is × ε

In particular, σ = q perfect polarization → E = 0 and ε = ∞

→ Metal (E = 0 in a metal)

Always $P > 0$ → ε > 1

Curie Paramagnetism



Magnetic moment from unpaired electons

$\mu = \gamma \hbar S = -g\mu_B S$

Zeemann splitting due to the magnetic field $\boldsymbol{H}$

$E = -g\mu_B HS = -\mu H$

Split to two for $S = 1/2$. In thermal equilibrium:

$$\frac{N_\uparrow}{N} = \frac{e^{\mu H/k_BT}}{e^{\mu H/k_BT} + e^{-\mu H/k_BT}} \qquad \frac{N_\downarrow}{N} = \frac{e^{-\mu H/k_BT}}{e^{\mu H/k_BT} + e^{-\mu H/k_BT}}$$

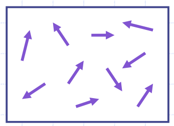
lead to

$$M = \mu_B(N_\uparrow - N_\downarrow) = N\mu \tanh\frac{\mu H}{k_BT} \approx N\mu\left(\frac{\mu H}{k_BT}\right) \leftarrow \frac{\mu H}{k_BT} << 1 \quad \text{so}$$

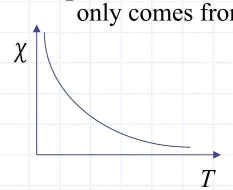
$$\chi = \frac{M}{H} = \frac{N\mu^2}{k_BT} = \frac{C}{T}$$ Curie constant

Except for S=1/2 $\quad C = \frac{NS(S+1)g^2\mu_B^2}{3k_B}$

χ is inversely proportional to T. only comes from S.



Random spins
Aligned under magnetic field.
More aligned at low T.



Magnetic Order

Ferromagnetism：all parallel
The whole material is a magnet.

$J>0$
$S_i // S_j$ is stable

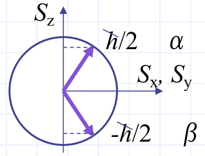
Antiferromagnetism：
alternately opposite directions

$J<0$
Antiparallel S_i and S_j

Spin Hamiltoniam

$$\hat{H} = -\sum_{i,j} 2J_{ij}\bar{S}_i\bar{S}_j - g\mu_B H\sum_i \bar{S}_i$$

Interaction　Zeemann splitting



S_i is a vector like (S_x, S_y, S_z): (Heisenberg model).
When spin is always directed in one direction (z) due to the large magnetic anisotropy coming from the crystal field, we only consider S_z.
(Ising model)

When $S_i = 1/2$, $S_j = 1/2$, (Interaction) $= -J/2$
When $S_i = 1/2$, $S_j = -1/2$, (Interaction) $= J/2$
} Energy difference J

Note: (Interaction) is defined as $-\sum_{i,j} J_{ij}\bar{S}_i\bar{S}_j$ in old literatures.
J is twice larger.

Molecular Field (Mean Field) Approximation

Focusing on S_i, and use average sum for Σj

$$\hat{H} = \sum_i S_i\left(-\sum_j 2J_{ij}S_j - g\mu_B H\right) = -g\mu_B (H_{\text{eff}} + H)\sum_i S_i$$

$$H_{\text{eff}} = \frac{1}{g\mu_B}\sum_j 2J_{ij} < S_j >$$

Interaction with S_j is replaced by a field (effective or internal field)(有効 or 内部磁場) generated on S_i.

S_j changes every moment, but Sj is approximated by the average $<S_j>$
(分子場近似 or 平均場近似 Molecular Field or Mean Field Approximation)

Statistical distribution similar to the Curie paramagnetism gives

$$M = \frac{N\mu^2 H}{k_B T} \xrightarrow{H \to H_{\text{eff}} + H} M = \chi_0 (H_{\text{eff}} + H)$$

where $M = Ng\mu_B <S>$ leads to

分子磁場係数

$$H_{\text{eff}} = \frac{\sum_j 2J_{ij} < S_j >}{N(g\mu_B)^2} M = aM$$

Put this in the above eq. to give

$$M = \chi_0 (aM + H)$$

$$M\left[(1 - \chi_0 a)\right] = \chi_0 H \to \chi = \frac{M}{H} = \frac{\chi_0}{1 - \chi_0 a} = \frac{C}{T - \theta}$$

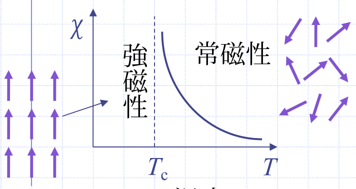
Curie-Weiss則

$$\theta = \frac{1}{k_B}\sum_j 2J_{ij} = \frac{2zJ}{k_B}$$

← Coordination number z for nearest neighbor J's

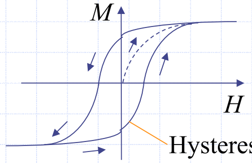
Weiss温度

$J>0 \to \theta>0$　Ferromagnetism



Curie温度

$T \to T_c$: $\chi \to \infty$
$T < T_c$: $M \neq 0$ for $H=0$
Spontaneous Magnetism → Magnet
T_c　Fe　1043 K　Ni　627 K



Magnetization of Ferromagnet

Usual ferromagnet has randomly oriented magnetic domains (磁区), but magnetic field aligns the spin orientation to make a bulk magnet.

Antiferromagnetism　Molecular fiedl for $J<0$：two sublattices $\uparrow M_1$, $\downarrow M_2$

$$\uparrow M_1 = \chi_0 (aM_2 + H)$$
$$\downarrow M_2 = \chi_0 (aM_1 + H)$$

$$a = \frac{\sum_j 4zJ_{ij}}{N(g\mu_B)^2} < 0 \qquad \chi_0 = \frac{C}{2T}$$

Half sites in the sublattice

add two equations

$$M = M_1 + M_2 = \chi_0 (a(M_1 + M_2) + 2H) = \chi_0 (aM + 2H)$$

$$\chi = \frac{M}{H} = \frac{2\chi_0}{1 - \chi_0 a} = \frac{C}{T - \theta}$$

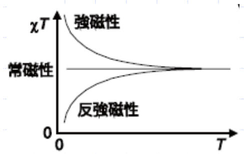
M_1, M_2→matrix

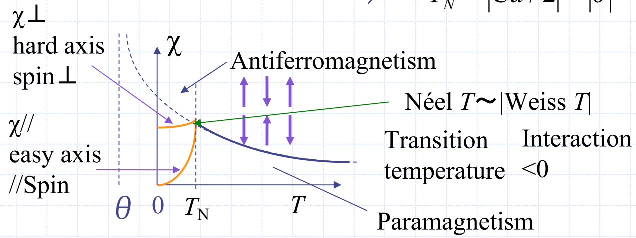
$$\begin{pmatrix} -\frac{1}{\chi_0} & a \\ a & -\frac{1}{\chi_0} \end{pmatrix}\begin{pmatrix} M_1 \\ M_2 \end{pmatrix} = \begin{pmatrix} H \\ H \end{pmatrix}$$

Determinant = 0 at $H \to 0$

$$\begin{vmatrix} -2T/C & a \\ a & -2T/C \end{vmatrix} = 0$$

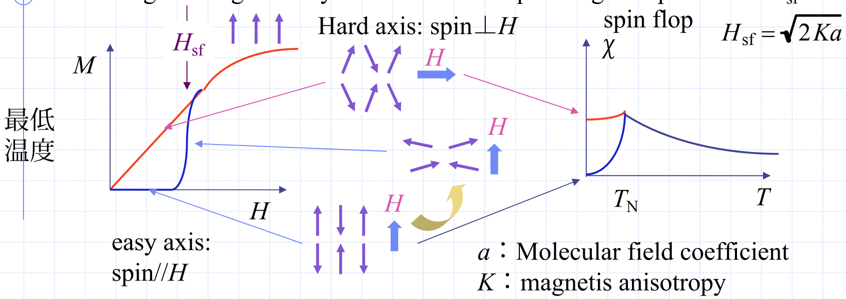
$$\to T_N = |Ca/2| = |\theta|$$





Easy axis of antiferromagnets

Spins in antiferromagnet are oriented in a particular direction due to
1) Dipole interaction 2) crystal field
Increasing H along the easy axis leads to abrupt change to spin $\perp H$ at H_{sf}.

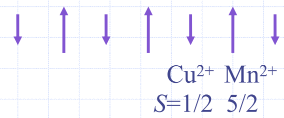


a：Molecular field coefficient
K：magnetis anisotropy
(difference of //and $\perp$)

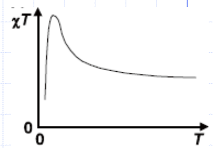
With increasing H // easy axis, suddenly spin becomes $\perp H$ at H_{sf}
Enery difference between easy and hard axis K (magnetic anisotropy) **spin flop**

$$\frac{1}{2}\chi_\perp H^2 - \frac{1}{2}\chi_{//} H^2 = K \longrightarrow H_{sf} = \sqrt{\frac{2K}{\chi_\perp - \chi_{//}}} = \sqrt{2K|a|}$$

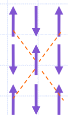
Ferrimagnetism



Alternating spins with different S
(e.g. different metals) lead to remaining moment
even for antiparallel order for J<0.
Ferrite Fe_3O_4 has Fe^{3+} and Fe^{2+}.
Most molecular magnets.

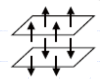


Magnetic frustration



Including a' from the next neighbor

$$M_1 = \chi_0(aM_2 - a'M_1 + H)$$
$$M_2 = \chi_0(aM_1 - a'M_2 + H)$$



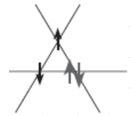
Add two equations

$$M = M_1 + M_2 = \chi_0((a-a')(M_1+M_2)+2H) = \chi_0((a-a')M + 2H)$$

or

$$\theta = \frac{2(zJ - z'J')}{k_B}$$ loss of a' (frustration)

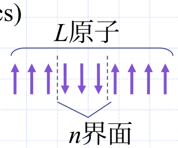
Antiferromagnetim does not happen
in a triangular lattice because the third
spin orientation is not determined (spin liquid).



Low dimensional fluctuation

1D Magnet does not exist (Landau, Lifshitz Statistical Physics)

Statistical weight of a state with n boundaries in a 1D
ferromagnet (length L): $W = \frac{L!}{(L-n)!n!}$



$$\ln W = L \ln L - (L-n)\ln(L-n) - n \ln n$$
$$= L \ln \frac{L}{L-n} + n \ln \frac{L-n}{n} \approx -n \ln \frac{n}{L} \qquad n<<L \to 第1項\sim 0$$

The free energy is $G = G_0 - TS + nJ = G_0 + k_B T n \ln \frac{n}{L} + nJ$

Realized n is obtained by minimizing G:

$$\frac{\partial G}{\partial n} = k_B T \ln \frac{n}{L} + J \quad (=0)$$

ln(n/L) takes a large negative value for small n/L, so near $n\sim 0$: $\frac{\partial G}{\partial n} < 0$

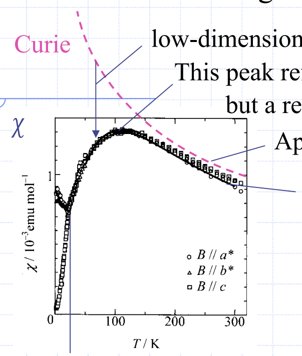
With increasing n, G decreases.
Accordingly, there is a minimum of G at finite $n \neq 0$.
For finite $T \neq 0$, many boundaries appear, and long-range magnetic order
is never established. Then there is no 1D ferromagnet.
Multi dimension increases the loss of J, and leads to long range magnetic order.

In general, a 1D system does not undergo any phase transitions at finite T.

Low-dimensional magnet ： large J only for 1 or 2 directions

Curie

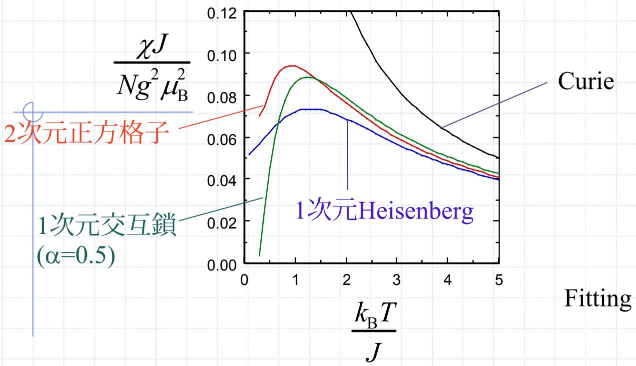
low-dimensional fluctuation
This peak reflects the short-range order due to J,
but a real phase transition does not take place.
Approaches to the Curie law at high T.



χ (T) is fitted to numerical calculations
Bonner & Fischer, *Phys. Rev.* A **135**, 640 (1964).
de Jongh & Miedema, *Experiments on Simple Magnetic Model Systems*, Tayler (1974).

3D long-range order due to interchain interaction.
(反強磁性)

β'-(BEDT-TTF)$_2$ICl$_2$



Fitting to polynomials

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