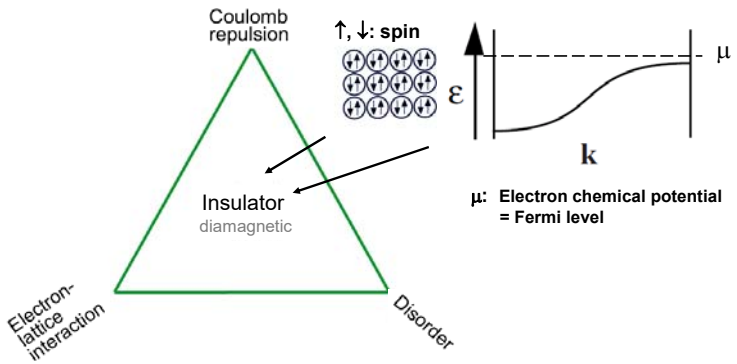
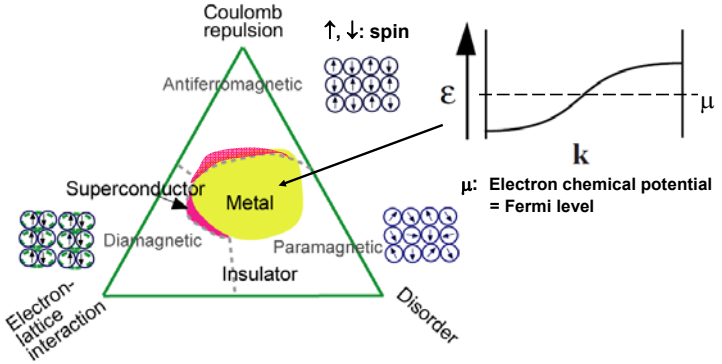
Electronic phase diagram of strongly correlated electron system at T = 0 K for n = 2



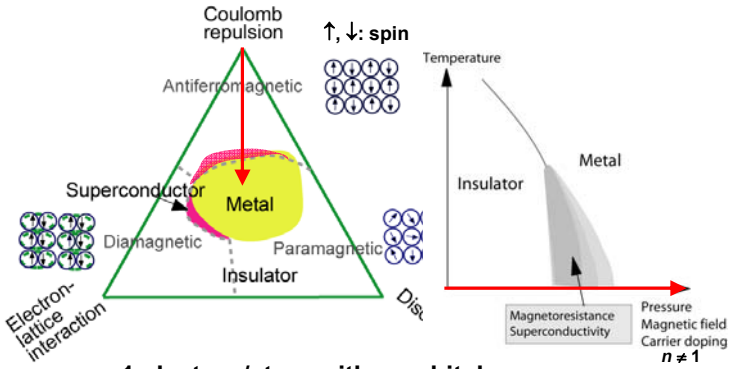
- **2 electrons/atom with *s* orbital**
- ***T* = 0 K**

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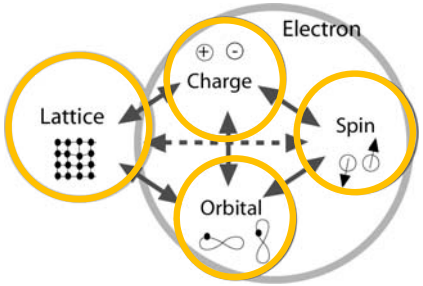
理・物理 藤森研ホームページ→講義→物質科学
URL: http://wyvern.phys.s.u-tokyo.ac.jp/f/lecture/matscig/index.htm

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

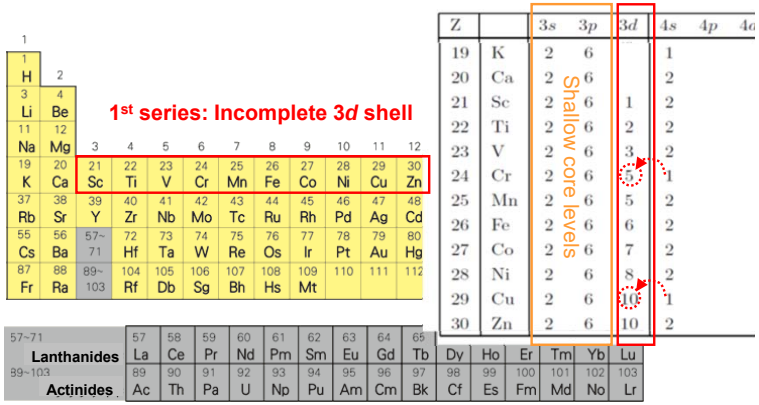
1. 藤森 淳「強相関物質の基礎 ― 原子，分子から固体へ」(内田老鶴圃，2005年)
2. M. Imada, A. Fujimori, and Y. Tokura: *Metal-Insulator Transitions*, Review in Modern Physics 70, 1039 (1998)
3. 津田惟雄，那須圭一郎，藤森 淳，白鳥紀一「電気伝導性酸化物(改訂版)」(裳華房，1993年)
   N. Tsuda, K. Nasu, A. Fujimori, K. Siratori: *Electronic Conduction in Oxides* (Springer-Verlag, 2000)

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



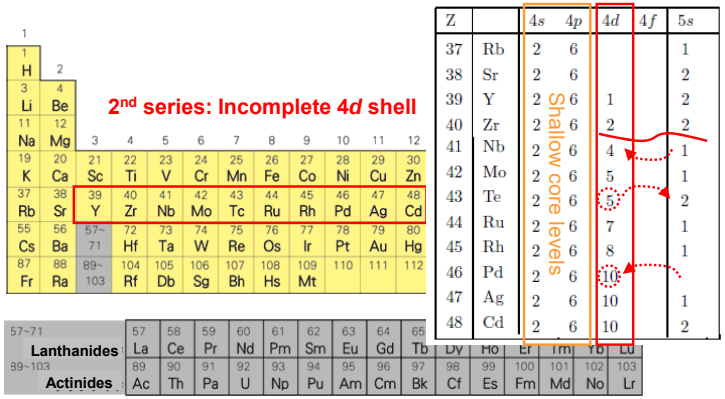
- many electrons/atom with *p, d, or f* orbitals
- $T = 0$ K

Transition elements



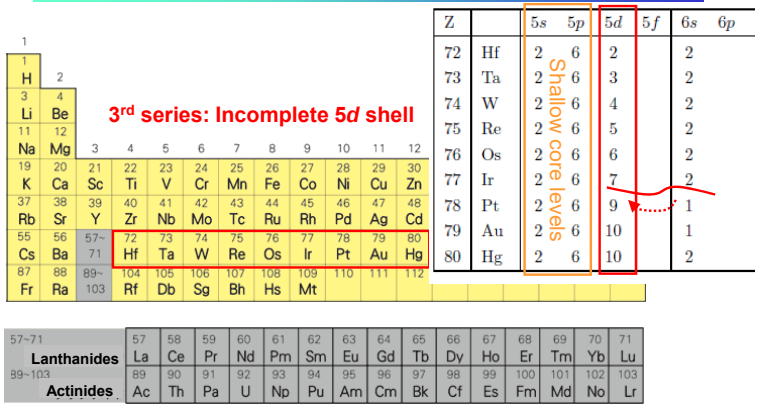
KEK home page

Transition elements



KEK home page

Transition elements



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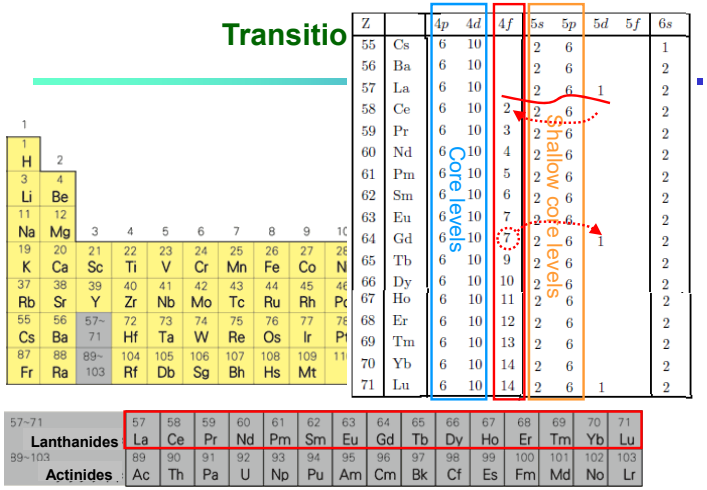
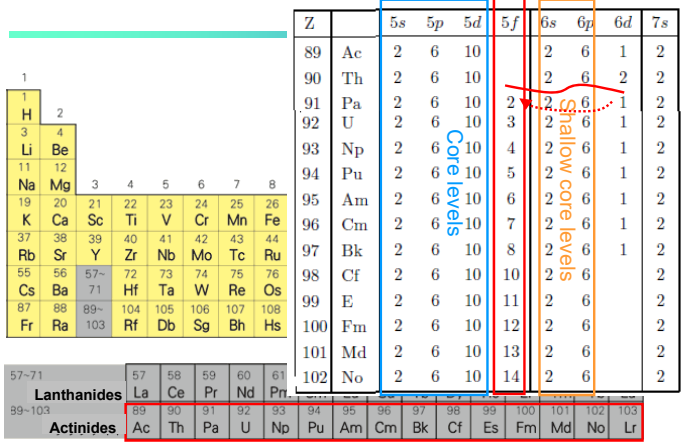
Transitio



Lanthanide series: Incomplete 4f shell

KEK home page

Transition elements



Actinide series: Incomplete 5f 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

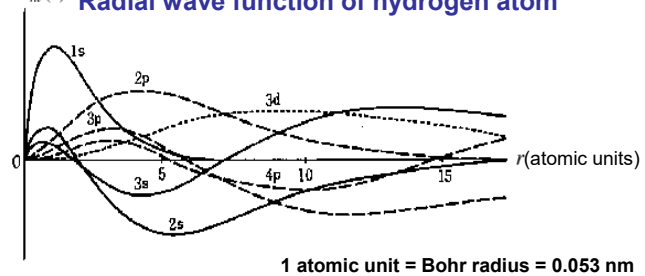
- 1.1 Atomic wave functions
- 1.2 Crystal-field splitting
- 1.3 Coulomb-exchange interaction
- 1.4 Multiplet splitting

1.1 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

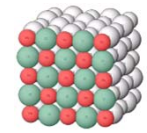


1 atomic unit = Bohr radius = 0.053 nm

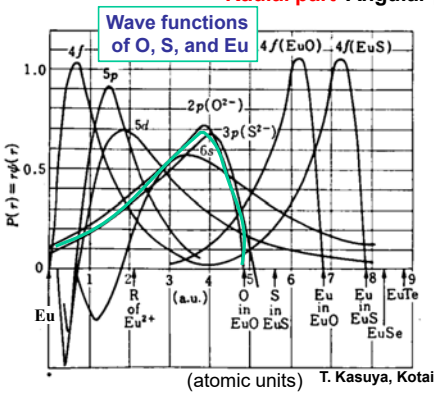
1.1 Atomic wave functions

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

Radial part Angular part (Spherical harmonics)



Eu O/S



1 atimic unit
= Bohr radius
= 0.053 nm

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

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

Radial part | Angular part (Spherical harmonics)

s orbital

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

p orbitals (complex)

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta, \qquad Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi},$$

d orbitals

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \qquad Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi},$$

$$Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi},$$

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

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

p orbitals (real)

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

d orbitals

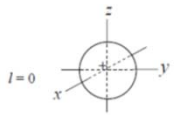
$$Y_2^0 \propto 3z^2 - r^2, \qquad \frac{1}{\sqrt{2}}[Y_2^1 \pm Y_2^{-1}] \propto yz, zx,$$

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

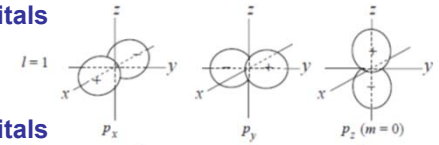
1. Electronic structure of transition-metal ions
1.1 Atomic wave functions

Spherical harmonics (complex) → Cubic harmonics (real)

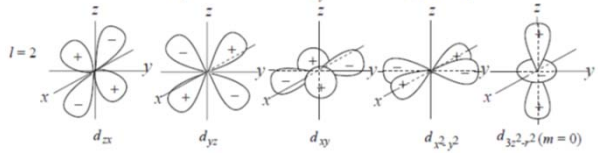
s orbital



p orbitals



d orbitals

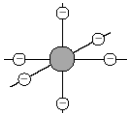


1. Electronic structure of transition-metal ions

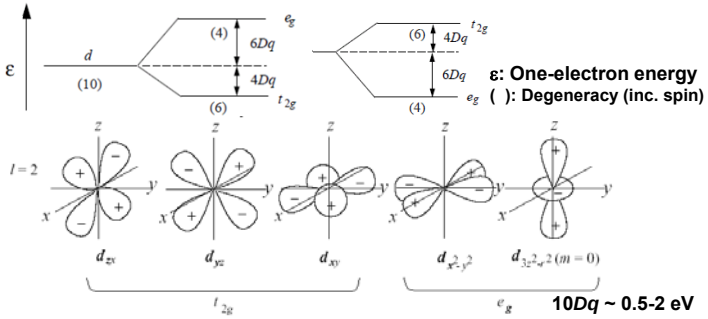
1.1 Atomic wave functions
1.2 Crystal-field splitting
1.3 Coulomb-exchange interaction
1.4 Multiplet splitting

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

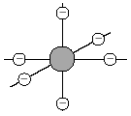


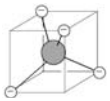
ε: One-electron energy
( ): Degeneracy (inc. spin)

10*Dq* ~ 0.5-2 eV

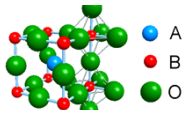
1. Electronic structure of transition-metal ions
1.2 Crystal-field splitting

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

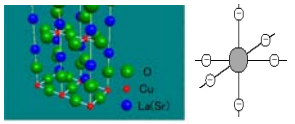
Octahedral coordination 

 Tetrahedral coordination

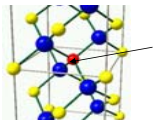
Giant magneto-resistive material
(Perovskite structure)



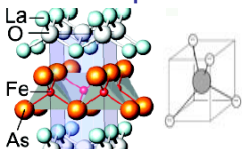
Cu-oxide High-Tc superconductor
(Layered perovskite str.)



Magnetic semiconductor
(Zinc Blende structure)

 Mn

Fe-based superconductor



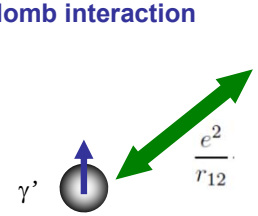
Lowered symmetry

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

Coulomb interaction



Electron 1

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

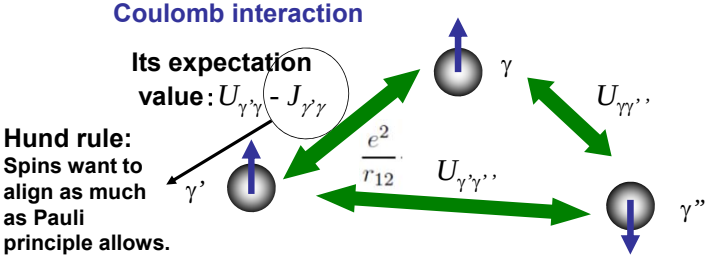
Electron 2

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

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

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

Coulomb interaction



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

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

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

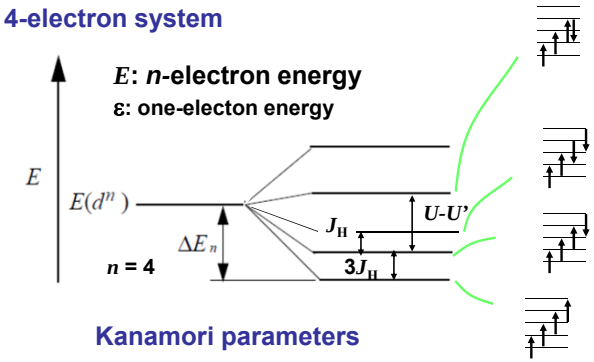
Exchange integral $J_{\gamma\gamma'} \equiv \langle \gamma'\gamma | v | \gamma\gamma' \rangle$ ~ 0.5-1 eV

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

1. Electronic structure of transition-metal ions

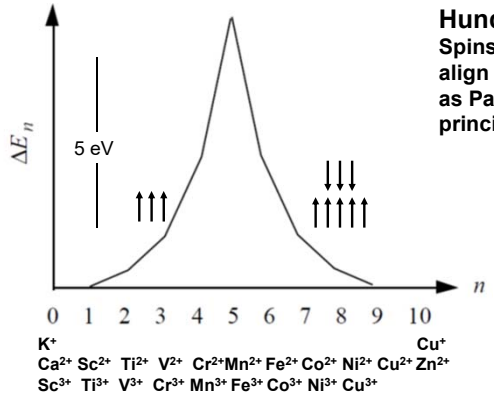
1.1 Atomic wave functions
1.2 Crystal-field splitting
1.3 Coulomb-exchange interaction
1.4 Multiplet splitting

4-electron system



Kanamori parameters

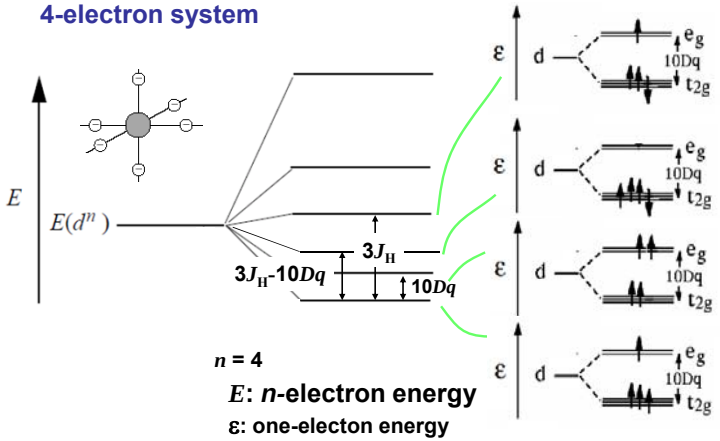
$$U \equiv U_{\gamma\gamma}, \quad U' \equiv U_{\gamma\gamma'}, \quad J_{\mathrm{H}} \equiv J_{\gamma\gamma'} \quad (\gamma \neq \gamma')$$
$$U - U' = 2J_{\mathrm{H}}$$



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

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

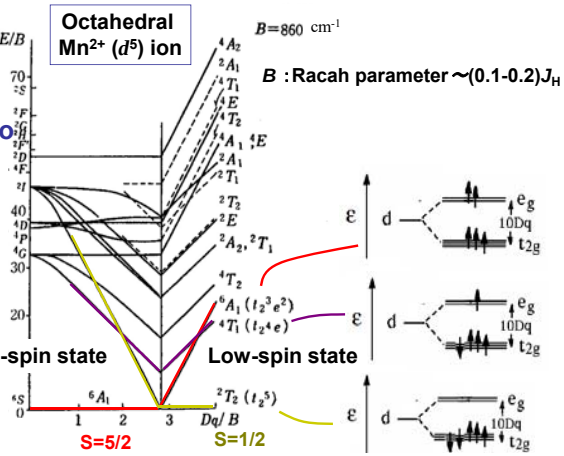
4-electron system



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)



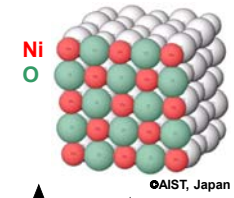
B : Racah parameter ~(0.1-0.2)J_H

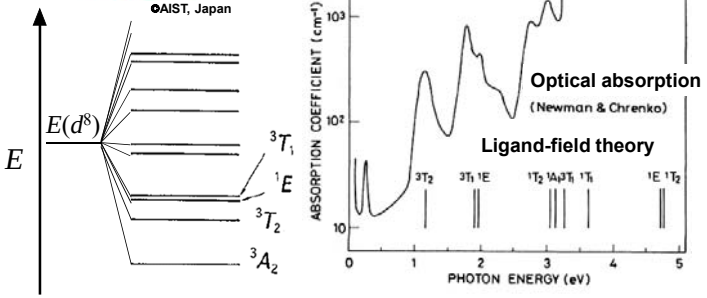
Ex ${}^6A_1$ $^{=2S+1}$

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 Ni2+ (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

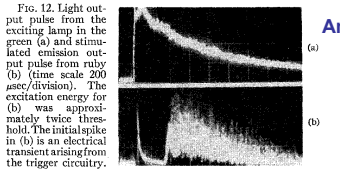
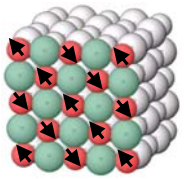


FIG. 12. Light output pulse from the exciting lamp in the green (a) and stimulated emission output pulse from ruby (b) (time scale 200 μsec/division). The excitation energy for (b) was approximately twice threshold. The initial spike in (b) is an electrical transient arising from the trigger circuitry.

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

Antiferromagnetic order of NiO



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