

Lecture on

2022.4.20 Lecture 3

10:25 – 11:55

# Magnetic Properties of Materials

## 磁性 (Magnetism)

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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

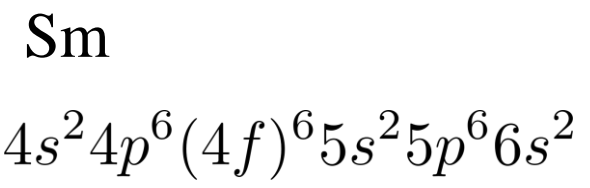
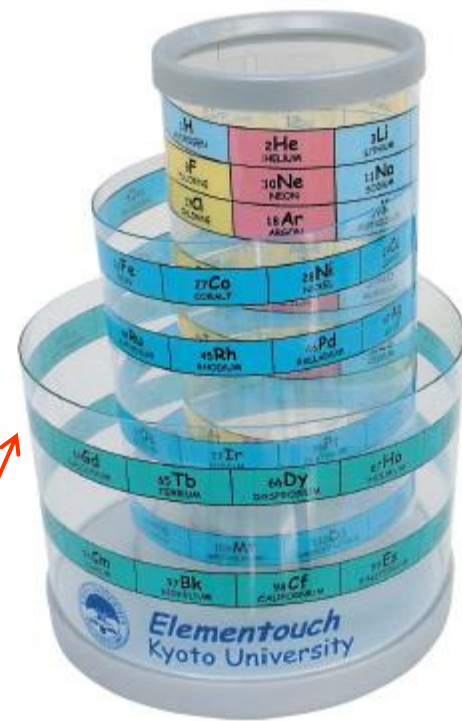
Octahedron potential

# Electronic states in magnetic ions (continued)

## Periodic table of elements

PubChem

1 <b>H</b> Hydrogen Nonmetal																	2 <b>He</b> Helium Noble Gas	
3 <b>Li</b> Lithium Alkali Metal	4 <b>Be</b> Beryllium Alkaline Earth Metal																	10 <b>Ne</b> Neon Noble Gas
11 <b>Na</b> Sodium Alkali Metal	12 <b>Mg</b> Magnesium Alkaline Earth Metal																	18 <b>Ar</b> Argon Noble Gas
19 <b>K</b> Potassium Alkali Metal	20 <b>Ca</b> Calcium Alkaline Earth Metal	21 <b>Sc</b> Scandium Transition Metal	22 <b>Ti</b> Titanium Transition Metal	23 <b>V</b> Vanadium Transition Metal	24 <b>Cr</b> Chromium Transition Metal	25 <b>Mn</b> Manganese Transition Metal	26 <b>Fe</b> Iron Transition Metal	27 <b>Co</b> Cobalt Transition Metal	28 <b>Ni</b> Nickel Transition Metal	29 <b>Cu</b> Copper Transition Metal	30 <b>Zn</b> Zinc Transition Metal	31 <b>Ga</b> Gallium Post-Transition Metal	32 <b>Ge</b> Germanium Metalloid	33 <b>As</b> Arsenic Metalloid	34 <b>Se</b> Selenium Nonmetal	35 <b>Br</b> Bromine Halogen	36 <b>Kr</b> Krypton Noble Gas	
37 <b>Rb</b> Rubidium Alkali Metal	38 <b>Sr</b> Strontium Alkaline Earth Metal	39 <b>Y</b> Yttrium Transition Metal	40 <b>Zr</b> Zirconium Transition Metal	41 <b>Nb</b> Niobium Transition Metal	42 <b>Mo</b> Molybdenum Transition Metal	43 <b>Tc</b> Technetium Transition Metal	44 <b>Ru</b> Ruthenium Transition Metal	45 <b>Rh</b> Rhodium Transition Metal	46 <b>Pd</b> Palladium Transition Metal	47 <b>Ag</b> Silver Transition Metal	48 <b>Cd</b> Cadmium Transition Metal	49 <b>In</b> Indium Post-Transition Metal	50 <b>Sn</b> Tin Post-Transition Metal	51 <b>Sb</b> Antimony Metalloid	52 <b>Te</b> Tellurium Metalloid	53 <b>I</b> Iodine Halogen	54 <b>Xe</b> Xenon Noble Gas	
55 <b>Cs</b> Cesium Alkali Metal	56 <b>Ba</b> Barium Alkaline Earth Metal		72 <b>Hf</b> Hafnium Transition Metal	73 <b>Ta</b> Tantalum Transition Metal	74 <b>W</b> Tungsten Transition Metal	75 <b>Re</b> Rhenium Transition Metal	76 <b>Os</b> Osmium Transition Metal	77 <b>Ir</b> Iridium Transition Metal	78 <b>Pt</b> Platinum Transition Metal	79 <b>Au</b> Gold Transition Metal	80 <b>Hg</b> Mercury Transition Metal	81 <b>Tl</b> Thallium Post-Transition Metal	82 <b>Pb</b> Lead Post-Transition Metal	83 <b>Bi</b> Bismuth Post-Transition Metal	84 <b>Po</b> Polonium Metalloid	85 <b>At</b> Astatine Halogen	86 <b>Rn</b> Radon Noble Gas	
87 <b>Fr</b> Francium Alkali Metal	88 <b>Ra</b> Radium Alkaline Earth Metal		104 <b>Rf</b> Rutherfordium Transition Metal	105 <b>Db</b> Dubnium Transition Metal	106 <b>Sg</b> Seaborgium Transition Metal	107 <b>Bh</b> Bohrium Transition Metal	108 <b>Hs</b> Hassium Transition Metal	109 <b>Mt</b> Meitnerium Transition Metal	110 <b>Ds</b> Darmstadtium Transition Metal	111 <b>Rg</b> Roentgenium Transition Metal	112 <b>Cn</b> Copernicium Transition Metal	113 <b>Nh</b> Nihonium Post-Transition Metal	114 <b>Fl</b> Flerovium Post-Transition Metal	115 <b>Mc</b> Moscovium Post-Transition Metal	116 <b>Lv</b> Livermorium Post-Transition Metal	117 <b>Ts</b> Tennessine Halogen	118 <b>Og</b> Oganesson Noble Gas	
			57 <b>La</b> Lanthanum Lanthanide	58 <b>Ce</b> Cerium Lanthanide	59 <b>Pr</b> Praseodymium Lanthanide	60 <b>Nd</b> Neodymium Lanthanide	61 <b>Pm</b> Promethium Lanthanide	62 <b>Sm</b> Samarium Lanthanide	63 <b>Eu</b> Europium Lanthanide	64 <b>Gd</b> Gadolinium Lanthanide	65 <b>Tb</b> Terbium Lanthanide	66 <b>Dy</b> Dysprosium Lanthanide	67 <b>Ho</b> Holmium Lanthanide	68 <b>Er</b> Erbium Lanthanide	69 <b>Tm</b> Thulium Lanthanide	70 <b>Yb</b> Ytterbium Lanthanide	71 <b>Lu</b> Lutetium Lanthanide	
			89 <b>Ac</b> Actinium Actinide	90 <b>Th</b> Thorium Actinide	91 <b>Pa</b> Protactinium Actinide	92 <b>U</b> Uranium Actinide	93 <b>Np</b> Neptunium Actinide	94 <b>Pu</b> Plutonium Actinide	95 <b>Am</b> Americium Actinide	96 <b>Cm</b> Curium Actinide	97 <b>Bk</b> Berkelium Actinide	98 <b>Cf</b> Californium Actinide	99 <b>Es</b> Einsteinium Actinide	100 <b>Fm</b> Fermium Actinide	101 <b>Md</b> Mendelevium Actinide	102 <b>No</b> Nobelium Actinide	103 <b>Lr</b> Lawrencium Actinide	



# Electronic states in magnetic ions (continued)

Ex) Lanthanoid:

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>
Lanthanum Lanthanide	Cerium Lanthanide	Praseodymium Lanthanide	Neodymium Lanthanide	Promethium Lanthanide	Samarium Lanthanide	Europium Lanthanide	Gadolinium Lanthanide	Terbium Lanthanide	Dysprosium Lanthanide	Holmium Lanthanide	Erbium Lanthanide	Thulium Lanthanide	Ytterbium Lanthanide	Lutetium 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

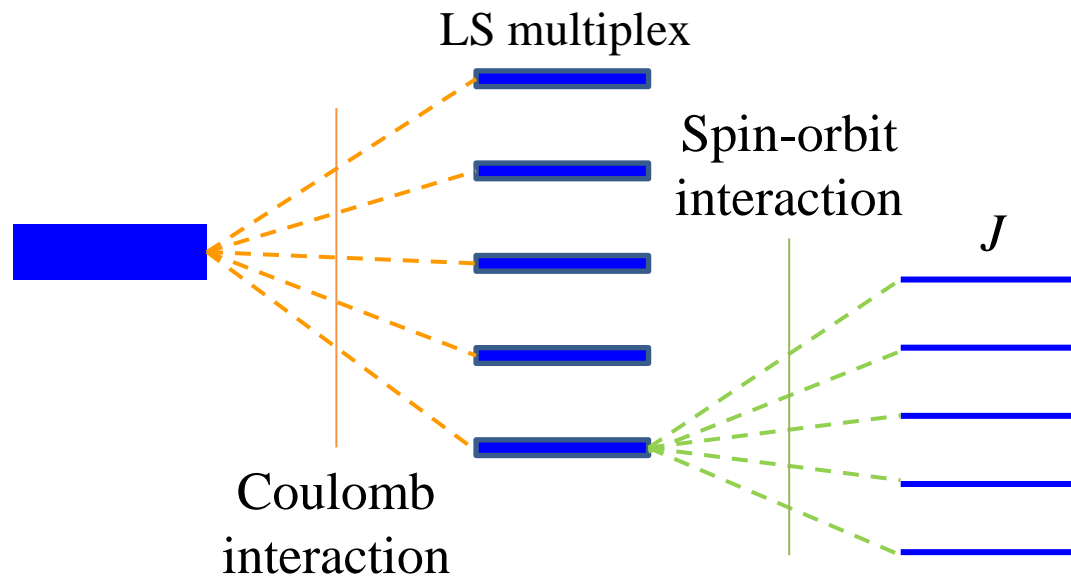
$$\mathcal{H}_L = \mathcal{H}_{L0} + \mathcal{H}_C + \mathcal{H}_{SOI} + \mathcal{H}_{CF}$$



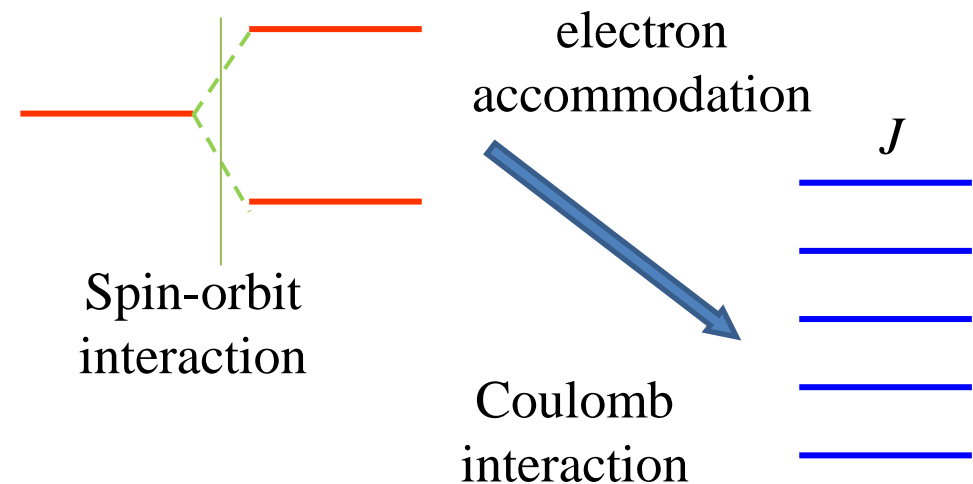
Lifting of degeneracy to LS multiplex

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: 
$$-\frac{e\hbar\boldsymbol{\sigma} \cdot \mathbf{p} \times \mathbf{E}}{4m^2c^2} = -\frac{e^2\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot (\mathbf{p} \times \nabla V) = \frac{e^2\hbar}{2m^2c^2}\zeta(r)\mathbf{s} \cdot \mathbf{l} \equiv \xi(r)\mathbf{l} \cdot \mathbf{s}$$

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

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)

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

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

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

# Total angular momentum

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \quad \longrightarrow \quad [\mathcal{H}, \mathbf{j}] = 0 \quad \mathbf{j} \text{ is a constant of motion}$$

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

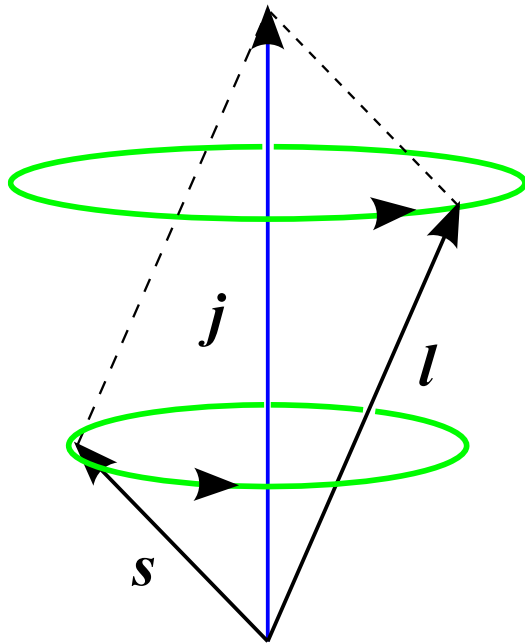
Zeeman-like term

$\mathbf{l}, \mathbf{s}$  : Precession around  $\mathbf{j}$

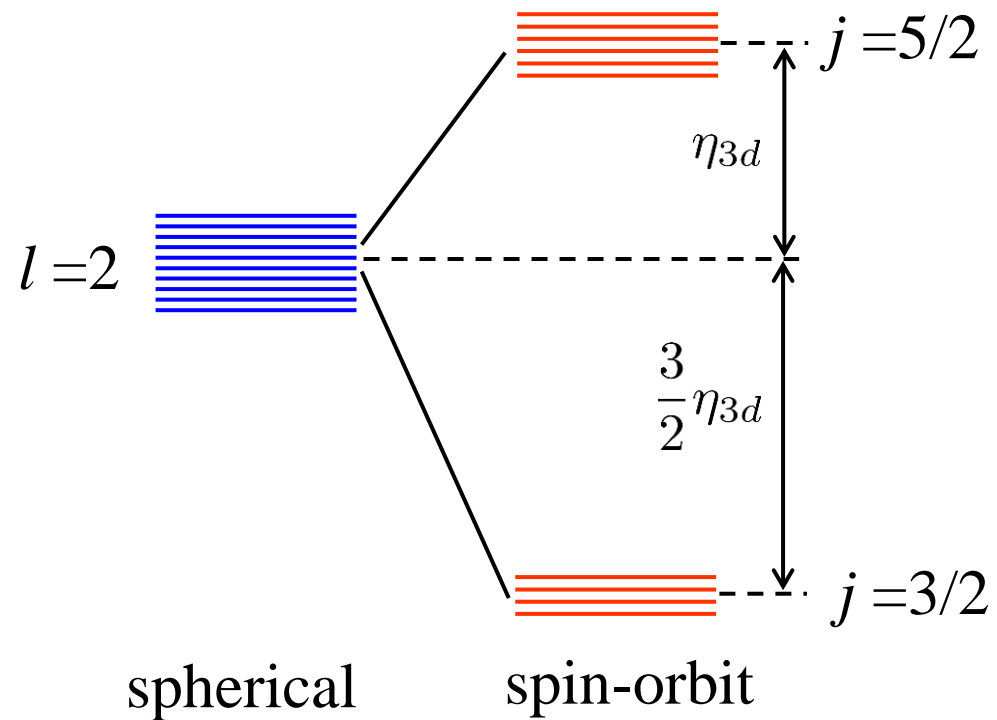
$$2\mathbf{l} \cdot \mathbf{s} = (\mathbf{l} + \mathbf{s})^2 - \mathbf{l}^2 - \mathbf{s}^2 = \mathbf{j}^2 - \mathbf{l}^2 - \mathbf{s}^2$$

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

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



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



Energy eigenvalues:

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

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

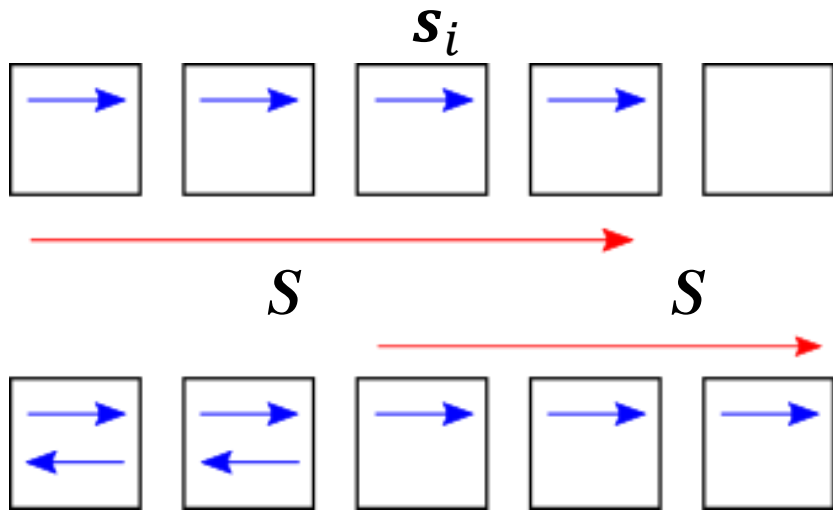
$j$  can take values:  $|l \pm 1/2|$



# Spin-orbit interaction in the ground state of LS multiplex

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

LS-coupling approach



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

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

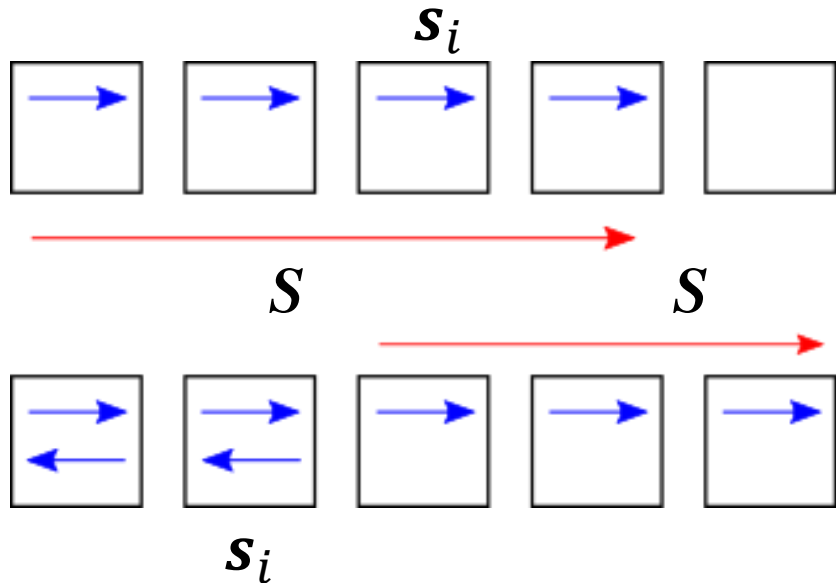
$\mathbf{L}, \mathbf{S}$  are not constant of motion.

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

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

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

# Spin-orbit interaction in the ground state of LS multiplex



$$n > 2l + 1$$

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

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

$$\begin{aligned} \mathcal{H}_{\text{SOI}} &= \xi \left[ \left( \sum_{i=1}^{2l+1} l_i \right) \cdot \mathbf{s} - \left( \sum_{i=2l+2}^n l_i \right) \cdot \mathbf{s} \right] \\ &= -\frac{\xi}{2S} \mathbf{L} \cdot \mathbf{S} = -\lambda \mathbf{L} \cdot \mathbf{S} \end{aligned}$$

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

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

Ground state

$$n \leq 2l + 1$$

$$J = |L - S|$$

$$n > 2l + 1$$

$$J = L + S$$

# Electron configuration of Lanthanoid ions

Elements (Lanthanoid)	Electronic Configuration	Electronic Configuration	Ground state				
	atom R	ion R <sup>3+</sup>	<i>L</i>	<i>S</i>	<i>J</i>	multiplex	<i>g<sub>j</sub></i>
La	5 <i>d</i> 6 <i>s</i> <sup>2</sup>		0	0	0	<sup>1</sup> <i>S</i> <sub>0</sub>	0
Ce	4 <i>f</i> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>1</sup>	3	1/2	5/2	<sup>2</sup> <i>F</i> <sub>5/2</sub>	6/7
Pr	4 <i>f</i> <sup>3</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>2</sup>	5	1	4	<sup>3</sup> <i>H</i> <sub>4</sub>	4/5
Nd	4 <i>f</i> <sup>4</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>3</sup>	6	3/2	9/2	<sup>4</sup> <i>I</i> <sub>9/2</sub>	8/11
Pm	4 <i>f</i> <sup>5</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>4</sup>	6	2	4	<sup>5</sup> <i>I</i> <sub>4</sub>	1/5
Sm	4 <i>f</i> <sup>6</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>5</sup>	5	5/2	5/2	<sup>6</sup> <i>H</i> <sub>5/2</sub>	2/7
Eu	4 <i>f</i> <sup>7</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>6</sup>	3	3	0	<sup>7</sup> <i>F</i> <sub>0</sub>	0
Gd	4 <i>f</i> <sup>7</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>7</sup>	0	7/2	7/2	<sup>8</sup> <i>S</i> <sub>7/2</sub>	2
Tb	4 <i>f</i> <sup>9</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>8</sup>	3	3	6	<sup>7</sup> <i>F</i> <sub>6</sub>	3/2
Dy	4 <i>f</i> <sup>10</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>9</sup>	5	5/2	15/2	<sup>6</sup> <i>H</i> <sub>15/2</sub>	4/3
Ho	4 <i>f</i> <sup>11</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>10</sup>	6	2	8	<sup>5</sup> <i>I</i> <sub>8</sub>	5/4
Er	4 <i>f</i> <sup>12</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>11</sup>	6	3/2	15/2	<sup>4</sup> <i>I</i> <sub>15/2</sub>	6/5
Tm	4 <i>f</i> <sup>13</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>12</sup>	5	1	6	<sup>3</sup> <i>H</i> <sub>6</sub>	7/6
Yb	4 <i>f</i> <sup>14</sup> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>13</sup>	3	1/2	7/2	<sup>2</sup> <i>F</i> <sub>7/2</sub>	8/7
Lu	4 <i>f</i> <sup>14</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>	4 <i>f</i> <sup>14</sup>	0	0	0	<sup>1</sup> <i>S</i> <sub>0</sub>	0

Spectroscopic symbol  
of multi-electron state

$$(L, S, J)$$

$$\downarrow$$

$$2S+1 L_J$$

2*S* + 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:  $\mathcal{H}_{\text{SOI}} = \sum_{mm'\sigma\sigma'} \lambda_{nl}(m\sigma, m'\sigma') a_{m\sigma}^\dagger a_{m'\sigma'}$ ,

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

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

# Clebsch-Gordan calculator on Wolfram alpha

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



Clebsch-Gordan calculator

自然言語 数字入力

拡張キーボード 例を見る アップロード ランダムな例を使う

計算に使う式・値を入力してください:

» j1:

» j2:

» m1:

» m2:

» j:

» m:

計算する

入力

(5 4 0 0 | 5 4 1 0)

( $j_1 j_2 m_1 m_2 | j_1 j_2 j m$ ) はクレブシュ(Clebsch)・ゴルダン(Gordan)係数です

結果 [表示桁数を増やす](#)

$\sqrt{\frac{5}{33}} \approx 0.389249$

ステップごとの  
数学, 代数,  
微積分ソルバ

ステップ 2

被積分関数  $\sec^{-1}(\sqrt{t})$  について,  
 $u = \sqrt{t}$  と  $du = \frac{1}{2\sqrt{t}} dt$  を置換する  
 $= 2 \int u \sec^{-1}(u) du$

ステップ 3 \* 積数の中間ステップ

\* 被積分関数  $u \sec^{-1}(u)$  について, 部分積分,  $\int f dg$   
を適用する. このとき,  
 $f = \sec^{-1}(u), dg = u du,$   
 $df = \frac{1}{u\sqrt{u^2-1}} du, g = \frac{u^2}{2}$  とする:  
 $= u^2 \sec^{-1}(u) - \int \frac{u}{\sqrt{u^2-1}} du$

[次のステップ](#) [すべてのステップを表示](#)

ステップごとに  
解いていきます.

学生価格

# j-j coupling (short comment)

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

Ground state

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

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

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

# 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.

$$\mathcal{H}_1 = \mu_B(\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} \qquad \mathcal{H}_1 = g_J\mu_B\mathbf{J} \cdot \mathbf{B}$$

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

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

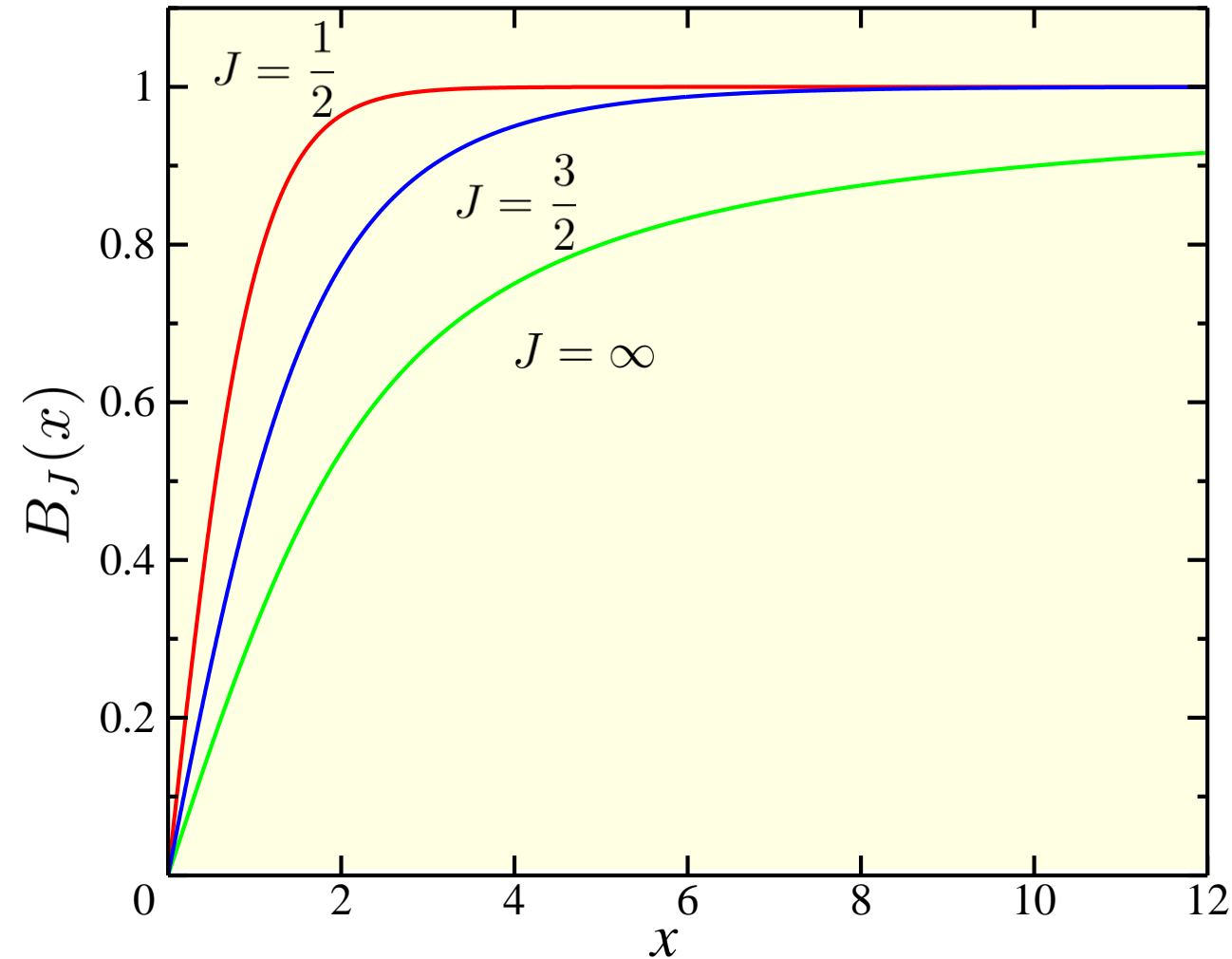
Expectation value of magnetization:

$$M = \langle -g_j\mu_B J_z \rangle = -\frac{\text{Tr}[g_j\mu_B J_z \exp(-g_j\mu_B J_z B/k_B T)]}{\text{Tr}[\exp(-g_j\mu_B J_z B/k_B T)]}$$
$$= k_B T \frac{\partial}{\partial B} \log \left[ \text{Tr} \left( \exp \frac{-g_j\mu_B J_z B}{k_B T} \right) \right]$$

Partition function:

$$\text{Tr} \left( \exp \frac{-g_j\mu_B J_z B}{k_B T} \right) = \frac{\sinh \left[ \frac{1}{2k_B T} g_J \mu_B \left( J + \frac{1}{2} \right) B \right]}{\sinh(g_J \mu_B B / 2k_B T)}$$

$$M = g_J \mu_B J B_J \left( \frac{g_J \mu_B J B}{k_B T} \right)$$



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

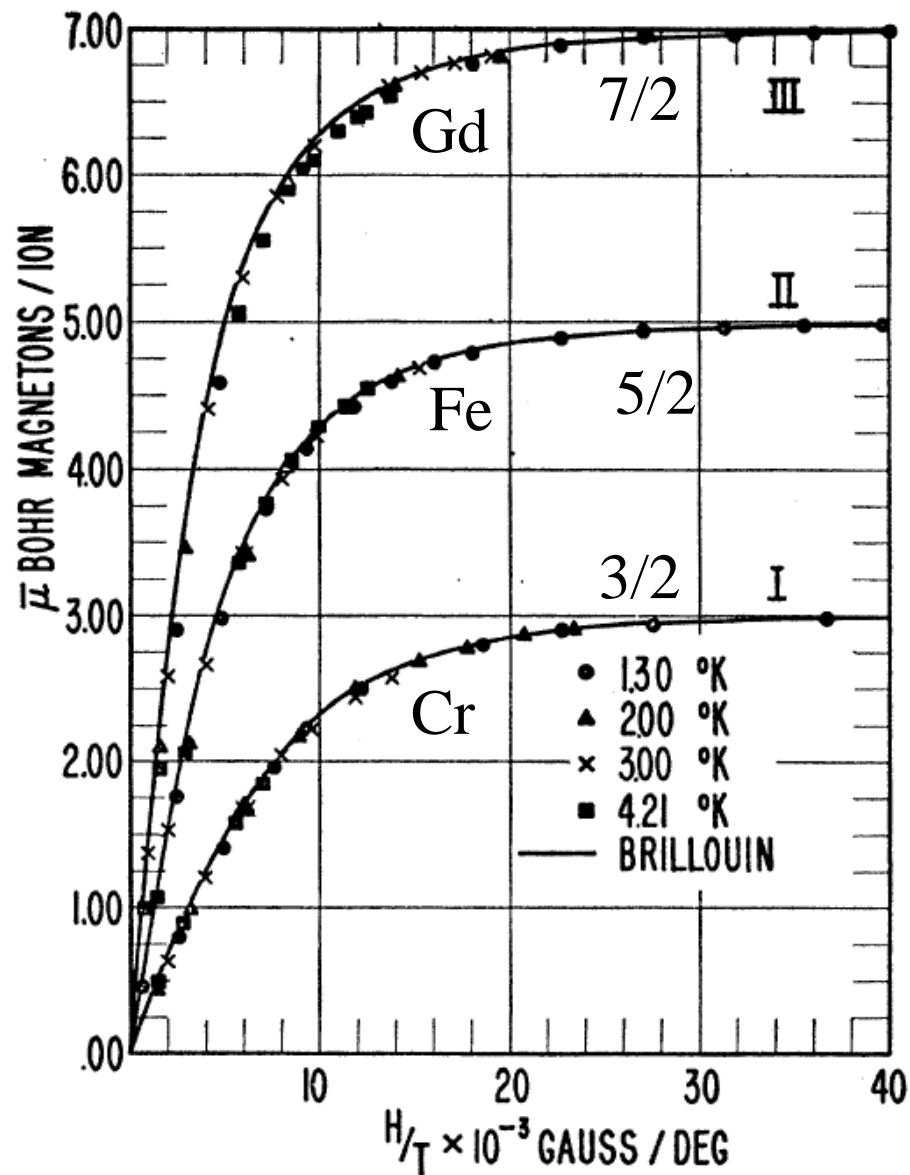
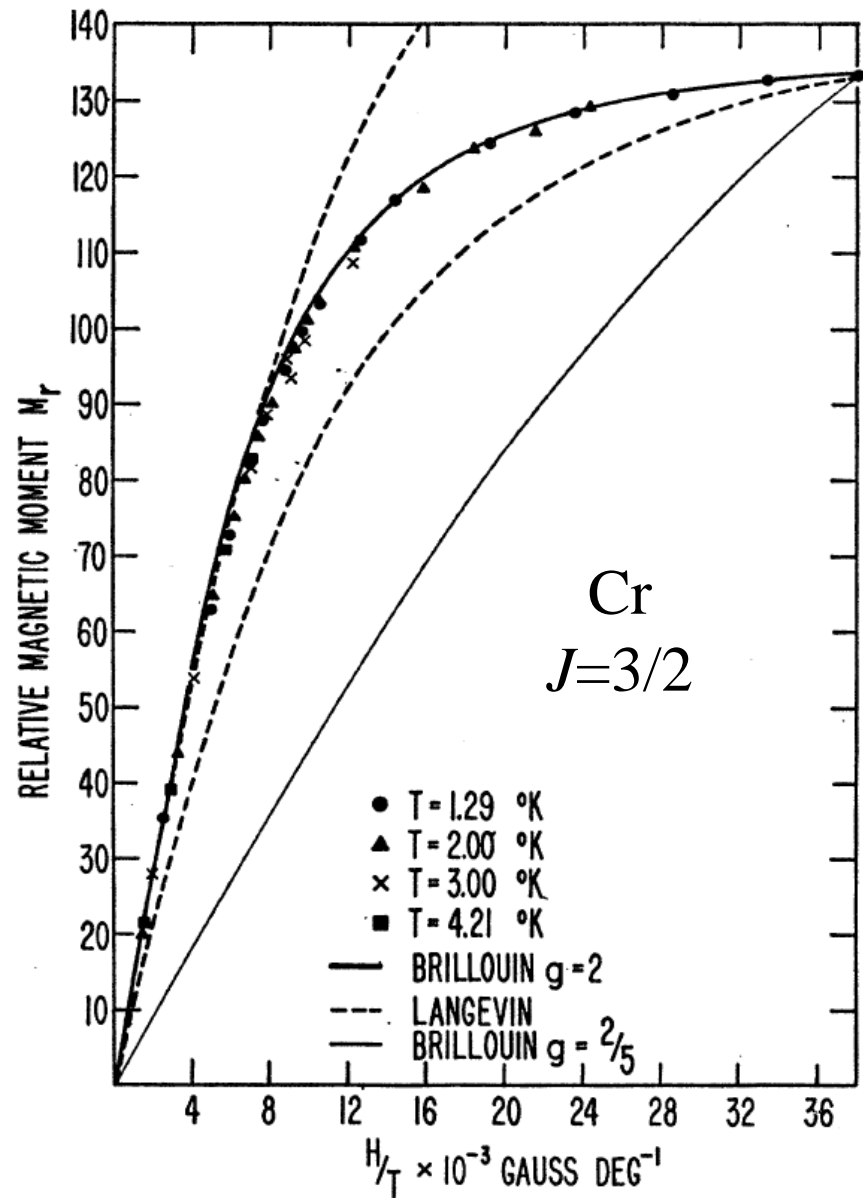
Brillouin function

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

$$\chi = \frac{dM}{dB} = (g_J \mu_B)^2 \frac{J(J+1)}{3k_B T}$$



# Examples of experiments



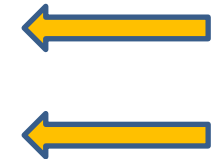
II

FeNH4(SO4)2 · 12H2O  
Iron Ammonium Alum

W. E. Henry, PR88,  
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 <sup>3+</sup>	2.5	2.54	2.56
$4f^2$	$^3H_4$	Pr <sup>3+</sup>	3.6	3.58	3.62
$4f^3$	$^4I_{9/2}$	Nd <sup>3+</sup>	3.8	3.62	3.68
$4f^5$	$^6H_{5/2}$	Sm <sup>3+</sup>	1.5	0.84	1.53
$4f^6$	$^7F_0$	Eu <sup>3+</sup>	3.6	0.00	3.40
$4f^7$	$^8S_{7/2}$	Gd <sup>3+</sup>	7.9	7.94	7.94
$4f^8$	$^7F_0$	Tb <sup>3+</sup>	9.7	9.72	9.7
$4f^9$	$^6H_{15/2}$	Dy <sup>3+</sup>	10.5	10.65	10.6
$4f^{10}$	$^5I_8$	Ho <sup>3+</sup>	10.5	10.61	10.6
$4f^{11}$	$^4I_{15/2}$	Er <sup>3+</sup>	9.4	9.58	9.6
$4f^{12}$	$^3H_6$	Tm <sup>3+</sup>	7.2	7.56	7.6
$4f^{13}$	$^2F_{7/2}$	Yb <sup>3+</sup>	4.5	4.54	4.5

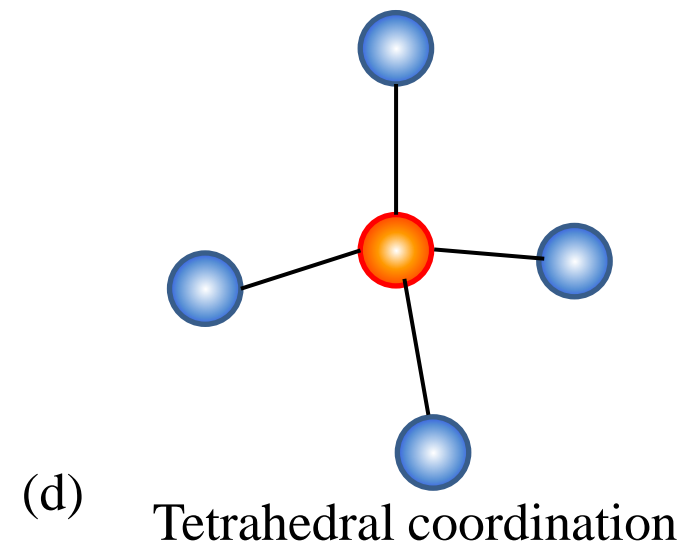
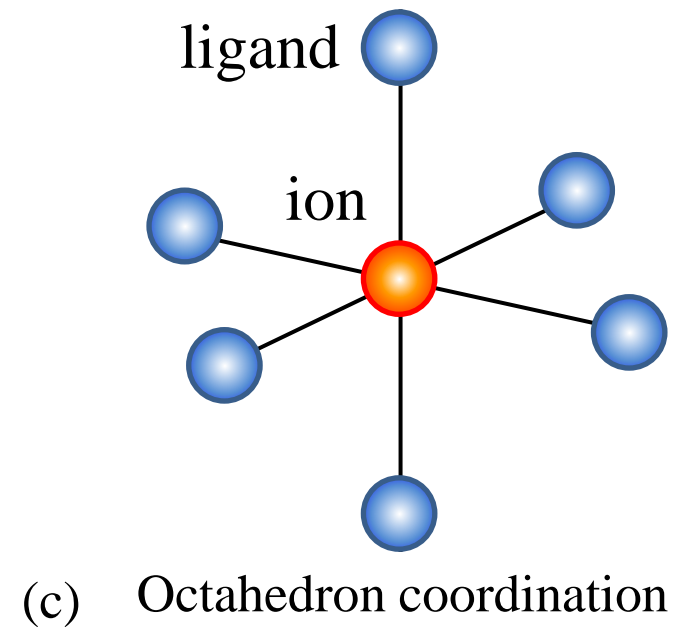
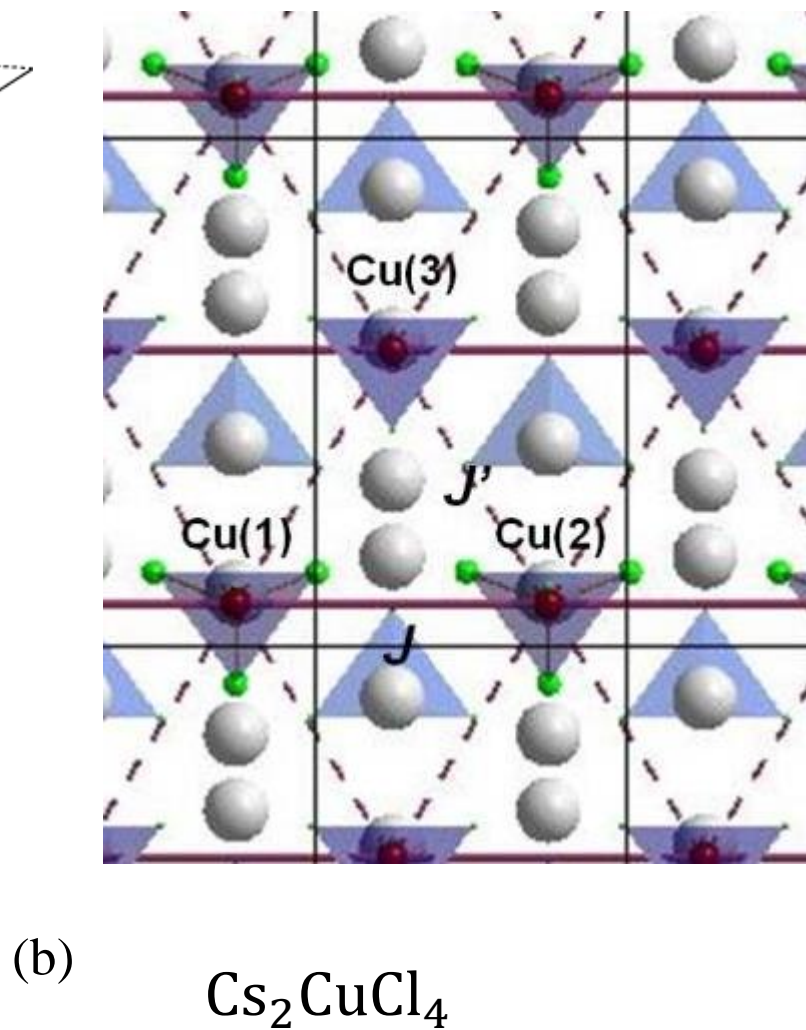
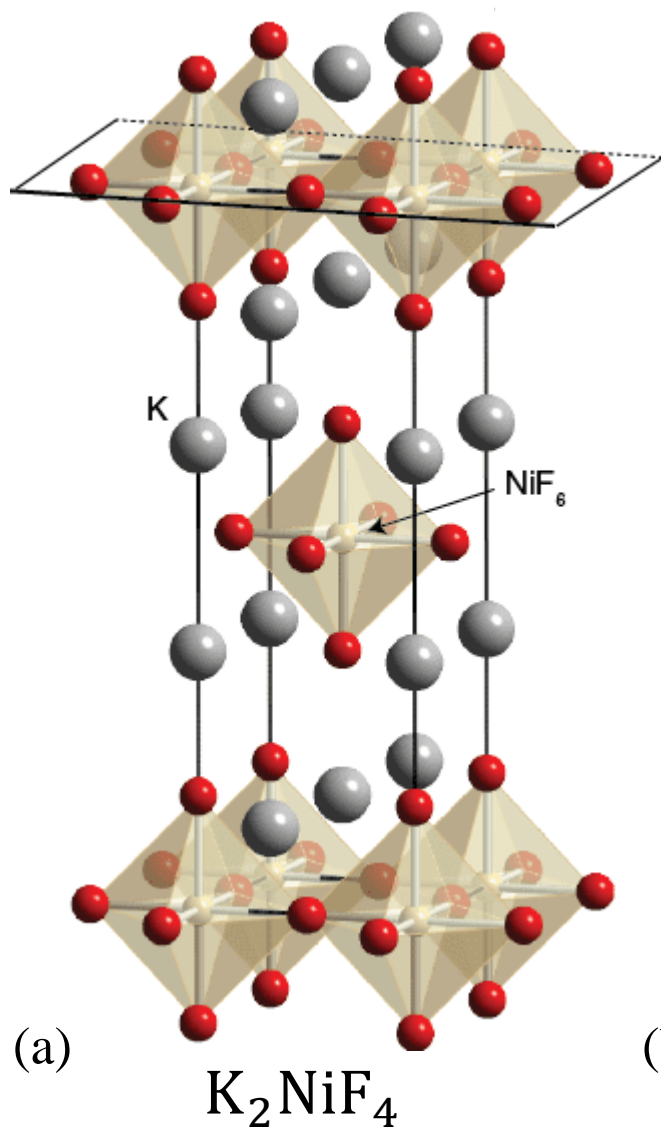


# 3d transition metals

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



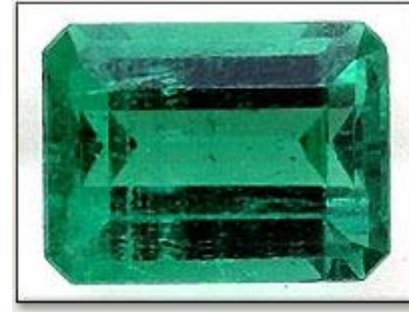
# Effect of ligand field

## Color centers in insulators



Ruby red in  $\text{Al}_2\text{O}_3$

$\text{Al}^{3+}$



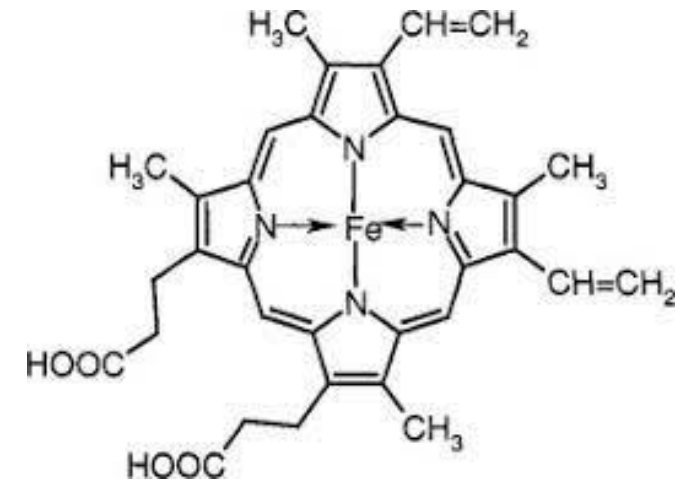
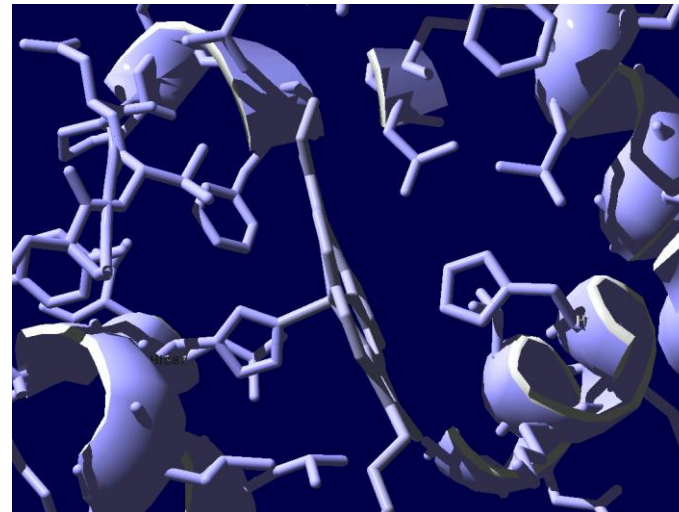
Emerald green in  $\text{Al}_2\text{O}_3$

$\text{Cr}^{3+}$



Sapphire blue in  $\text{Al}_2\text{O}_3$

$\text{Fe}^{2+}$



Hemoglobin: Fe

# Octahedron ligand field

$$v_c(\mathbf{r}) = \sum_i \frac{Z_i e^2}{|\mathbf{r} - \mathbf{R}_i|} = \sum_i \frac{Z e^2}{\sqrt{r^2 + R^2 - 2Rr \cos \omega_i}} \quad \text{Unit: CGS}$$

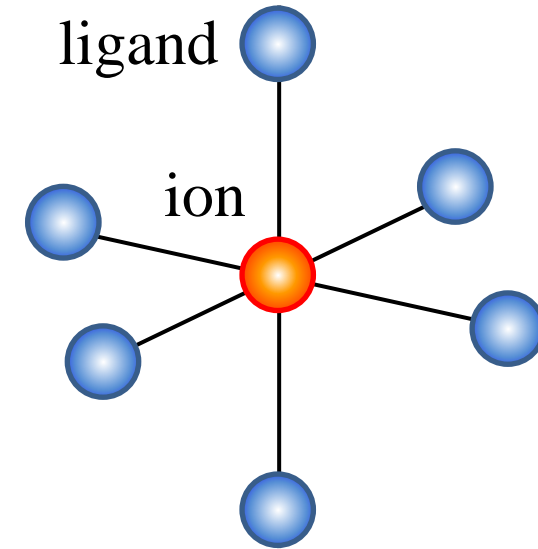
$$\mathbf{R}_i = (R, \theta_i, \varphi_i) \quad (\pm R, 0, 0), (0, \pm R, 0), (0, 0, \pm R)$$

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

$$\frac{r}{R} \ll 1 \quad \text{Expansion:} \quad v_c(\mathbf{r}) = \sum_i \frac{Z e^2}{R} \sum_{k=0}^{\infty} \left(\frac{r}{R}\right)^k P_k(\cos \omega_i)$$

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

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



# Octahedron ligand field (potential)

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

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

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

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

$$T_{km} = 0 \quad \text{for } k: \text{ odd}$$

# Octahedron ligand field potential

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

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

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



# 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  $3d$  transition metals

Ligand field approach

Octahedron potential