Lecture on

2022.4.20 Lecture 3

10:25 – 11:55

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

1. Spin-orbit interaction
2. Magnetism in quantum theory

Chapter 2 Magnetism in localized systems

1. Spherical potential
2. Larmor precession
3. Magnetism of inert gas
4. LS multiplex ground state of open shell ions and Hund’s rule

Agenda

Electronic states in magnetic ions

- LS coupling approach
- j-j coupling approach

Paramagnetism by magnetic ions in insulators

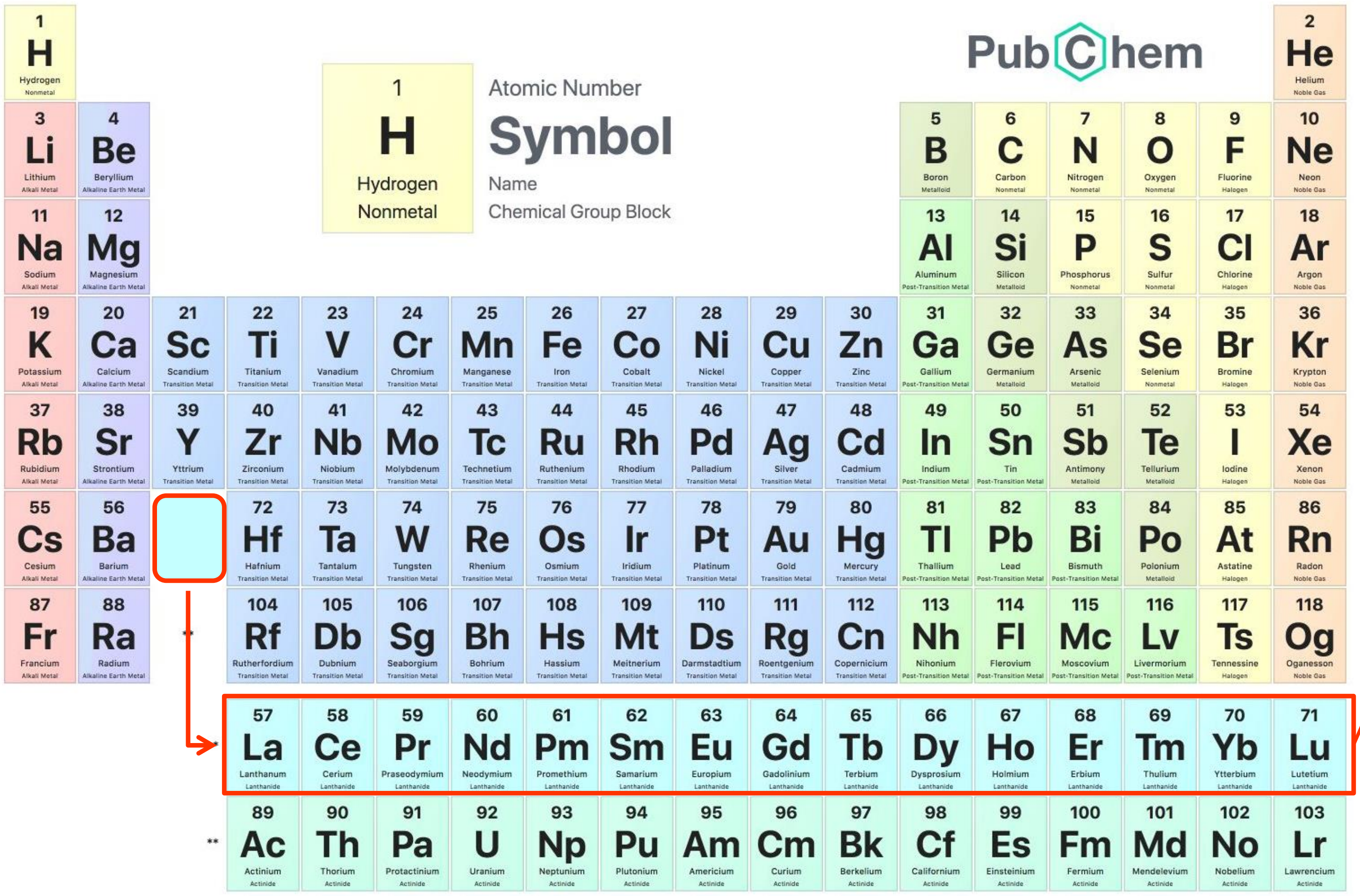
- Curie law
- Breakdown of LS coupling approach in $3d$ transition metals

Ligand field approach

- Octahedron potential

Electronic states in magnetic ions (continued)

Periodic table of elements



Sm

$$4s^2 4p^6 (4f)^6 5s^2 5p^6 6s^2$$

Electronic states in magnetic ions (continued)

Ex) Lanthanoid:

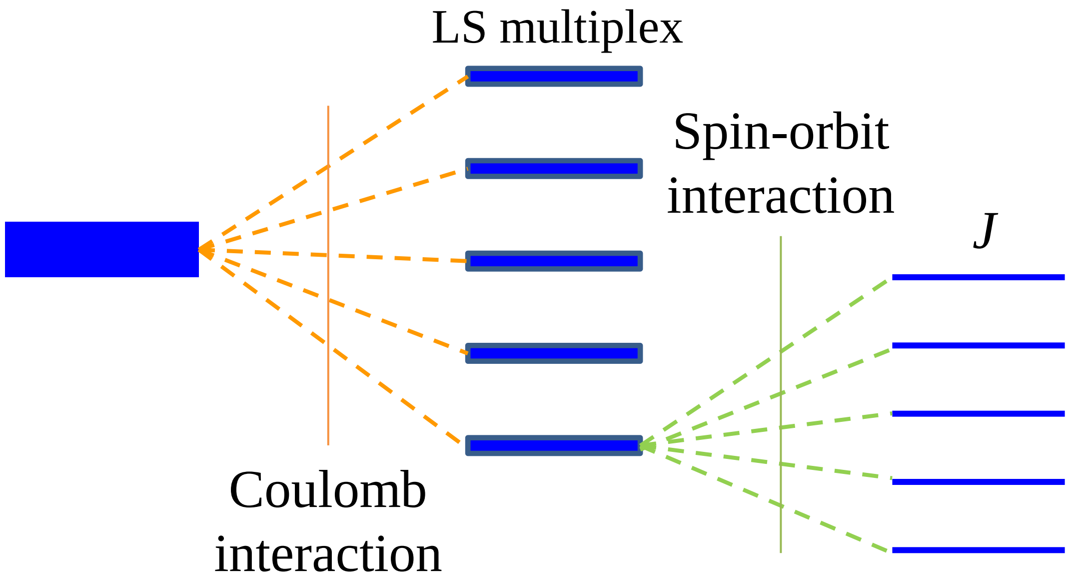
	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide	Lanthanide
Number of 4*f* electrons:	0	1	3	4	5	6	7	7	9	10	11	12	13	14	15
Number of 4*f* electrons (3+ion):	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

$$\mathcal{H}_{\mathrm{L}} = \underline{\mathcal{H}_{\mathrm{L0}} + \mathcal{H}_{\mathrm{C}}} + \mathcal{H}_{\mathrm{SOI}} + \mathcal{H}_{\mathrm{CF}}$$

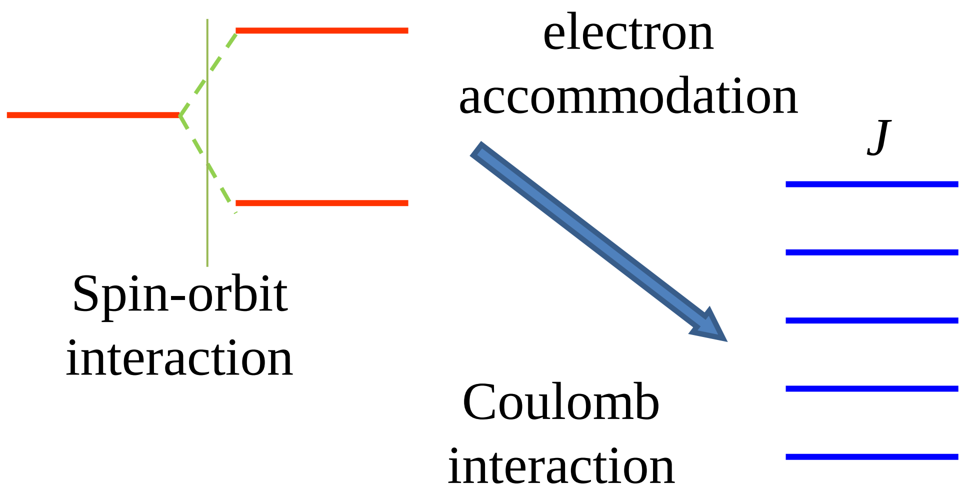
Lifting of degeneracy to LS multiplex

Hund's rule to find the ground LS multiplex

LS coupling (Russell-Saunders)



j-j coupling



Spin-orbit splitting of multiplex in single-electron problem

Spin-orbit term in the Pauli approximation:
$$-\frac{e\hbar\boldsymbol{\sigma}\cdot\boldsymbol{p}\times\boldsymbol{E}}{4m^2c^2} = -\frac{e^2\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{p}\times\nabla V) = \frac{e^2\hbar}{2m^2c^2}\zeta(r)\boldsymbol{s}\cdot\boldsymbol{l} \equiv \xi(r)\boldsymbol{l}\cdot\boldsymbol{s}$$

Coulomb potential: $V(r) = -\dfrac{Ze^2}{4\pi\epsilon_0 r}$ then $\xi(r) = \dfrac{Ze^2}{2m^2c^2}\dfrac{1}{(4\pi\epsilon_0)r^3}$

The expression tells that the SOI is more important for larger Z and orbitals closer to the nucleus.

Lanthanoid: (effect of spin-orbit interaction) > (that of crystal field)

Spin-orbit single electron hamiltonian:
$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\rm so} = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) + \xi(r)\boldsymbol{l}\cdot\boldsymbol{s}$$

$[\mathcal{H}, \boldsymbol{l}] \neq 0 \quad [\mathcal{H}, \boldsymbol{s}] \neq 0$ $\quad$ $\boldsymbol{l}, \boldsymbol{s}$: not constants of motion

$$[\boldsymbol{l}\cdot\boldsymbol{s}, \hat{l}_z] = i\hbar(-l_y s_x + l_x s_y), \quad [\boldsymbol{l}\cdot\boldsymbol{s}, \hat{s}_z] = i\hbar(-l_x s_y + l_y s_x) = -[\boldsymbol{l}\cdot\boldsymbol{s}, \hat{l}_z]$$

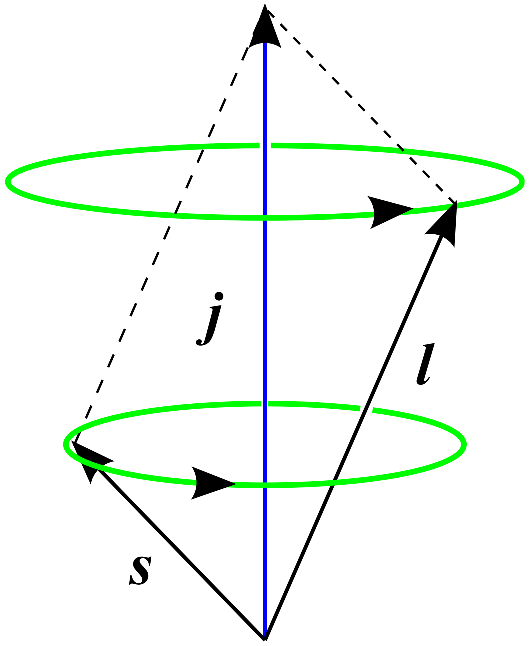
Total angular momentum

$$\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s} \longrightarrow [\mathcal{H}, \boldsymbol{j}] = 0$$

j is a constant of motion

$$\boldsymbol{l} \cdot \boldsymbol{s} = (\boldsymbol{l} + \boldsymbol{s}) \cdot \boldsymbol{s} - \boldsymbol{s}^2 = \underline{\boldsymbol{j} \cdot \boldsymbol{s}} - \boldsymbol{s}^2 \qquad [\mathcal{H}, \boldsymbol{s}^2] = 0$$

Zeeman-like term



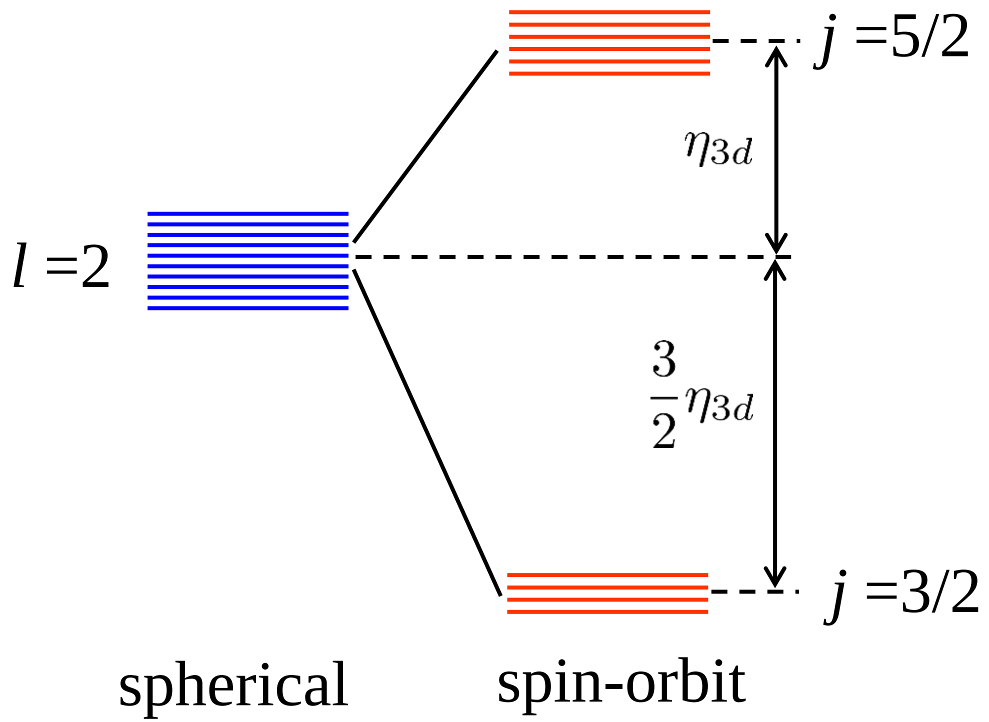
l, ***s*** : Precession around ***j***

$$2\boldsymbol{l} \cdot \boldsymbol{s} = (\boldsymbol{l} + \boldsymbol{s})^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2 = \boldsymbol{j}^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2$$

Eigenvalue of $\boldsymbol{l} \cdot \boldsymbol{s}$

$$[j(j+1) - l(l+1) - s(s+1)]/2 = \frac{1}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$$

Spin-orbit splitting of multiplex in single-electron problem (2)



Energy eigenvalues:

$$\epsilon_{nlj} = \epsilon_{nl} + \frac{\eta_{nl}}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$$

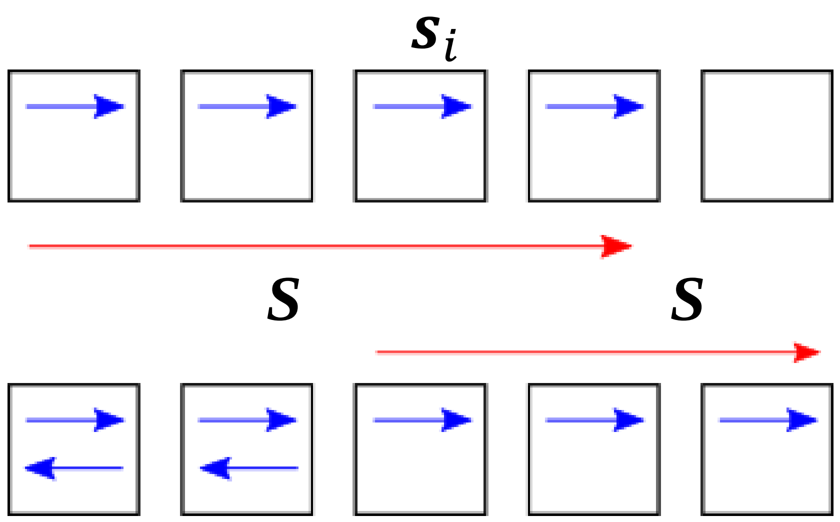
$$\eta_{nl} = \int_0^\infty \xi(r) R_{nl}(r)^2 r^2 dt$$

j can take values: $|l \pm 1/2|$

Spin-orbit interaction in the ground state of LS multiplex

Multi-electron hamiltonian: $\mathcal{H}_{\rm SOI} = \sum_i \xi(r_i)\boldsymbol{l}_i \cdot \boldsymbol{s}_i \rightarrow \sum_i \xi_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i \rightarrow \xi \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i$

LS-coupling approach



Hund's rule $\longrightarrow$ LS multiplex ground state
$(2L+1)(2S+1)$ degeneracy

$[\mathcal{H}, \boldsymbol{L}] \neq 0 \quad [\mathcal{H}, \boldsymbol{S}] \neq 0$

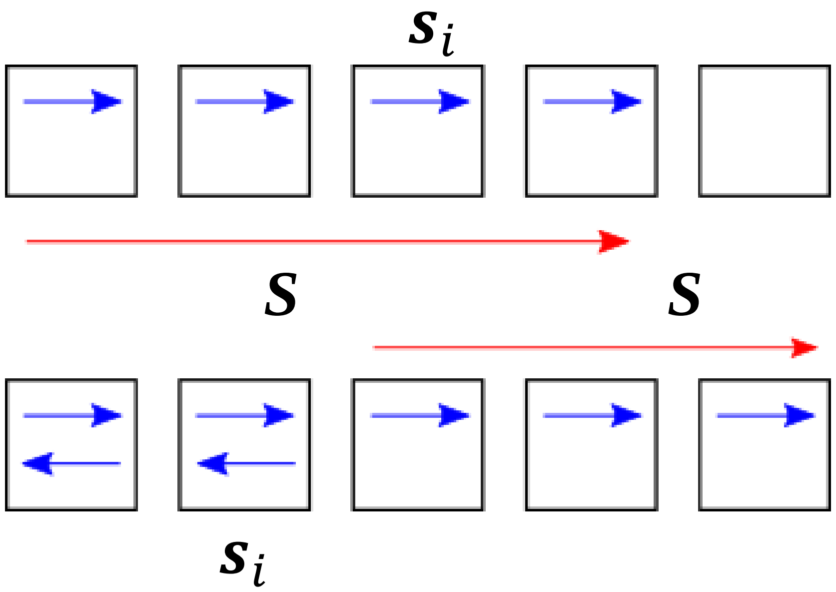
$\boldsymbol{L}$, $\boldsymbol{S}$ are not constant of motion.

$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$: a constant of motion

$$\boldsymbol{s}_i = \frac{1}{n}\boldsymbol{S} = \frac{1}{2S}\boldsymbol{S} \quad (n \leq 2l+1)$$

$$\mathcal{H}_{\rm SOI} = \xi \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i = \xi \left(\sum_i \boldsymbol{l}_i\right) \cdot \boldsymbol{s} = \frac{\xi}{2S}\boldsymbol{L} \cdot \boldsymbol{S} \equiv \lambda \boldsymbol{L} \cdot \boldsymbol{S}$$

Spin-orbit interaction in the ground state of LS multiplex



$n > 2l + 1$

Summation on all m_l: $\sum l_i = 0$

Residual part: $\boldsymbol{s}_i$ and $\boldsymbol{S}$ are inverted

$$\mathcal{H}_{\mathrm{SOI}} = \xi \left[\left(\sum_{i=1}^{2l+1} \boldsymbol{l}_i \right) \cdot \boldsymbol{s} - \left(\sum_{i=2l+2}^{n} \boldsymbol{l}_i \right) \cdot \boldsymbol{s} \right]$$

$$= -\frac{\xi}{2S} \boldsymbol{L} \cdot \boldsymbol{S} = -\lambda \boldsymbol{L} \cdot \boldsymbol{S}$$

$$J = |L - S|, |L - S| + 1, \cdots, L + S$$

$$\boldsymbol{L} \cdot \boldsymbol{S} = \frac{1}{2}(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2) = \frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]$$

Ground state

$n \leq 2l + 1 \qquad J = |L - S|$

$n > 2l + 1 \qquad J = L + S$

Electron configuration of Lanthanoid ions

Elements (Lanthanoid)	Electronic Configuration atom R	Electronic Configuration ion R^{3+}	L	S	J	Ground state multiplex	g_j
La	$5d6s^2$		0	0	0	${}^1S_0$	0
Ce	$4f5d6s^2$	$4f^1$	3	1/2	5/2	${}^2F_{5/2}$	6/7
Pr	$4f^36s^2$	$4f^2$	5	1	4	${}^3H_4$	4/5
Nd	$4f^46s^2$	$4f^3$	6	3/2	9/2	${}^4I_{9/2}$	8/11
Pm	$4f^56s^2$	$4f^4$	6	2	4	${}^5I_4$	1/5
Sm	$4f^66s^2$	$4f^5$	5	5/2	5/2	${}^6H_{5/2}$	2/7
Eu	$4f^76s^2$	$4f^6$	3	3	0	${}^7F_0$	0
Gd	$4f^75d6s^2$	$4f^7$	0	7/2	7/2	${}^8S_{7/2}$	2
Tb	$4f^96s^2$	$4f^8$	3	3	6	${}^7F_6$	3/2
Dy	$4f^{10}6s^2$	$4f^9$	5	5/2	15/2	${}^6H_{15/2}$	4/3
Ho	$4f^{11}6s^2$	$4f^{10}$	6	2	8	${}^5I_8$	5/4
Er	$4f^{12}6s^2$	$4f^{11}$	6	3/2	15/2	${}^4I_{15/2}$	6/5
Tm	$4f^{13}6s^2$	$4f^{12}$	5	1	6	${}^3H_6$	7/6
Yb	$4f^{14}6s^2$	$4f^{13}$	3	1/2	7/2	${}^2F_{7/2}$	8/7
Lu	$4f^{14}5d6s^2$	$4f^{14}$	0	0	0	${}^1S_0$	0

Spectroscopic symbol of multi-electron state

$$(L, S, J)$$
$$\downarrow$$
$${}^{2S+1}L_J$$

$2S + 1$: number
L: symbol
J: number

Eigenfunction and second quantization representation

Eigenfunction for (J, M): $$|J, M\rangle = \sum_{M_l M_s} \underbrace{\langle L, M_l; S, M_s | J, M\rangle}_{\text{Clebsch-Gordan coefficient}} |L, M_l; S, M_s\rangle$$

Second quantization representation: $$\mathcal{H}_{\mathrm{SOI}} = \sum_{mm'\sigma\sigma'} \lambda_{nl}(m\sigma, m'\sigma') a^{\dagger}_{m\sigma} a_{m'\sigma'},$$

$$\lambda_{nl}(m\sigma, m'\sigma') \equiv \frac{Z_{\mathrm{eff}} e^2 \hbar^2 \langle r^3 \rangle}{2m^2c^2(4\pi\epsilon_0)} \langle m|\boldsymbol{l}|m'\rangle_{nl} \cdot \left(\frac{\boldsymbol{\sigma}}{2}\right)_{\sigma\sigma'}$$

Effective Coulomb potential: $$V(r) = -\frac{Z_{\mathrm{eff}} e^2}{4\pi\epsilon_0 r}$$

Clebsch-Gordan calculator on Wolfram alpha

https://www.wolframalpha.com/input/?i=Clebsch-Gordan+calculator

j-j coupling (short comment)

$(4f)^2$ Pr^{3+} $\quad l = 2 \quad j = 3 \pm \frac{1}{2} = \underline{\frac{5}{2}}, \frac{7}{2}$

Ground state

$$J_{\max} = \frac{5}{2} + \frac{3}{2} = 4$$: same as LS coupling

$$|J, M\rangle = |4, +4\rangle = a^\dagger_{+5/2} a^\dagger_{+3/2} |0\rangle$$

$$a^\dagger_{j_z} = \sum_{m,s} \langle 3, m; 1/2, s | 5/2, j_z \rangle \, a^\dagger_{ms} = \sqrt{\frac{7 + 2j_z}{14}} a^\dagger_{j_z + 1/2 \downarrow} - \sqrt{\frac{7 - 2j_z}{14}} a^\dagger_{j_z - \uparrow}$$

Paramagnetism by magnetic ions in insulators

Free local moment and Curie law

Due to the g-factor, the magnetization is not parallel with the total momentum, hence the magnetization is not a constant of motion.

$$\mathcal{H}_1 = \mu_\mathrm{B}(\boldsymbol{L} + g\boldsymbol{S}) \cdot \boldsymbol{B} \qquad \mathcal{H}_1 = g_J \mu_\mathrm{B} \boldsymbol{J} \cdot \boldsymbol{B}$$

$$g_J \boldsymbol{J} = \boldsymbol{L} + g\boldsymbol{S}, \quad \boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

Average gives effective g-factor: $$g_J = \frac{1+g}{2} - \frac{g-1}{2}\frac{L(L+1) - S(S+1)}{J(J+1)}$$ Lande g-factor

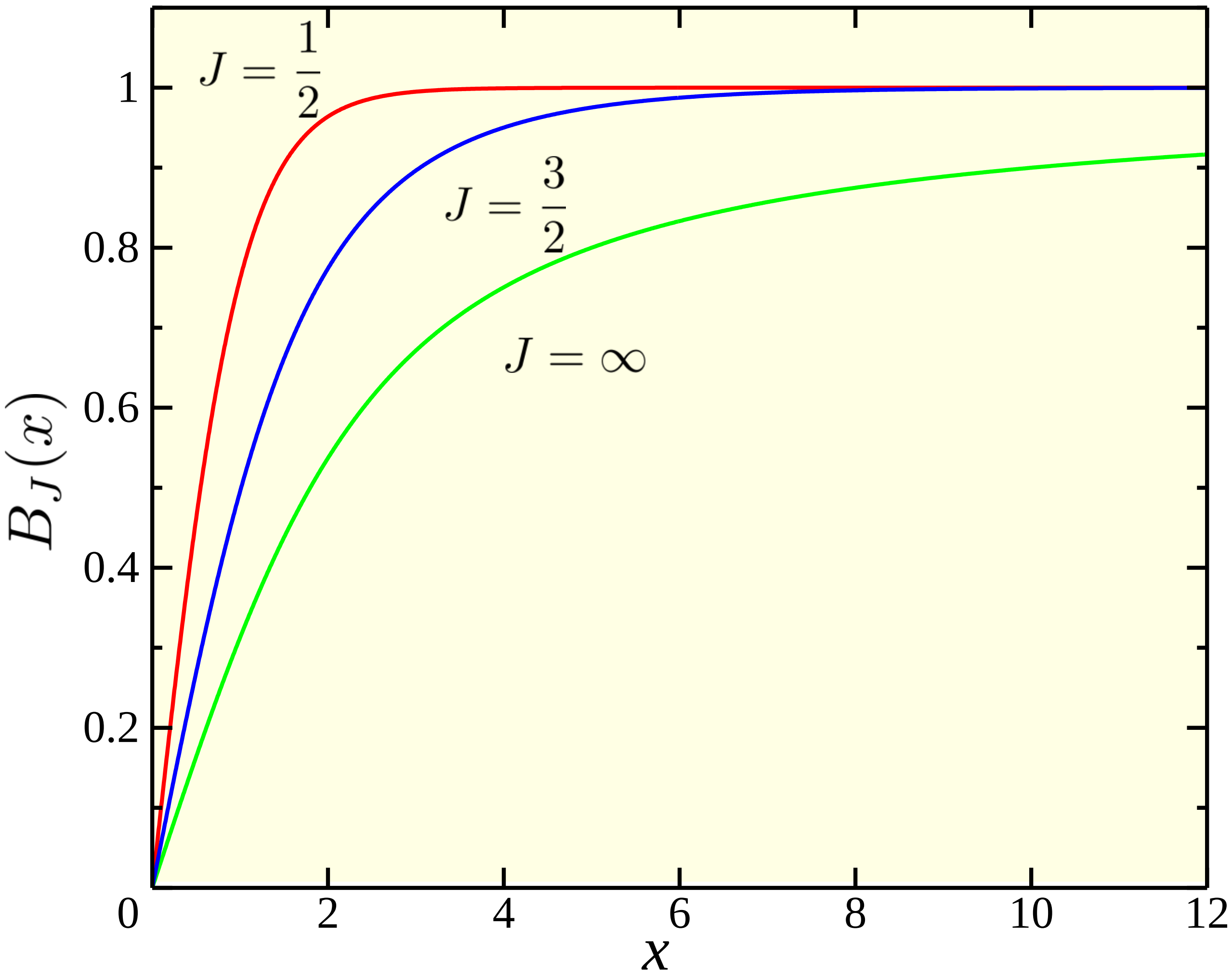
Expectation value of magnetization:

$$M = \langle -g_j \mu_\mathrm{B} J_z \rangle = -\frac{\mathbf{Tr}[g_j \mu_\mathrm{B} J_z \exp(-g_j \mu_\mathrm{B} J_z B / k_\mathrm{B} T)]}{\mathrm{Tr}[\exp(-g_j \mu_\mathrm{B} J_z B / k_\mathrm{B} T)]}$$

$$= k_\mathrm{B} T \frac{\partial}{\partial B} \log\left[\mathrm{Tr}\left(\exp \frac{-g_j \mu_\mathrm{B} J_z B}{k_\mathrm{B} T}\right)\right]$$

Partition function: $$\mathrm{Tr}\left(\exp \frac{-g_j \mu_\mathrm{B} J_z B}{k_\mathrm{B} T}\right) = \frac{\sinh\left[\frac{1}{2k_\mathrm{B}T} g_J \mu_\mathrm{B}\left(J + \frac{1}{2}\right) B\right]}{\sinh(g_J \mu_\mathrm{B} B / 2k_\mathrm{B} T)}$$

$$M = g_J \mu_{\rm B} J B_J\left(\frac{g_J \mu_{\rm B} J B}{k_{\rm B} T}\right)$$



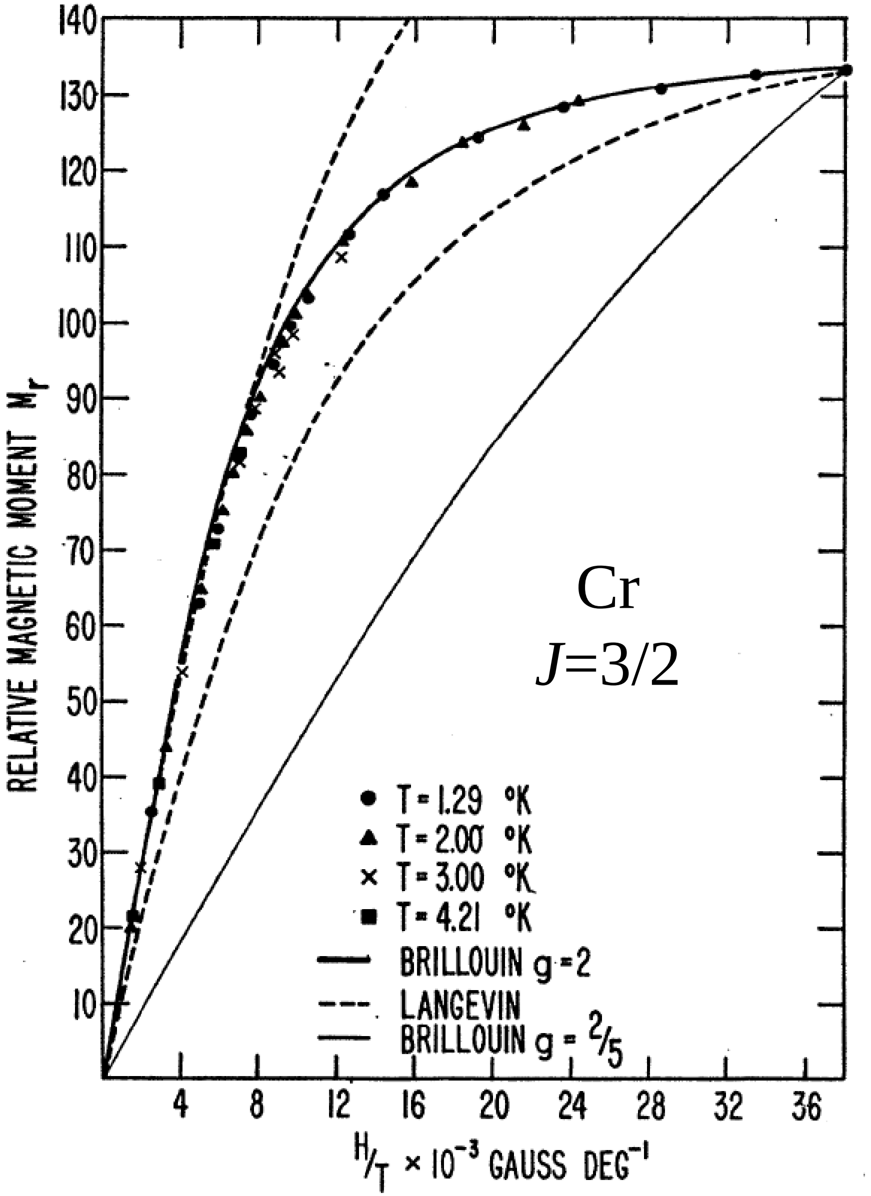
$$B_J(x) = \frac{2J+1}{2J}\coth\frac{2J+1}{2J}x - \frac{1}{2J}\coth\frac{x}{2J}$$

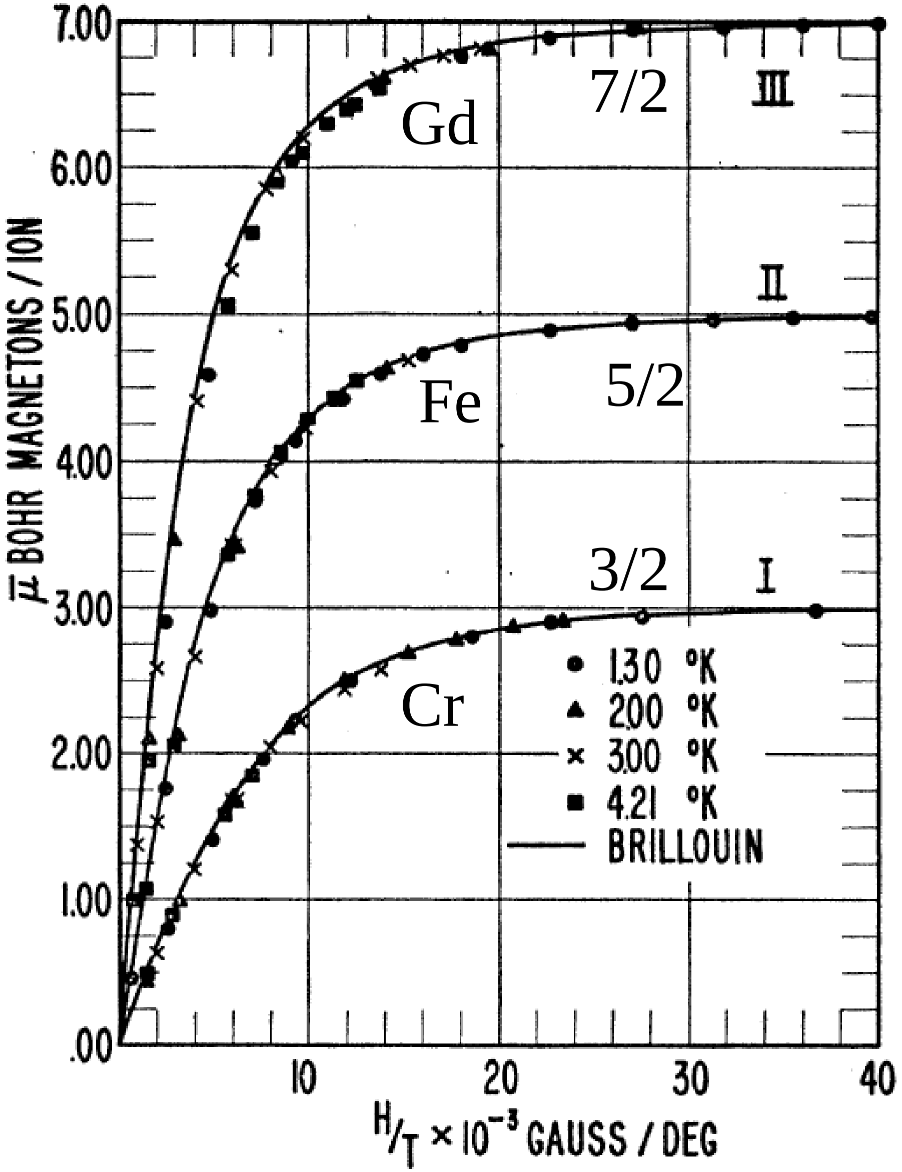
Brillouin function

$$x \ll 1 \rightarrow B_J(x) \sim (J+1)x/3J$$

$$\chi = \frac{dM}{dB} = (g_J\mu_{\rm B})^2\frac{J(J+1)}{3k_{\rm B}T}$$

Examples of experiments





II

$FeNH_4(SO_4)_2 \cdot 12H_2O$

Iron Ammonium Alum

W. E. Henry, PR **88**, 556, 1952

LS coupling approach for Lanthanoid (rare earth)

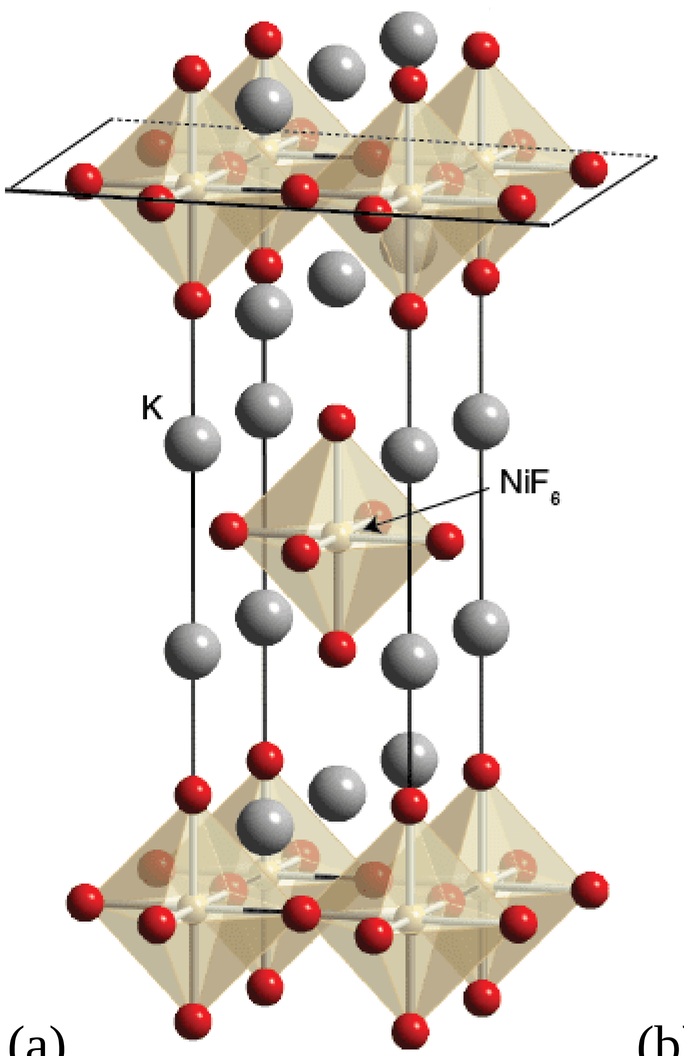
Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$4f^1$	$^2F_{5/2}$	Ce^{3+}	2.5	2.54	2.56
$4f^2$	$^3H_4$	Pr^{3+}	3.6	3.58	3.62
$4f^3$	$^4I_{9/2}$	Nd^{3+}	3.8	3.62	3.68
$4f^5$	$^6H_{5/2}$	Sm^{3+}	1.5	0.84	1.53
$4f^6$	$^7F_0$	Eu^{3+}	3.6	0.00	3.40
$4f^7$	$^8S_{7/2}$	Gd^{3+}	7.9	7.94	7.94
$4f^8$	$^7F_0$	Tb^{3+}	9.7	9.72	9.7
$4f^9$	$^6H_{15/2}$	Dy^{3+}	10.5	10.65	10.6
$4f^{10}$	$^5I_8$	Ho^{3+}	10.5	10.61	10.6
$4f^{11}$	$^4I_{15/2}$	Er^{3+}	9.4	9.58	9.6
$4f^{12}$	$^3H_6$	Tm^{3+}	7.2	7.56	7.6
$4f^{13}$	$^2F_{7/2}$	Yb^{3+}	4.5	4.54	4.5

3d transition metals

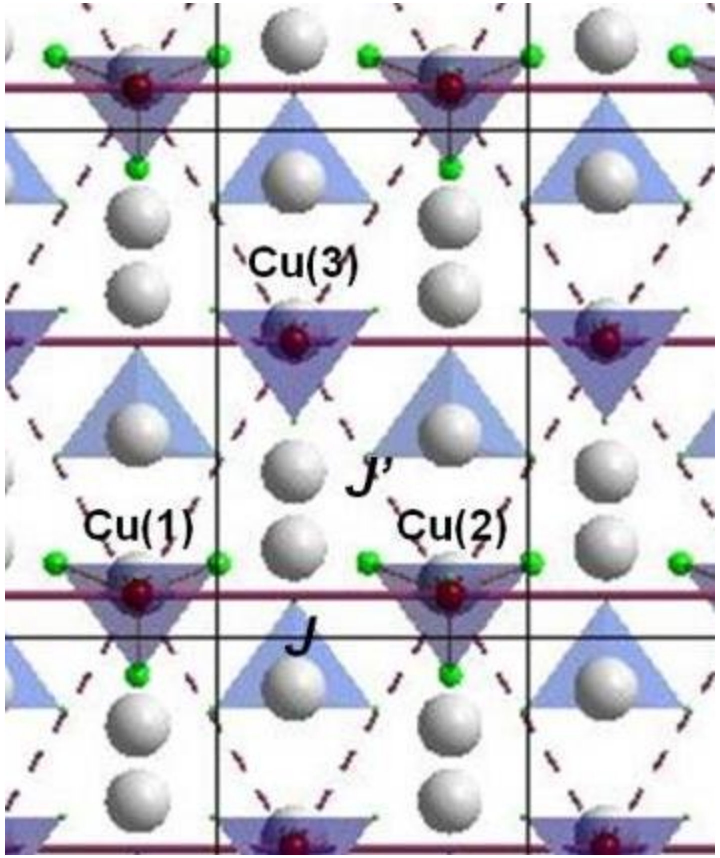
Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$3d^1$	$^2D_{3/2}$	V^{4+}	1.8	1.55	1.73
$3d^2$	$^3F_2$	V^{3+}	2.8	1.63	2.83
$3d^3$	$^4F_{3/2}$	V^{2+}	3.8	0.77	3.87
		Cr^{3+}	3.7	0.77	3.87
		Mn^{4+}	4.0	0.77	3.87
$3d^4$	$^5D_0$	Cr^{2+}	4.8	0	4.90
		Mn^{3+}	5.0	0	4.90
$3d^5$	$^6S_{5/2}$	Mn^{2+}	5.9	5.92	5.92
		Fe^{3+}	5.9	5.92	5.92
$3d^6$	$^5D_4$	Fe^{2+}	5.4	6.7	4.90
$3d^7$	$^4F_{9/2}$	Co^{2+}	4.8	6.63	3.87
$3d^8$	$^3F_4$	Ni^{2+}	3.2	5.59	2.83
$3d^9$	$^2D_{5/2}$	Cu^{2+}	1.9	3.55	1.73

The discrepancy tells that we need to take the effect of crystal field into account before going into the spin-orbit interaction.

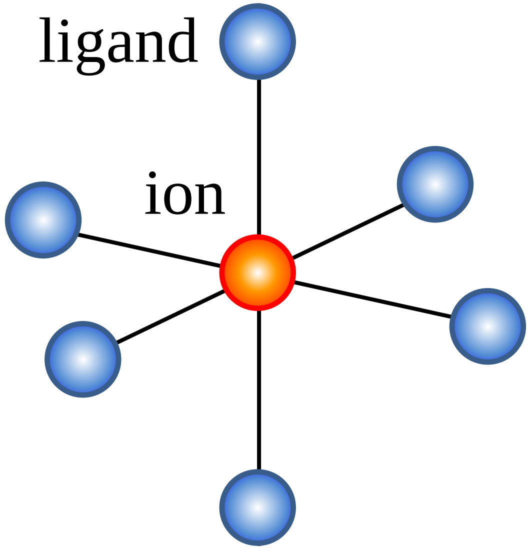
Magnetic ions in insulating crystals: ligands configuration



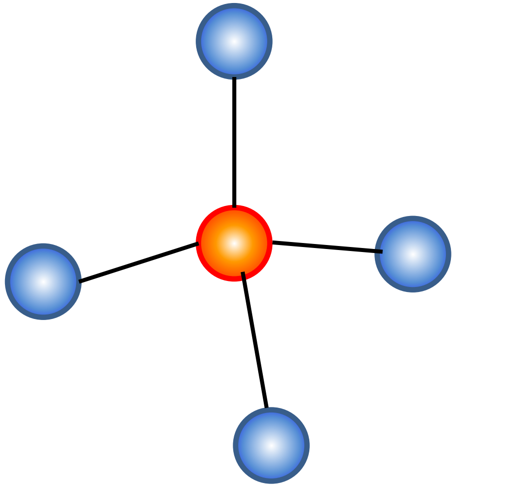
(a) K_2NiF_4



(b) Cs_2CuCl_4



(c) Octahedron coordination



(d) Tetrahedral coordination

Effect of ligand field

Color centers in insulators

Ruby red in Al_2O_3

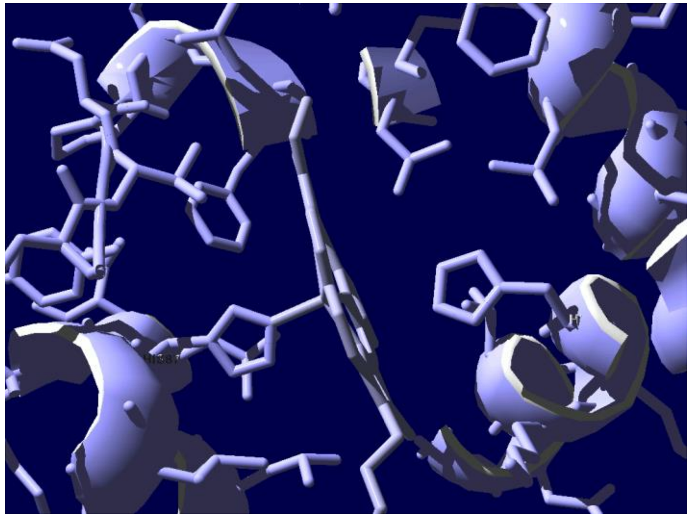
Al^{3+}

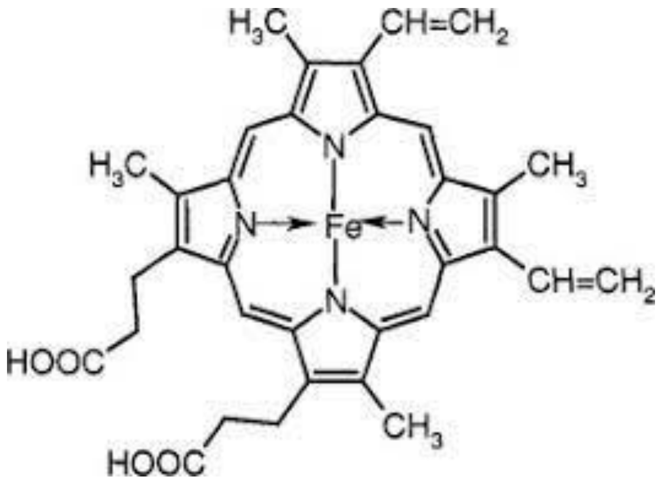
Emerald green in Al_2O_3

Cr^{3+}

Sapphire blue in Al_2O_3

Fe^{2+}



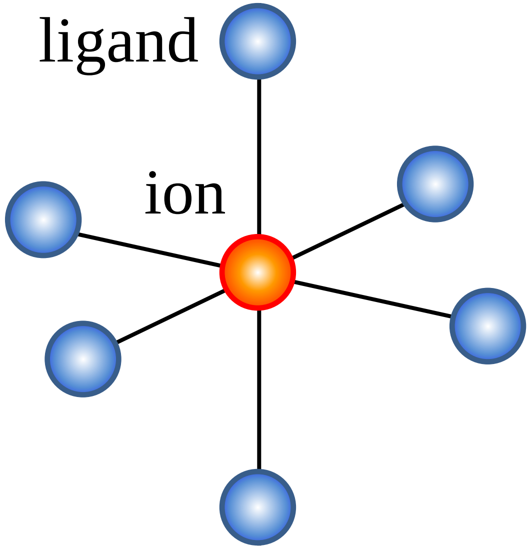


Hemoglobin: Fe

Octahedron ligand field

$$v_{\mathrm{c}}(\boldsymbol{r}) = \sum_i \frac{Z_i e^2}{|\boldsymbol{r} - \boldsymbol{R}_i|} = \sum_i \frac{Ze^2}{\sqrt{r^2 + R^2 - 2Rr\cos\omega_i}}$$

Unit: CGS



$$\boldsymbol{R}_i = (R, \theta_i, \varphi_i) \qquad (\pm R, 0, 0), (0, \pm R, 0), (0, 0, \pm R)$$

$$(\pi/2, 0),\ (\pi/2, \pi/2),\ (0, 0),\ (\pi/2, \pi),\ (\pi/2, 3\pi/2),\ (\pi, 0)$$

$$\frac{r}{R} \ll 1$$

Expansion: $$v_{\mathrm{c}}(\boldsymbol{r}) = \sum_i \frac{Ze^2}{R} \sum_{k=0}^{\infty} \left(\frac{r}{R}\right)^k P_k(\cos\omega_i)$$

Legendre function: $$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n}[(x^2 - 1)]$$

$$P_k(\cos\omega_i) = \frac{4\pi}{2k+1} \sum_{m=-k}^{k} Y_{km}(\theta, \varphi) Y^*_{km}(\theta_i, \varphi_i)$$

Octahedron ligand field (potential)

Define $$T_{km} \equiv \sqrt{\frac{4\pi}{2k+1}} \frac{Ze^2}{R^{k+1}} \sum_i Y_{km}(\theta_i, \varphi_i), \quad C_{km} \equiv \sqrt{\frac{4\pi}{2k+1}} Y_{km}(\theta, \varphi)$$

then we write $$v_c(\boldsymbol{r}) = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} r^k T_{km} C_{km}(\theta, \varphi)$$

$$\begin{cases} T_{km} = 0 \quad \text{for } m\text{: odd} \\ T_{k0} = \sqrt{\frac{2}{2k+1}} \frac{Ze^2}{R^{k+1}} \left[\Theta_{k0}(0) + 4\Theta_{k0}\left(\frac{\pi}{2}\right) + \Theta_{k0}(\pi) \right], \\ T_{km} = \sqrt{\frac{8}{2k+1}} \frac{Ze^2}{R^{k+1}} \Theta_{km}\left(\frac{\pi}{2}\right)\left(1 + \cos\frac{m\pi}{2}\right) \end{cases}$$

$$Y_{km}(\theta, \varphi) = \Theta_{km}(\theta) e^{im\varphi}$$

$T_{km} = 0$ for k: odd

Octahedron ligan field potential

$$v_{\mathrm{c}}(\boldsymbol{r}) = \frac{6Ze^2}{R} + \frac{2}{5}Der^4\left[C_{40}(\theta,\varphi) + \sqrt{\frac{5}{14}}(C_{44}(\theta,\varphi) + C_{4-4}(\theta,\varphi))\right]$$

$$D = \frac{35Ze}{4R^5}$$

$$\boxed{v_{\mathrm{cb}}(\boldsymbol{r}) = eD\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right)}$$

Summary

- Electronic states in magnetic ions
  - LS coupling approach
  - j-j coupling approach
- Paramagnetism by magnetic ions in insulators
  - Curie law
  - Breakdown of LS coupling approach in 3*d* transition metals
- Ligand field approach
  - Octahedron potential