2010 winter term Global Focus on Knowledge

"The World of Diverse Matter"

Lecture 7

"The Diversity of Matter Born from the Actions of Atoms, Electrons, and Molecules"

Advanced Functionality Produced by Molecular Assembly

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Univ. of Tokyo Executive Vice President

Global Focus on Knowledge 2010, 2010.11.18

My Research

Research area: Chemistry (Physical Chemistry of Molecular Assembly)

Physical chemistry deals with physical and chemical properties of elements, and its aim is to manipulate them to invent various kinds of molecular assemblies, developing new functionalities and new physical-chemical phenomena. It is the core of material sciences.

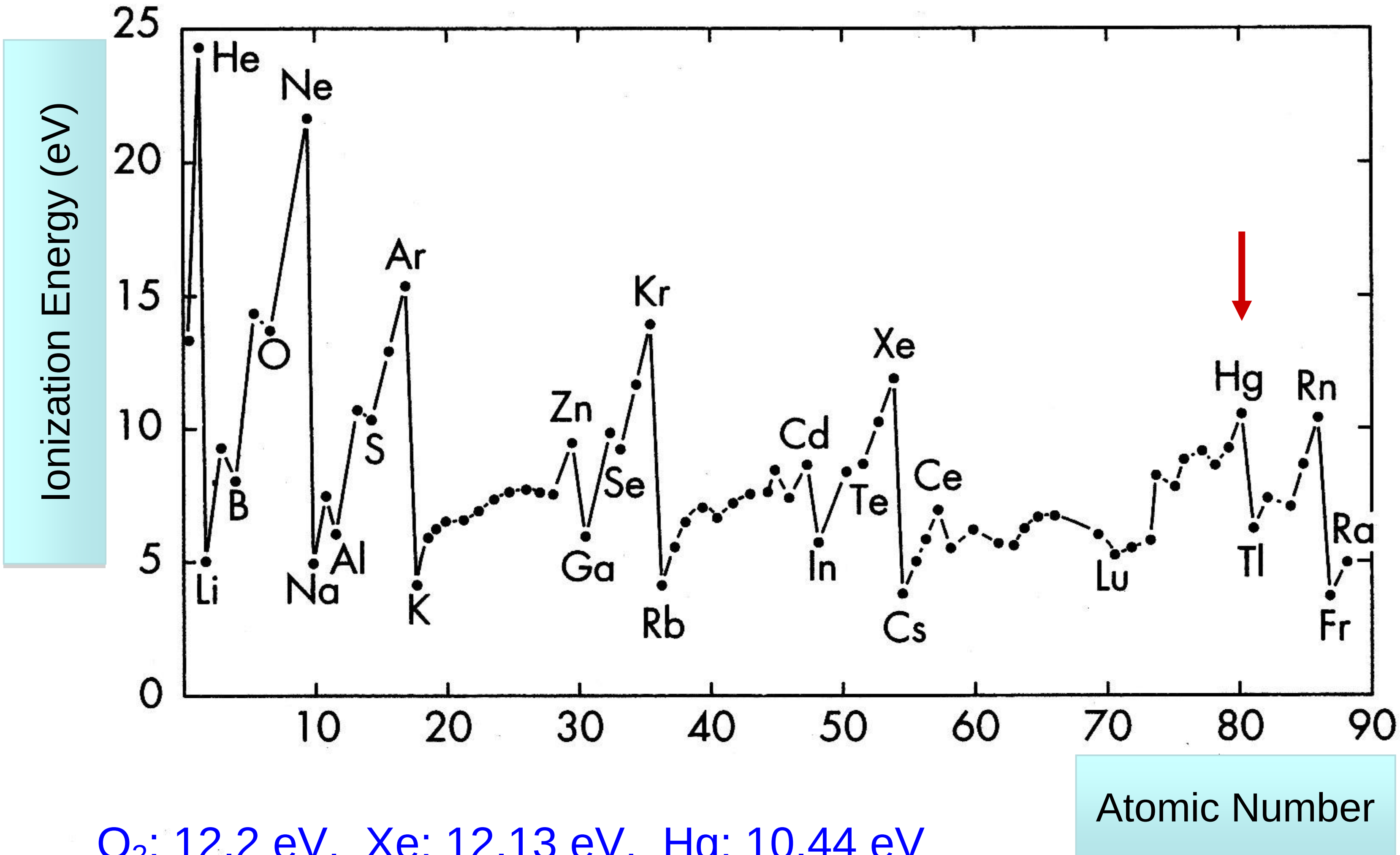
Main research subject

- **Transformation from insulators to metals (valence transition for metal complex)**
- **Manipulating properties of magnets with light (photo-magnetism), investigating magnets with light (magneto-optics)**
- **Realization of higher order functionalities based on the photo-induced transformation of molecules (design of photo-responsive organic-inorganic hybrid complexes)**

In the distant future: transformation from insulators to metals and superconductors with light.

Survey on Physical and Chemical Properties of Elements

Periodicity of the Ionization Energy

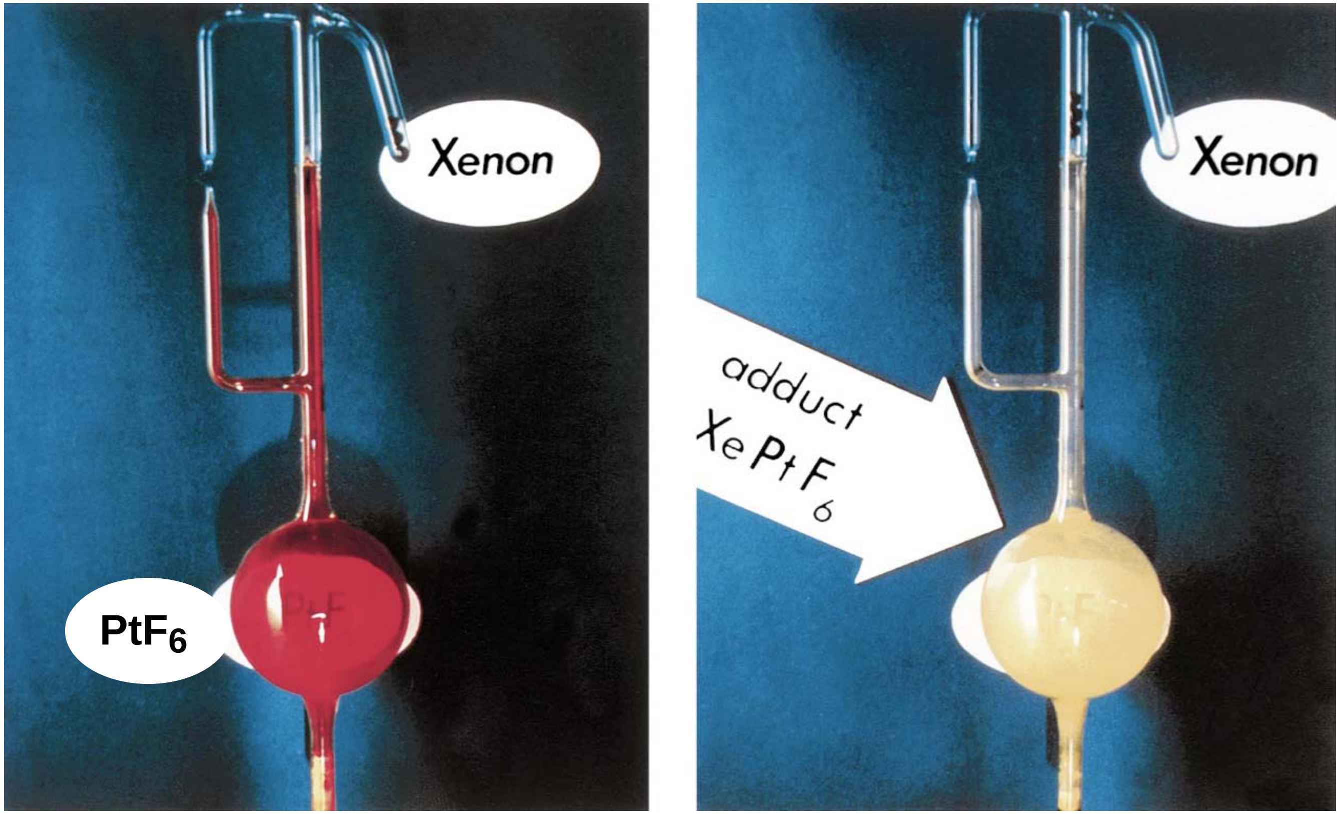


O_2: 12.2 eV, Xe: 12.13 eV, Hg: 10.44 eV

Why the ionization energy of mercury is so high?

The First Synthesis of Rare Gas Compound, $Xe^{+}[PtF_6]^{-}$

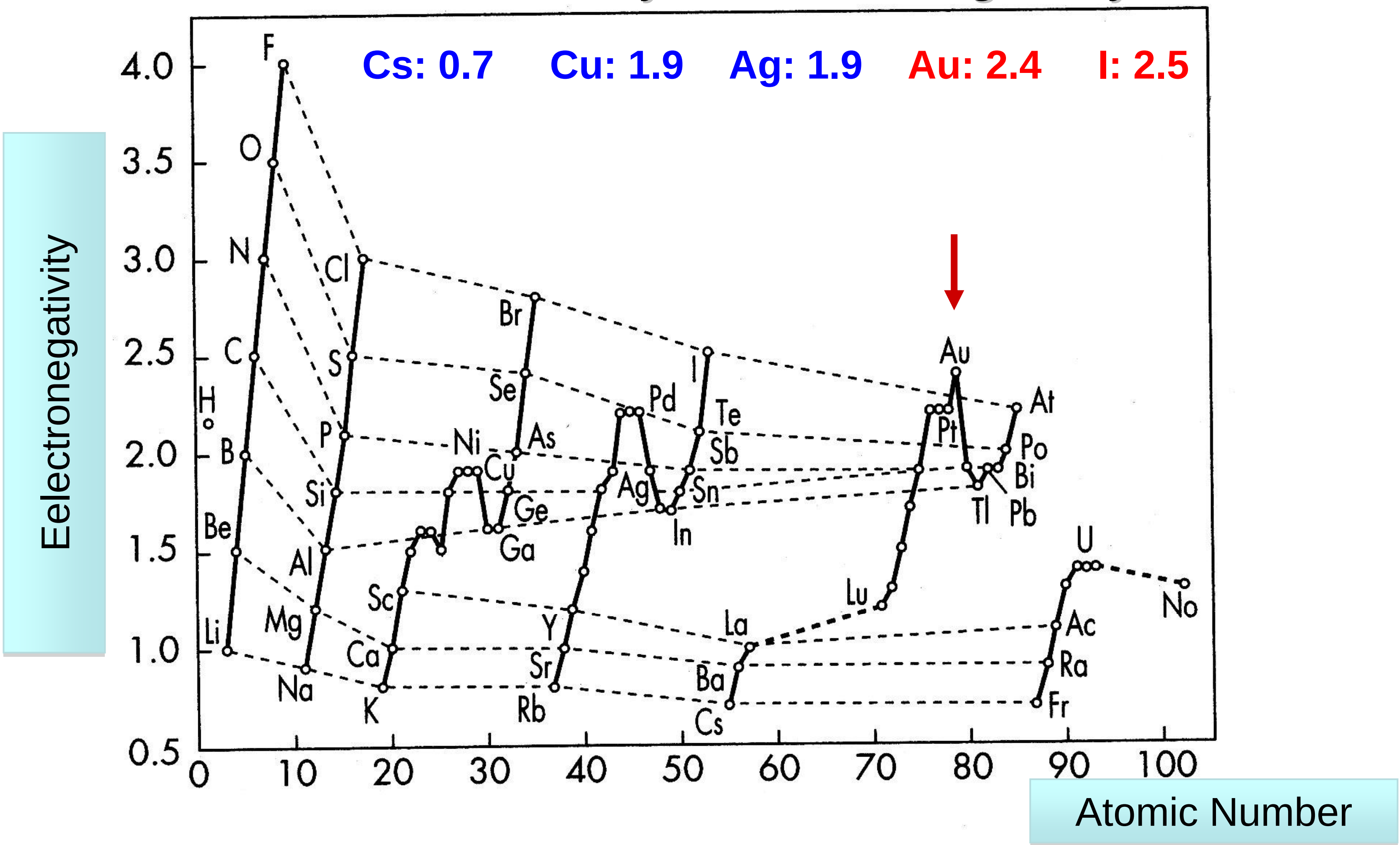
L. Graham, O. Graudejus, N.K. Jha and N. Bartlett, *Coord. Chem. Rev*., **197**, 321 (2000).



- N. Bartlett removed one electron from O_2 molecule with a strong oxidant PtF_6 and obtained $O_2^{+}[PtF_6]^{-}$.
- He noticed the ionization energy of Xe is almost equal to that of O_2 molecule and removed one electron from Xe with PtF_6, obtaining $Xe^{+}[PtF_6]^{-}$ (1962).

Survey on Physical and Chemical Properties of Elements

The Periodicity of Electronegativity



Cs + Au → $Cs^{+}Au^{-}$（ionic crystal） Cs + Ag → CsAg（alloy）

Cs + Cu → CsCu（alloy）

The Origin of Extraordinary Physical/Chemical Characteristics of Heavy Elements

～Relativistic Effects on Heavy Elements～

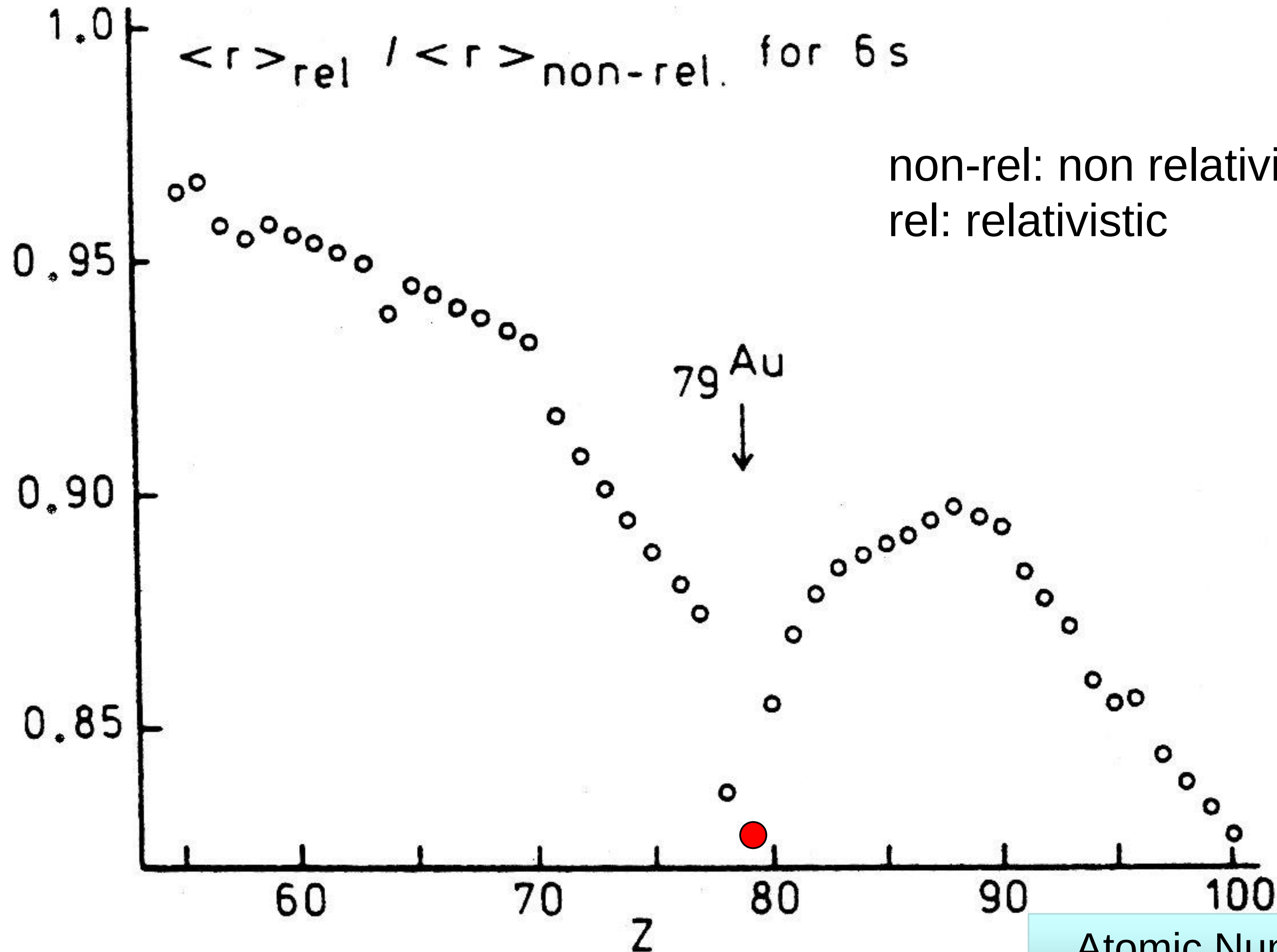
$$m = m_0 / \{1-(v/c)^2\}^{1/2}$$ （**mass of moving electron)**

$$r_n = n^2 h^2 \varepsilon_0 / \pi m Z e^2$$ （**radius of ns orbital**）

$$E_n = -\frac{m Z^2 e^2}{8 \varepsilon_0^2 h^2 n^2}$$ （**energy of ns orbital**）

Mean velocity of 1s electron of Hg is as high as 60 % of light speed.

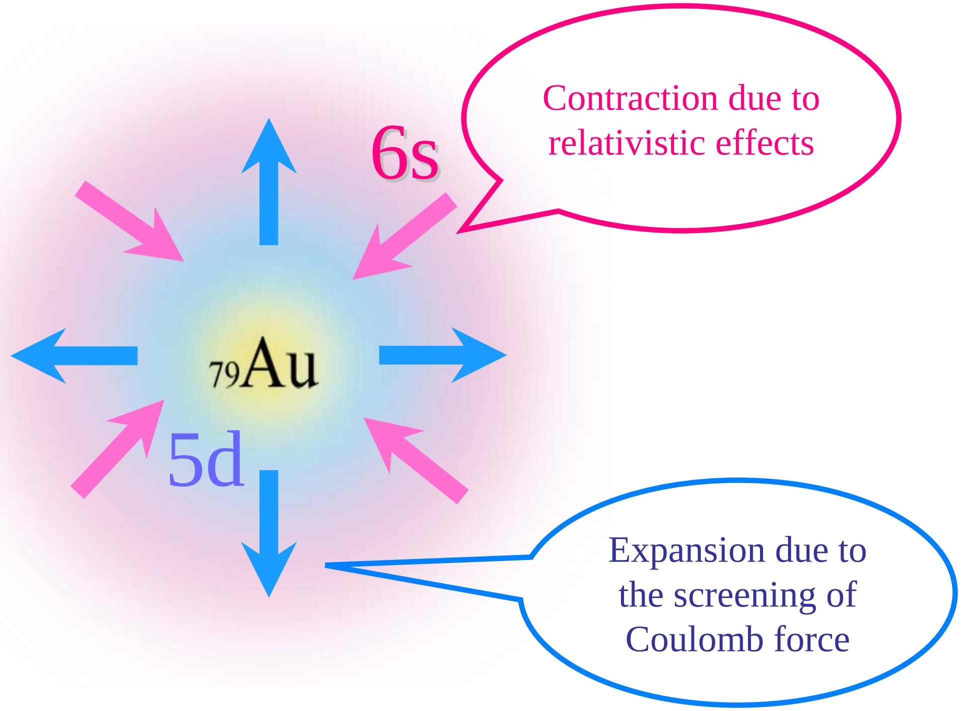
Relativistic Contraction of the Radius <*r*> of 6s Orbital

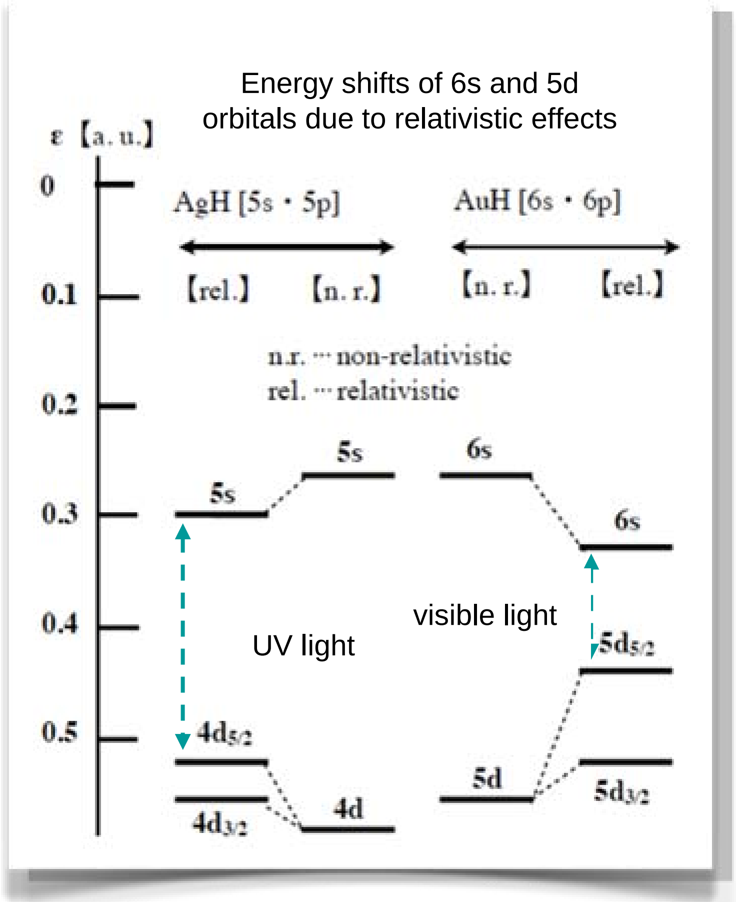


non-rel: non relativistic
rel: relativistic

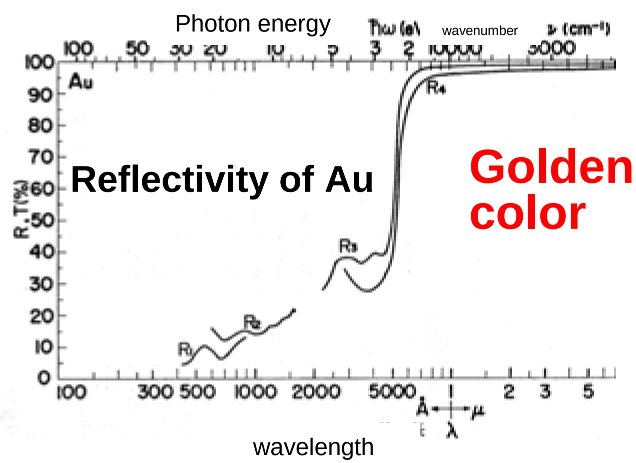
Atomic Number

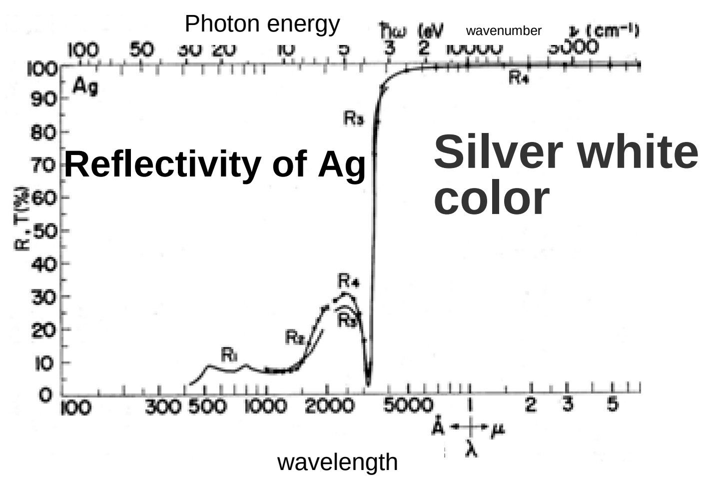
P. Pyykkö, et al., *Accounts of Chemical Research*, 12, 276 (1979).





If the relativistic effects on 6s electron were negligible, the color of Au would be silver white.





Mystery of Relativistic Effects on Heavy Elements

- Mercury (Hg) is liquid at room temperature due to relativistic effect

  ＊6s orbital is closed shell, and its characteristics is similar to those of rare gases.

- Gold (Au) exhibits golden color due to relativistic effect

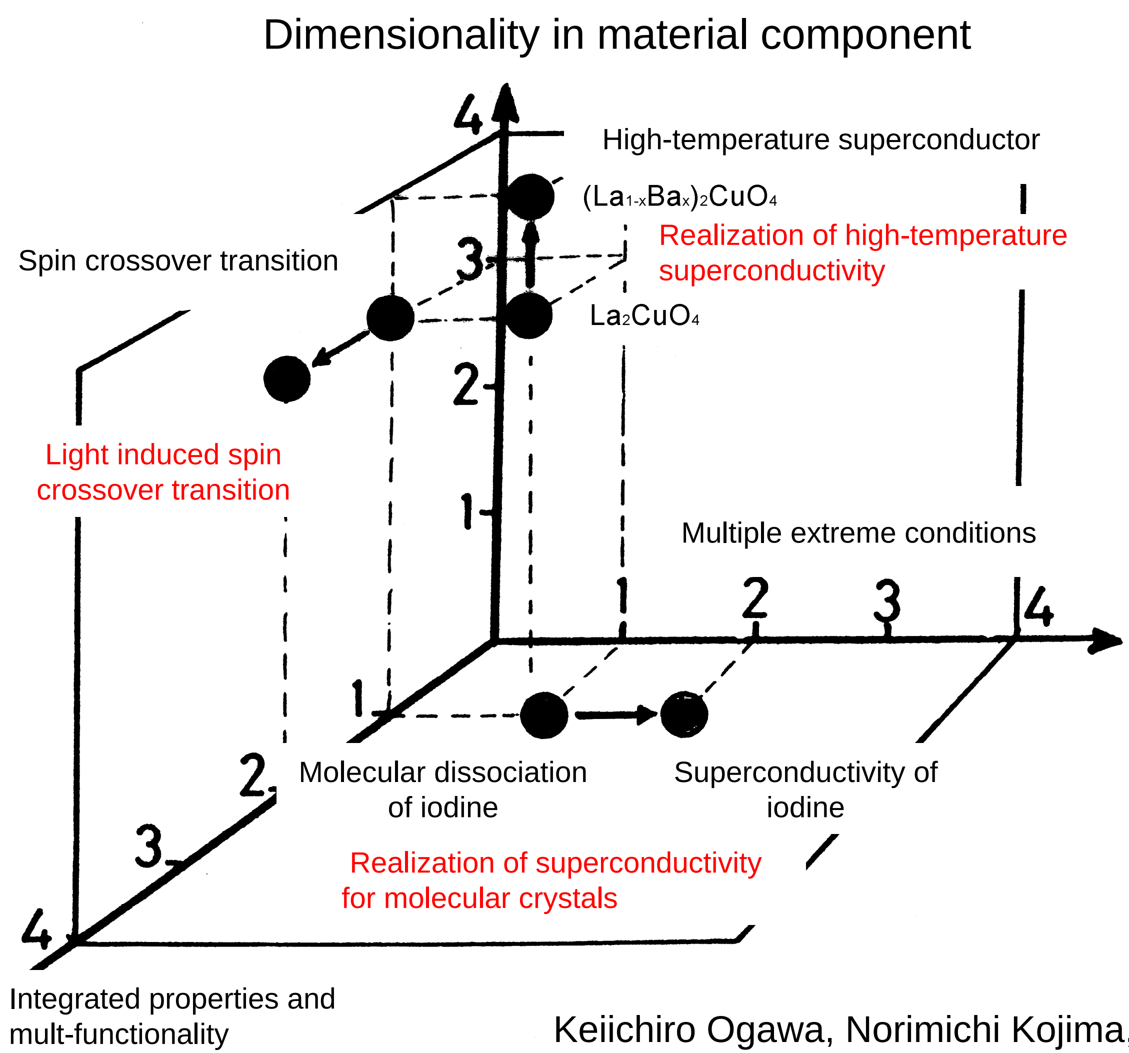
  ＊If the relativistic effect on 6s electron was negligible, the color of Au would be silver white.

- Anomalous electronegativity of Au

- Anomalous ionization energy of Hg

Viewpoint for Materials

Our viewpoint at room temperature and ambient pressure is only one point in the multiple coordinates for materials.



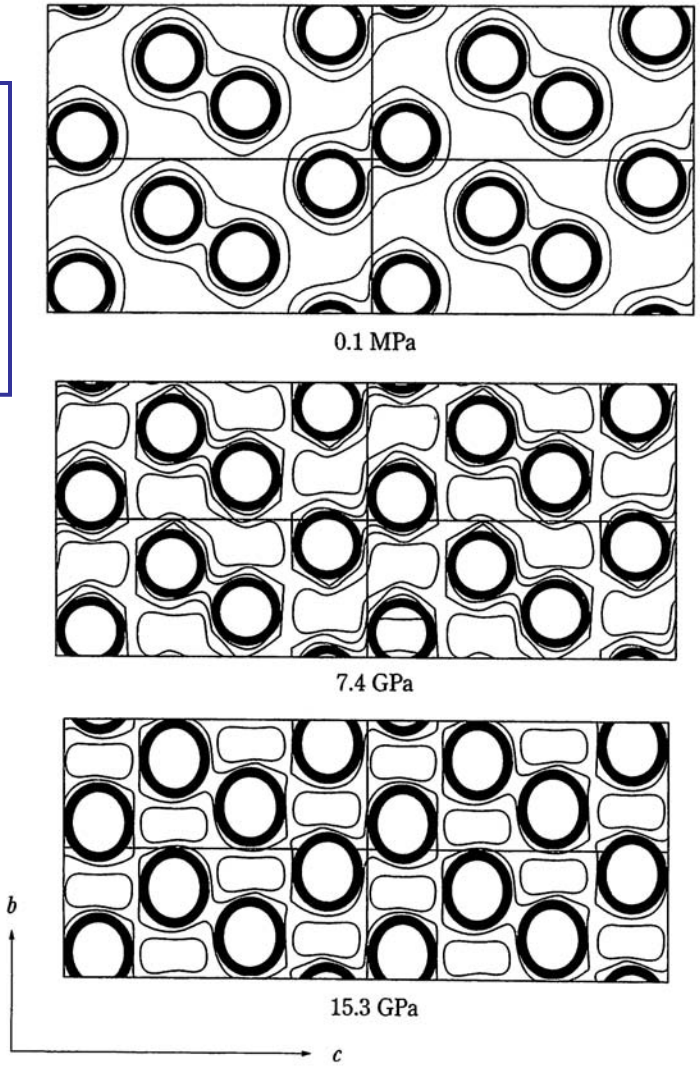
Keiichiro Ogawa, Norimichi Kojima, eds., New "Bussei Kagaku no Kiso" (in Japanese) Kodansha (2010)

Distribution of Electron Density in Solid Iodine at 0.1 MPa, 7.4 GPa, and 15.3 GPa

Pressure dependence of the distribution of electron density in solid iodine was measured by means of X-ray structural analysis under high pressures.

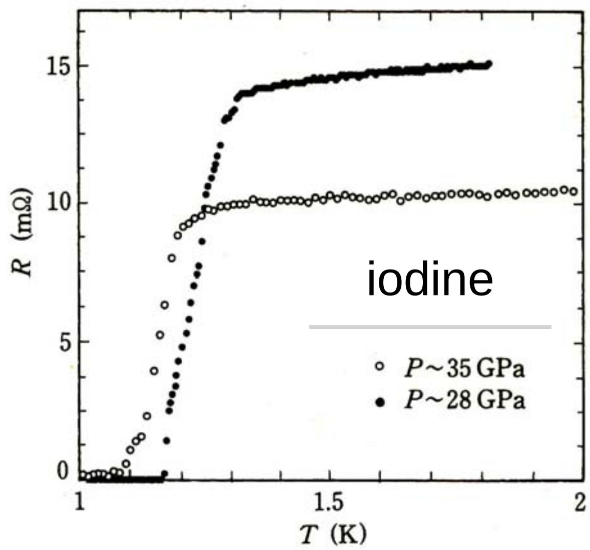
Ambient pressure ≈ 0.1 MPa

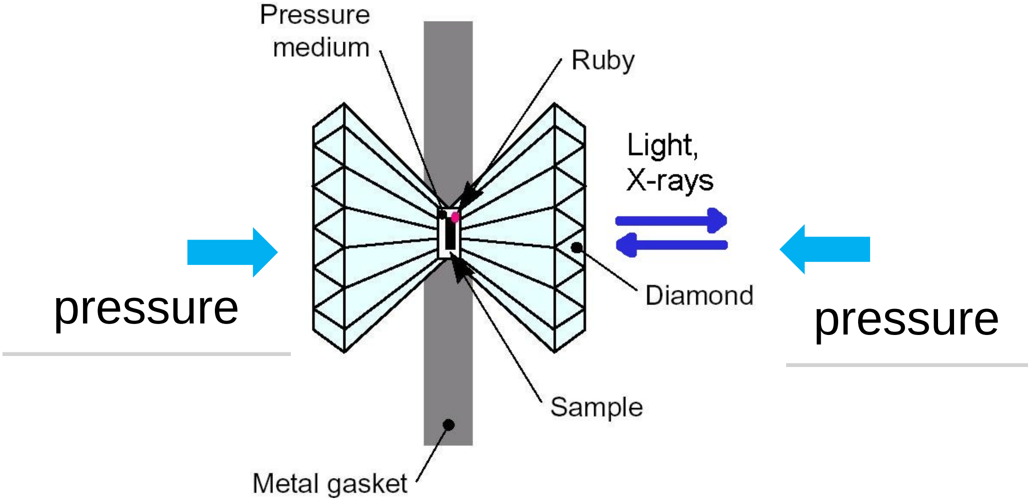
1 GPa = 10^3 MPa

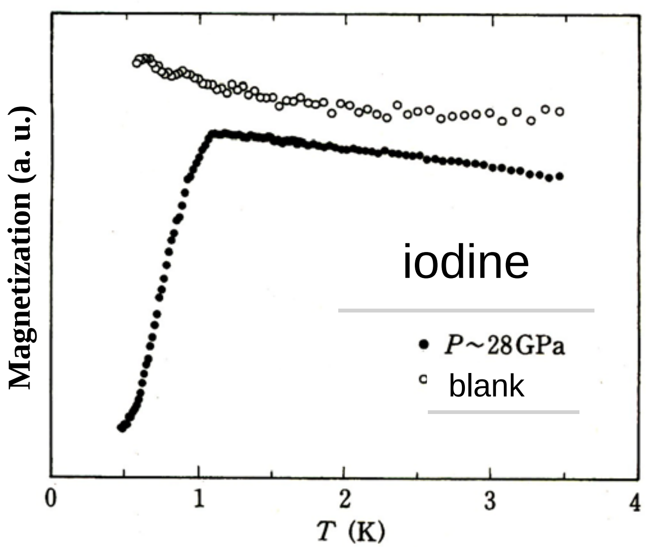


Yuji Fujihisa, “The Review of High Pressure Science and Technology (in Japanese)”, **5**, 160 (1996).

Superconductivity of Solid Iodine



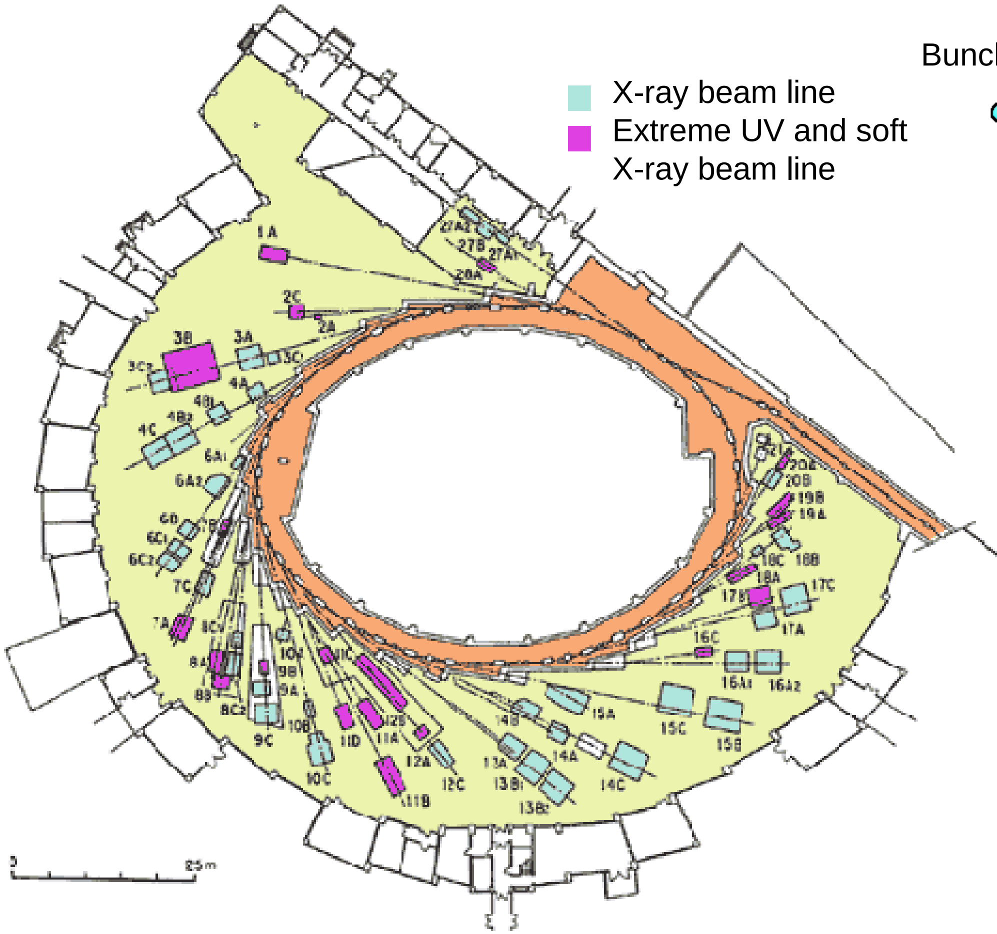




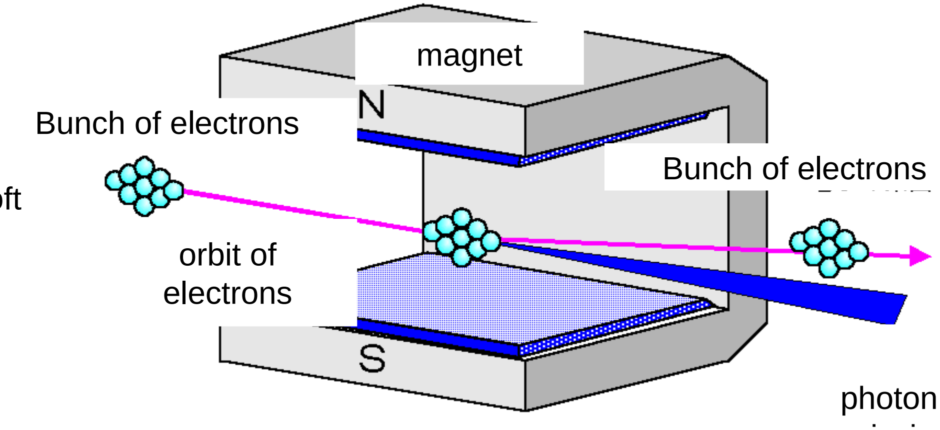
Kiichi Amaya, Mamoru Ishizuka, Katsuya Shimizu, et al., "Solid State Physics (in Japanese)", **28,** 435 (1993).

Photon Factory and the Principles of Synchrotron Radiation

When the orbit of electrons with high speed comparable to light speed is suddenly deflected, photons are emitted into the tangent direction, which is called synchrotron radiation.

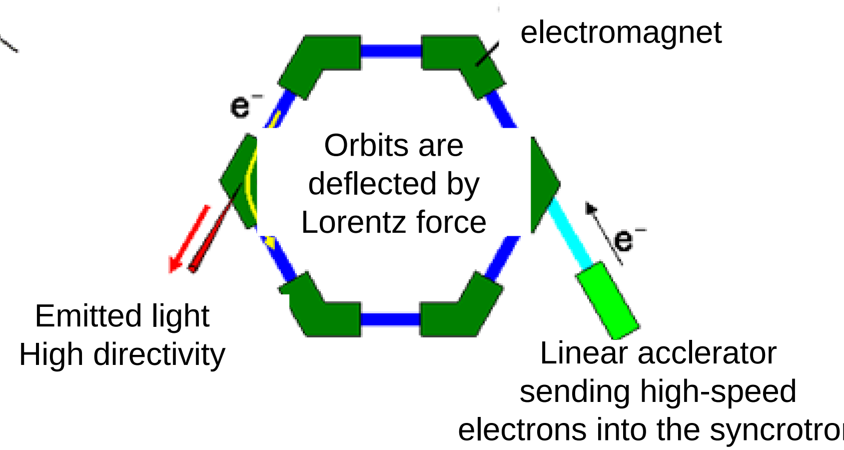


KEK
http://www.kek.jp/ja/index.html



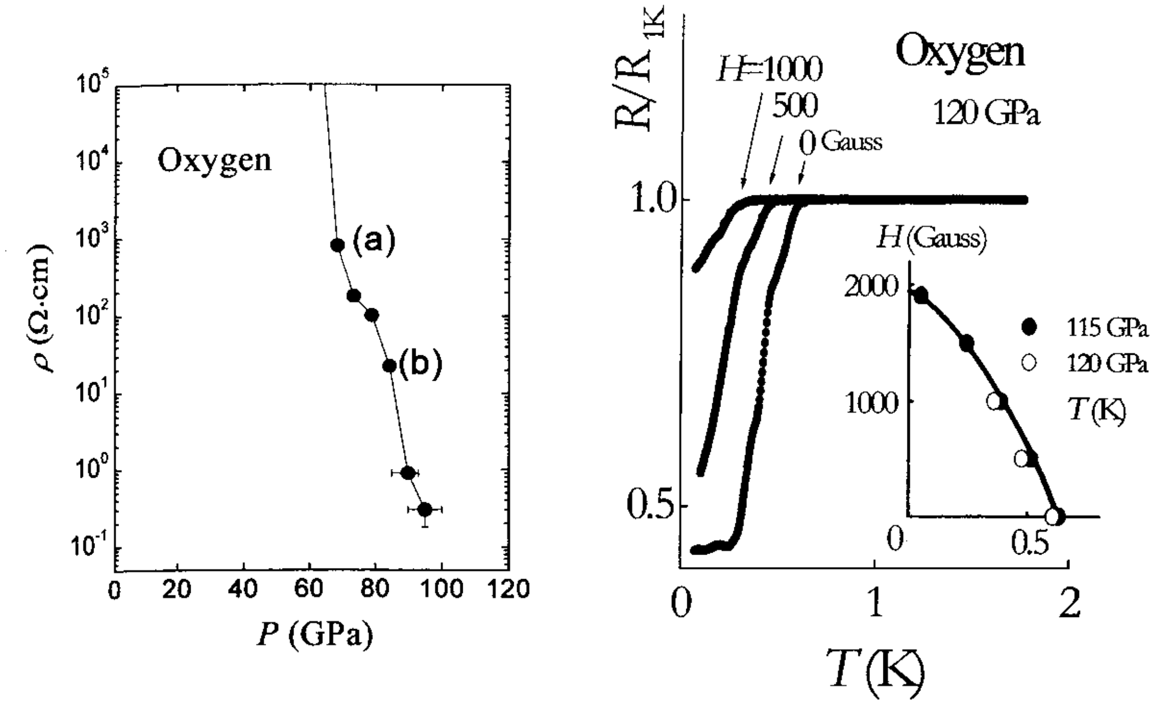
The principles of synchrotron radiation

From Spring-8 brochure (October 1997), page 11



Geological Survey of Japan, AIST
http://staff.aist.go.jp/a.ohta/MyHome.htm

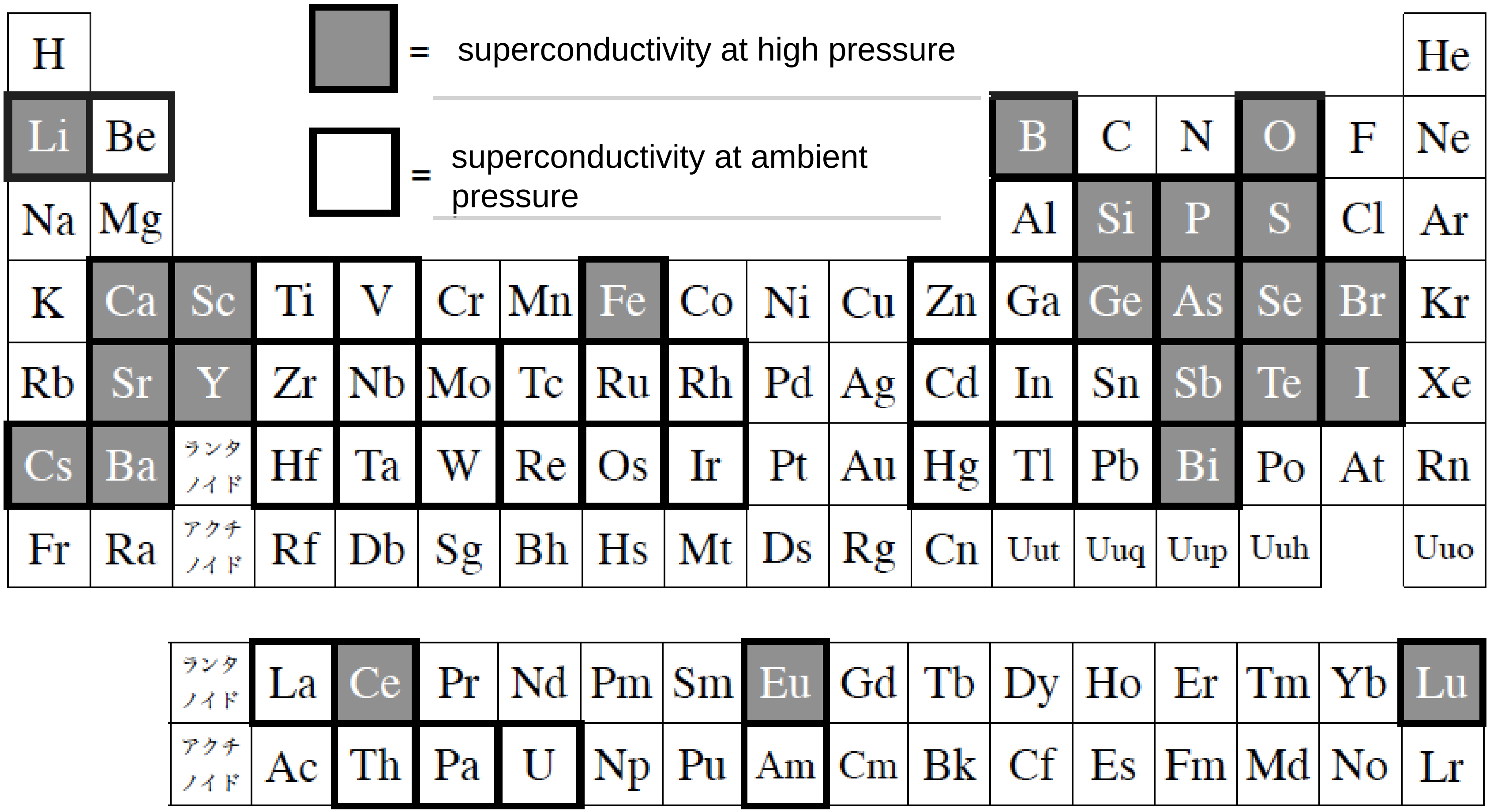
Superconductivity appears in solid oxygen at high pressures.



Solid oxygen exhibits the superconductivity at 115 GPa and 0.6 K.

Katsuya Shimizu, “The Review of High Pressure Science and Technology (in Japanese)”, **10**, 194 (2000).

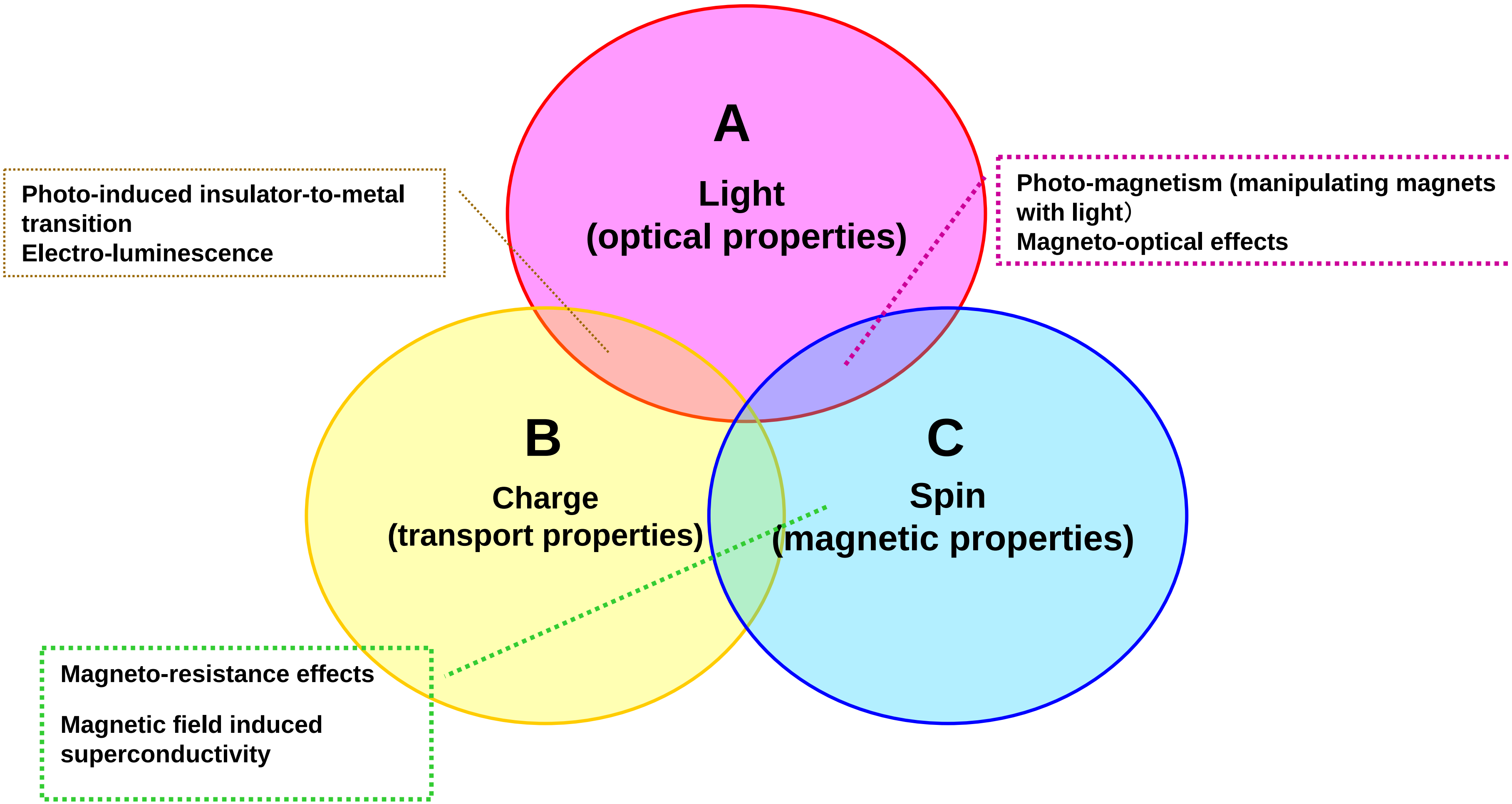
Elements exhibiting superconductivity (simple substance)



Keiichiro Ogawa, Norimichi Kojima, eds., New “Bussei Kagaku no Kiso” (in Japanese) Kodansha (2010)

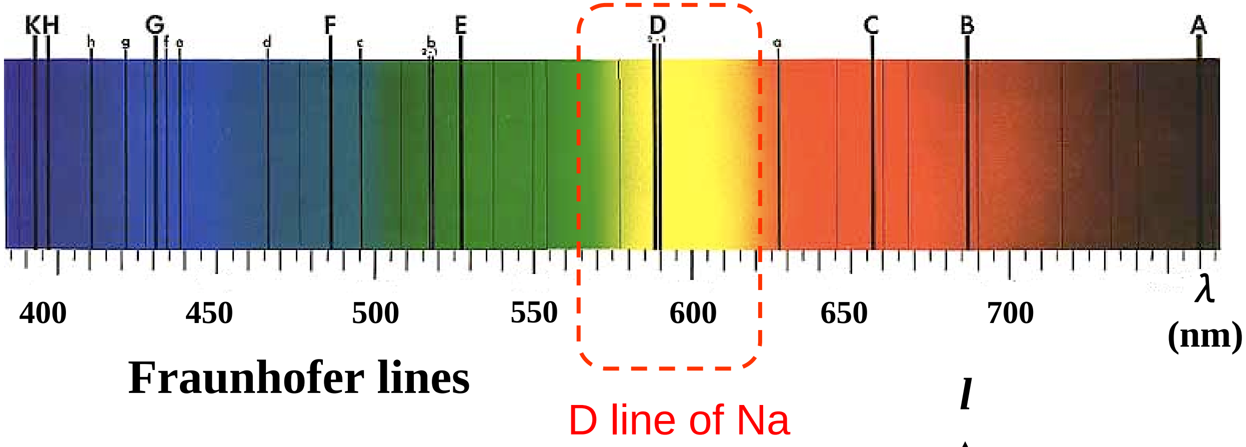
Concept of Multifunctionality

～Advanced functionality based on molecular assembly～



Multifunctionality（A + B, B + C,   A + C, A + B + C）

(C) Spin (magnetic properties)



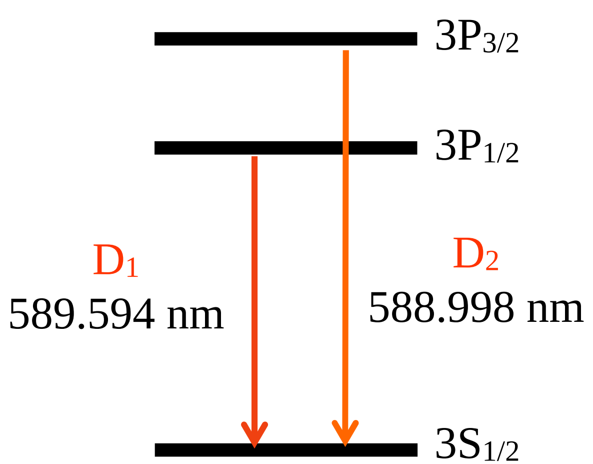
Fraunhofer lines

Splitting of D line of Na

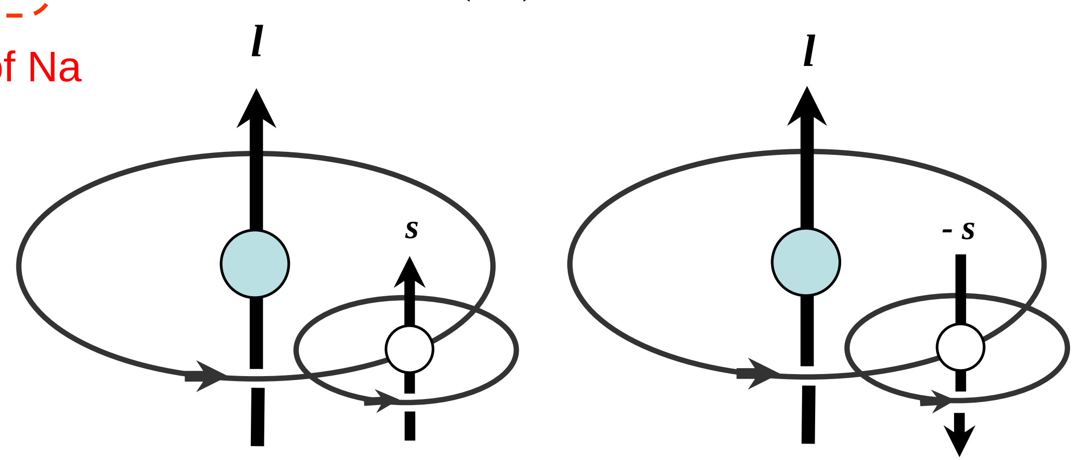
↓

Discovery of electron spin (S = ½)

Uhlenbeck & Goudsmit (1925)



3p→3s transition of Na atom



An electron with clockwise orbital rotation and clockwise spin rotation (total angular momentum = $\boldsymbol{l} + \boldsymbol{s}$)

An electron with clockwise orbital rotation and anticlockwise spin rotation (total angular momentum = $\boldsymbol{l} - \boldsymbol{s}$)

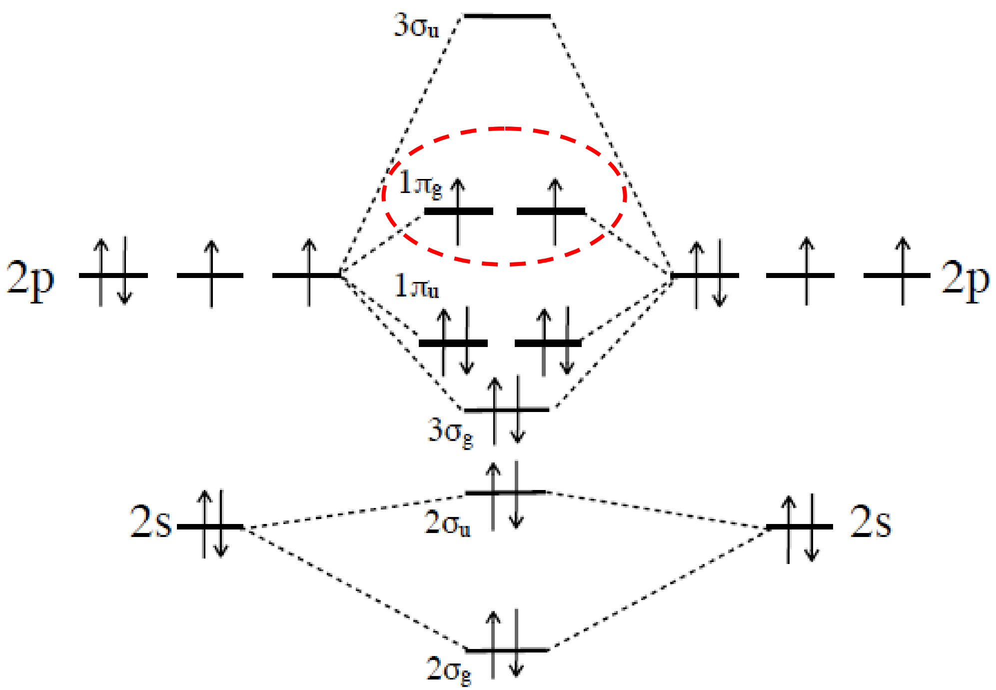
An electron feels the following magnetic field when it is rotating around an atomic nucleus

$$H = \frac{1}{2} Z e \frac{[r \times v]}{r^3} = \frac{e\hbar}{2\mathrm{m}} \frac{Z}{r^3} l$$

$$(\hbar l = [r \times P])$$

(C) Spin (magnetic properties)

Paramagnetism of O_2 molecules



Molecular orbitals of O_2

Liquid oxygen is pale blue and its boiling point is 90K. Liquid oxygen is attracted to a magnet.

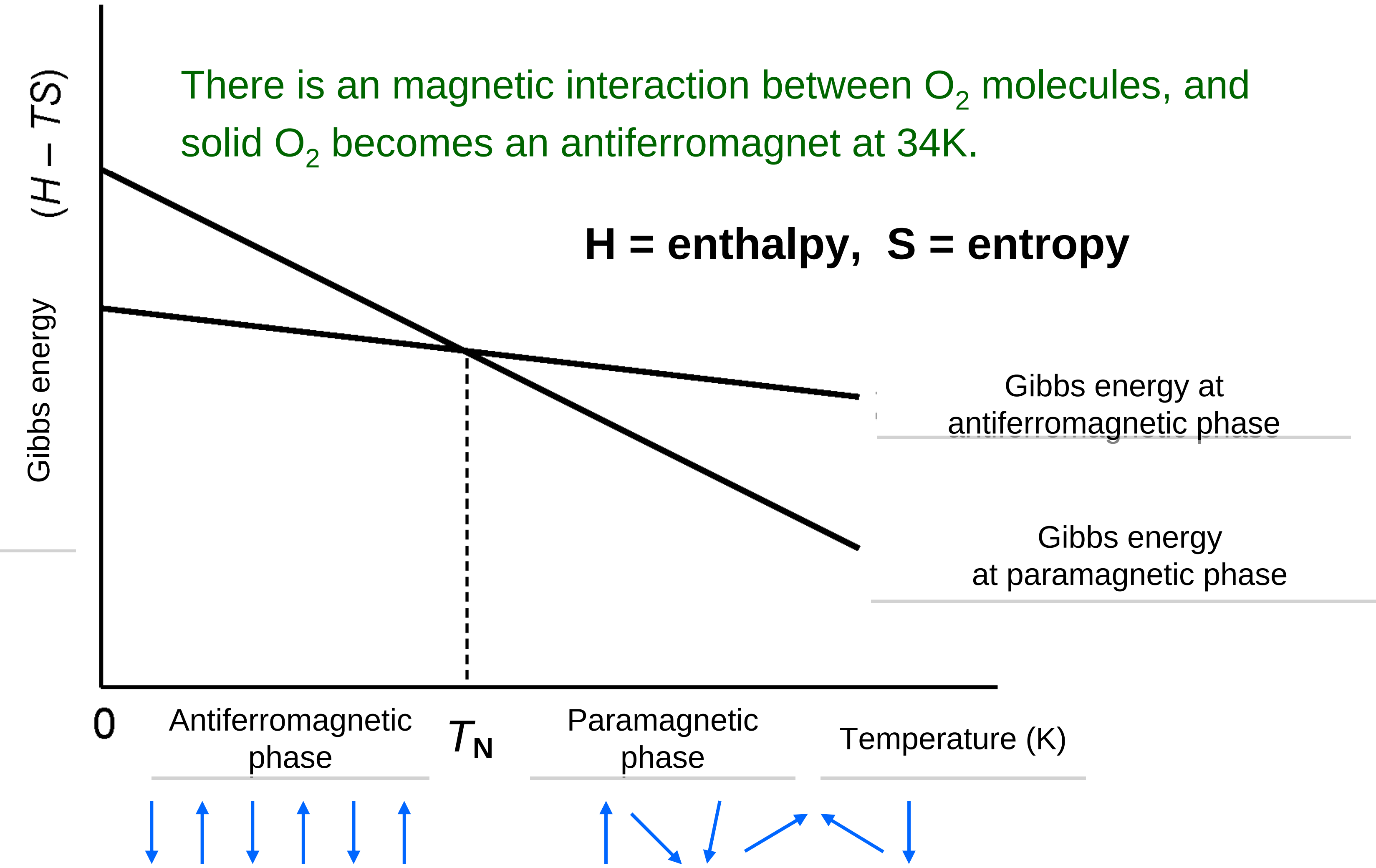
Keiichiro Ogawa, Norimichi Kojima, eds., New “Bussei Kagaku no Kiso” (in Japanese) Kodansha (2010)

(C) Spin (magnetic properties)

Paramagnetic phase and magnetically ordered phase

There is an magnetic interaction between O_2 molecules, and solid O_2 becomes an antiferromagnet at 34K.

H = enthalpy, S = entropy



(A) Light (optical properties) The origin of 15 types for colors of matter

【 Vibrations and Simple Excitations 】

1. **Black-body radiation:** filament lamps, sunlight (blackbody radiation at 5700 ℃)
2. **Excitations of gas:** sodium lamp, neon light, aurora
3. **Excitations of vibrations and rotations:** blue color of water (optical absorption by higher harmonic oscillations)

【 Transitions Involving Ligand Field Effects 】

4. **Color of transition metal compounds (transitions in d orbitals):** blue color of copper sulfate
5. **Color of transition metal as impurities:** red color of ruby

【 Transitions Between Molecular Orbitals 】

6. **Organic compound:** color of organic pigments, color of organic charge-transfer complexes
7. **Color due to charge transfer:** blue sapphire, Prussian blue

【 Transition Involving Energy Bands 】

8. **Metallic luster:** color of gold, golden color of brass, color of silver
9. **Color of pure semiconductors:** silver white of silicon, red color of cinnabar
10. **Color of n(p) semiconductors:** colored diamonds, semiconductor laser
11. **Color center:** amethyst, smoky quartz

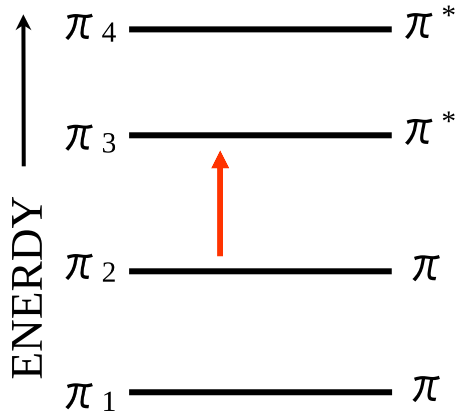
【 Geometrical and Physical Optics 】

12. **Dispersive refraction:** rainbow, halos
13. **Scattering of light:** Rayleigh scattering, Raman scattering
14. **Interference of light:** color of soap bubbles,
15. **Diffraction of light:** color of liquid crystals, opal

The Physics and Chemistry of Color, by K. Nassau (John Wiley & Sons, 1983)

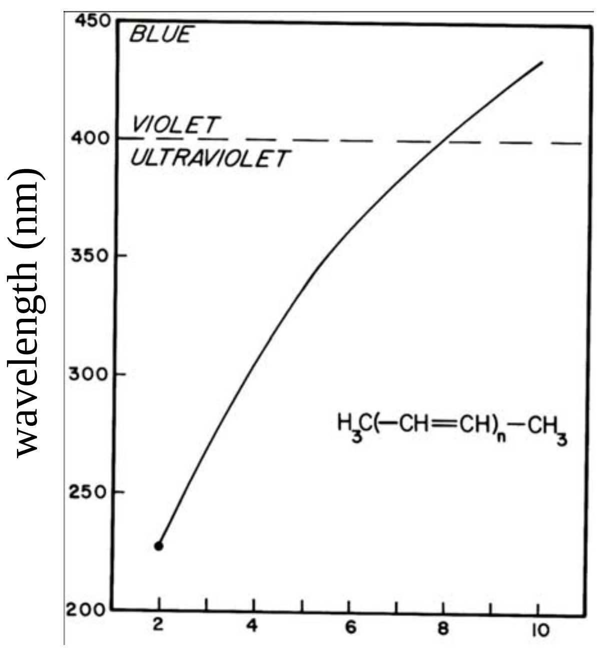
(A) Light (optical properties)

Color change of organic molecules due to external fields

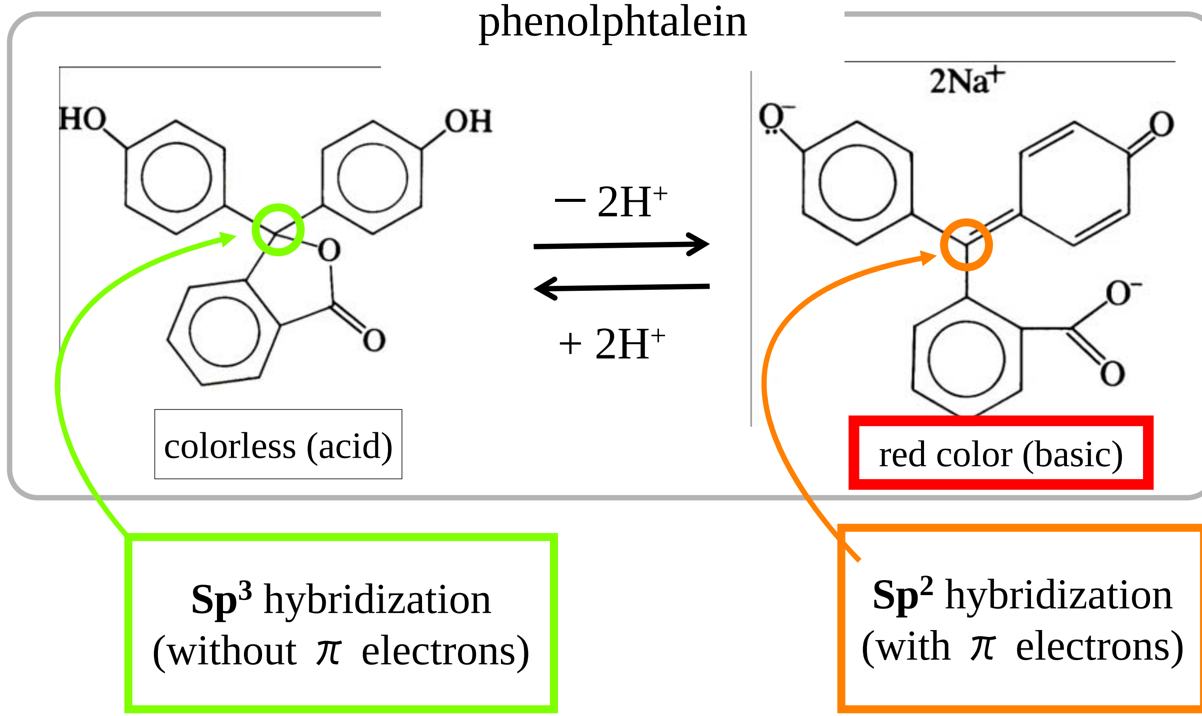


LUMO（lowest unoccupied molecular orbital）

HOMO（highest occupied molecular orbital）



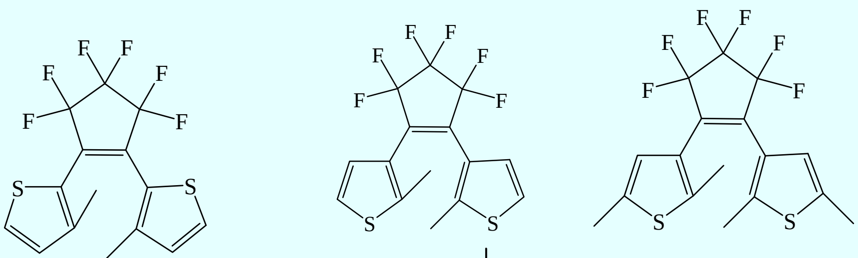
The HOMO – LUMO gap as a function of the number of double bonds in conjugated polyene.



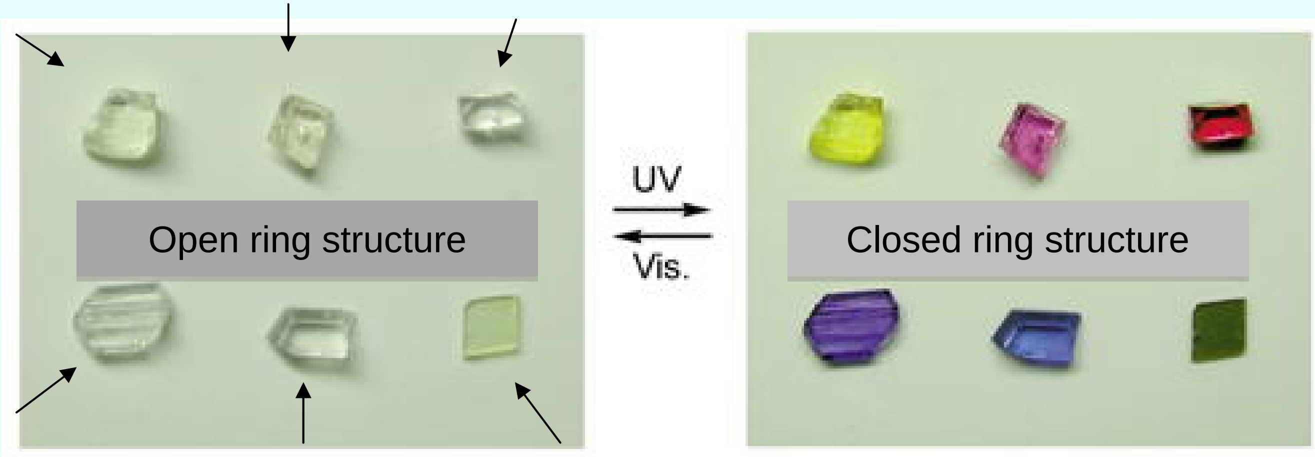
In alkaline solution of phenolphtalein, π electrons are delocalized in the molecule and the π - π * transition is in visible region.

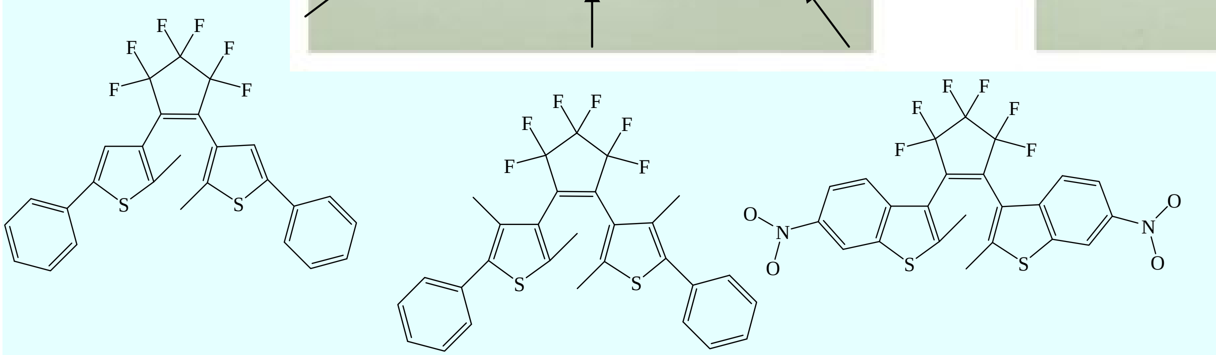
Color change and photoisomerization of Diarylethene

T. Fukaminato, S. Kobatake, T. Kawai, and M.Irie, *Proc. Japan Acad., Ser. B*, 77, 30 (2001).



In closed ring structure, π electrons are delocalized in the molecule and the π - π * transition is in visible region.

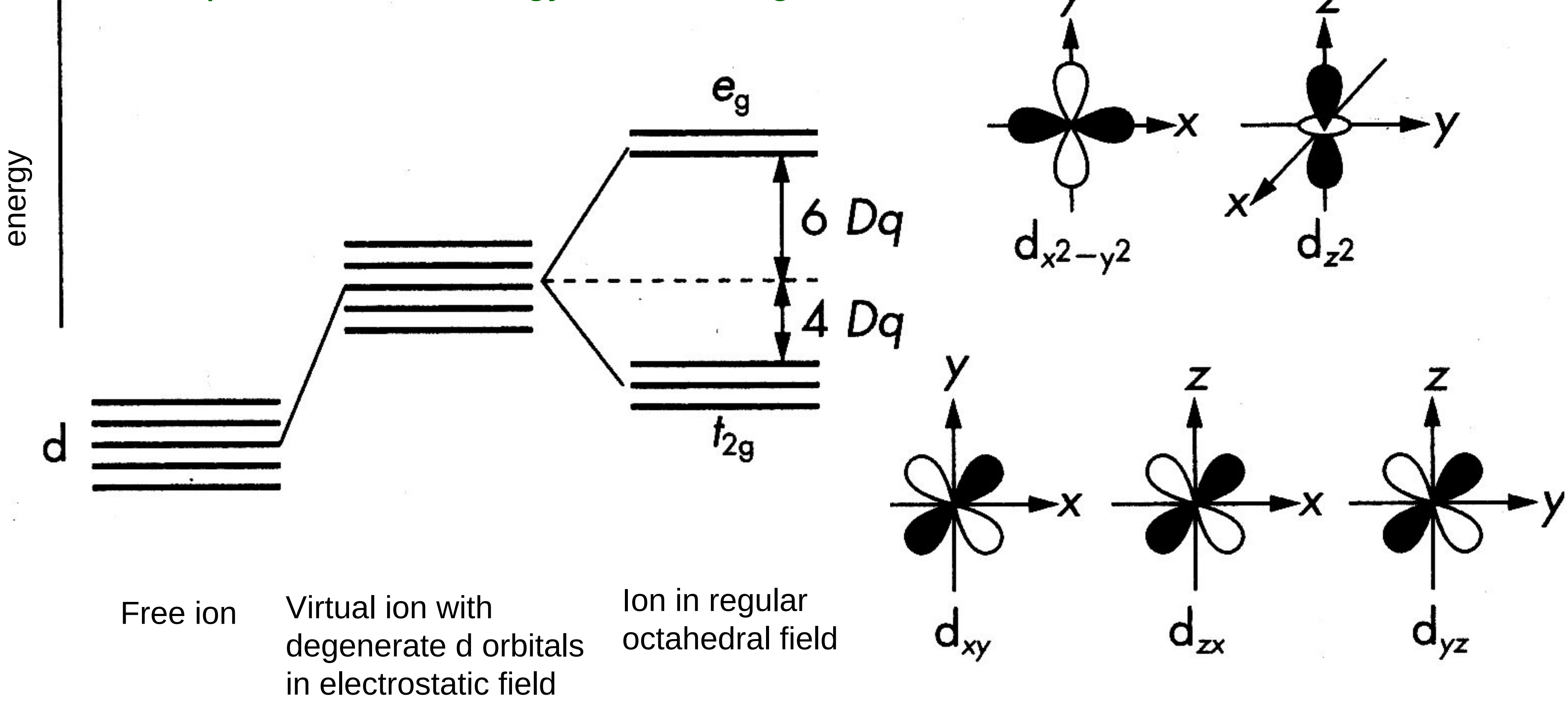




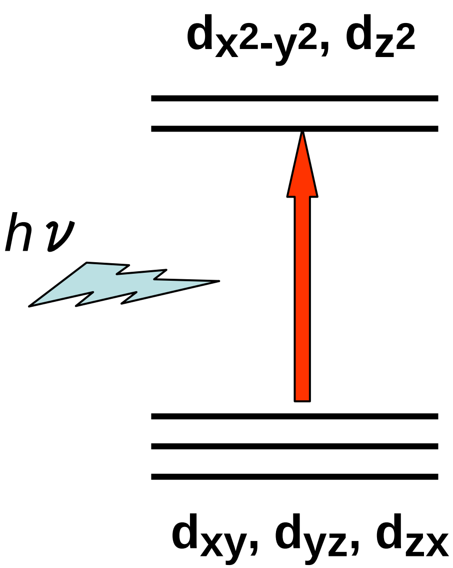
(A) Light (optical properties)

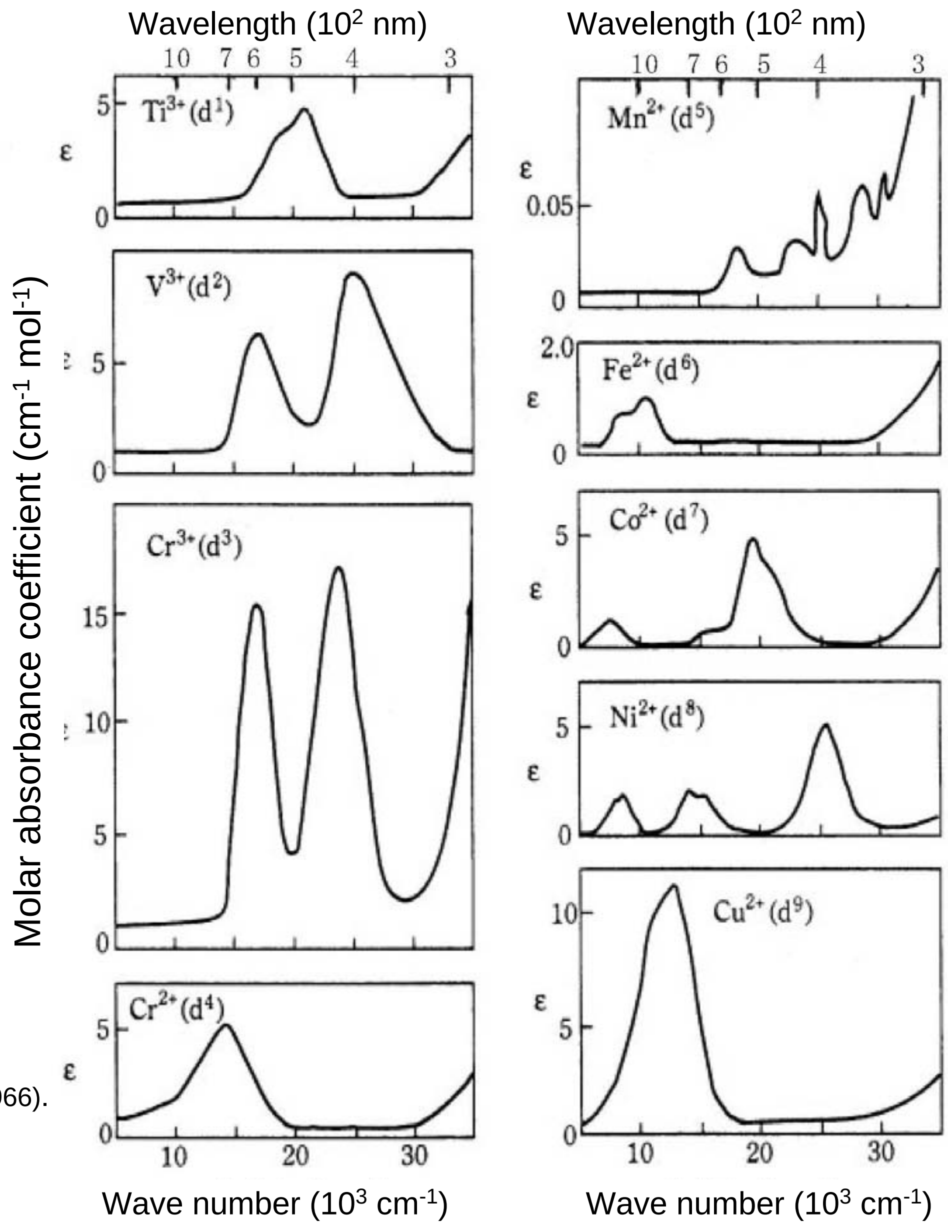
Splitting of d orbitals by the formation of metal complex

Origin of colors of transition metal complexes: The splitting (10Dq) of d orbitals corresponds to the energy of visible light.



Optical Absorption Spectra of $[M(H_2O)_6]^{n+}$ due to d-d Transition





B. Figgis, *Introduction to Ligand Fields*, Wiley-Interscience (1966).

(A) Light (optical properties)

The origin of colors of transitional metal complex

（1）Transition between d orbitals（d-d transition）

（2）Charge transfer transition

①Charge transfer from ligand to d orbitals of transition metal ions:
LMCT (Ligand-to-Metal Charge Transfer)

ex. Magenta color of Permanganate, $[MnO_4]^-$

②Charge transfer from d orbitals of transition metal ion to ligands:
MLCT (Metal-to-Ligand Charge Transfer)

ex. Red color of $[Fe(phen)_3]^{2+}$(phen = phenanthroline**)**

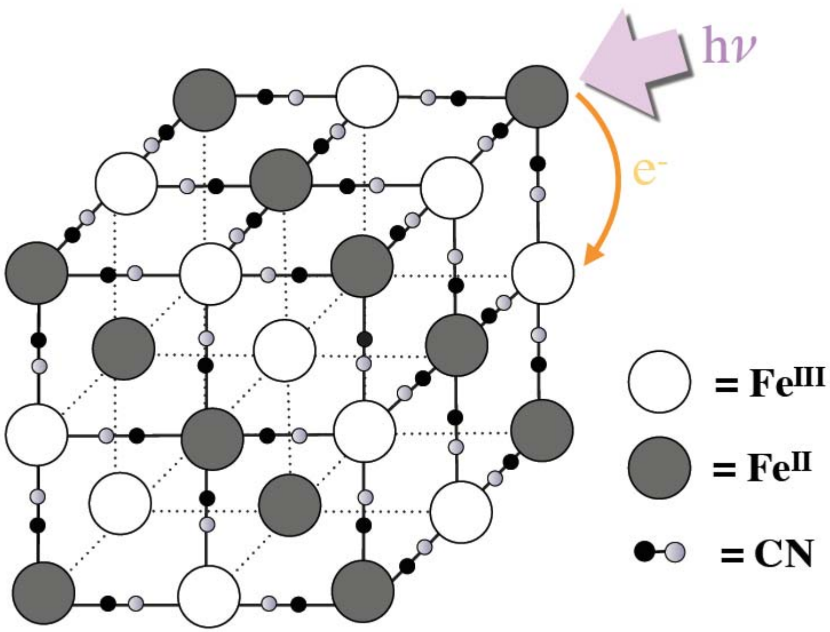
③Charge transfer between transition metal ions:
IVCT (Inter-Valence Charge Transfer)

ex. Ultramarine color of Prussian blue, $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 15H_2O$

(A) Light (optical properties)

IVCT (Inter-Valence Charge Transfer)

Ultramarine color of Prussian blue



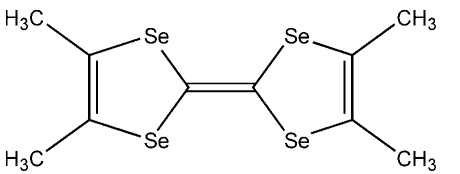
Crystal structure of Prussian blue,
($Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 15H_2O$)

Hokusai Katsushika
Fugaku Sanjūrokkei

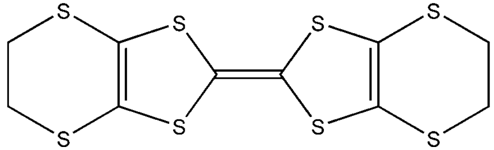
『Kanagawa-oki namiura』

Hokusai Katsushika in the Edo era used imported Prussian blue as a ultramarine colored pigment to draw his Fugaku Sanjūrokkei series.

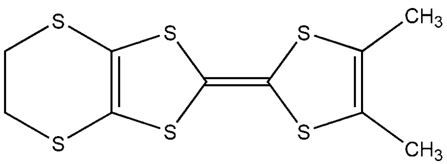
(B) Charge (transport properties)



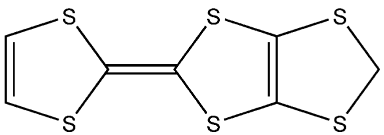
TMTSF



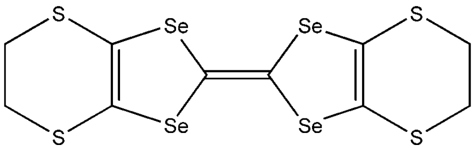
BEDT-TTF (ET)



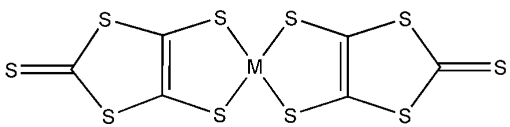
DMET



MDT-TTF

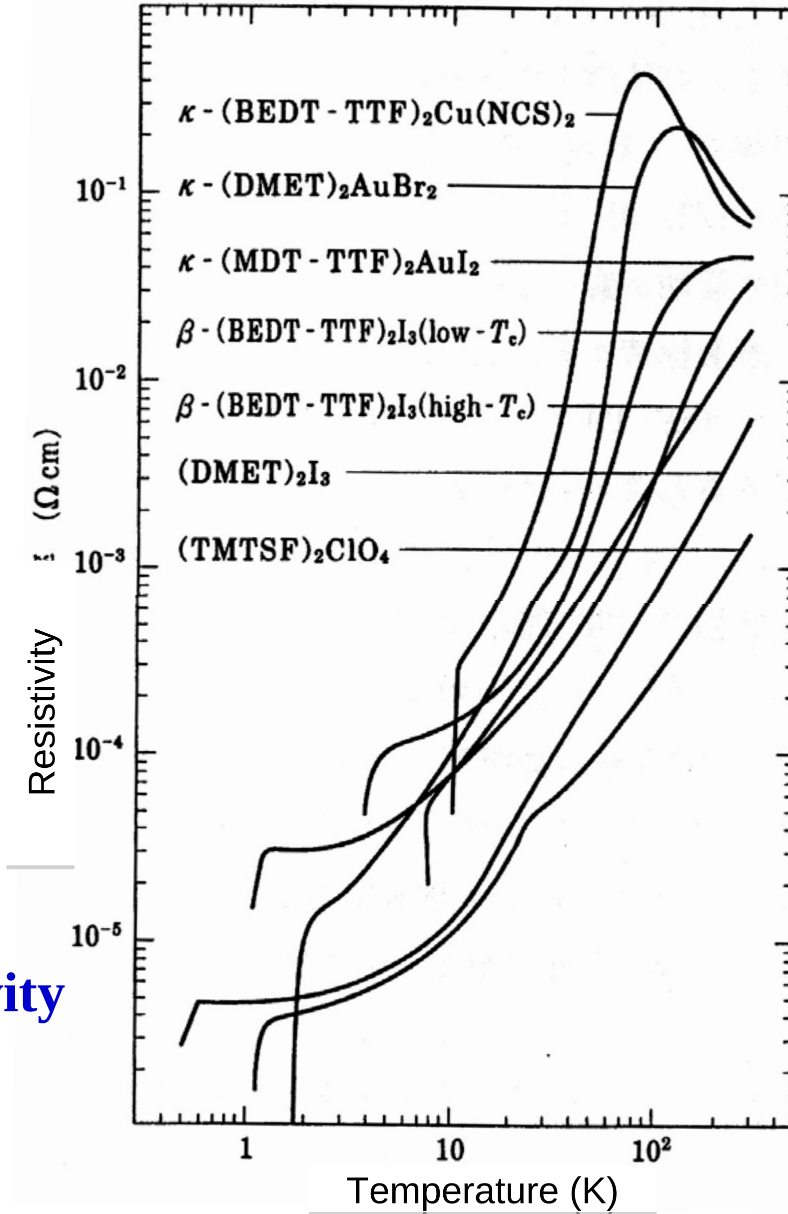


BEDT-TSF (BETS)



M(dmit)$_2$ (M = Ni,Pd)

Organic molecules producing superconductivity



Temperature dependence of the electrical resistivity of typical organic superconductors

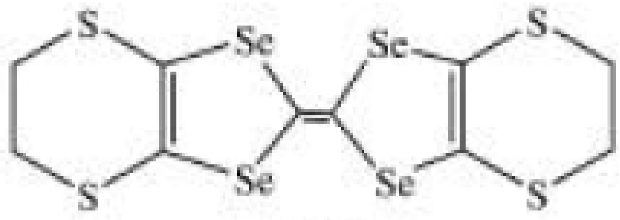
From "Low-dimensional conductors" Seiichi Kagoshima (Shoka-bou, 2000)

1979 The discovery of organic superconductivity
$(TMTSF)_2PF_6$ (T_c = 0.9 K at 1.2 GPa)

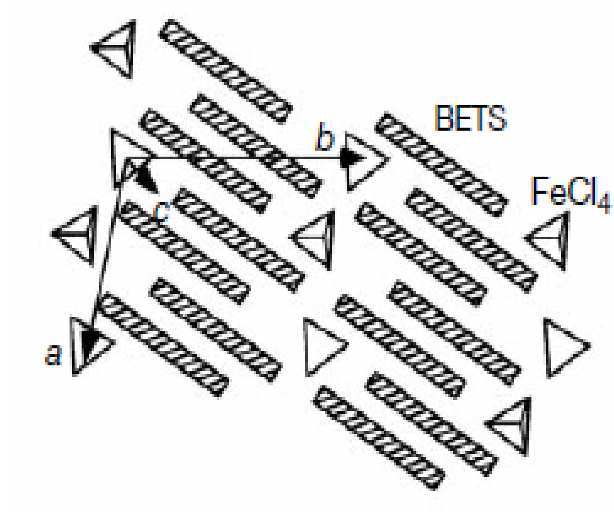
1988 Organic superconductor at T_c > 10K
$(BEDT\text{-}TTF)_2Cu(NCS)_2$ (T_c = 10.4 K)

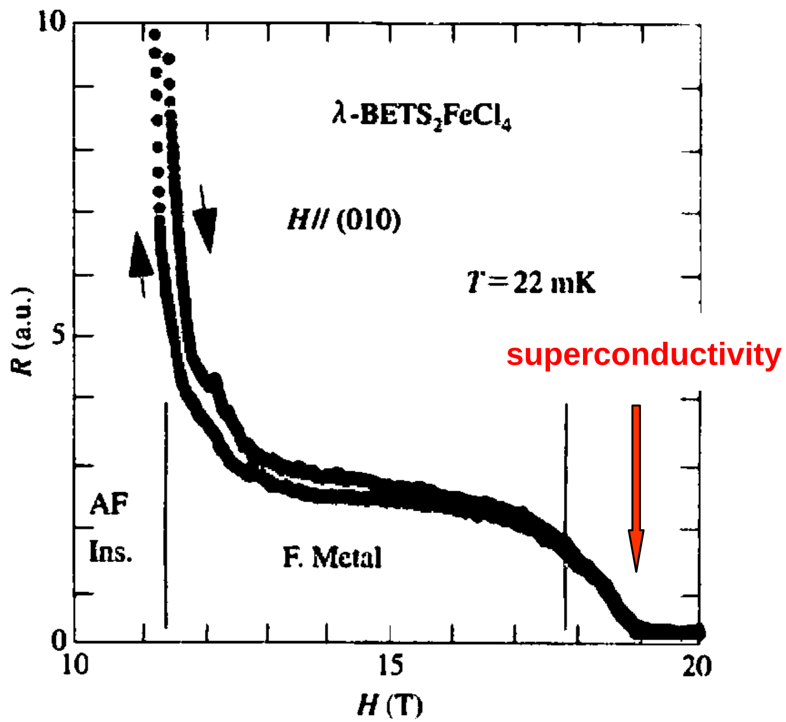
(B + C) Cooperative phenomenon coupled with charge and spin:

Magnetic field induced superconductivity of λ-$(BETS)_2FeCl_4$

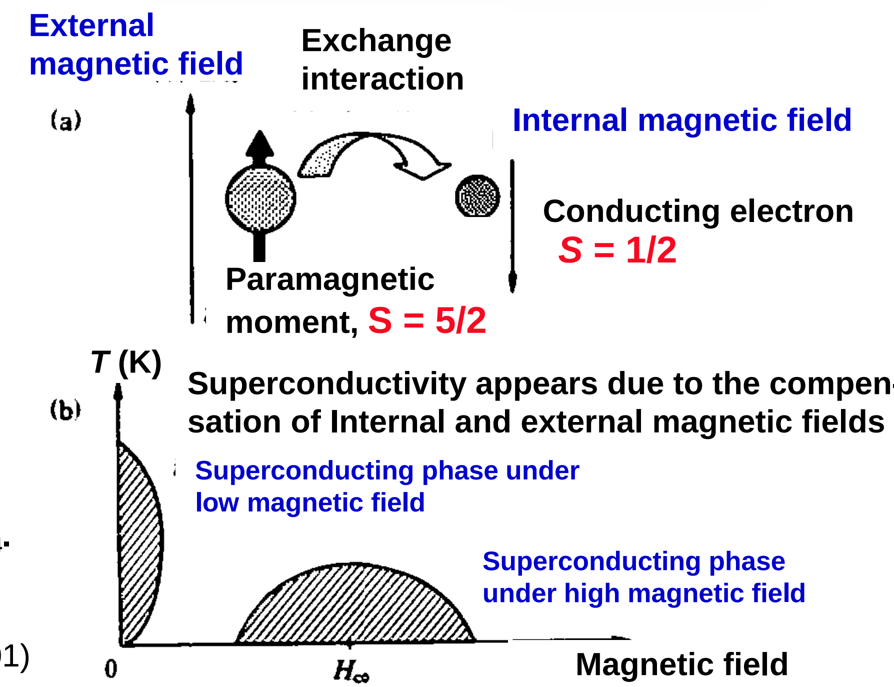


BETS





Magnetic field dependence of the resistivity of λ-$(BETS)_2FeCl_4$.

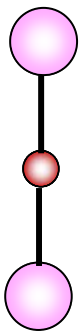


Shinya Uji, "Solid State Physics (in Japanese)", Vol. 36, No. 6, (2001)

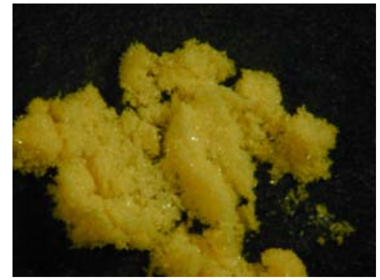
(A) Light (optical properties): Color of $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$

The origin of golden color: Charge transfer from Au(I) to Au(III) (IVCT)

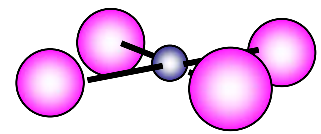
colorless



$(C_4H_9)_4N[Au^{I}Cl_2]$



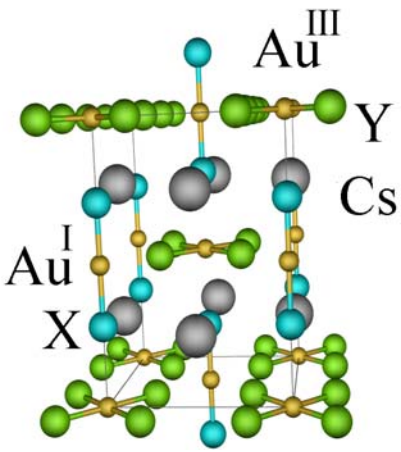
yellow



$(C_4H_9)_4N[Au^{III}Cl_4]$

$C_6H_5SO_3Cs$

0°C

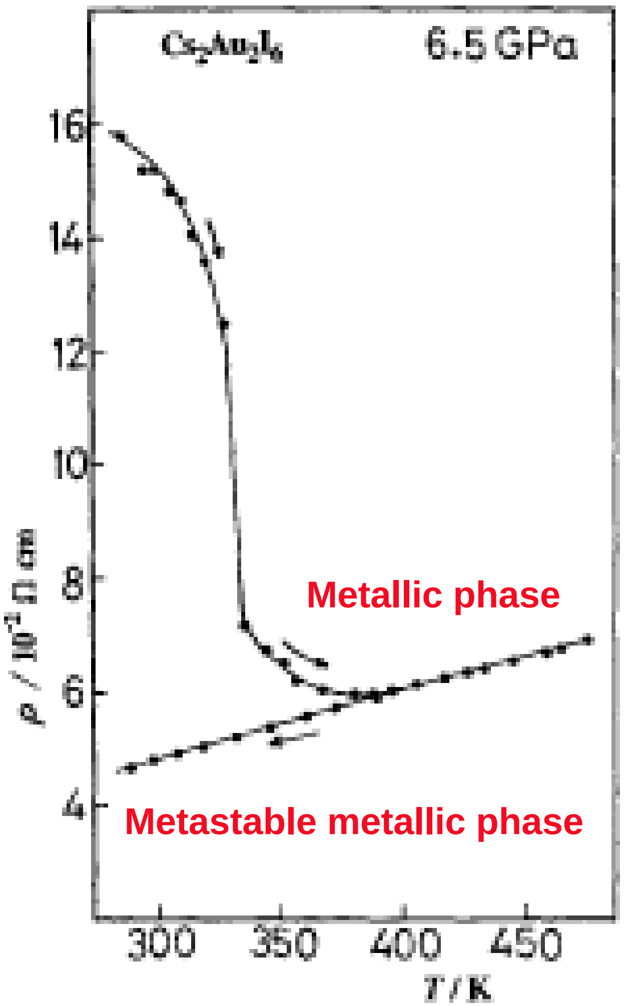


golden color

$Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$

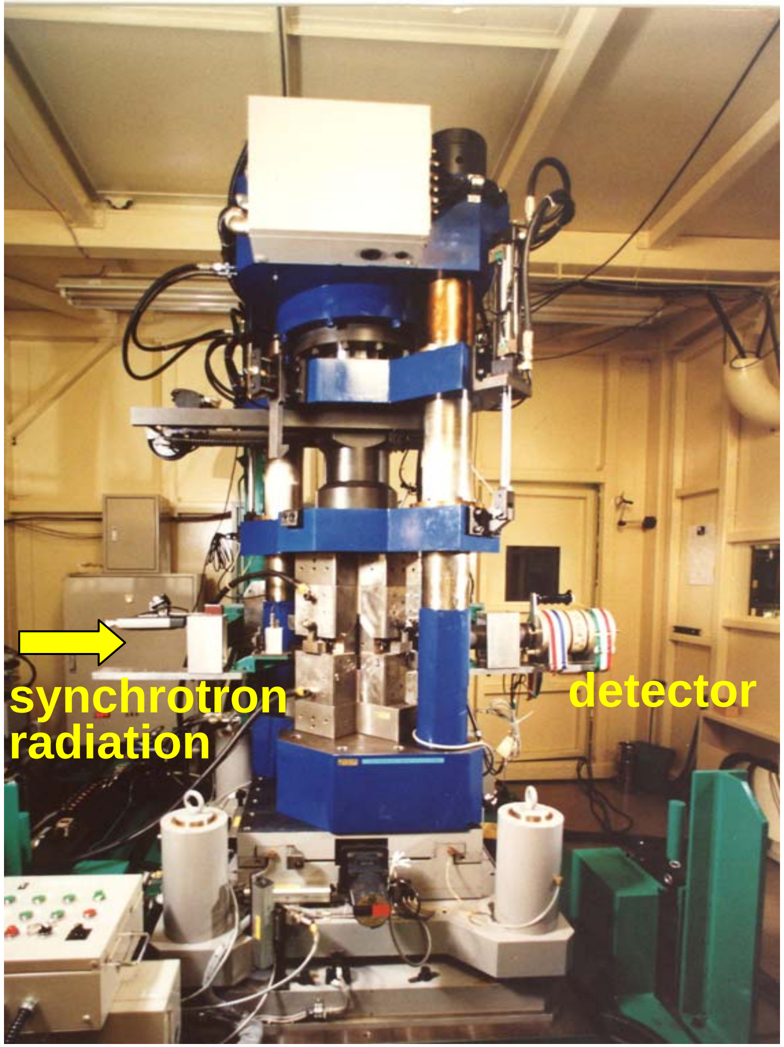
(B) Charge (transport properties)

Appearance of Metallic Phase in $Cs_2[Au^{I}I_2][Au^{III}I_4]$ under High Pressures and High Temperatures

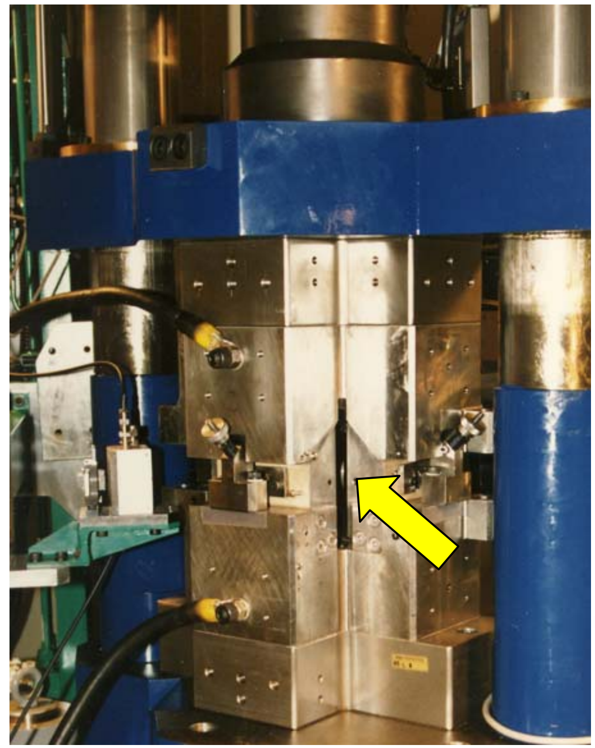


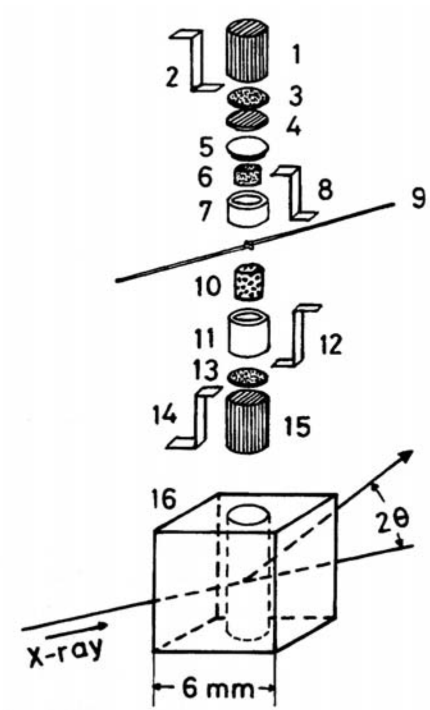
N. Kojima, et al., *Solid State Commun*. 73, 743(1990)

X-ray structural analysis with synchrotron radiation under high pressure



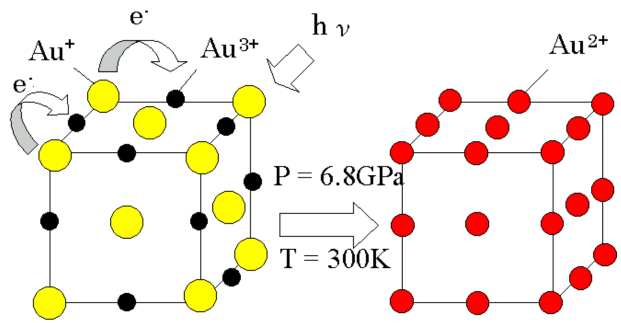
P = 0 ~ 14 GPa
T = r.t. ~ 1000 K

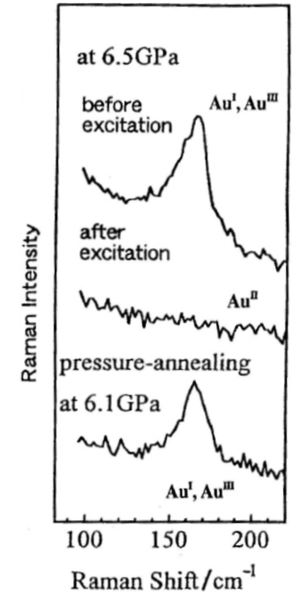




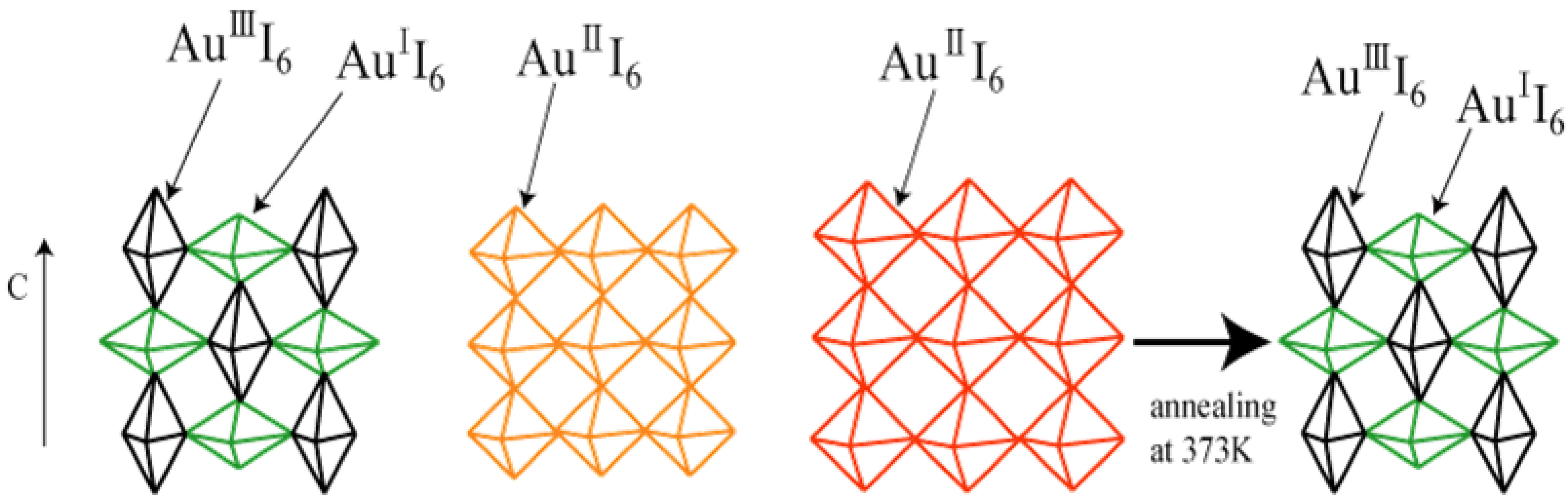
Cubic anvil type high-pressure apparatus (MAX90)
in the National Laboratory for High Energy Physics, Tsukuba, Japan

Pressure-induced and photo-induced gold valence transition for $Cs_2[Au^{I}Br_2][Au^{III}Br_4]$





X. J. Liu, Y. Moritomo, M. Ichida, A. Nakamura and N. Kojima, *Phys. Rev.* **B 61,** 20(2000).



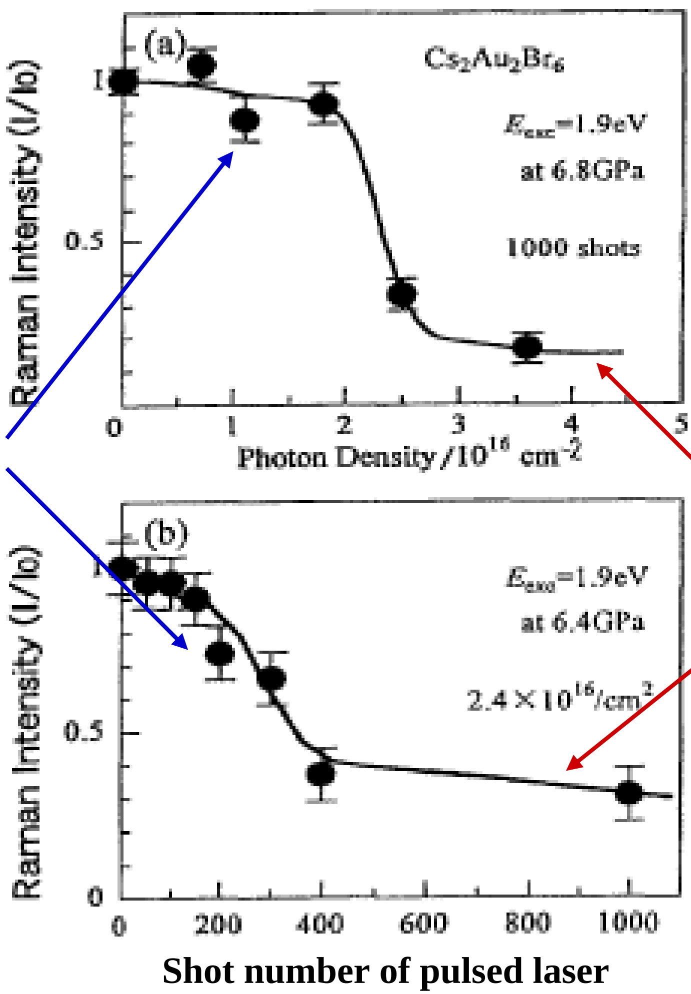
Insulator phase	**Metallic phase**	**Metastable metallic phase**	**Insulator phase**
P = ambient pressure *T* = room temperature	*P* = 6.5 GPa *T* = 100 ℃	*P* = ambient pressure *T* = room temperature	*P* = ambient pressure *T* = room temperature

N. Kojima, *Bull. Chem. Soc. Jpn.*, **73**, 1445(2000).

The Photo-induced Gold Valence Transition of $Cs_2[Au^{I}Br_2][Au^{III}Br_4]$

The Extinction of Insulator Phase by Laser and the Appearance of Metallic Phase

Mixed valence state of Au^{I} & Au^{III} (insulator phase)

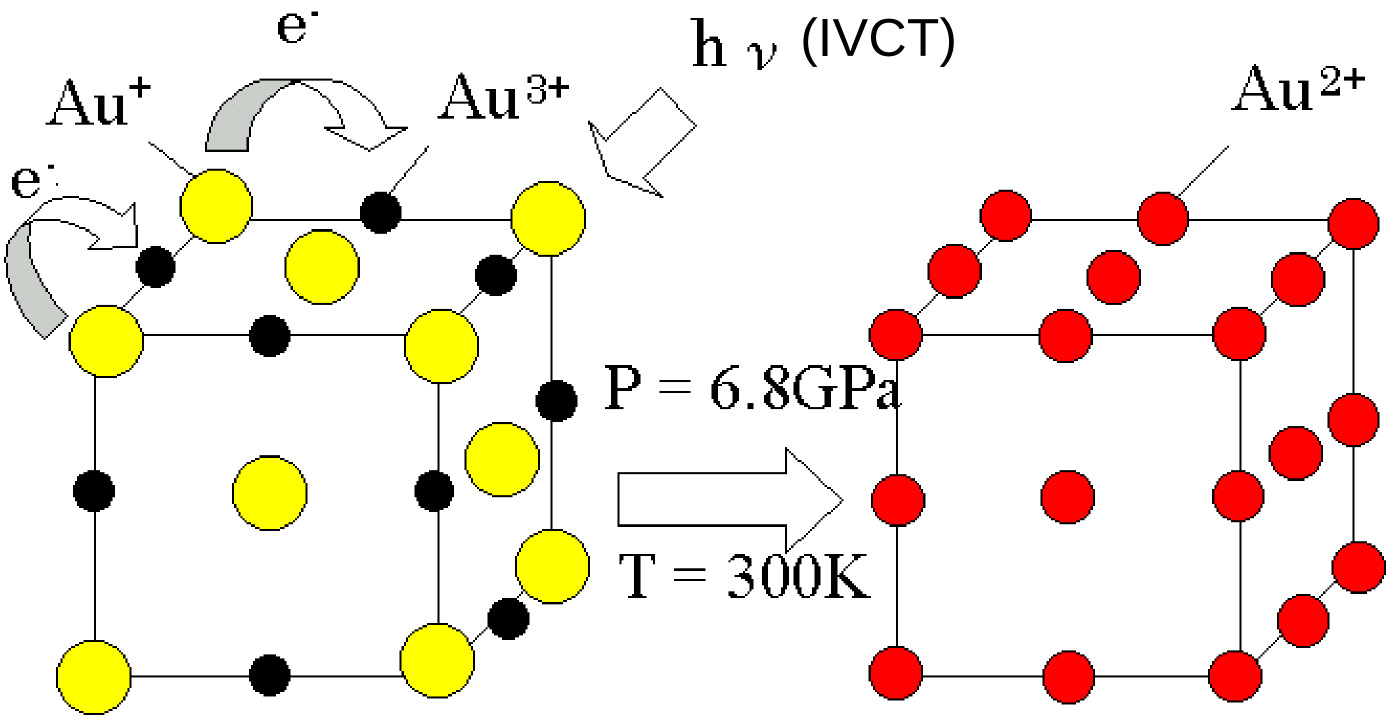


Single valence state of Au^{II} (metallic phase)

X. J. Liu, Y. Moritomo, N. Kojima, et al., *Phys*. *Rev*. B, **61**, 20 (2000).

A（light） + B（charge）

Transforming $Cs_2[Au^IBr_2][Au^{III}Br_4]$ from Insulator to Metal with Light



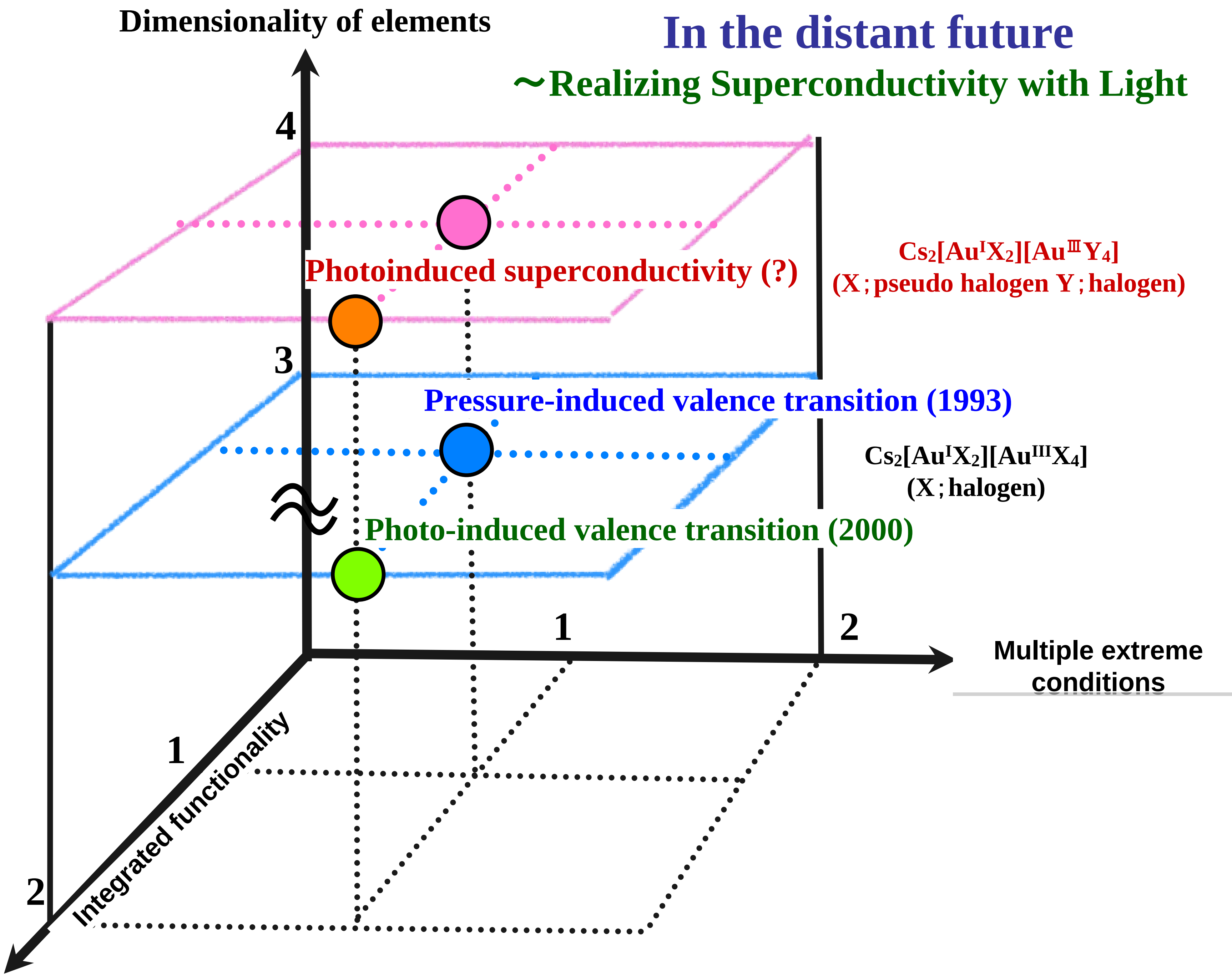
Mixed valence state (insulator phase)

Single valence state (metallic phase)

X. J. Liu, Y. Moritomo, N. Kojima, et al., *Phys*. *Rev*. B, **61**, 20 (2000).

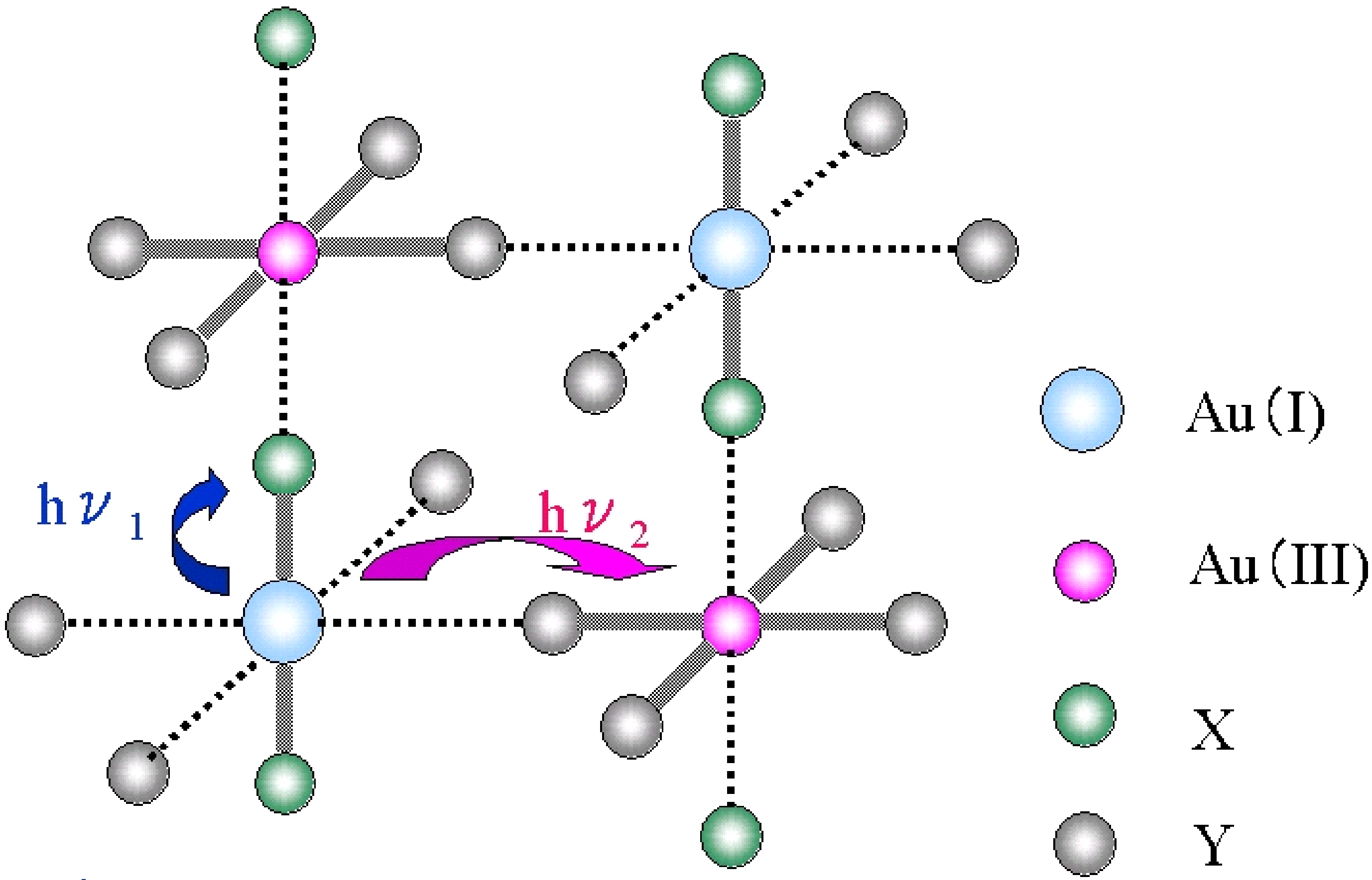
In the distant future

～Realizing Superconductivity with Light



A(light）+ B(charge）

Search for the photo-induced superconductivity with simultaneous irradiation of two kinds of light

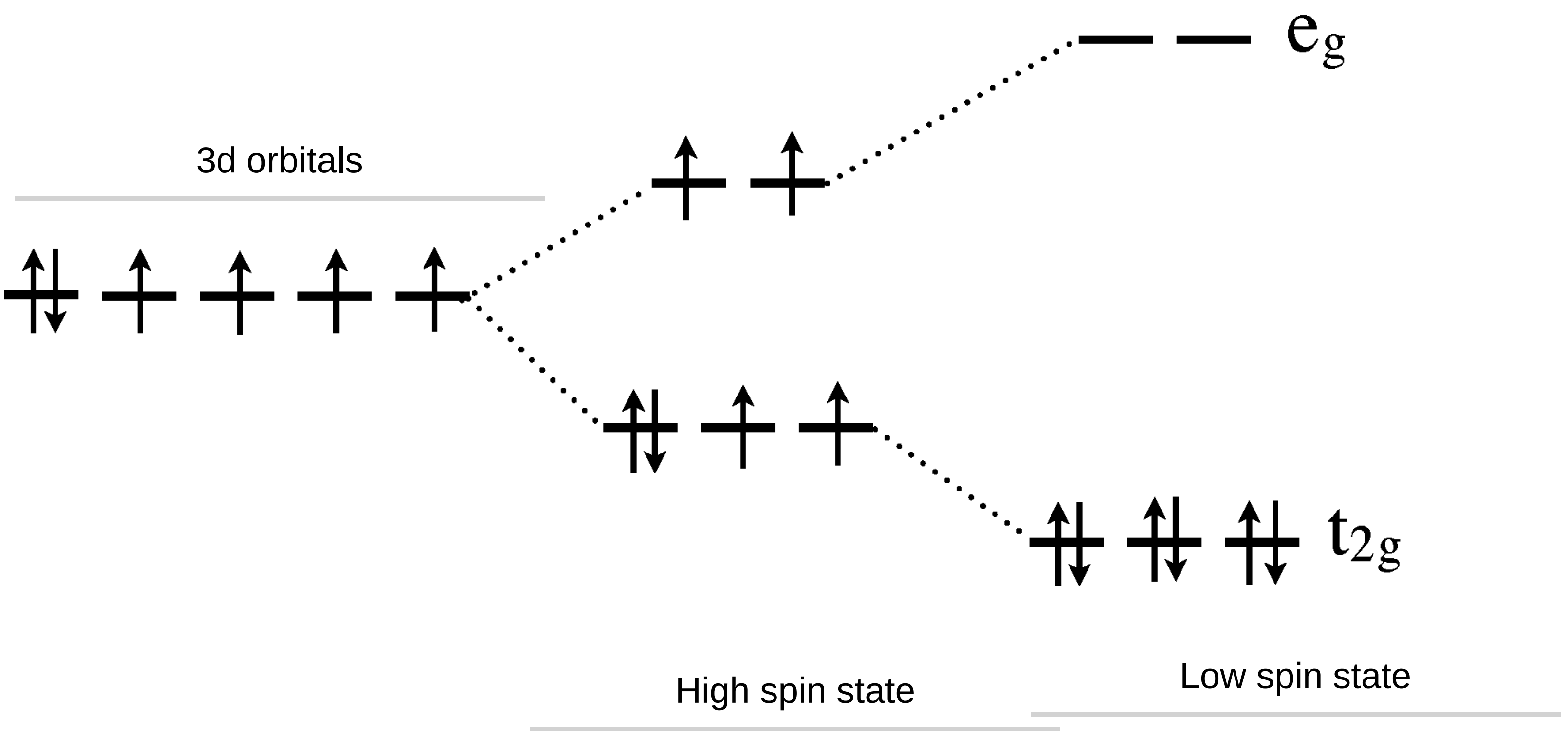


$h\nu_1$: Light for carrier control

$h\nu_2$: Light for Au valence transition

X: pseudohalogen having π^* orbital

Electron Configuration in 3d orbitals of Fe(II) Complex



Free Fe ion

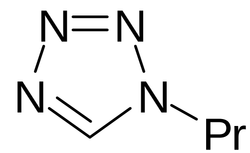
Fe ion in regular octahedral field

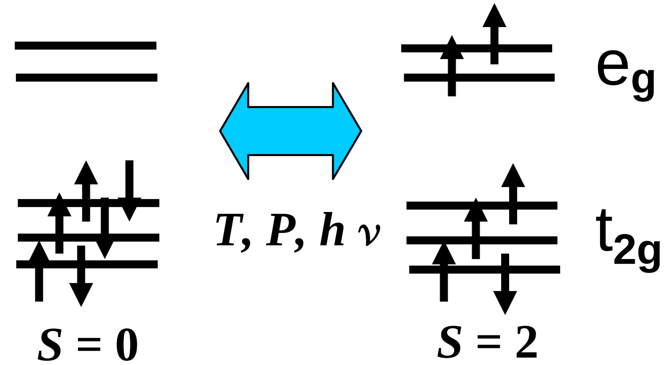
A(light) + C(spin): Transforming Spin State with Light

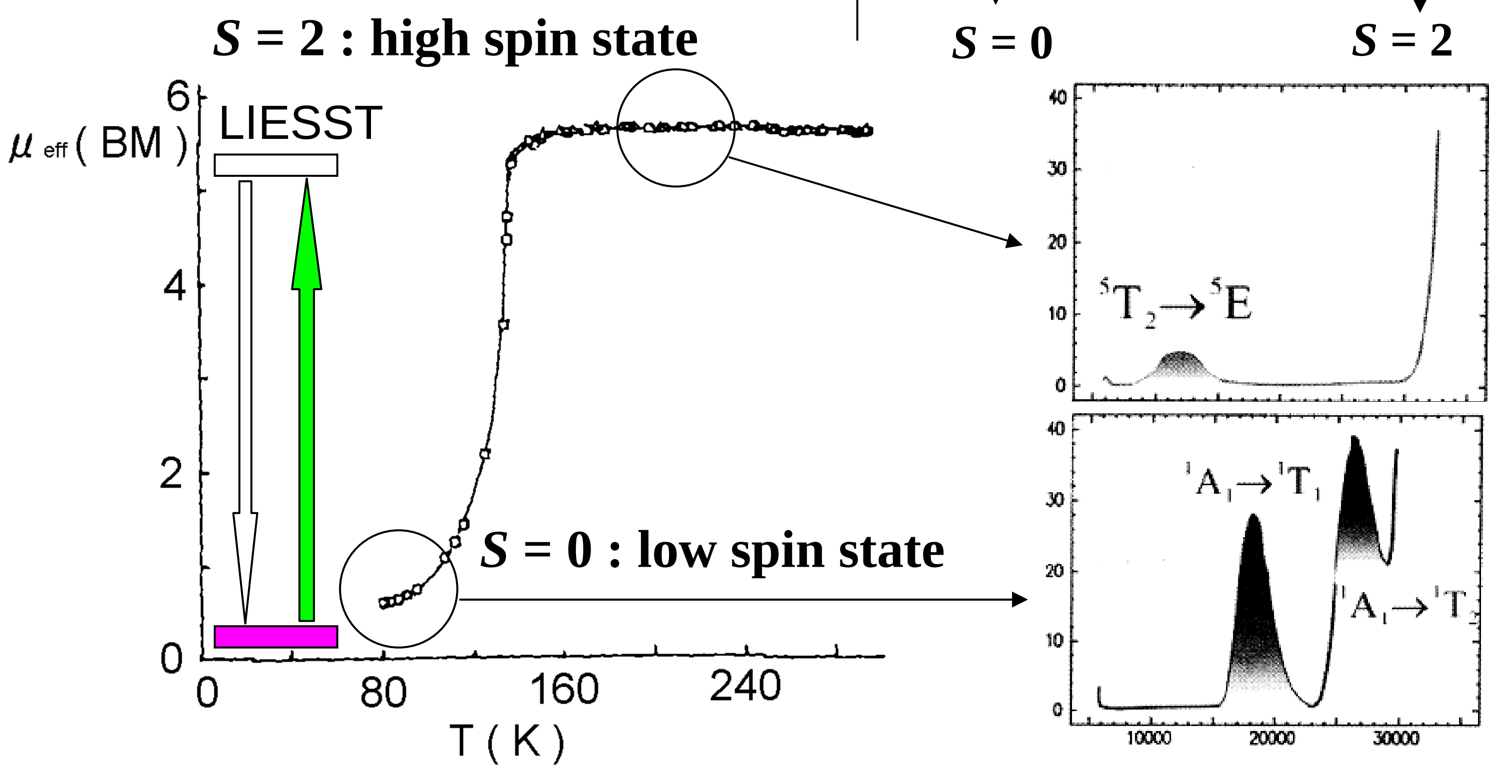
Light Induced Excited Spin State Trapping (LIESST)

$[Fe^{II}(ptz)_6](BF_4)_2$

Ptz =

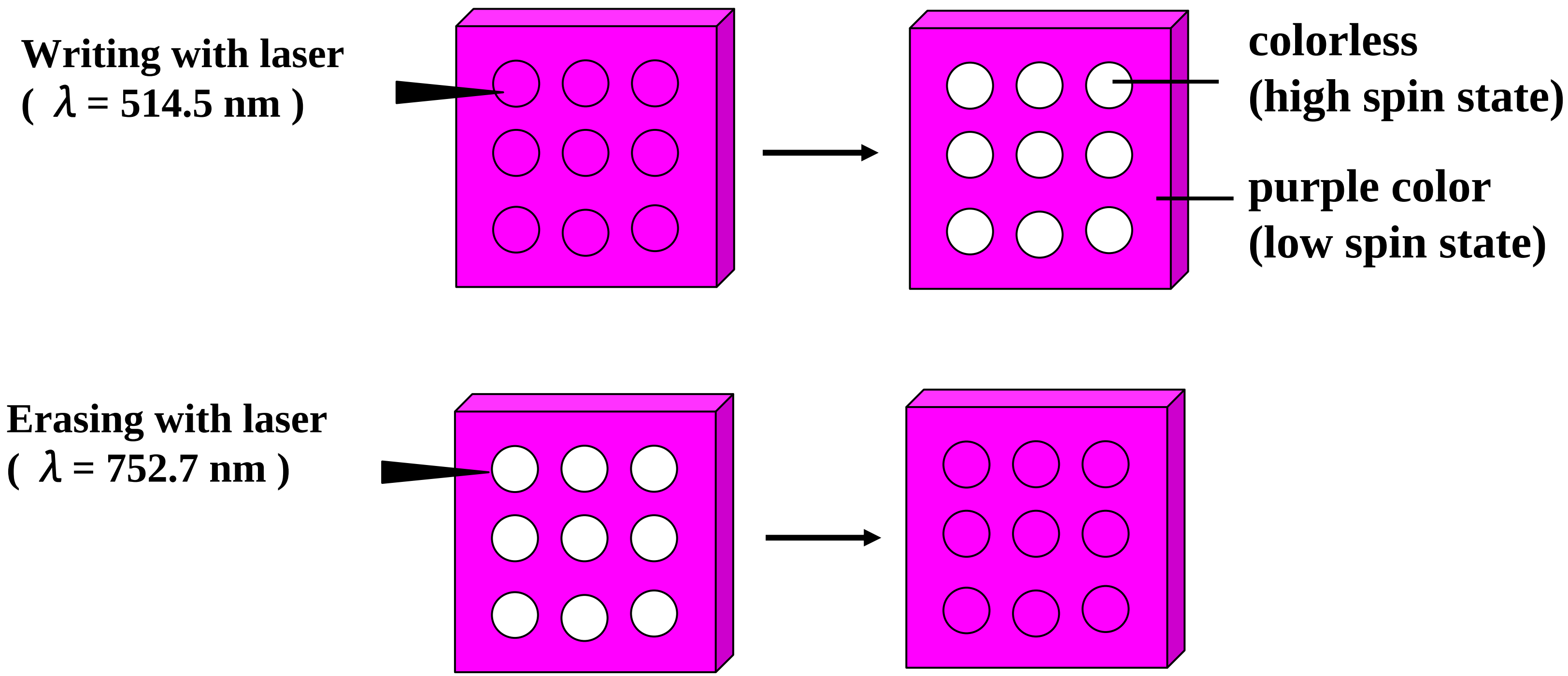




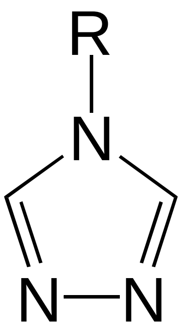


P. L. Franke, et al. *Inorg. Chim. Acta*, **59** (1982) 5, S. Decurtins et al. *Chem. Phys. Lett.* **105** (1984) 1

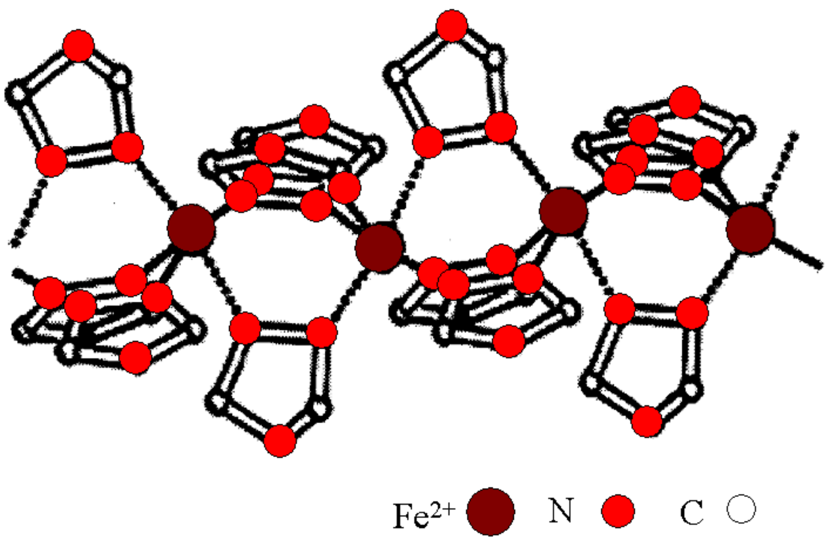
Molecular Memory with Photo-induced Spin Crossover Transition



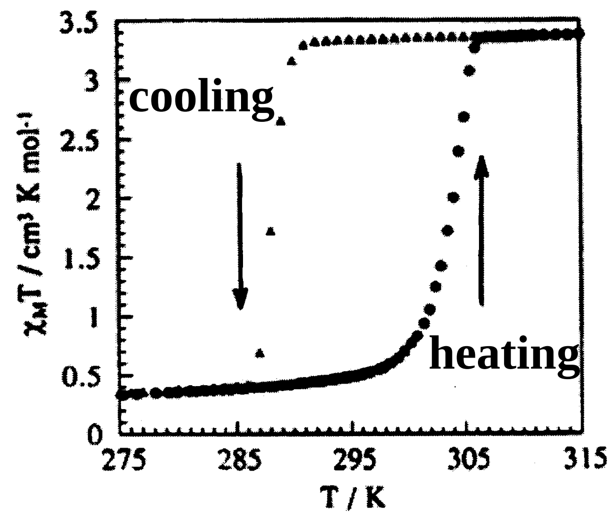
Spin Crossover Transition of $[Fe^{II}(R\text{-}trz)_3]A_2 \cdot nH_2O$



1,2,4-R-triazole
R = H, NH_2, C_nH_{2n+1},etc



$\chi_M T$ vs. T for $[Fe(H\text{-}trz)_{2.85}(NH_2\text{-}trz)_{0.15}](ClO_4)_2$

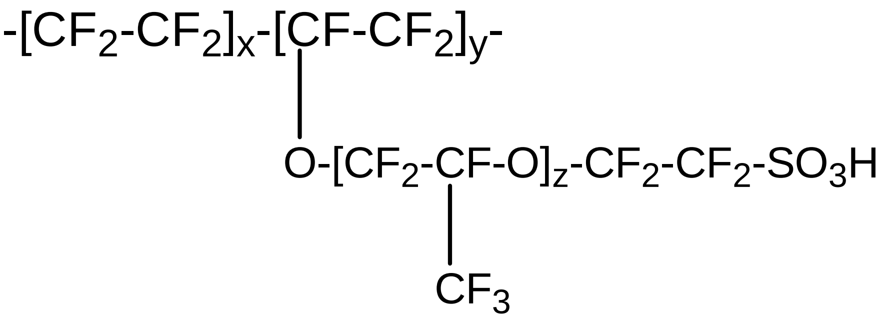


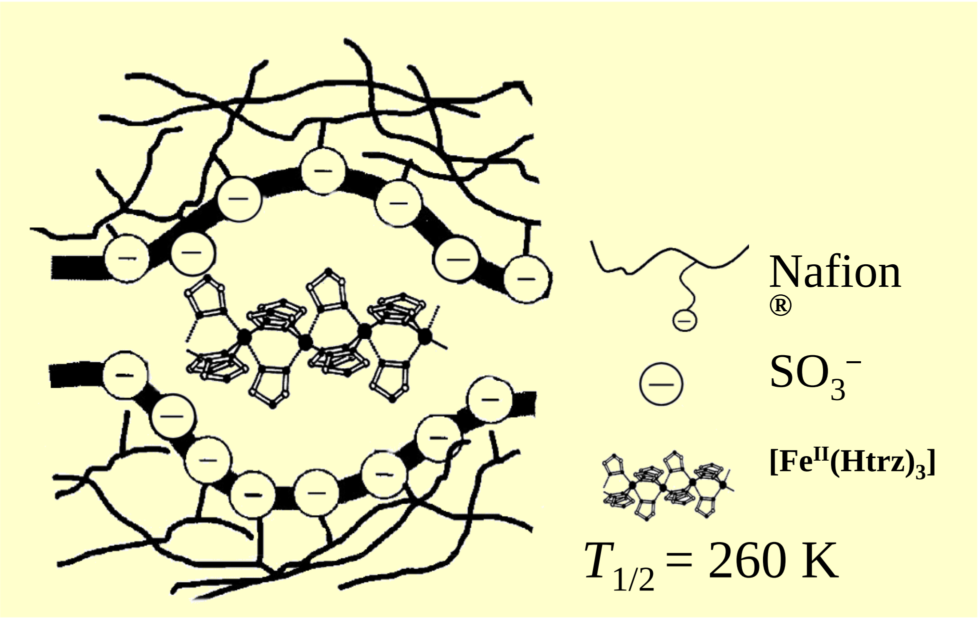
J. Kröber et al, J. Am. Chem. Soc. (1993)

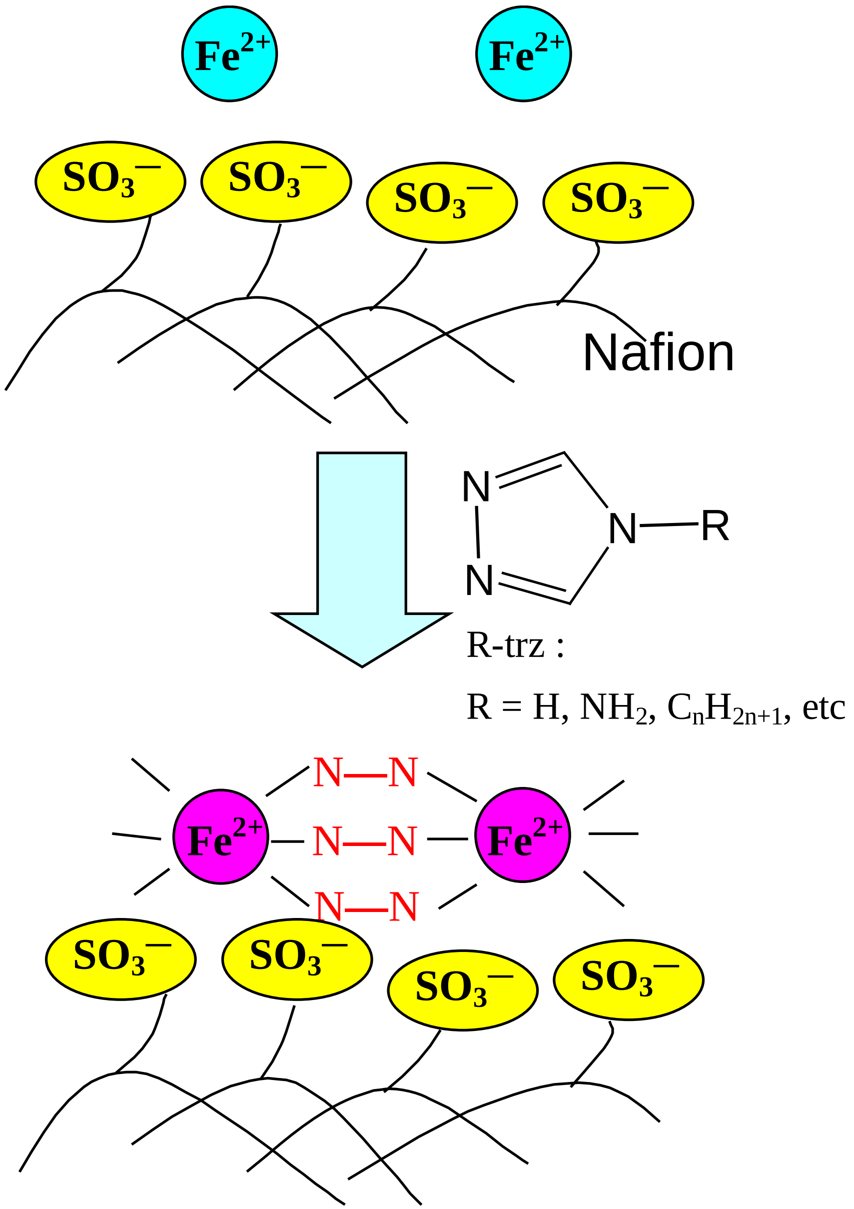
memory, display device

Producing Transparent Spin Crossover Complex Film

Nafion: ion exchange resin



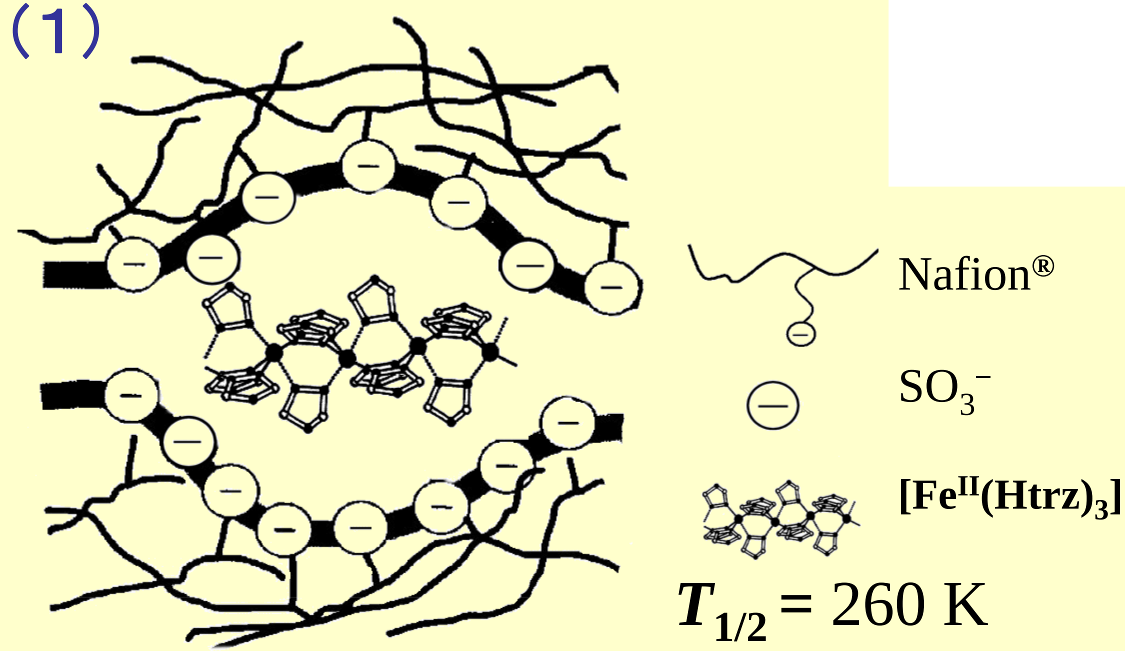


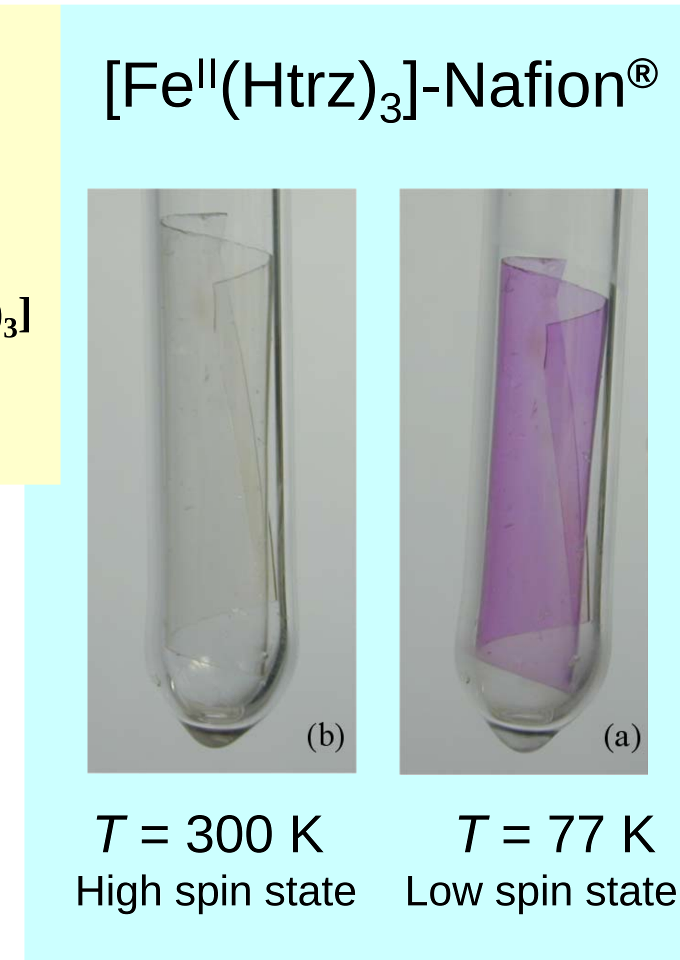


(1) Development of Transparent Spin Crossover Complex Film

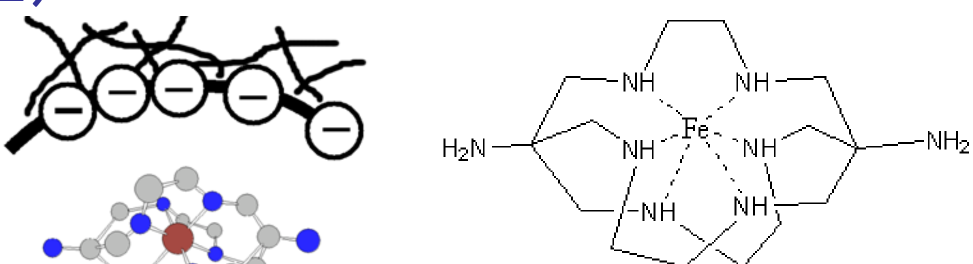
(2) Visualization of Proton Flow Using Transparent Spin Crossover Complex Film

(1)





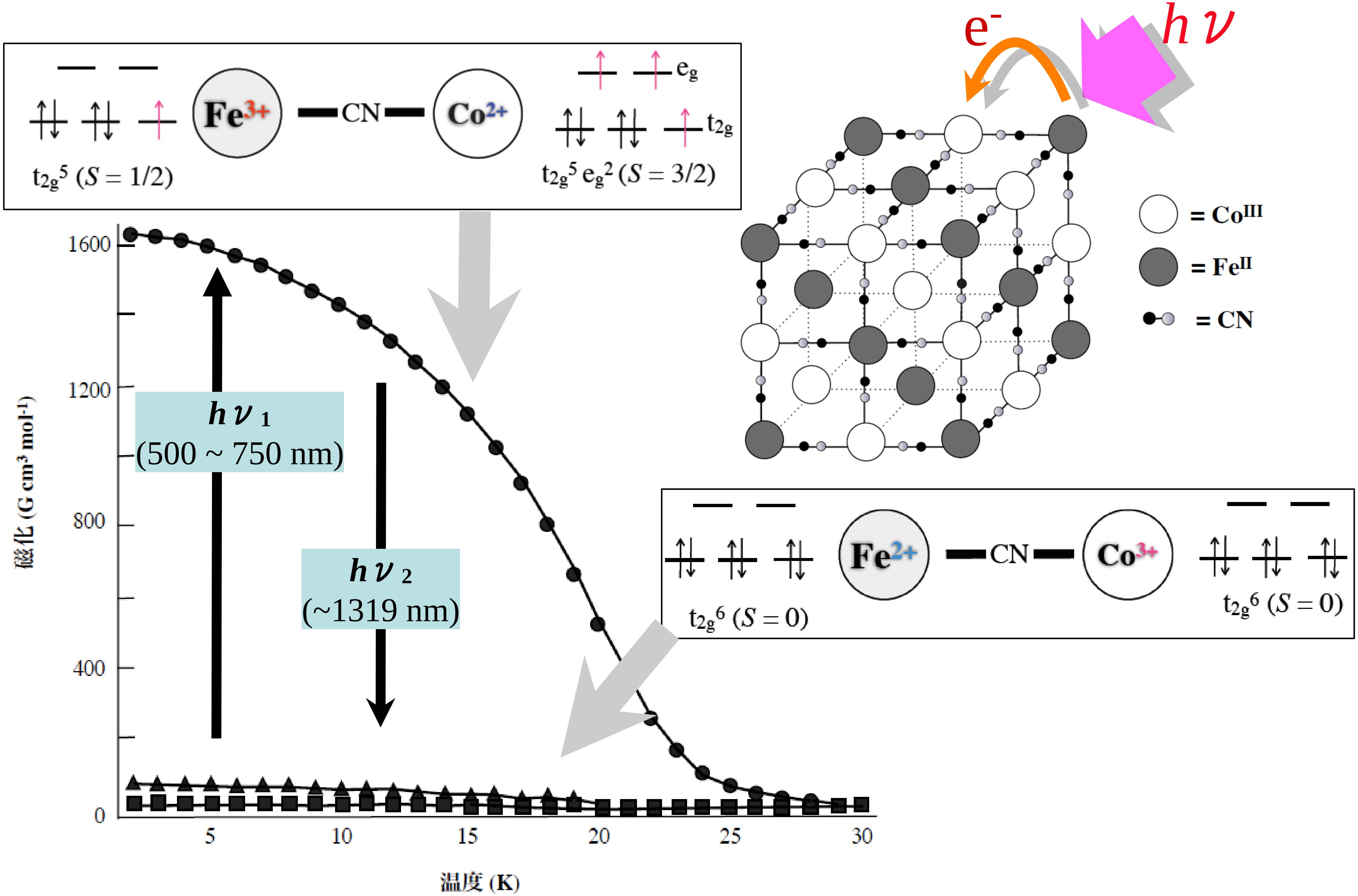
(2)



pH 4.5 : $T_{1/2}$ = 290 K

pH 8.5 : $T_{1/2}$ = 390 K

A（light）+ C（spin）: Producing Magnets with Light

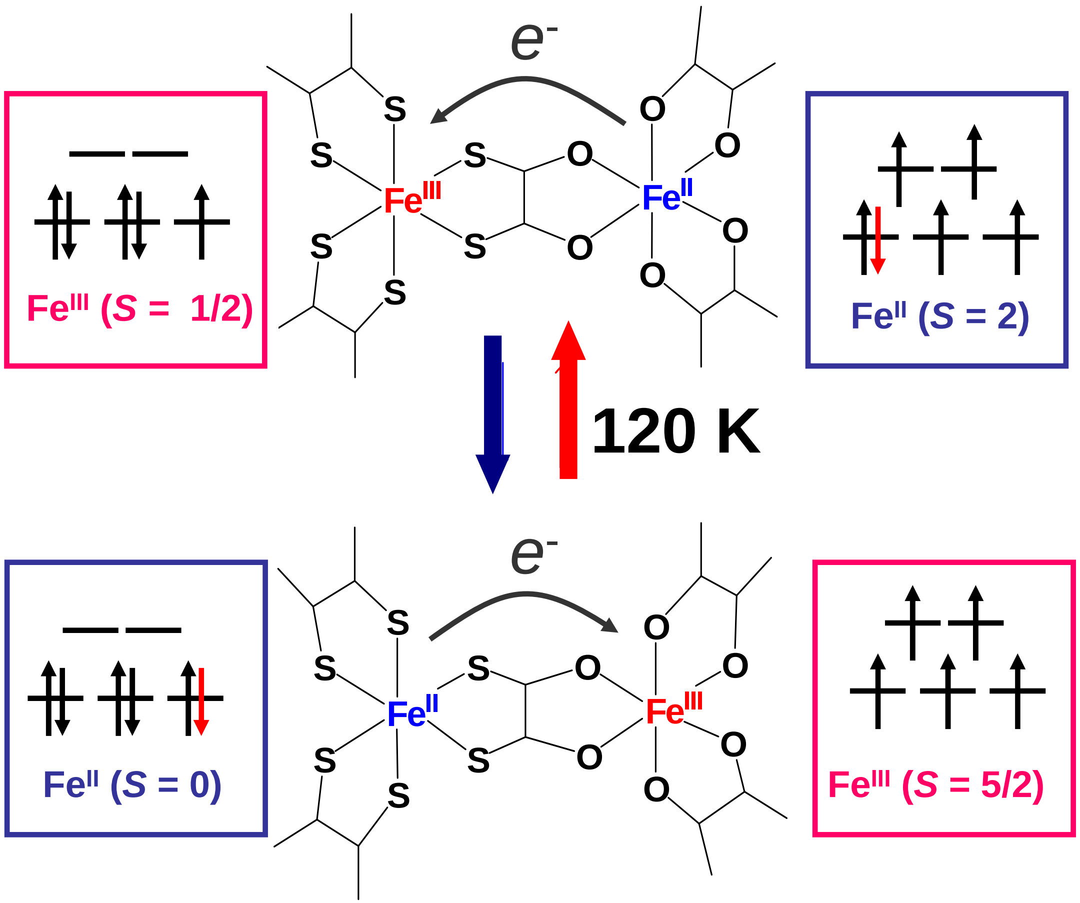


O. Sato, Y. Einaga, T. Oyoda, A. Fujishima and K. Hashimoto, *J. Electrochem. Soc.*, **114**, L11 (1997)

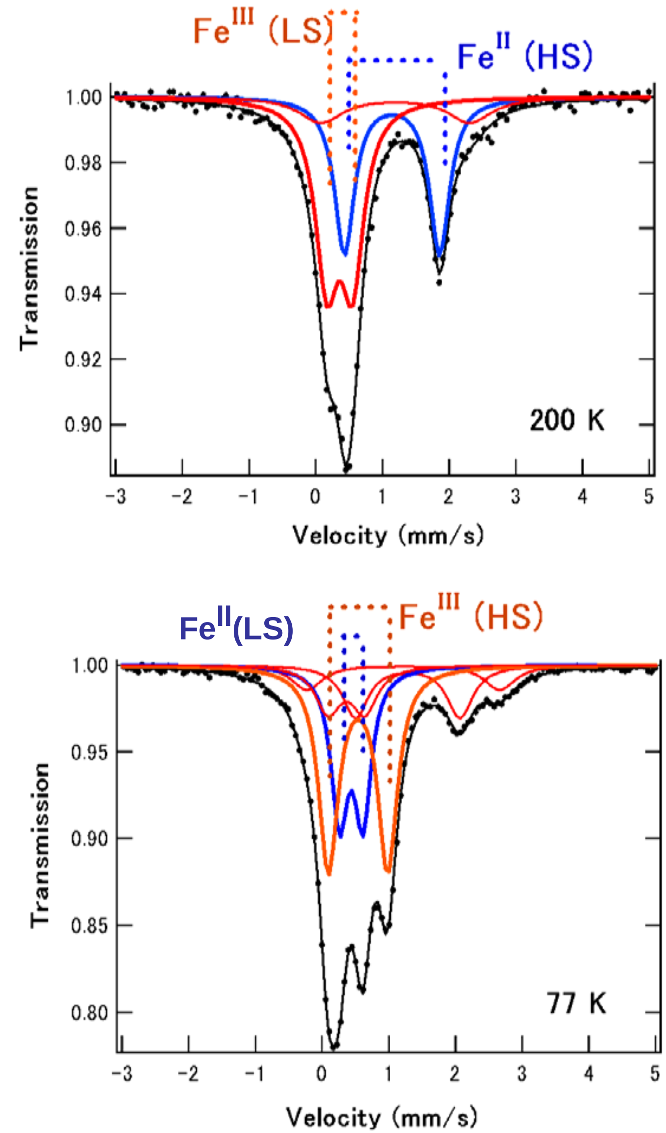
B（charge）＋C（spin）:

Charge Transfer Phase Transition of $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3](dto = C_2O_2S_2)$

Although this complex is an insulator, the electrons transfer at around 120K and the recombination between the Fe^{II} and Fe^{III} sites occurs.



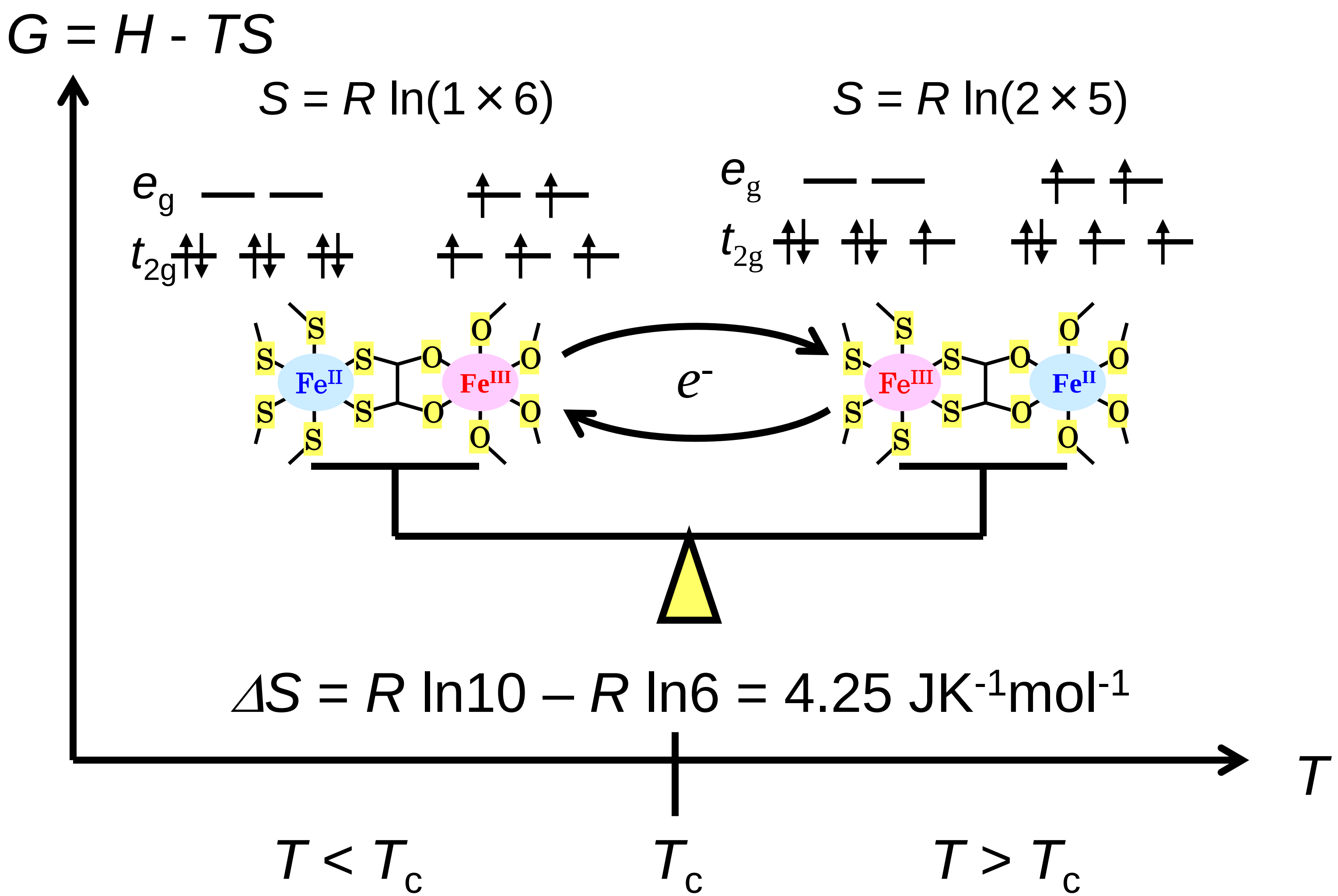
N. Kojima, et al., *Solid State Commun.* **120**, 165 (2001)



Nuclear absorption spectrum of ^{57}Fe

Charge Transfer Phase Transition of $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$

The difference of spin entropy is the driving force for the charge transfer.



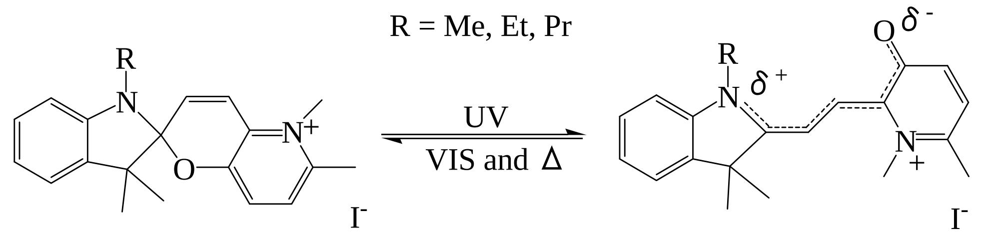
Molecular Design: The Photoisomerization of Intercalated Molecule is the Driving Force for the Charge Transfer from Fe(II) to Fe(III)

(SP)[$Fe^{II}Fe^{III}(dto)_3$]

cation

Photochromic molecule Spiropyran(SP)

Photo-isomerization in solid state



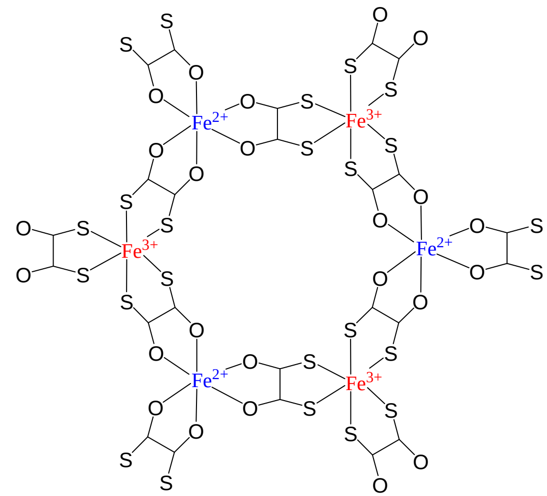
SP-close (SP type) yellow

SP-open (MC type) red

anion

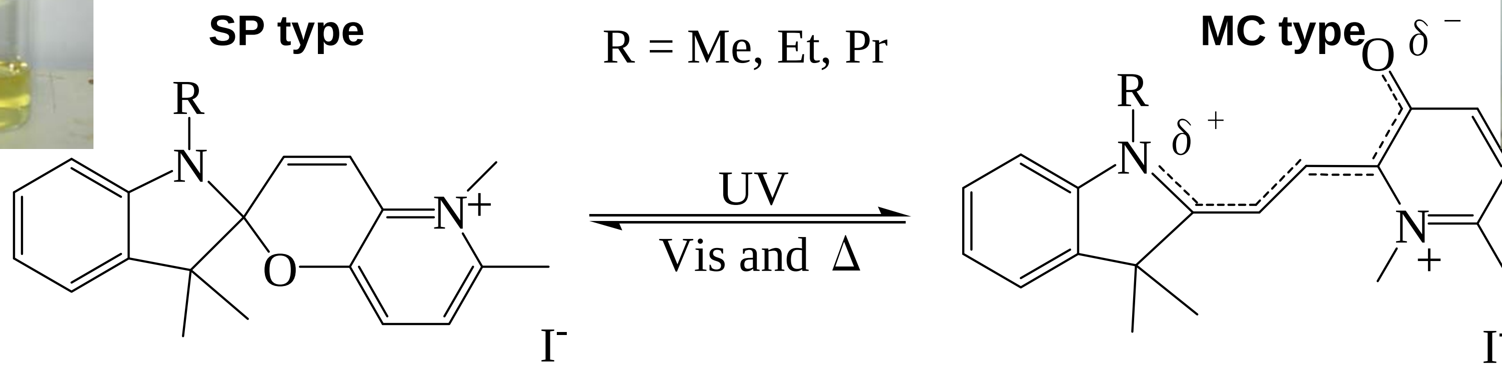
2D iron mixed-valence complex [$Fe^{II}Fe^{III}(dto)_3]_n^{n-}$

Charge transfer phase transition
Ferromagnetism



N. Kida, M. Enomoto, N. Kojima, et al., *J. Am. Chem. Soc*. **131**, 212 (2009)

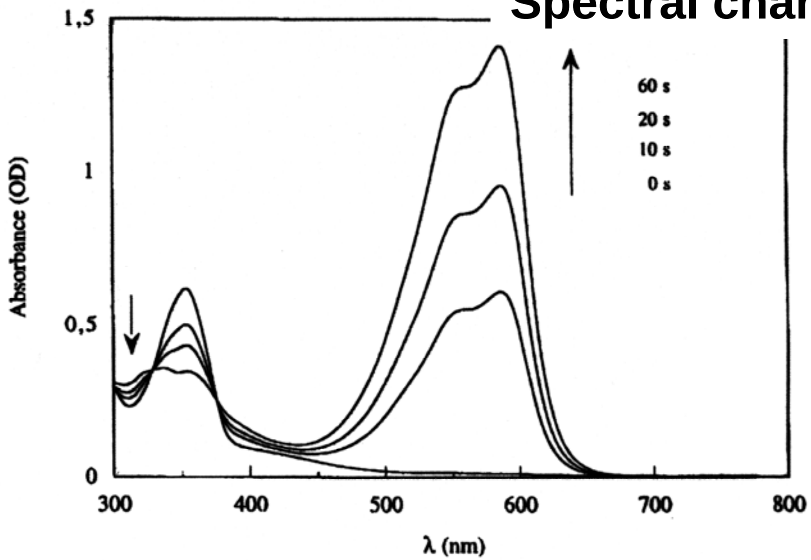
Photoisomerization and Color Change of Spiropyran (SP)



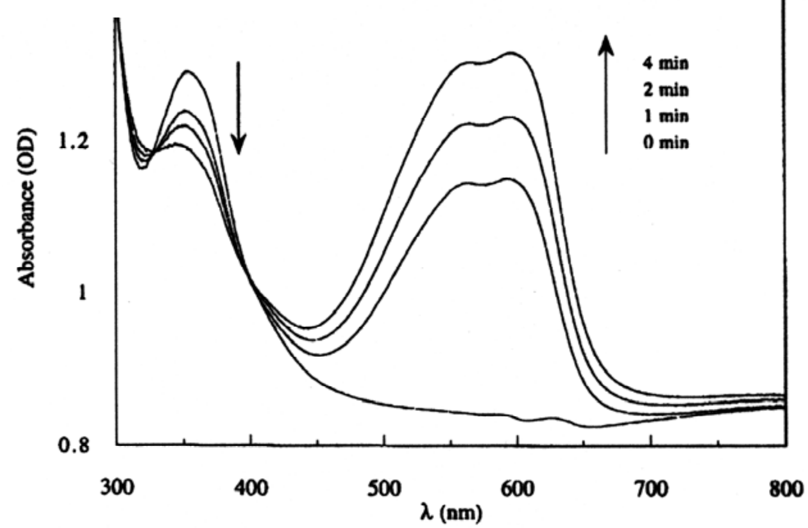
yellow close form (CF)

red open form (OF)

Spectral change by UV irradiation



chloroform solution*



Solid state (KBr pellet)*

* S. Bernard, P. Yu, *Adv. Mater.*, **12**, 48 (2000).

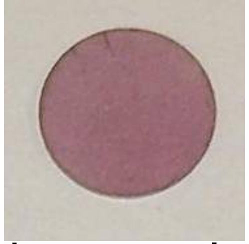
$(SP)[Fe^{II}Fe^{III}(dto)_3]$ UV-vis Absorption Spectrum (KBr Pellet)

N. Kida, M. Enomoto, N. Kojima, et al.,
J. Am. Chem. Soc. **131**, 212 (2009)

black

UV →

← vis. or Δ

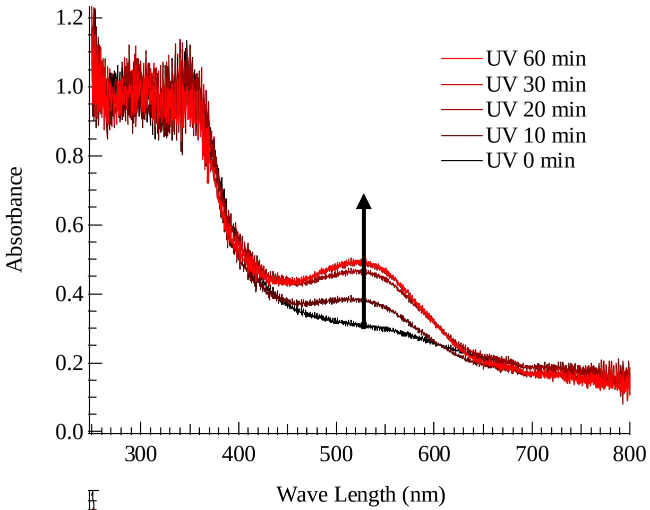


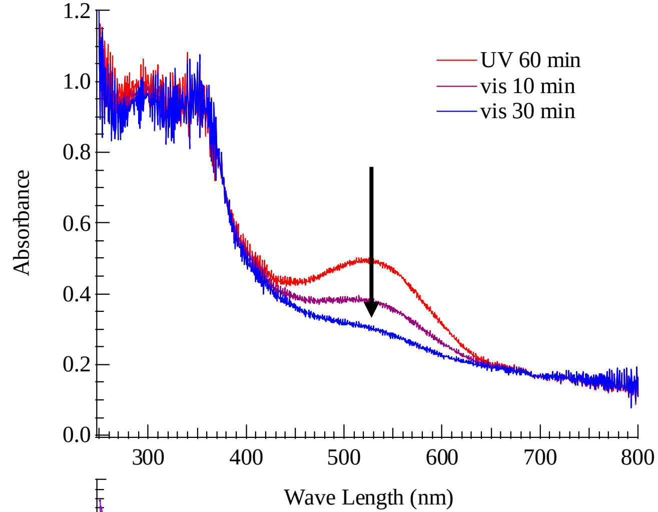
deep purple

UV (350 nm) irradiation

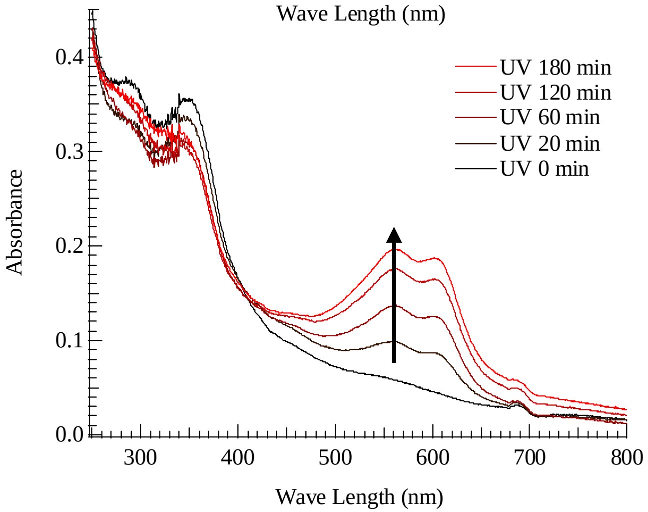
After the saturation of spectrum at 550 nm, visible light (550 nm) was irradiated.

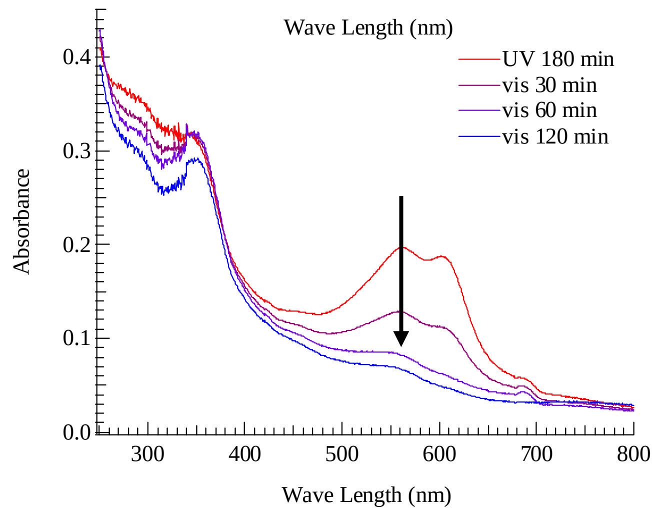
300 K



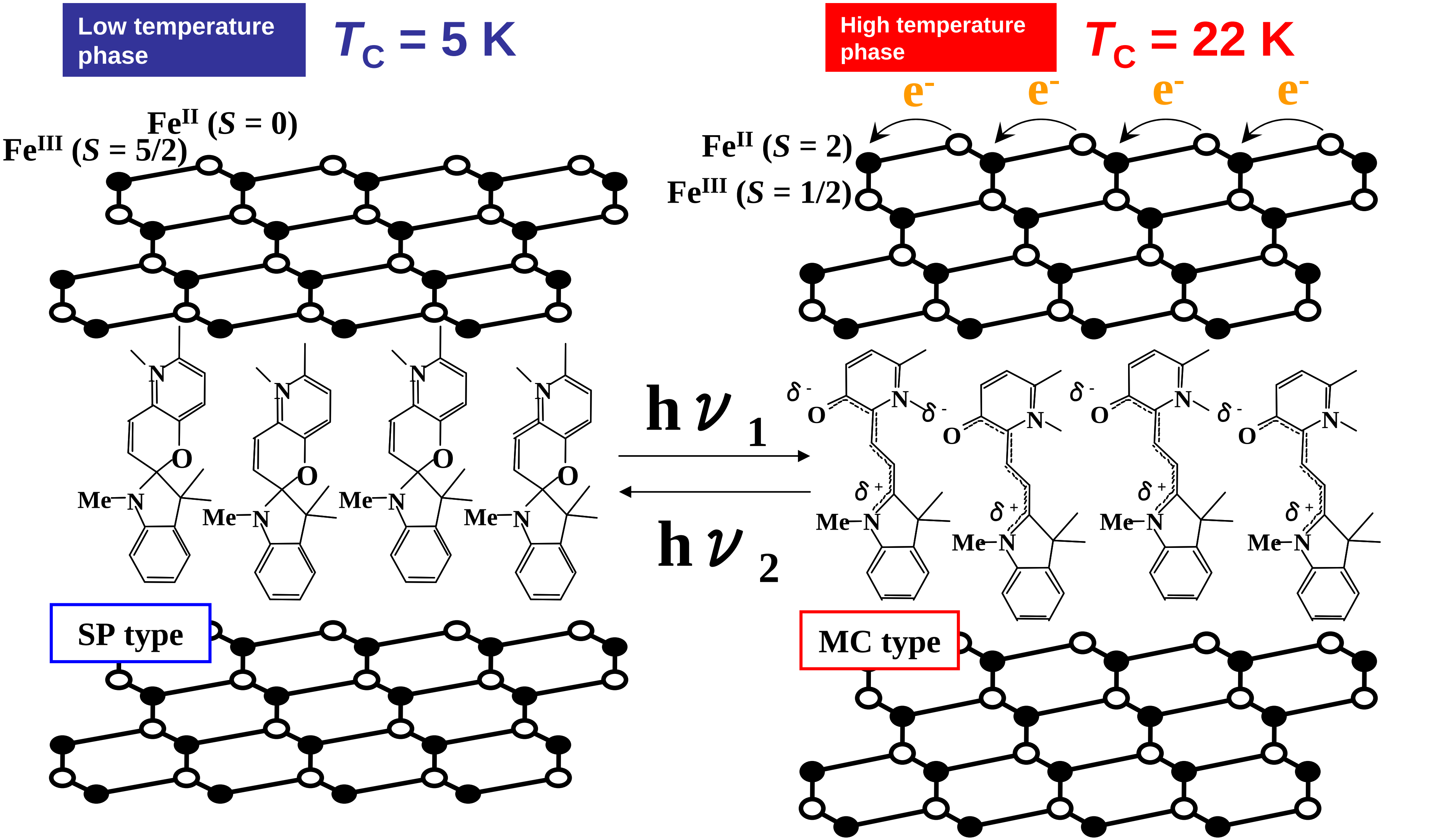


70 K



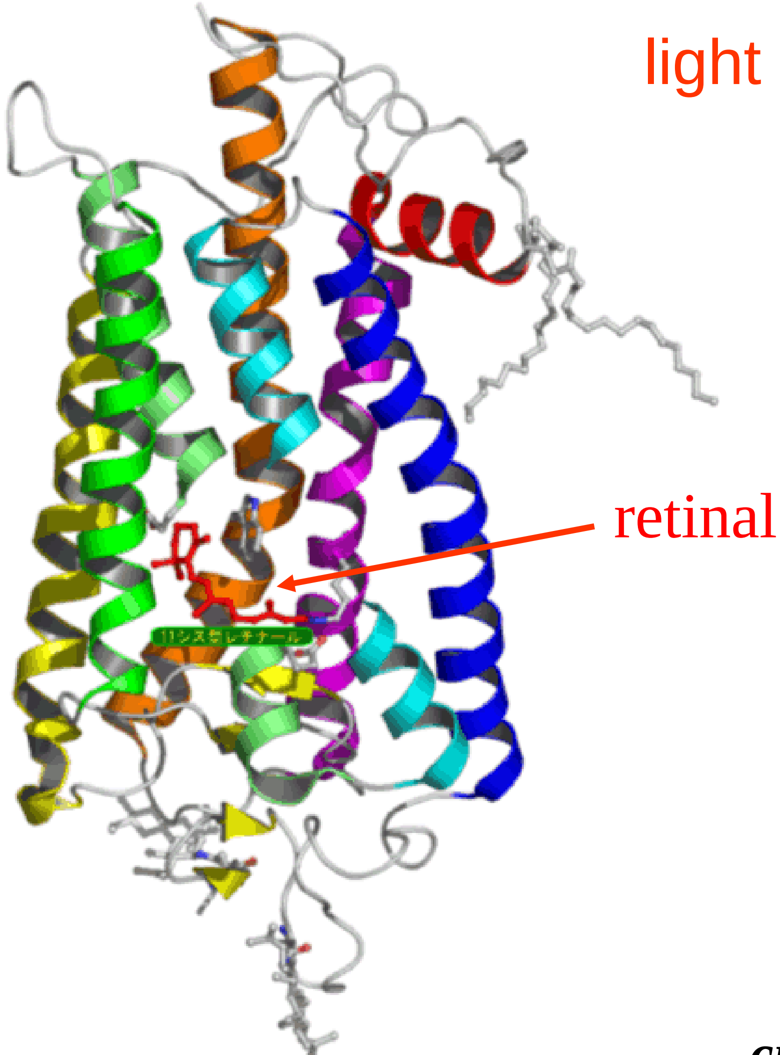


A(light) + B(charge) + C(spin): Fe(II)-Fe(III) Charge Transfer Driven by Photoisomerization of Spiropyran

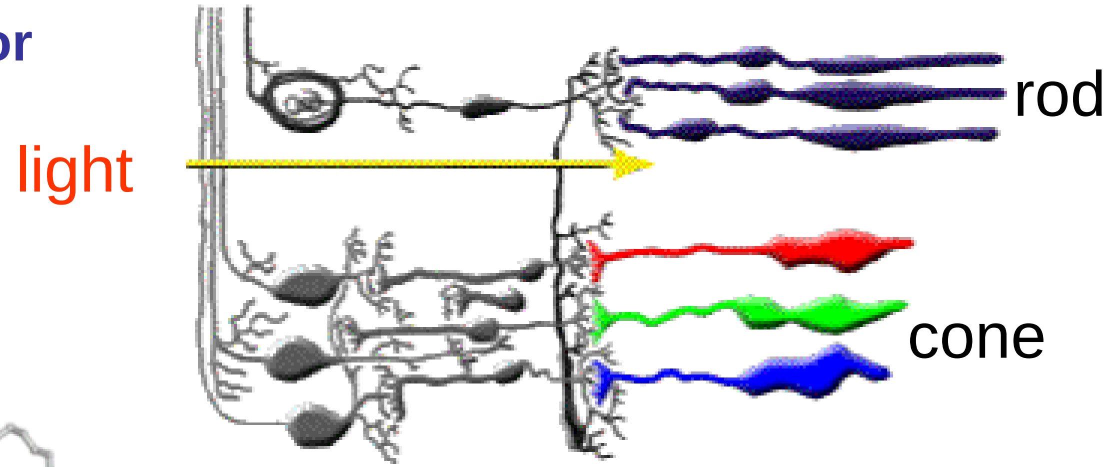


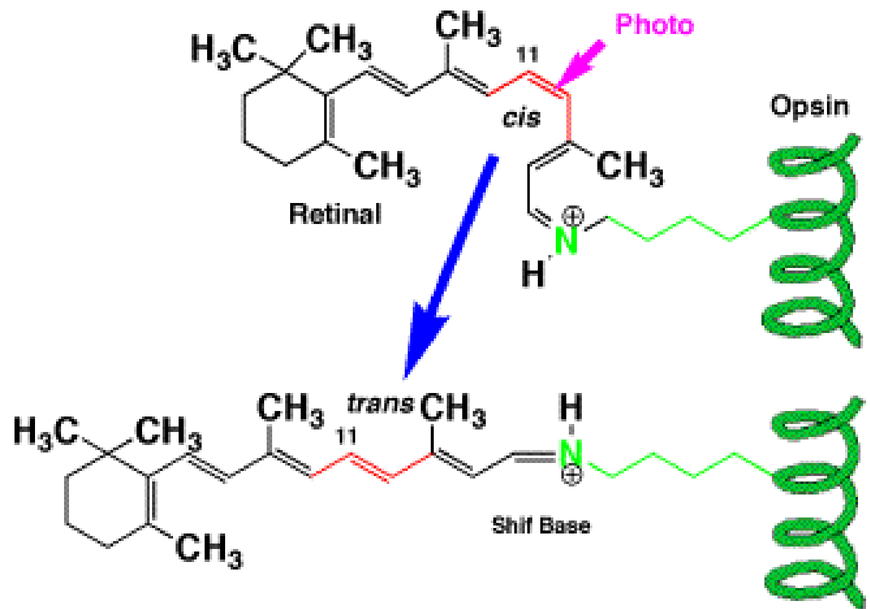
N. Kida, M. Enomoto, N. Kojima, et al., *J. Am. Chem. Soc*. **131**, 212 (2009)

Mechanism of Photoreceptor



Structure of rhodopsin



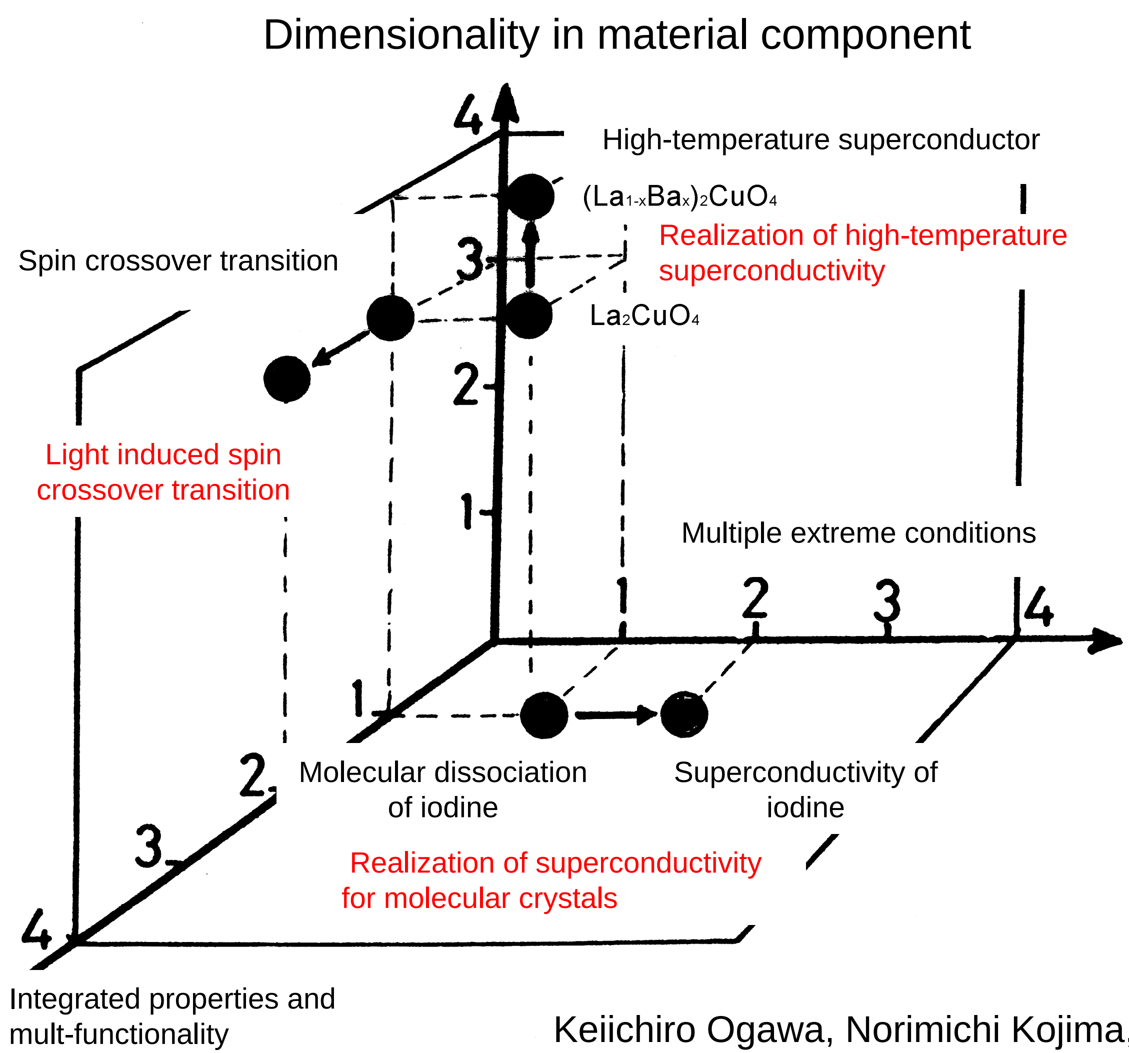


***cis-trans* photoisomerization of retinal**

Kiriya chemical, http://www.kiriya-chem.co.jp/q&a/q52.html

Viewpoint for Materials

Our viewpoint at room temperature and ambient pressure is only one point in the multiple coordinates for materials.



Keiichiro Ogawa, Norimichi Kojima, eds., New “Bussei Kagaku no Kiso” (in Japanese) Kodansha (2010)