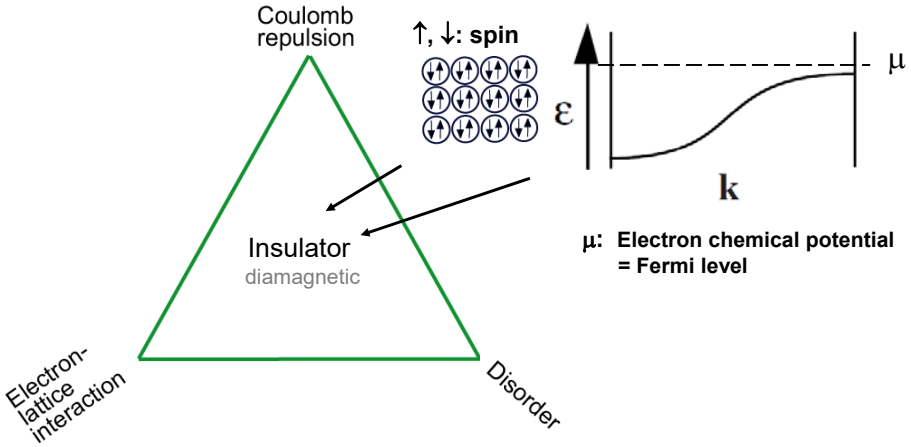
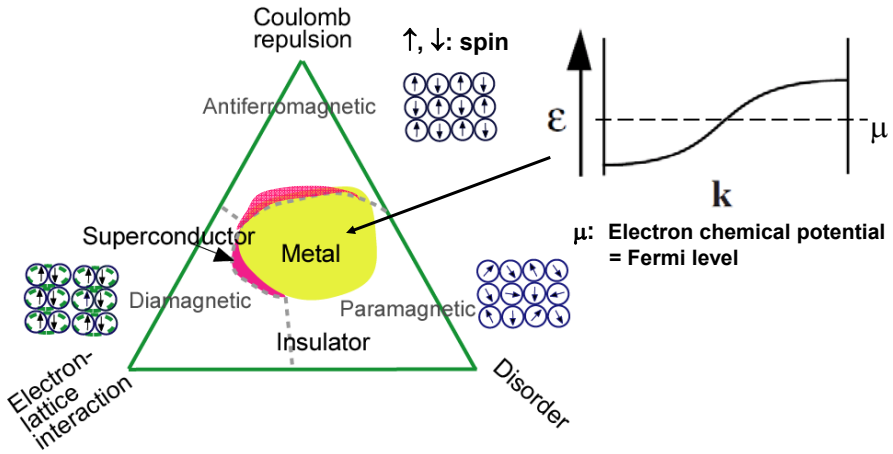
Electronic phase diagram of strongly correlated electron system at T = 0 K for n = 2



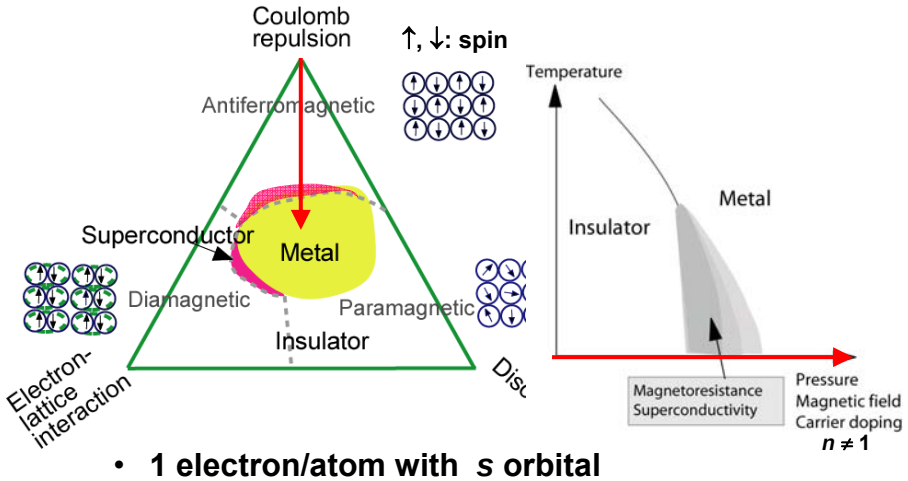
- **2 electrons/atom with *s* orbital**
- ***T* = 0 K**

Electronic phase diagram of strongly correlated electron system at T = 0 K for n = 1



- **1 electron/atom with *s* orbital**
- ***T* = 0 K**

Electronic phase diagram of strongly correlated electron system at finite *T*



- **1 electron/atom with *s* orbital**
- ***T* = 0 K**

Material Science

I. *p* electron systems

Kanoda

II. *d* electron systems

Fujimori

Download lecture note
講義ノートのダウンロード

For your convenience, you can download the lecture note prior to each class.
各講義時間の前に講義ノートをダウンロードできます。

English

Fujimori group home, Department of Physics, School of Science
→ Courses → Material Science
URL: http://wyvern.phys.s.u-tokyo.ac.jp/f/lecture/matscig/index_en.htm

日本語

理・物理 藤森研ホームページ→講義→物質科学
URL: http://wyvern.phys.s.u-tokyo.ac.jp/f/lecture/matscig/index.htm

If you cannot attend a class due to an unavoidable conflicting schedule, please let Fujimori know by email.
公用でやむを得ず欠席する場合は，藤森までメールで連絡下さい。

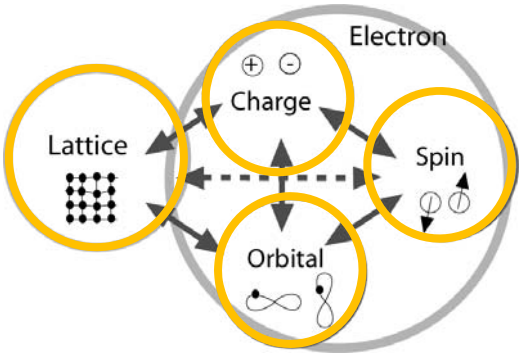
References

1. 藤森 淳「強相関物質の基礎 ― 原子，分子から固体へ」（内田老鶴圃，2005年）

2. M. Imada, A. Fujimori, and Y. Tokura: *Metal-Insulator Transitions*, Review in Modern Physics 70, 1039 (1998)

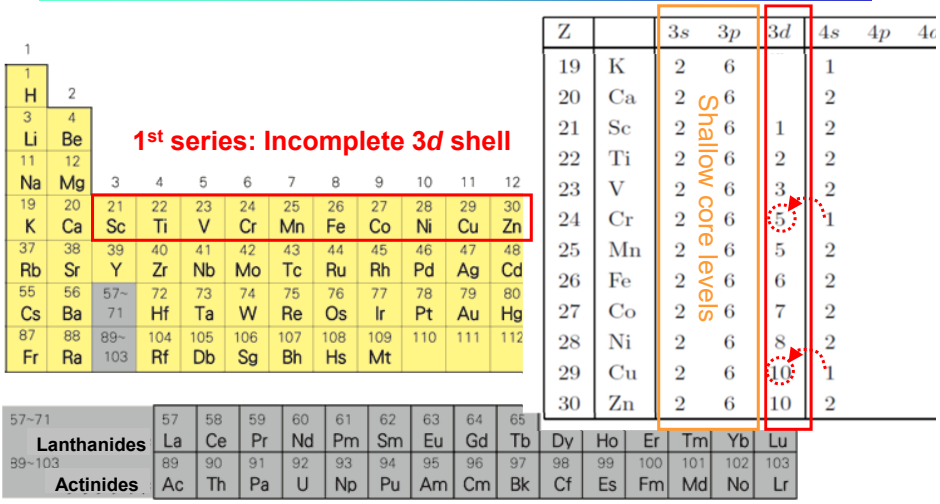
3. 津田惟雄，那須圭一郎，藤森 淳，白鳥紀一「電気伝導性酸化物（改訂版）」（裳華房，1993年）
   N. Tsuda, K. Nasu, A. Fujimori, K. Siratori: *Electronic Conduction in Oxides* (Springer-Verlag, 2000)

Electronic phase diagram of strongly correlated electron system for $n > 1$



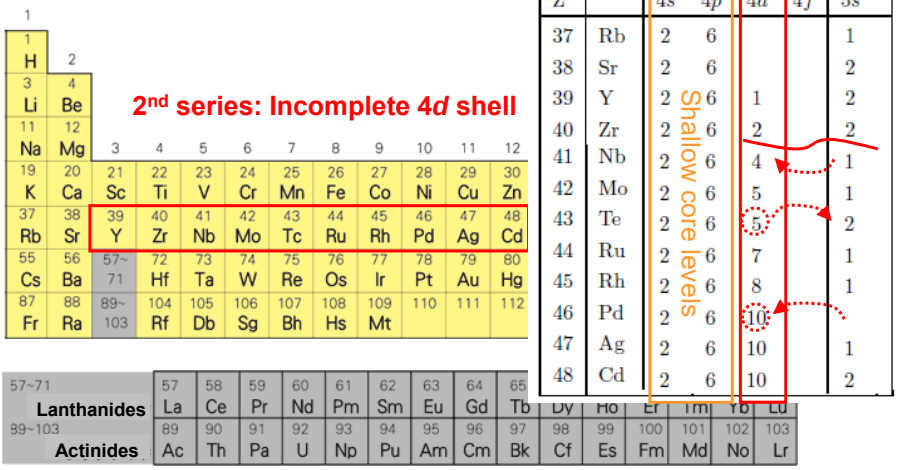
- many electrons/atom with *p, d, or f* orbitals
- $T = 0$ K

Transition elements



KEK home page

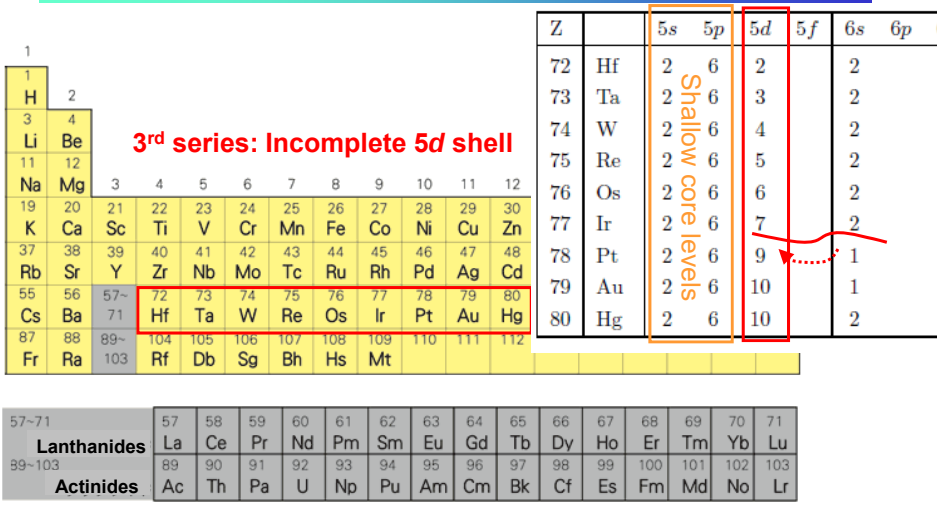
Transition elements



Z		4s	4p	4d	4f	5s
37	Rb	2	6			1
38	Sr	2	6			2
39	Y	2	6	1		2
40	Zr	2	6	2		2
41	Nb	2	6	4		1
42	Mo	2	6	5		1
43	Tc	2	6	5		2
44	Ru	2	6	7		1
45	Rh	2	6	8		1
46	Pd	2	6	10		
47	Ag	2	6	10		1
48	Cd	2	6	10		2

KEK home page

Transition elements



Z		5s	5p	5d	5f	6s	6p
72	Hf	2	6	2		2	
73	Ta	2	6	3		2	
74	W	2	6	4		2	
75	Re	2	6	5		2	
76	Os	2	6	6		2	
77	Ir	2	6	7		2	
78	Pt	2	6	9		1	
79	Au	2	6	10		1	
80	Hg	2	6	10		2	

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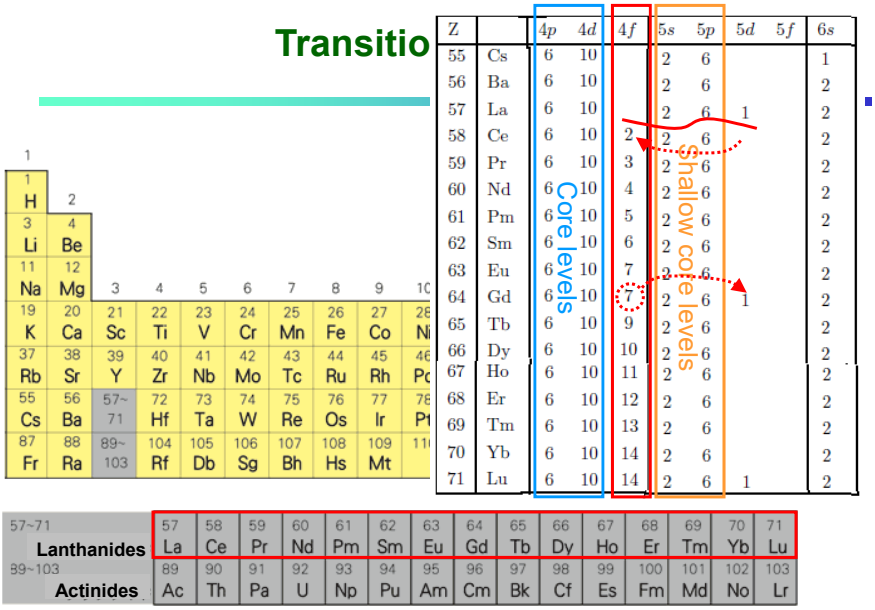
Transitio

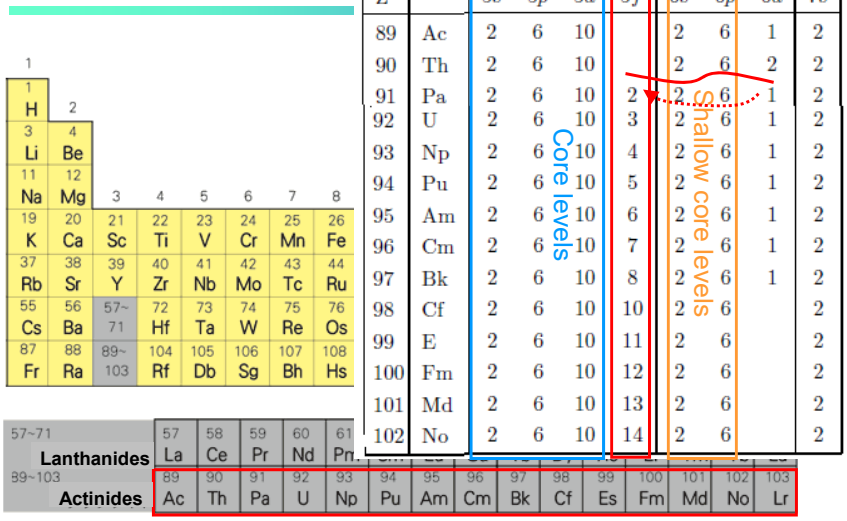


Z		4p	4d	4f	5s	5p	5d	5f	6s
55	Cs	6	10		2	6			1
56	Ba	6	10		2	6			2
57	La	6	10		2	6	1		2
58	Ce	6	10	2	2	6			2
59	Pr	6	10	3	2	6			2
60	Nd	6	10	4	2	6			2
61	Pm	6	10	5	2	6			2
62	Sm	6	10	6	2	6			2
63	Eu	6	10	7	2	6			2
64	Gd	6	10	7	2	6	1		2
65	Tb	6	10	9	2	6			2
66	Dy	6	10	10	2	6			2
67	Ho	6	10	11	2	6			2
68	Er	6	10	12	2	6			2
69	Tm	6	10	13	2	6			2
70	Yb	6	10	14	2	6			2
71	Lu	6	10	14	2	6	1		2

Lanthanide series: Incomplete 4*f* shell

KEK home page

Transition elements



Z		5s	5p	5d	5f	6s	6p	6d	7s
89	Ac	2	6	10		2	6	1	2
90	Th	2	6	10		2	6	2	2
91	Pa	2	6	10	2	2	6	1	2
92	U	2	6	10	3	2	6	1	2
93	Np	2	6	10	4	2	6	1	2
94	Pu	2	6	10	5	2	6	1	2
95	Am	2	6	10	6	2	6	1	2
96	Cm	2	6	10	7	2	6	1	2
97	Bk	2	6	10	8	2	6	1	2
98	Cf	2	6	10	10	2	6		2
99	E	2	6	10	11	2	6		2
100	Fm	2	6	10	12	2	6		2
101	Md	2	6	10	13	2	6		2
102	No	2	6	10	14	2	6		2

Actinide series: Incomplete 5*f* shell

KEK home page

Material Science
II. *d* Electron systems

1. Electronic structure of transition-metal ions (May 23)

Two weeks break in between

2. Crystal structure and band structure (June 13)
3. Mott insulators (June 20)
4. Metal-insulator transition (June 27)
5. High-temperature superconductivity (July 4)
6. Spin-related phenomena (July 11)

1. Electronic structure of transition-metal ions

- 1.1 Atomic wave functions
- 1.2 Crystal-field splitting
- 1.3 Coulomb-exchange interaction
- 1.4 Multiplet splitting

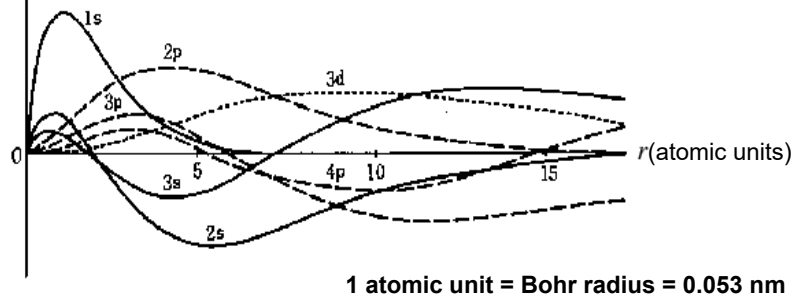
1. Electronic structure of transition-metal ions

1.1 Atomic wave functions

$$\phi_{nlm}(\mathbf{r}) = \phi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$$

Radial part **Angular part (Spherical harmonics)**

$rR_{nl}(r)$ **Radial wave function of hydrogen atom**



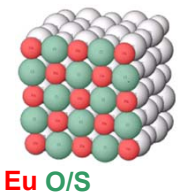
1 atomic unit = Bohr radius = 0.053 nm

1. Electronic structure of transition-metal ions

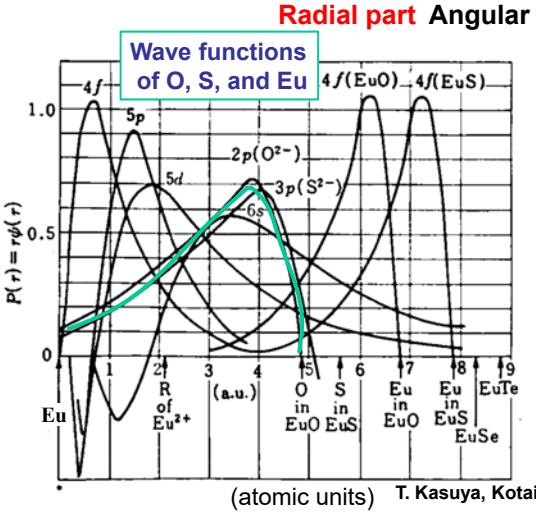
1.1 Atomic wave functions

$$\phi_{nlm}(\mathbf{r}) = \phi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$$

Radial part **Angular part (Spherical harmonics)**



Eu O/S



T. Kasuya, Kotai Butsuri 12, 650 (1977)

1 atimic unit
= Bohr radius
= 0.053 nm

1. Electronic structure of transition-metal ions

1.1 Atomic wave functions

$$\phi_{nlm}(\mathbf{r}) = \phi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$$

Radial part Angular part (Spherical harmonics)

s orbital

$$Y_0^0 = 1/\sqrt{4\pi},$$

complex

p orbitals

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta, \qquad Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi},$$

d orbitals

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \qquad Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi},$$

$$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi},$$

1. Electronic structure of transition-metal ions

1.1 Atomic wave functions

$$\phi_{nlm}(\mathbf{r}) = \phi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$$

Radial part Angular part (Spherical harmonics)

s orbital

$$Y_0^0 = 1/\sqrt{4\pi},$$

real

p orbitals

$$Y_1^0 \propto z, \qquad \frac{1}{\sqrt{2}}[Y_1^1 \pm Y_1^{-1}] \propto x, y,$$

d orbitals

$$Y_2^0 \propto 3z^2 - r^2, \qquad \frac{1}{\sqrt{2}}[Y_2^1 \pm Y_2^{-1}] \propto yz, zx,$$

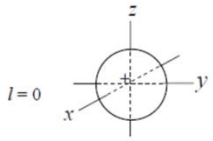
$$\frac{1}{\sqrt{2}}[Y_2^2 + Y_2^{-2}] \propto x^2 - y^2, \qquad \frac{1}{\sqrt{2}}[Y_2^2 - Y_2^{-2}] \propto xy,$$

1. Electronic structure of transition-metal ions

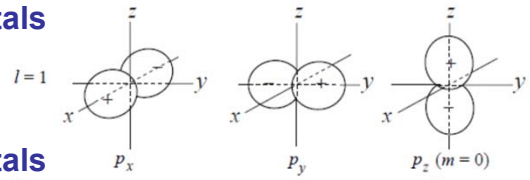
1.1 Atomic wave functions

Spherical harmonics complex → Cubic harmonics real

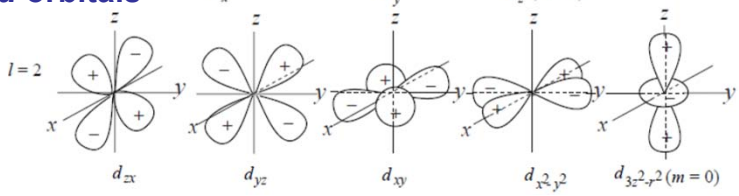
s orbital



p orbitals



d orbitals



1. Electronic structure of transition-metal ions

1.1 Atomic wave functions

➡ 1.2 Crystal-field splitting

1.3 Coulomb-exchange interaction

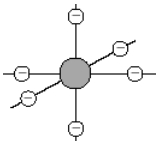
1.4 Multiplet splitting

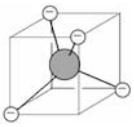
1. Electronic structure of transition-metal ions

1.2 Crystal-field splitting

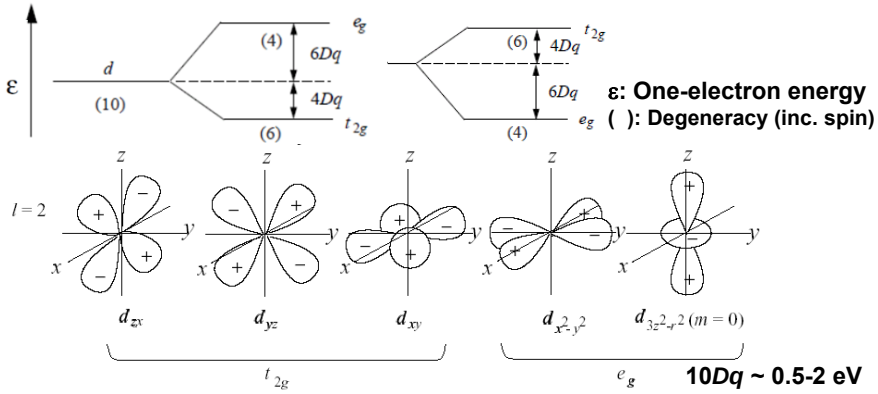
Crystal fields from anion ligands (e.g., O^{2-}, F^{-})

Octahedral coordination





Tetrahedral coordination



ε: One-electron energy

( ): Degeneracy (inc. spin)

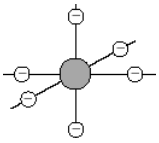
$10Dq$ ~ 0.5-2 eV

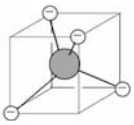
1. Electronic structure of transition-metal ions

1.2 Crystal-field splitting

Crystal fields from anion ligands (e.g., O^{2-}, F^{-})

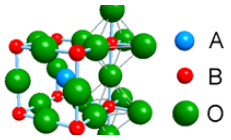
Octahedral coordination



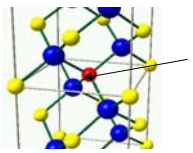


Tetrahedral coordination

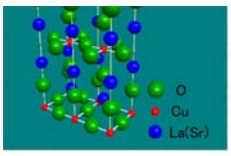
Giant magneto-resistive material
(Perovskite structure)

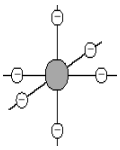


Magnetic semiconductor
(Zinc Blende structure)

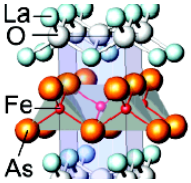


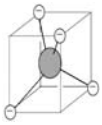
Cu-oxide High-Tc superconductor
(Layered perovskite str.)





Fe-based superconductor





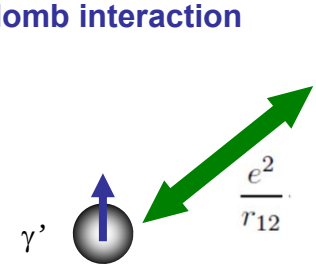
Lowered symmetry

1. Electronic structure of transition-metal ions

1.1 Atomic wave functions
1.2 Crystal-field splitting
1.3 Coulomb-exchange interaction
1.4 Multiplet splitting

1.3 Coulomb-exchange interaction

Coulomb interaction



Electron 1

$$\psi_q(\mathbf{x}) \equiv \underbrace{\phi_\gamma(\mathbf{r})}_{\text{Orbital part}} \underbrace{\chi_\sigma(s)}_{\text{Spin part}}$$

Electron 2

$$\psi_{q'}(\mathbf{x}) \equiv \underbrace{\phi_{\gamma'}(\mathbf{r})}_{\text{Orbital part}} \underbrace{\chi_{\sigma'}(s)}_{\text{Spin part}}$$

$\mathbf{X} \equiv (\boldsymbol{r}, \mathbf{s})$
$\boldsymbol{r}$: Spatial coordinate
$\boldsymbol{s}$: Spin coordinate (=1, 2)

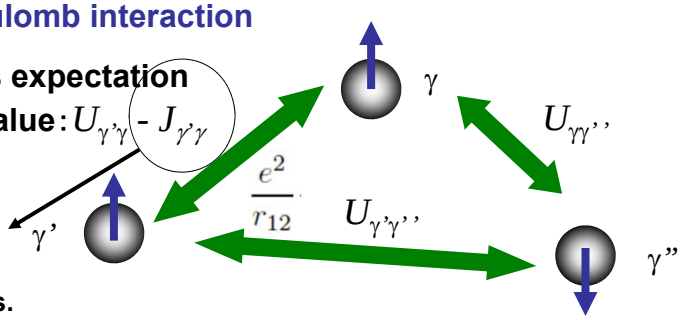
$\boldsymbol{q} \equiv (\gamma, \sigma)$
γ: Orbital quantum number
σ: Spin quantum number (=↑,↓)

1. Electronic structure of transition-metal ions
1.3 Coulomb-exchange interaction

Coulomb interaction

Its expectation value: $U_{\gamma'\gamma} - J_{\gamma'\gamma}$

Hund rule:
Spins want to align as much as Pauli principle allows.



Coulomb integral $U_{\gamma\gamma'} \equiv \langle\gamma\gamma'|v|\gamma\gamma'\rangle$ ~ 4-8 eV

Exchange integral $J_{\gamma\gamma'} \equiv \langle\gamma'\gamma|v|\gamma\gamma'\rangle$ ~ 0.5-1 eV

$$\langle\gamma\gamma'|v|\gamma''\gamma'''\rangle \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi^*_\gamma(\mathbf{r}_1)\phi^*_{\gamma'}(\mathbf{r}_2)\frac{e^2}{r_{12}}\phi_{\gamma''}(\mathbf{r}_1)\phi_{\gamma'''}(\mathbf{r}_2)$$

1. Electronic structure of transition-metal ions
1.3 Coulomb-exchange interaction

Kanamori parameters (2 independent parameters)

$$U \equiv U_{\gamma\gamma}, \quad U' \equiv U_{\gamma\gamma'}, \quad J_{\mathrm{H}} \equiv J_{\gamma\gamma'} \quad (\gamma \neq \gamma')$$
$$U - U' = 2J_{\mathrm{H}}$$

Coulomb integral $U_{\gamma\gamma'} \equiv \langle\gamma\gamma'|v|\gamma\gamma'\rangle$ ~ 4-8 eV

Exchange integral $J_{\gamma\gamma'} \equiv \langle\gamma'\gamma|v|\gamma\gamma'\rangle$ ~ 0.5-1 eV

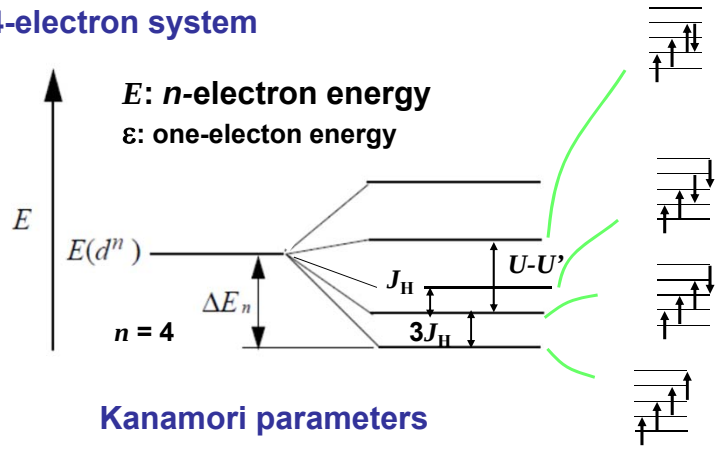
$$\langle\gamma\gamma'|v|\gamma''\gamma'''\rangle \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi^*_\gamma(\mathbf{r}_1)\phi^*_{\gamma'}(\mathbf{r}_2)\frac{e^2}{r_{12}}\phi_{\gamma''}(\mathbf{r}_1)\phi_{\gamma'''}(\mathbf{r}_2)$$

1. Electronic structure of transition-metal ions

1.1 Atomic wave functions
1.2 Crystal-field splitting
1.3 Coulomb-exchange interaction
1.4 Multiplet splitting

1.4 Multiplet splitting

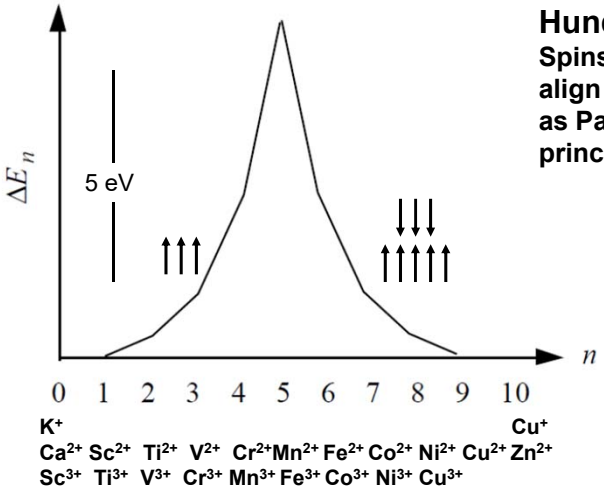
4-electron system



Kanamori parameters

$$U \equiv U_{\gamma\gamma},\quad U' \equiv U_{\gamma\gamma'},\quad J_{\mathrm{H}} \equiv J_{\gamma\gamma'}\quad (\gamma \neq \gamma')$$
$$U - U' = 2J_{\mathrm{H}}$$

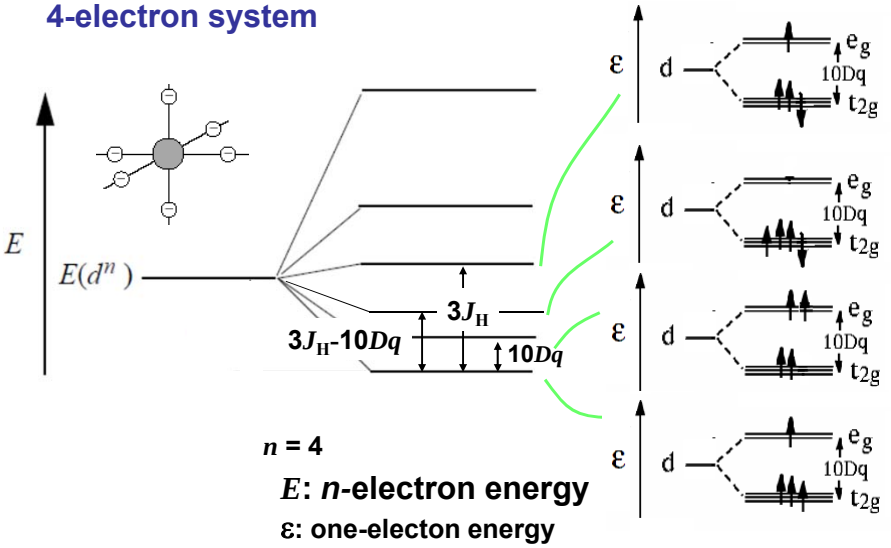
1. Electronic structure of transition-metal ions
1.4 Multiplet splitting



Hund rule:
Spins want to align as much as Pauli principle allows.

1. Electronic structure of transition-metal ions
1.4 Multiplet splitting

4-electron system



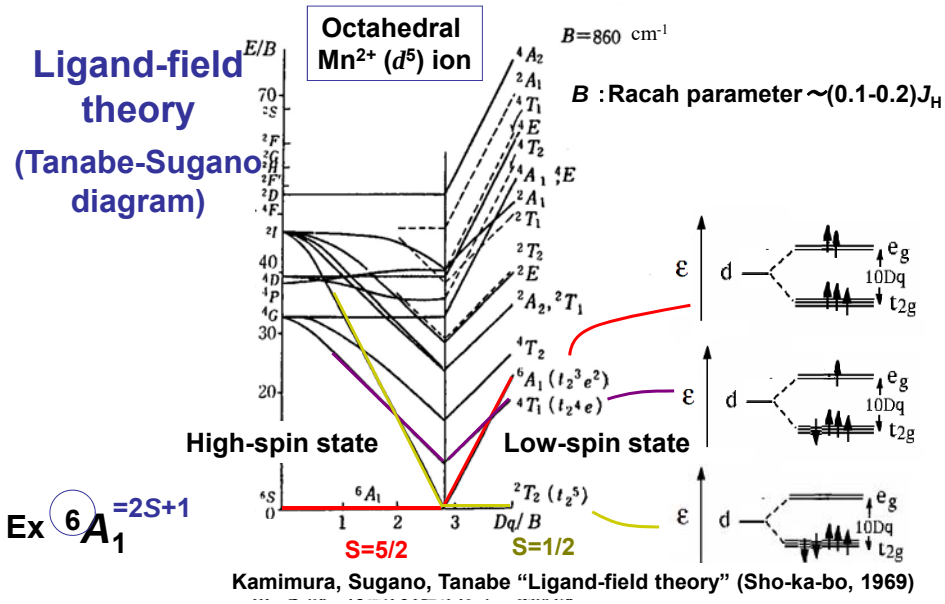
$n = 4$

E: n-electron energy

ε: one-electon energy

1. Electronic structure of transition-metal ions
1.4 Multiplet splitting

Ligand-field theory
(Tanabe-Sugano diagram)

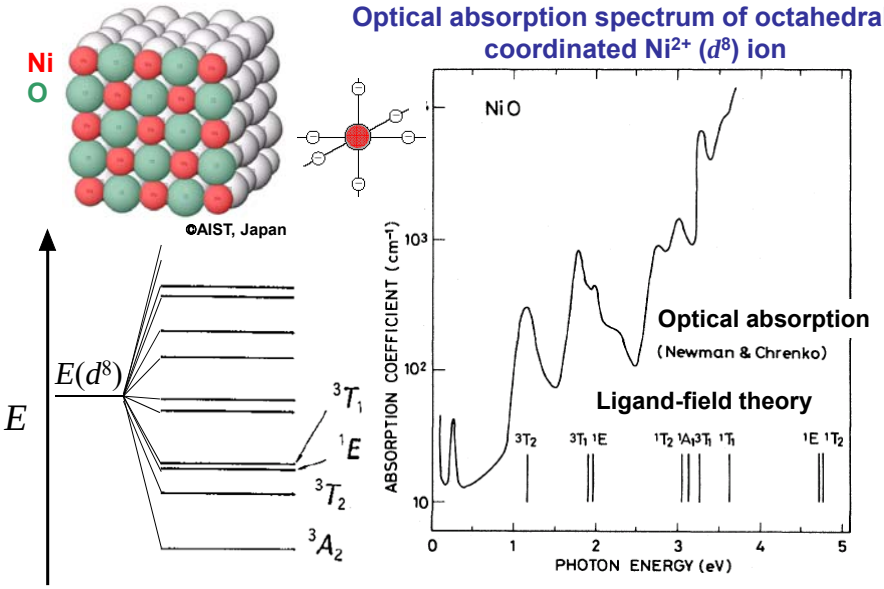


Ex $^{6}A_{1}$ =2S+1

Kamimura, Sugano, Tanabe "Ligand-field theory" (Sho-ka-bo, 1969)

1. Electronic structure of transition-metal ions
1.4 Multiplet splitting

Optical absorption spectrum of octahedrally coordinated Ni^{2+} (d^8) ion



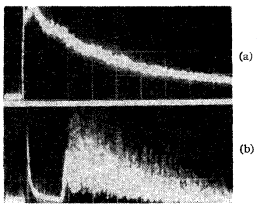
1.4 Multiplet splitting

Ligand-field theory explains:

- **Optical spectra – Color, Laser emission**

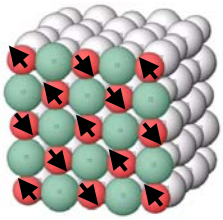
First Laser emission:
Ruby (Cr^{3+} in Al_2O_3) *R* line

FIG. 12. Light output pulse from the exciting lamp in the green (a) and stimulated emission output pulse from ruby (b) (time scale 200 μsec/division). The excitation energy for (b) was approximately twice threshold. The initial spike in (b) is an electrical transient arising from the trigger circuitry.



T.H. Maiman *et al.*, Phys. Rev. 123, 1151 (1961)

Antiferromagnetic order of NiO



- **Antiferromagnetism ($T < T_N$)**
- **Paramagnetism following the Curie-Weiss law ($T > T_N$)**