

LBMO

2019/9/4 Lecture 9 (9:00-10:30)

Functional Oxide Spintronics and the material design

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STO(100)

2 nm



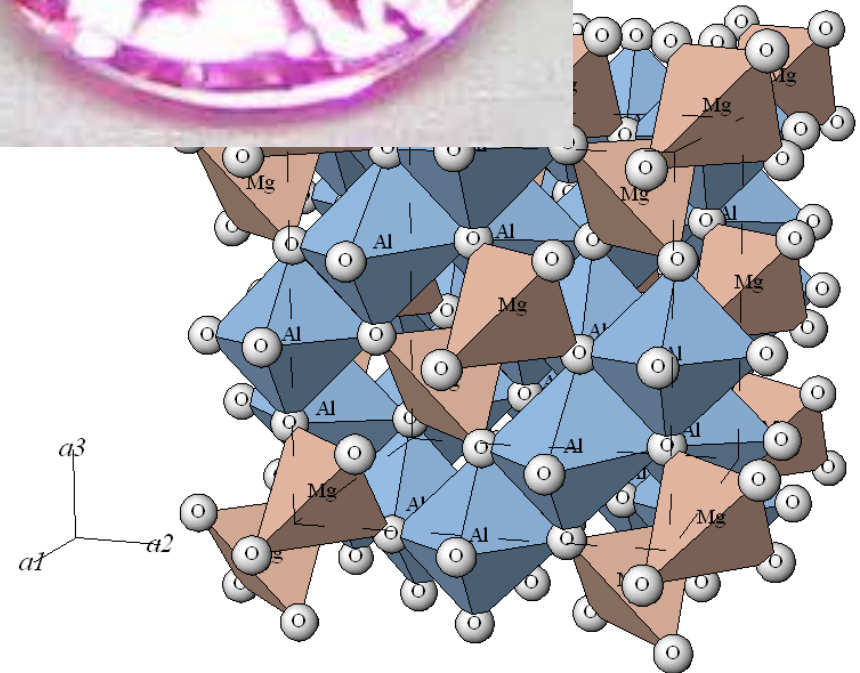


Ceramics



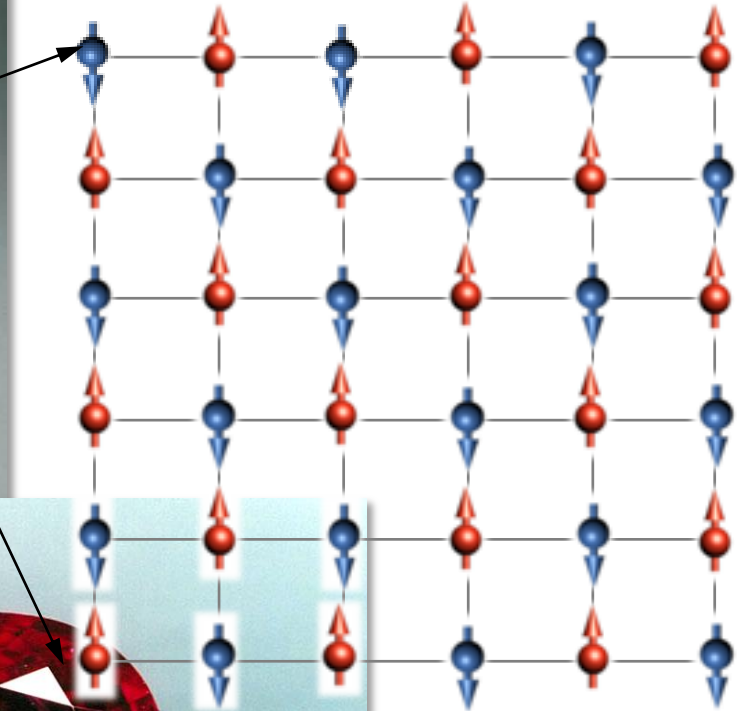


Jewelry (Spinel, Garnet)



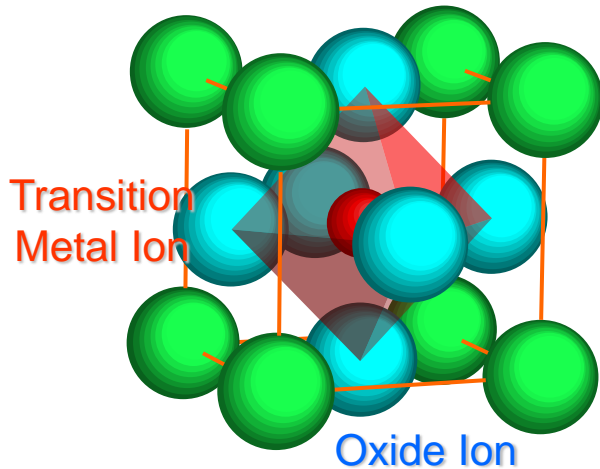


Functional Oxides





Transition Metal Oxides

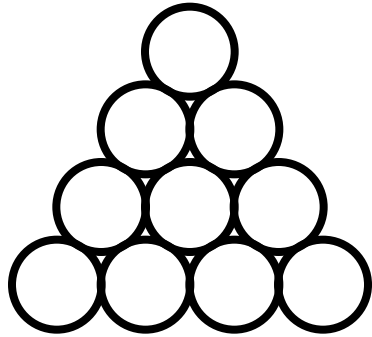


22 Ti 47.87 チタン Titanium	23 V 50.94 バナジウム Vanadium	24 Cr 52.00 クロム Chromium	25 Mn 54.94 マンガン Manganese	26 Fe 55.85 鉄 Iron	27 Co 58.93 コバルト Cobalt	28 Ni 58.69 ニッケル Nickel	29 Cu 63.55 銅 Copper
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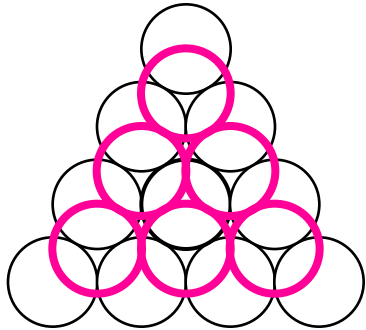
Ferro dielectrics	Anti-/Ferro magnetics	High temperature superconductors
Piezoelectrics	Colossal MR	Conductors
Memory (DRAM, FRAM, RRAM)	Magnetic head	Magnetic recorder
	Memory (MRAM)	Josephson junction electrode
Piezoelectric devices		SQUID
		Bolometer

Information processing and data storage materials related with our daily life

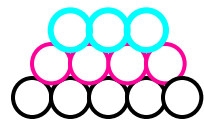
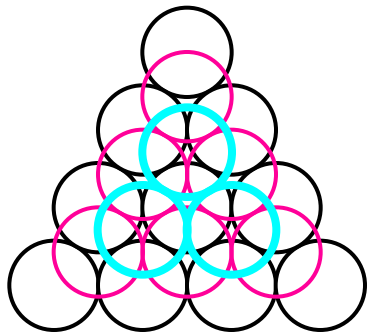
Face-centered cubic => Closed pack structure



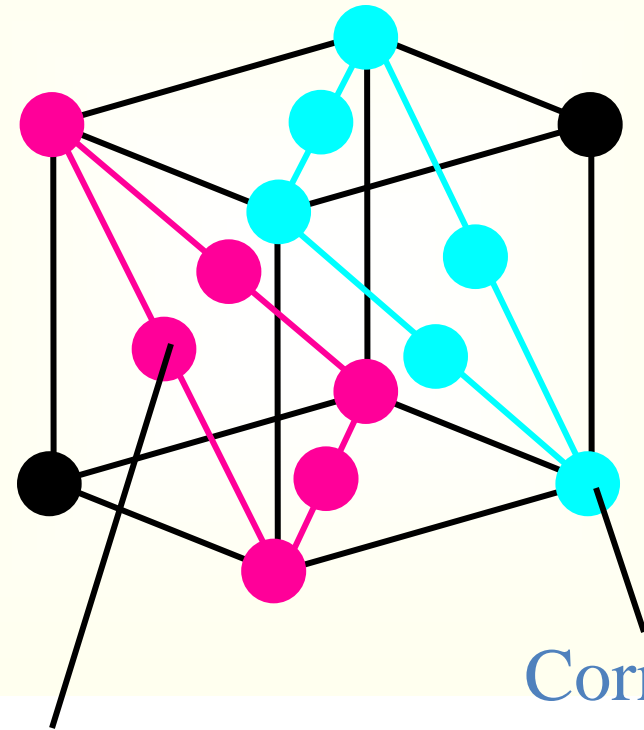
1st layer



2nd layer



3rd layer



Center face

$1/2 \times 6$ parts

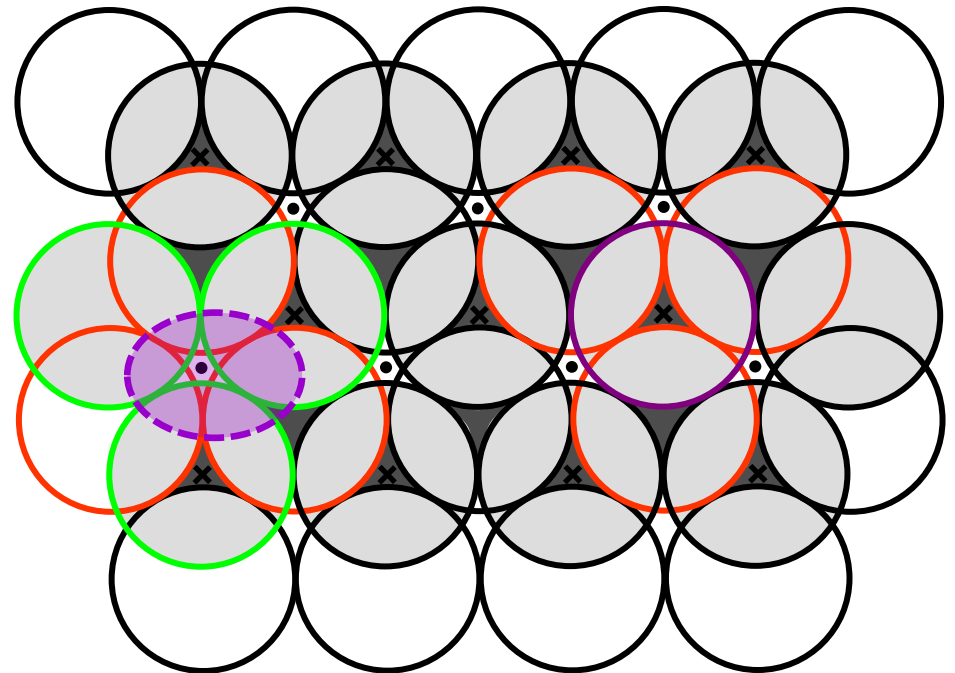
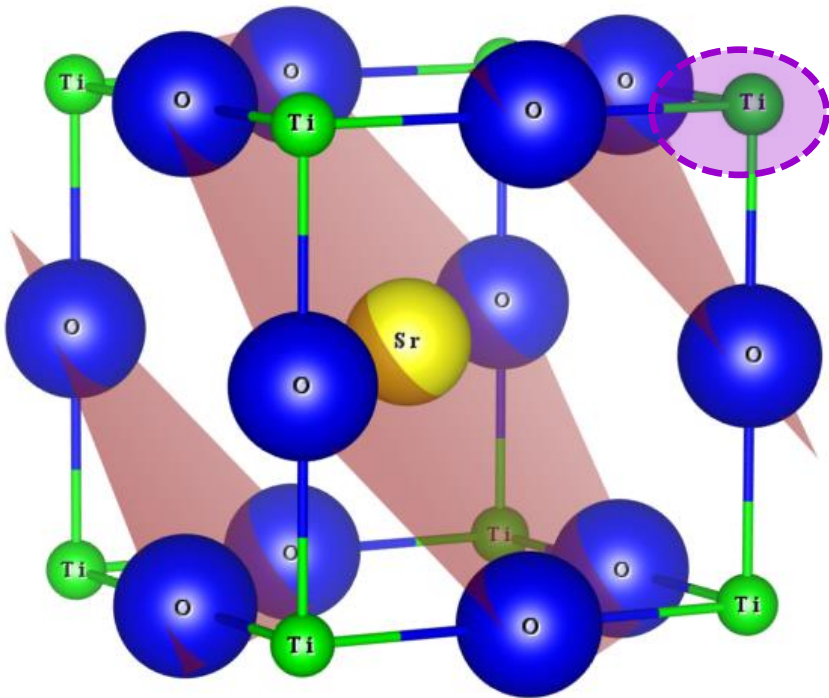
Corner

$1/8 \times 8$ parts

Perovskite structure: ABO_3 e.g. $SrTiO_3$

Interspace of close packed oxide ions : Octahedral interspace

$$\geq 0.414r \quad O^{2-}=1.40\text{\AA}, \quad Sr^{2+}=1.26\text{\AA}, \quad Ti^{4+}=0.61\text{\AA},$$





Orbital bonding

Bonding and Antibonding states

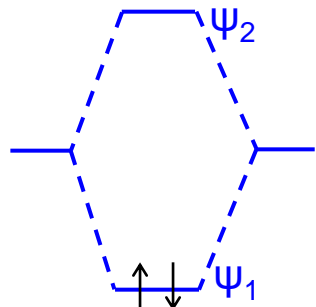


Valence and Conduction band

Covalent bonding H H₂ H

$$\psi_2 = \chi_A - \chi_B$$

Energy ↑

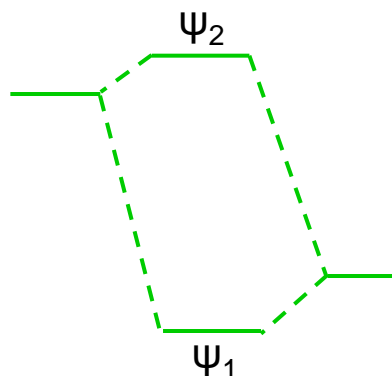


$$\psi_1 = \chi_A + \chi_B$$

A A-B B

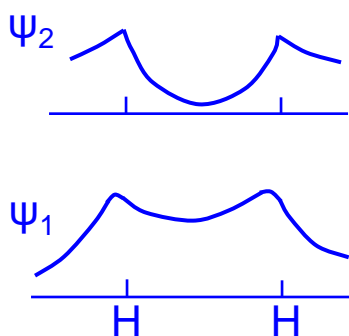
Ion bonding

$$\psi_2 = a_2\chi_A - b_2\chi_B$$

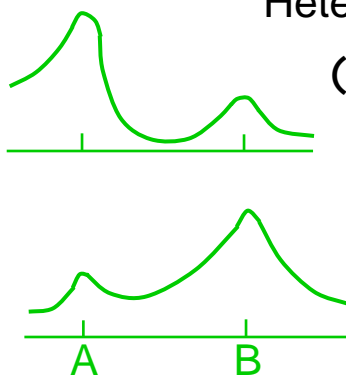


$$\psi_1 = a_1\chi_A + b_1\chi_B$$

Electron density ↑



Antibonding



Bonding

Heteronuclear diatomic molecule

(Covalent or Ionic characters)

↓
Different orbital level

[Electronegativity
Ionization potential

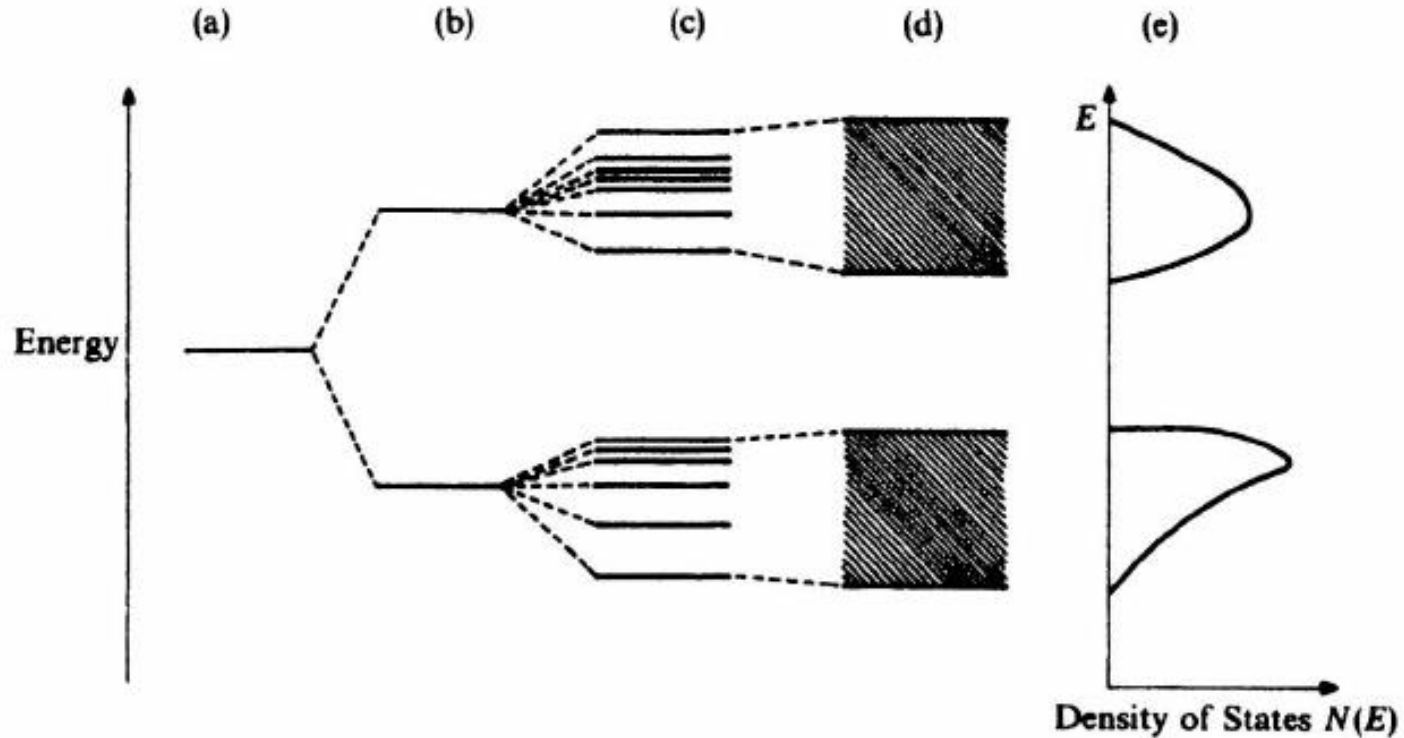
(a)

(b)

Electron distributions and energies of molecular orbitals in (a) H₂ and a heteronuclear molecule AB



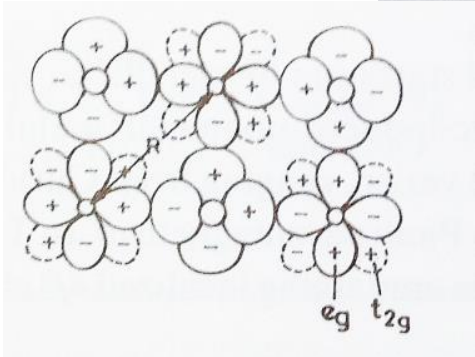
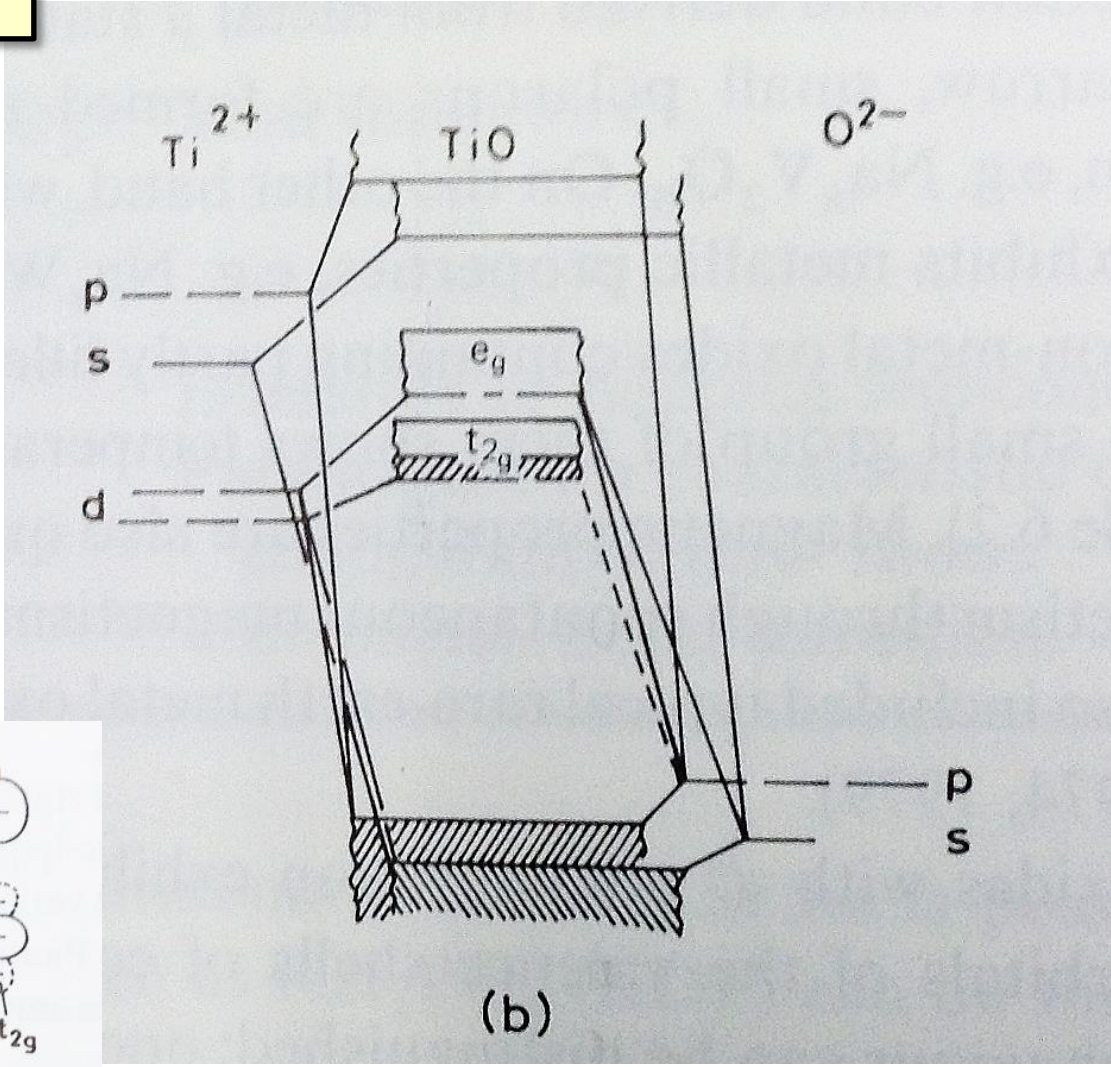
From orbital to band formation



Orbital energies of (a) atom, (b) small molecule, (c) large molecule, (d) solid, and (e) density of states corresponding to (d)

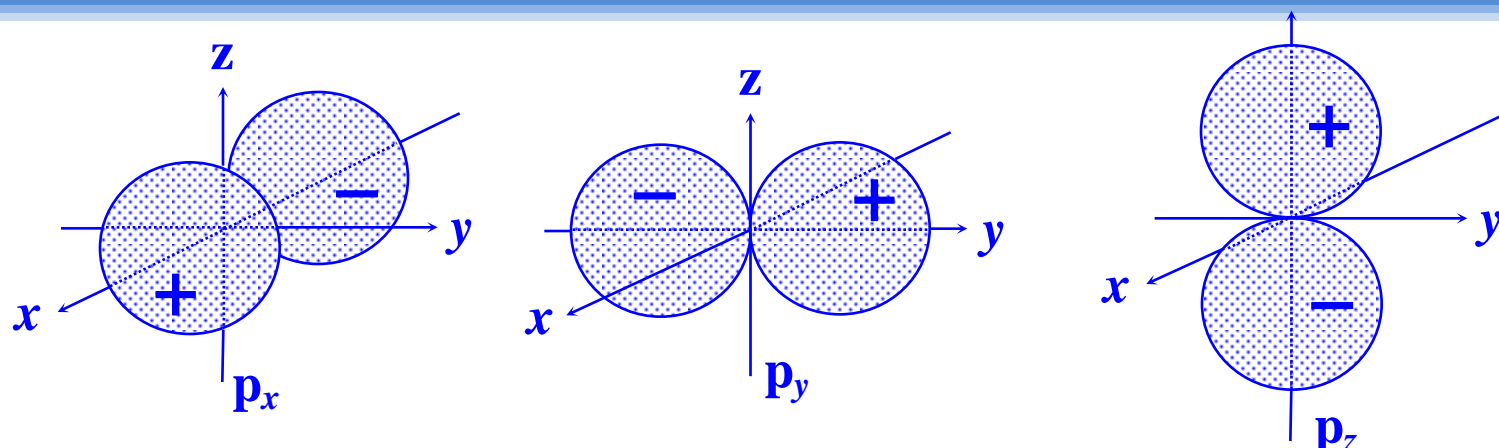


TiO

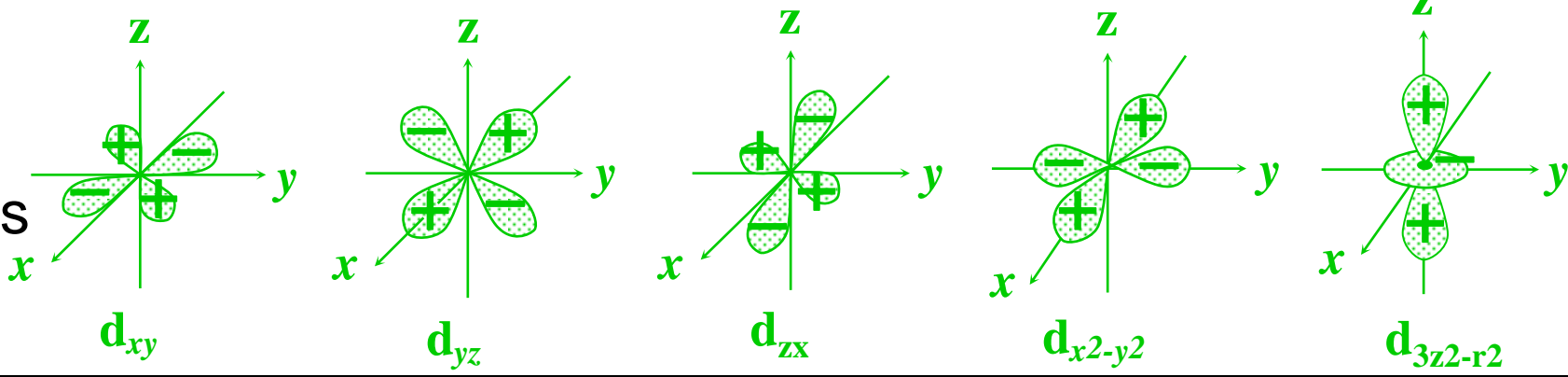


Existence of electrons - Orbital shape

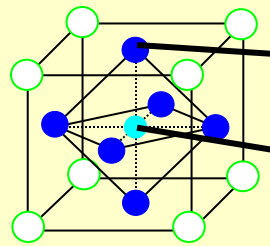
p orbitals



d orbitals

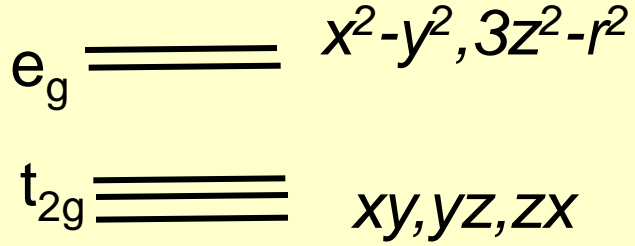


Perovskite structure



Oxygen atom
3d transition metal

Ligand field splitting
(Crystal field splitting)



Periodic Table of the Elements

2

18

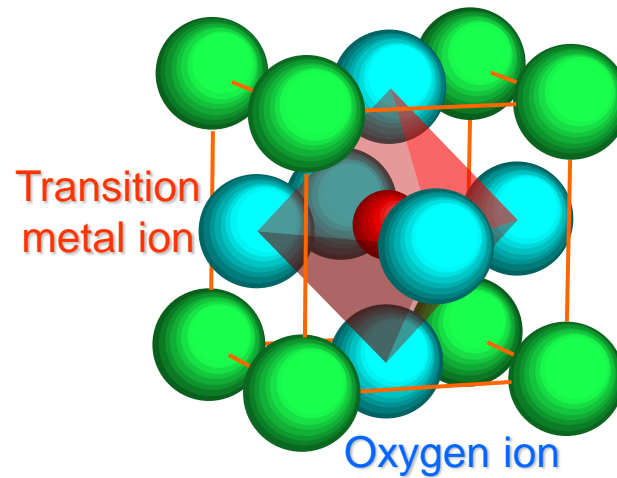
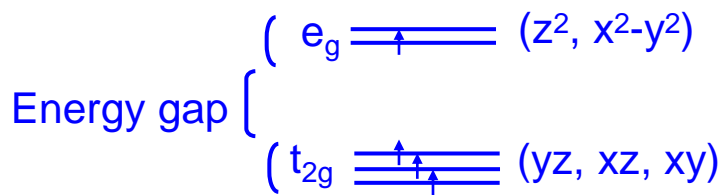
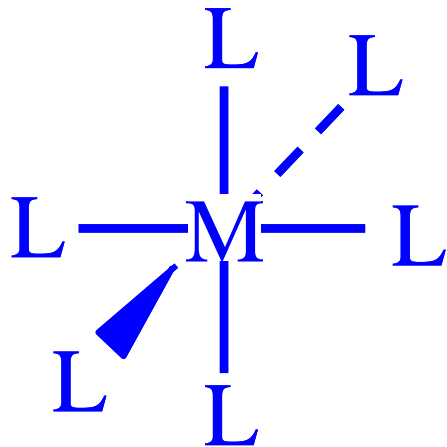
<p>oxidation states in compounds: important, most important (for easier reading, arabic numerals are used instead of the correct roman ones)</p> <p>electron configuration</p> <p>atomic number</p> <p>name (IUPAC)</p> <ul style="list-style-type: none"> ● element essential to all biological species investigated ● essential to at least one biological species ● biological function suggested ○ essential to humans ○ suggested to be essential to humans <p>atomic radius in pm (half the interatomic distance for the element; α-Fe in this example) covalent radius for single bonds in pm (after Pauling; radii for polar and multiple bonds are shorter) ionic radius in pm with coordination number (Cr, Mn, Fe, Co: values for high-spin complexes) van der Waals radius in pm</p> <p>reduction potential E^\ominus in V with number (n) of electrons for: $E^{n+} + ne^- \rightleftharpoons E(s)$ (metals) $E + ne^- \rightleftharpoons E^{n-}$ $EO_{2,3} + nH^+ + ne^- \rightleftharpoons E(s) + n/2 H_2O$ $1/2 O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O(l)$</p> <p>electronegativity (Allred and Rochow)</p> <p>abundance (mass fraction in % of the element in the earth's lithosphere (upper 16 km) plus hydrosphere (oceans) plus atmosphere; mass fraction calculated from natural radioactive series or other natural nuclear reactions)</p>																	
<p>13 14 15 16 17</p> <p>3B IIIA 4B IVA 5B VA 6B VIA 7B VIIA</p> <p>5B 6B 7B 8 9 10 11 12</p> <p>3A IIIB 4A IVB 5A VIB 6A VIIB 7A VIIIB 8 VIII 9 VIIIB 10 VIII 11 IB 12 IIB</p>																	
<p>3d² 3d³ 3d⁵ 3d⁵ 3d⁶ 3d⁷ 3d⁸ 3d¹⁰ 3d¹⁰</p> <p>4s² 4s² 4s¹ 4s² 4s² 4s² 4s² 4s² 4s¹ 4s²</p>																	
<p>37 to 71</p> <p>La - Lu</p> <p>88 to 103</p> <p>Ac - Lr</p>																	
<p>Distribution: VCH Verlagsgesellschaft, P.O. Box 1260/1280, D-6940 Weinheim (Federal Republic of Germany) USA and Canada: VCH Publishers, 303 N.W. 12th Avenue, Deerfield Beach, FL 33442-1705 (USA) Order number 10 10 109</p> <p>VCH: The international name in scientific publishing</p>																	



<p>6</p> <p>57 La 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu</p> <p>7</p> <p>89 Ac 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr</p> <p>Actinium Thorium Protactinium Uranium Neptunium Plutonium Americium Curium Berkelium Californium Einsteinium Fermium Mendeleevium Nobelium Lawrencium</p>																	
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Crystal field splitting of perovskite structure

Octahedral ligands





Required interaction for material design

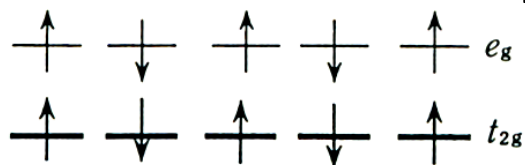
Superexchange interaction

Double exchange interaction

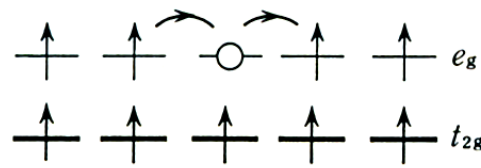
LaMnO₃

Carrier doping

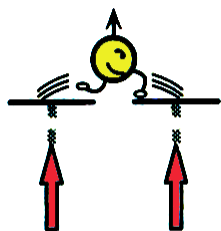
(La,Sr)MnO₃



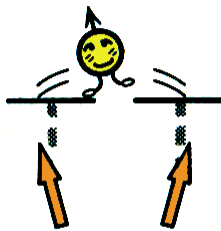
(a) LaMnO₃



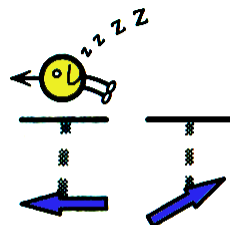
(b) La_{1-x}Sr_xMnO₃ ($T \ll T_c$)



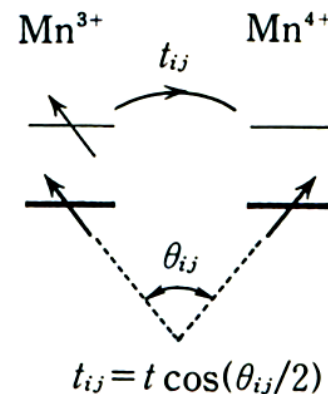
(a)



(b)



(c)



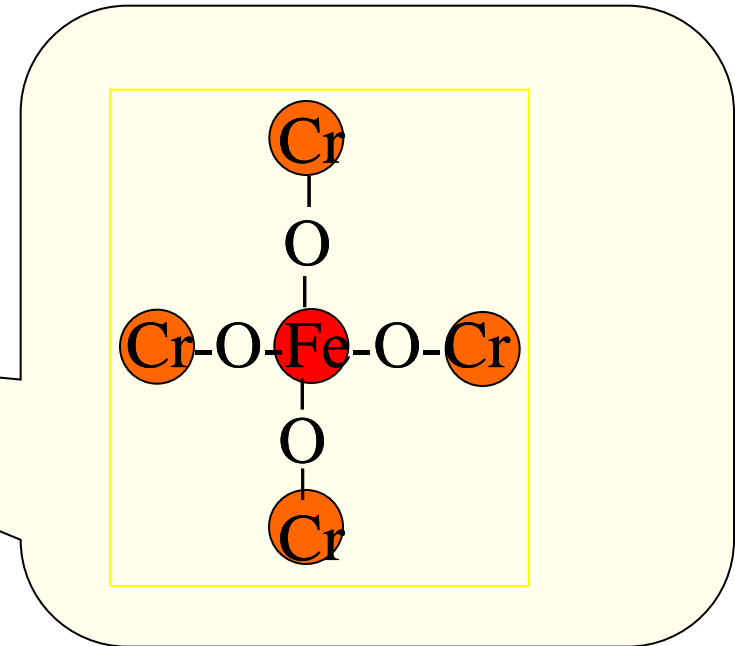
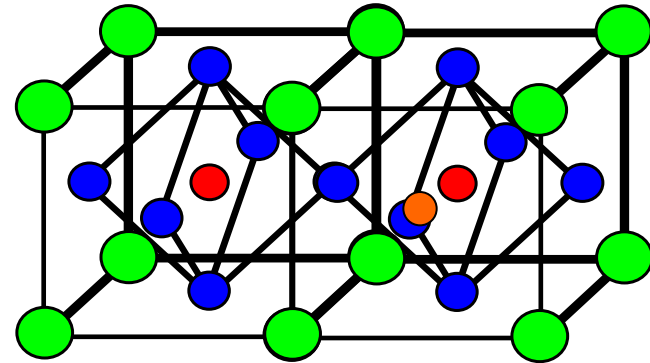
$$H = -t_{\text{Mn-Mn}} \cos\left(\frac{\theta}{2}\right) - K_{\text{Hund}} \sigma S_{\text{Mn}} - J_{t2g} \sum_{\text{LMnO}} S_{\text{Mn}}^{t2g} S_{\text{Mn}}^{t2g}$$



Kanamori-Goodenough rules

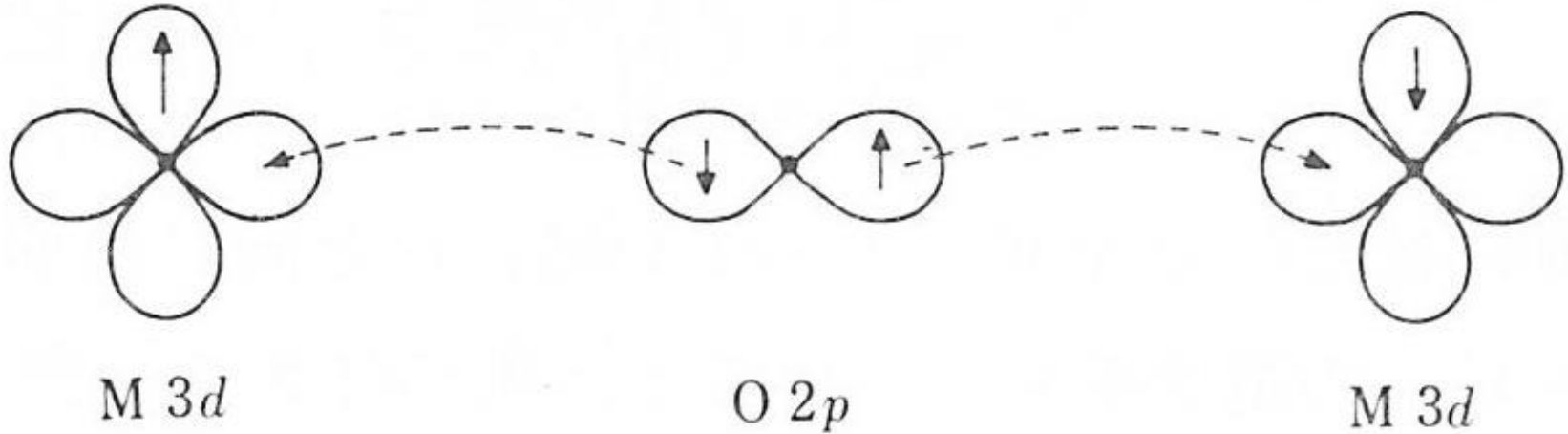
60 years ago

Kanamori former
president of Osaka Univ.





Superexchange interaction

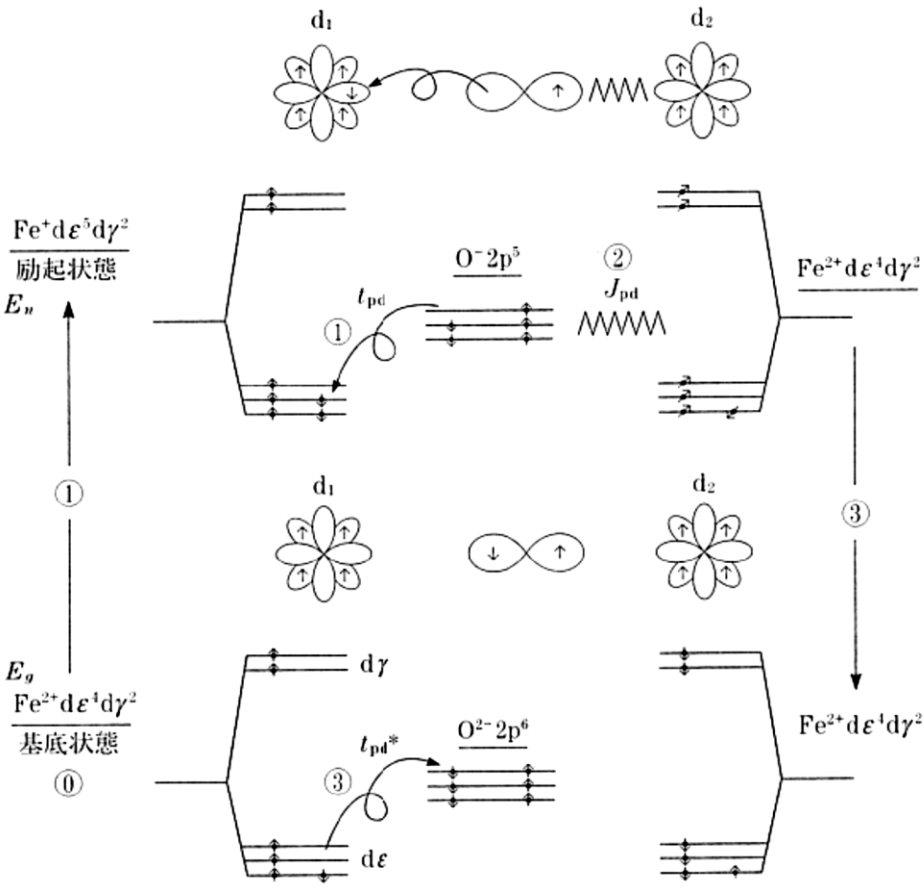


Superexchange interaction

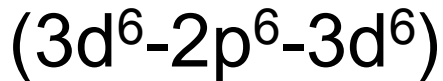
→ Indirect interaction between two magnetic atoms
through non-magnetic atom



Superexchange interaction



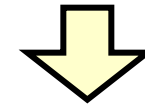
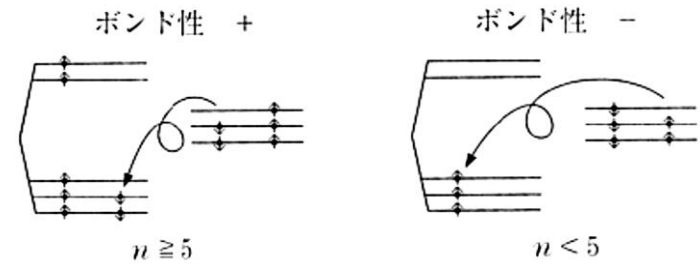
(a) Fe²⁺ - O²⁻ - Fe²⁺ 間の超交換相互作用模型



Considering an excited state in the case of electron transfer from 2p orbital to 3d orbital

(transfer integral) $t_{pd} = \int \phi_d^* V_{pd} \phi_p dr$

■ bonding rule



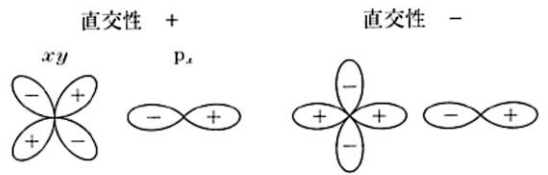
Considering a direct exchange interaction (J_{pd}) between 2p spin and 3d spin



Superexchange interaction

Sign of J_{pd} Ferromagnetic $J_{pd} > 0$, Antiferromagnetic $J_{pd} < 0$

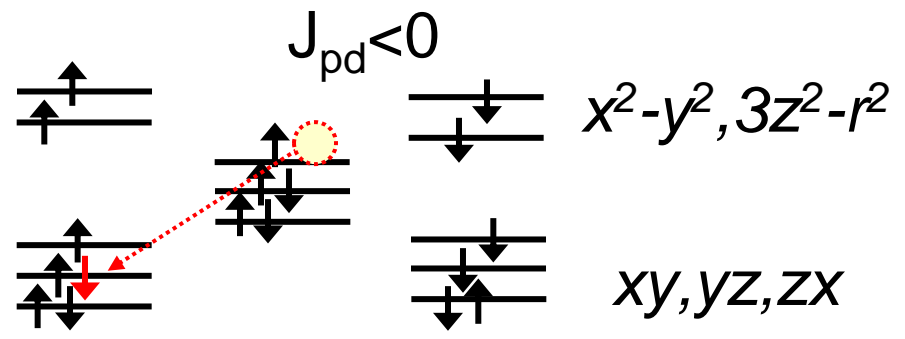
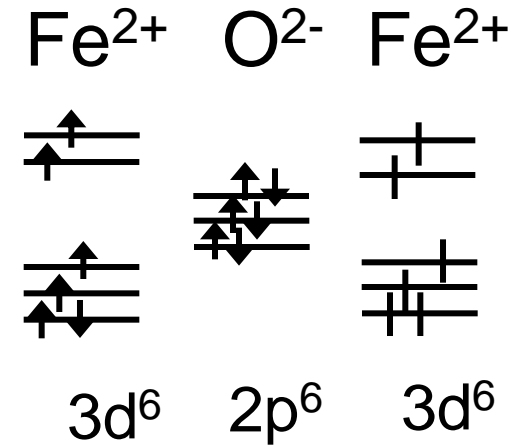
... Orthogonal character of J_{pd}



$\int \psi_p \psi_d dr = 0$ $\int \psi_p \psi_d dr \neq 0$

(+ : 直交, - : 非直交, (σ), (π) は σ および π 結合)

d		p_x	p_y	p_z	s
$3z^2 - r^2$	X	$-(\sigma)$	+	+	$-(\sigma)$
	Y	+	$-(\sigma)$	+	$-(\sigma)$
	Z	+	+	$-(\sigma)$	$-(\sigma)$
$x^2 - y^2$	X	$-(\sigma)$	+	+	$-(\sigma)$
	Y	+	$-(\sigma)$	+	$-(\sigma)$
	Z	+	+	+	+
xy	X	+	$-(\pi)$	+	+
	Y	$-(\pi)$	+	+	+
	Z	+	+	+	+
yz	X	+	+	+	+
	Y	+	+	$-(\pi)$	+
	Z	+	$-(\pi)$	+	+
zx	X	+	+	$-(\pi)$	+
	Y	+	+	+	+
	Z	$-(\pi)$	+	+	+



Orthogonal character table in case that d orbital function locates the origin and

FeO is an antiferromagnetic material

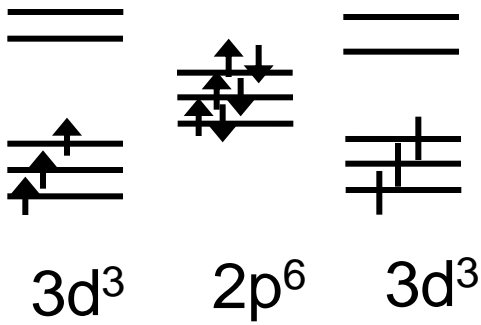
s and p orbitals arrange Orthogonal coordinates of X, Y and Z axes



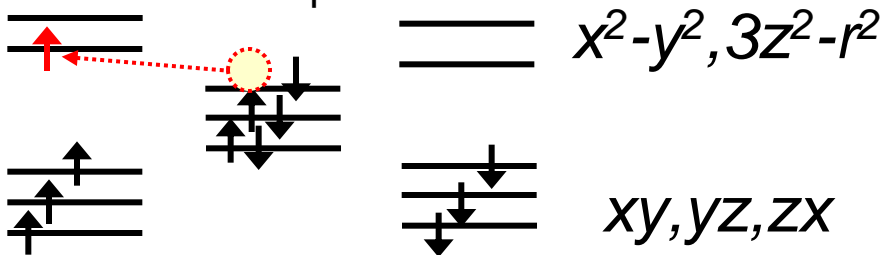
Superexchange interaction

Ex.) $\text{Mn}^{4+} - \text{O}^{2-} - \text{Mn}^{4+}$: Antiferromagnetic

Mn^{4+} O^{2-} Mn^{4+}



$J_{pd} > 0$



(+ : 直交, - : 非直交, (σ), (π) は σ および π 結合)

d		p_x	p_y	p_z	s
$3z^2 - r^2$	X	$-(\sigma)$	+	+	$-(\sigma)$
	Y	+	$-(\sigma)$	+	$-(\sigma)$
	Z	+	+	$-(\sigma)$	$-(\sigma)$
$x^2 - y^2$	X	$-(\sigma)$	+	+	$-(\sigma)$
	Y	+	$-(\sigma)$	+	$-(\sigma)$
	Z	+	+	+	+
xy	X	+	$-(\pi)$	+	+
	Y	$-(\pi)$	+	+	+
	Z	+	+	+	+
yz	X	+	+	+	+
	Y	+	+	$-(\pi)$	+
	Z	+	$-(\pi)$	+	+
zx	X	+	+	$-(\pi)$	+
	Y	+	+	+	+
	Z	$-(\pi)$	+	+	+



Double exchange interaction

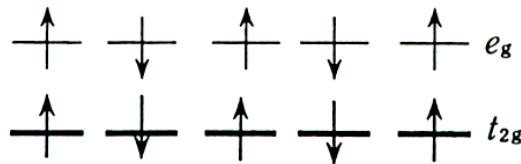
Superexchange interaction

Double exchange interaction

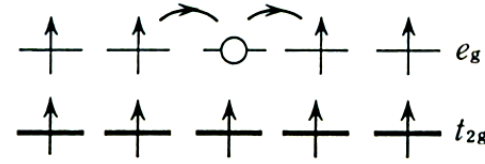
LaMnO₃

Carrier doping

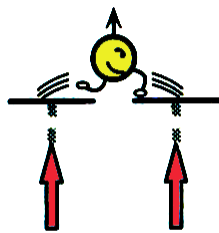
(La,Sr)MnO₃



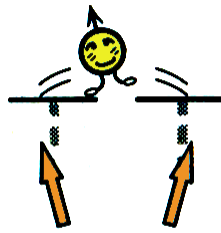
(a) LaMnO₃



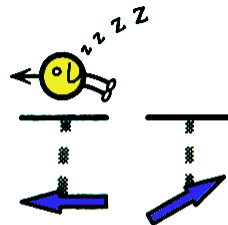
(b) $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($T \ll T_C$)



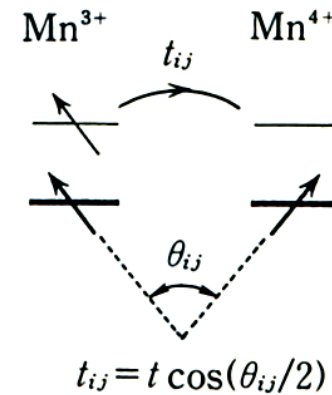
(a)



(b)



(c)

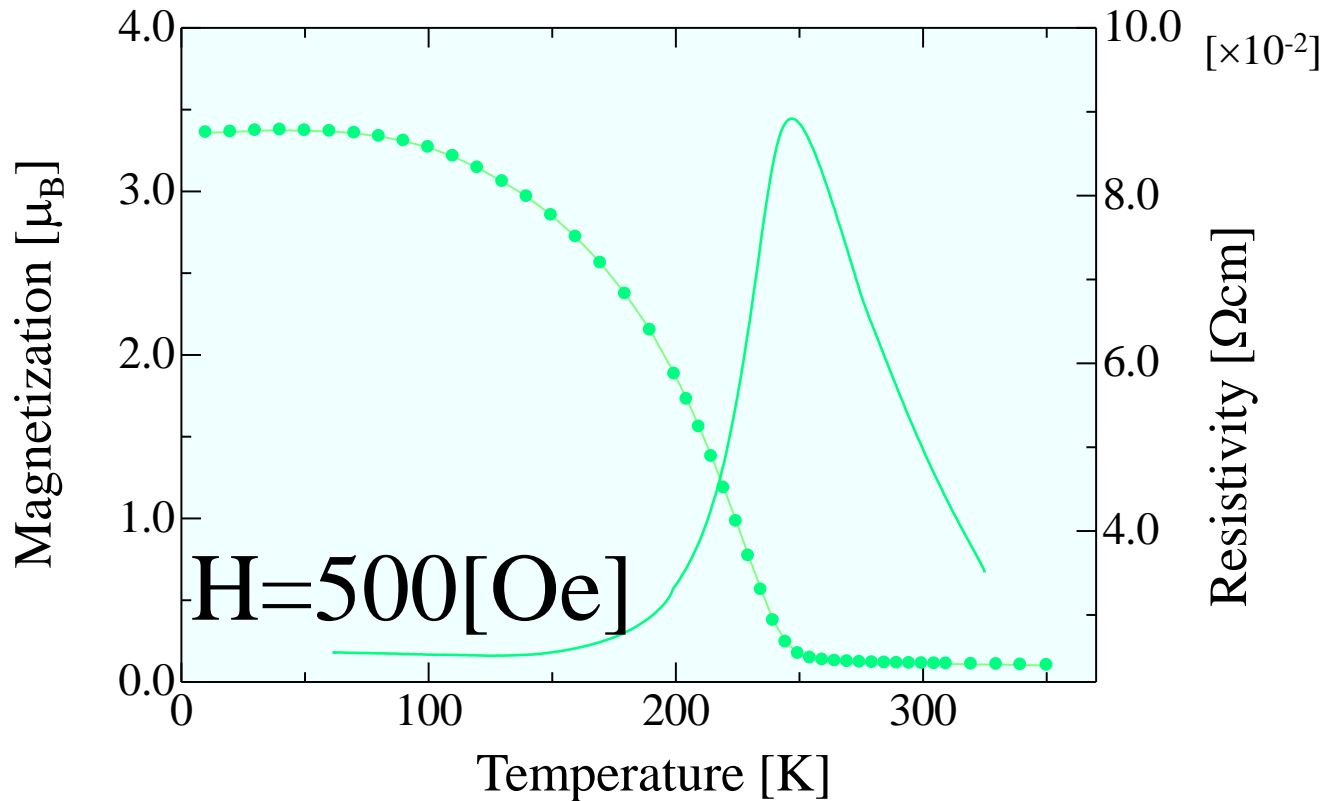


$$H = -t_{\text{Mn-Mn}} \cos\left(\frac{\theta}{2}\right) - K_{\text{Hund}} \sigma S_{\text{Mn}} - J_{t_{2g}} \sum_{\text{LMnO}} S_{\text{Mn}}^{t_{2g}} S_{\text{Mn}}^{t_{2g}}$$

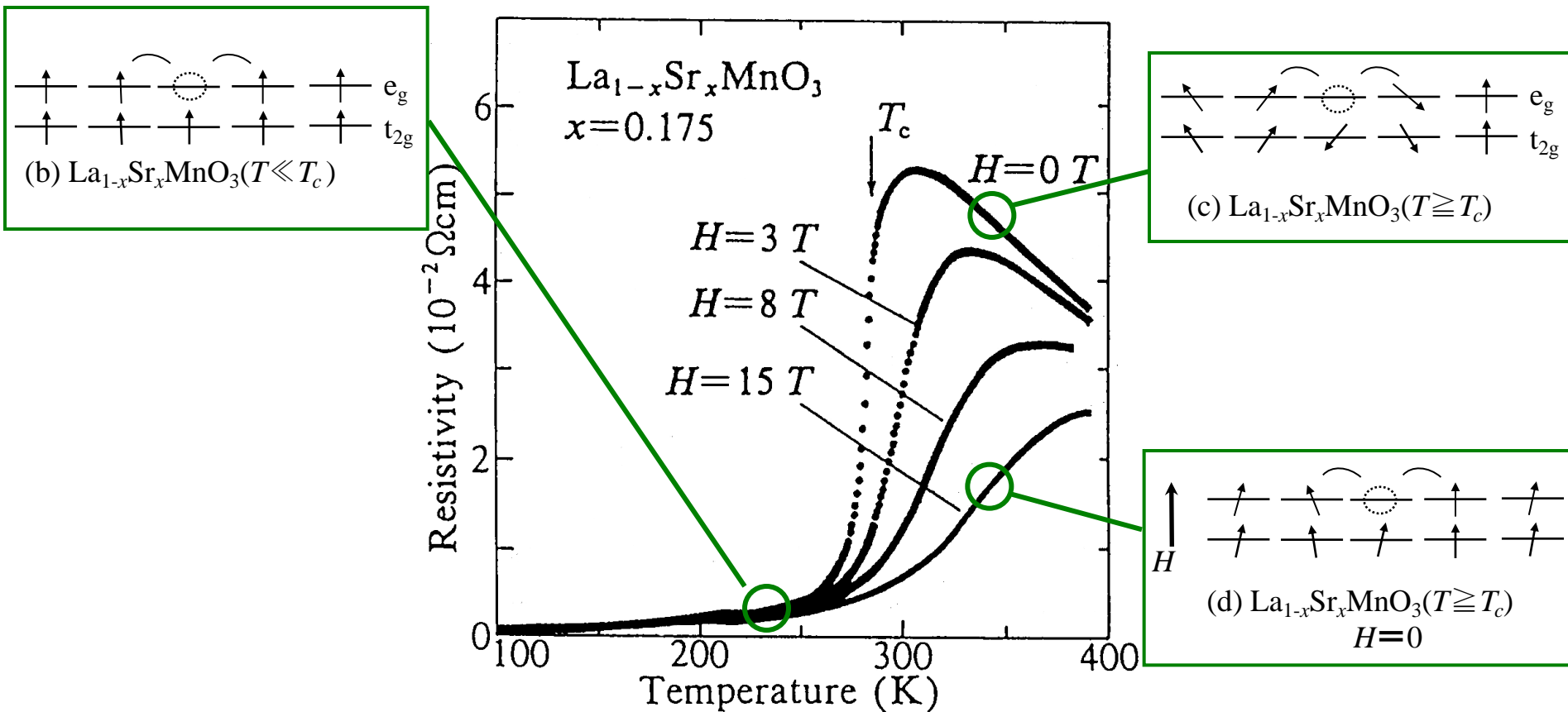


Magnetism modulation due to change of electron transfer integral

$$H = -t_{\text{Mn-Mn}} \cos\left(\frac{\theta}{2}\right) - K_{\text{Hund}} \sigma S_{\text{Mn}} - J_{t2g} \sum_{\text{LMnO}} S_{\text{Mn}}^{t2g} S_{\text{Mn}}^{t2g}$$

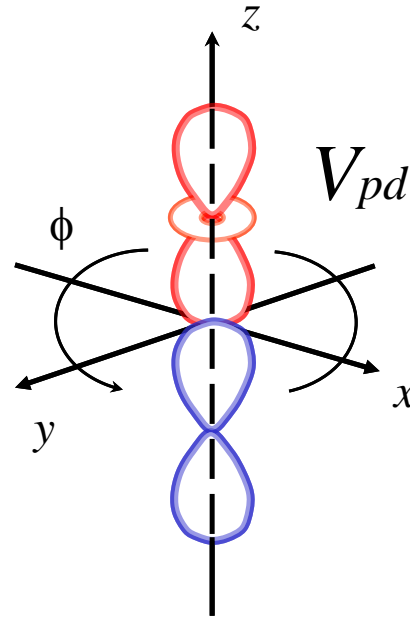
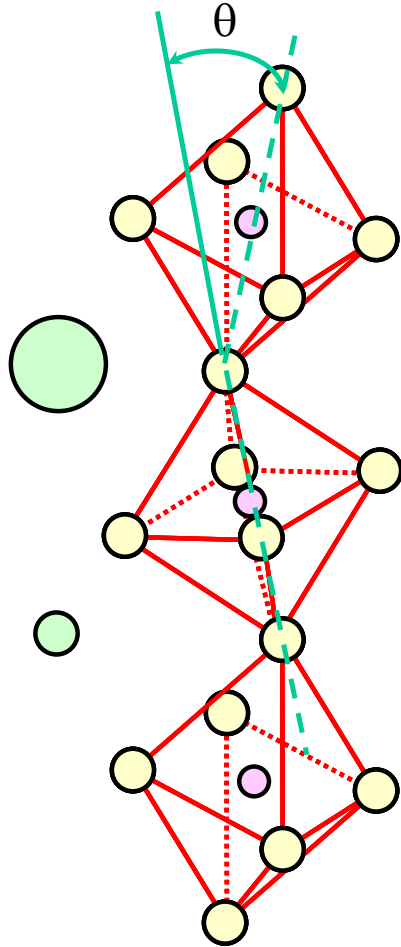


Colossal magneto resistance (CMR)



Temperature dependence of resistivity with a variety of magnetic fields in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ crystal (negative CMR) .
 T_c indicates the Curie temperature at $H=0$ T.

Main parameters of transfer integral changes



Harrison's equation

$$V_{pd\sigma} = \langle \varphi_d | H | \varphi_p \rangle \sim d^{-7/2}$$

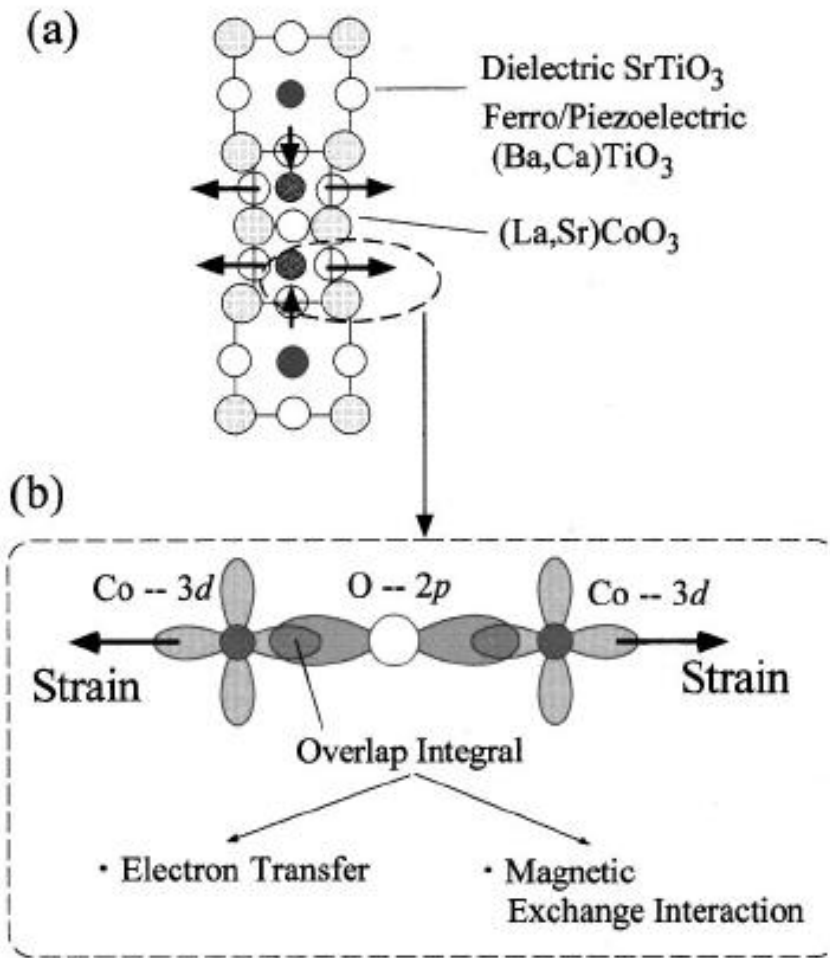
d : the distance between orbitals

ϕ : the bond angle

$$E_{3z^2-r^2, 3z^2-r^2} = \left[n^2 - \frac{1}{2}(l^2 + m^2) \right]^2 V_{dd\sigma} + 3n^2(l^2 + m^2) V_{dd\pi} + \frac{3}{4}(l^2 + m^2)^2 V_{dd\delta}$$

$$\approx \cos \phi$$

Main parameters of transfer integral changes



Tensile strain

$$V_{pd\sigma} \sim d^{-7/2}$$

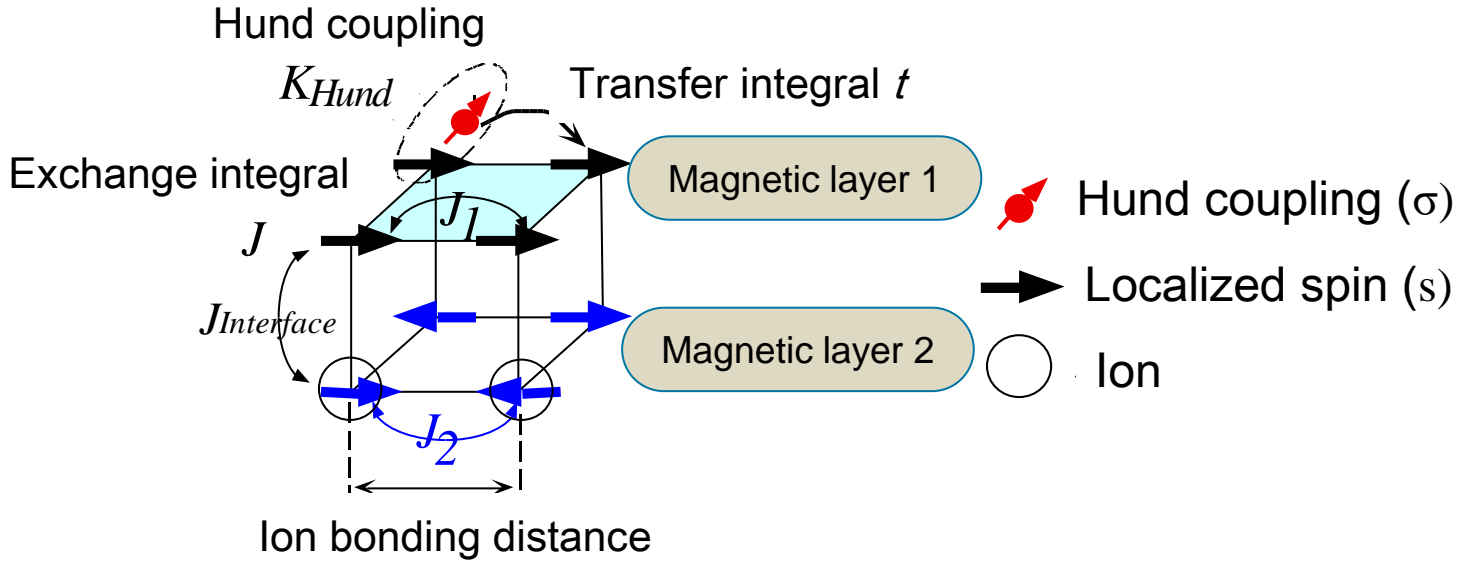
Compressive strain

Band width $W = 2zV$

z : Coordination number



Material design for oxide spintronics



$$\begin{aligned}
 H_{electron} = & \sum E_d + \frac{1}{2} \sum U + K_{Hund} \sum_i \sigma S_i + \sum_{i,j} J_{ij} S_i S_j \\
 & + \sum E_p + \sum t + A \sum_i d Q d
 \end{aligned}$$

d electron energy
Coulomb integral
Hund coupling
Exchange integral

E_d
 U
 K_{Hund}
 σS_i
 $J_{ij} S_i S_j$

E_p
 t
 $A \sum_i d Q d$

Transfer integral



Material design for oxide spintronics

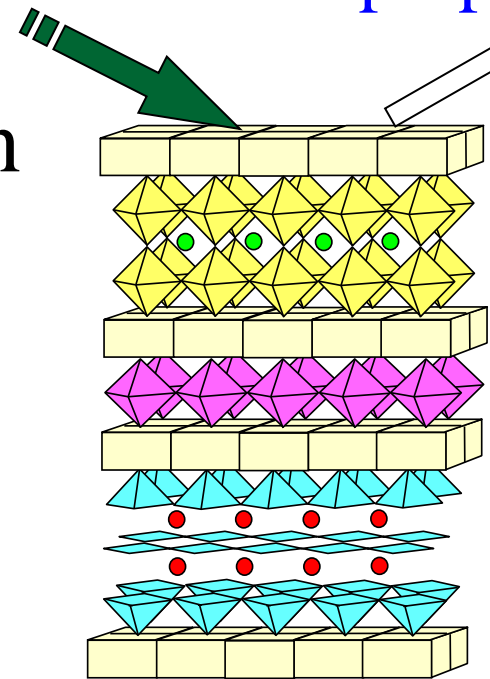
(1) Introduce strain effect

(2) Introduce magnetic interaction between different layers

(3) Integrate different functional materials

$h\nu$, H , E

Nobel
physical
properties

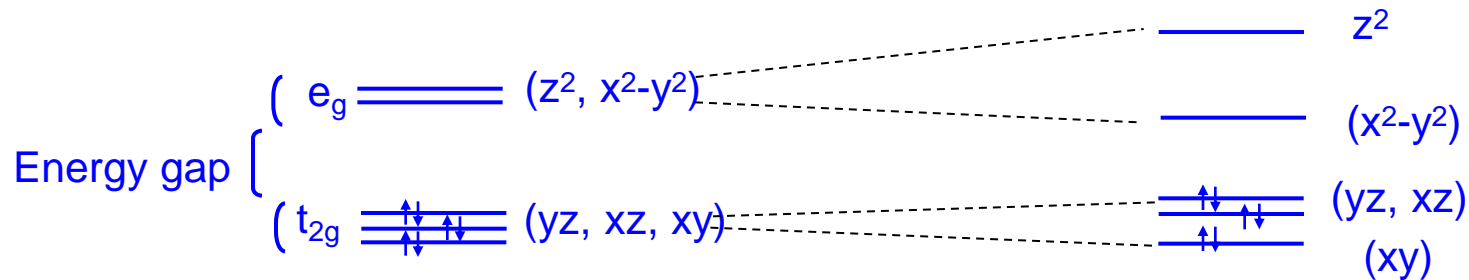
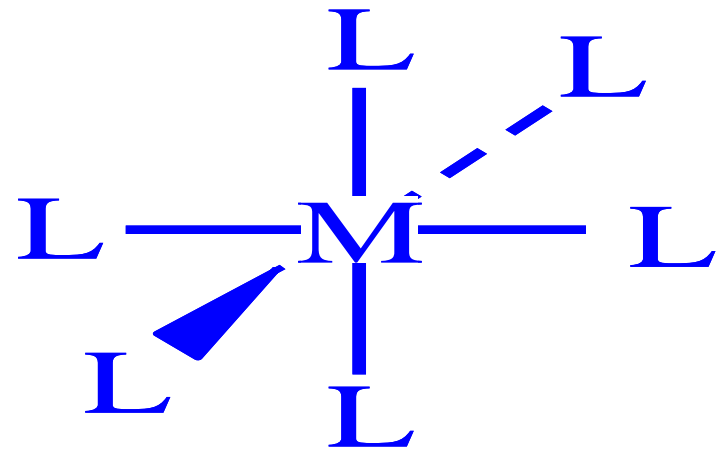
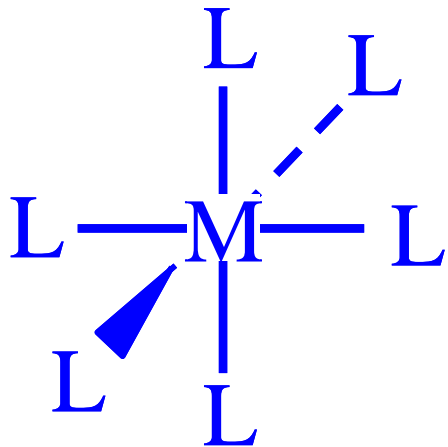




Control of crystal field splitting due to strain effect

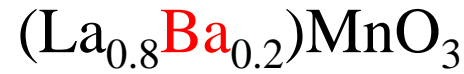
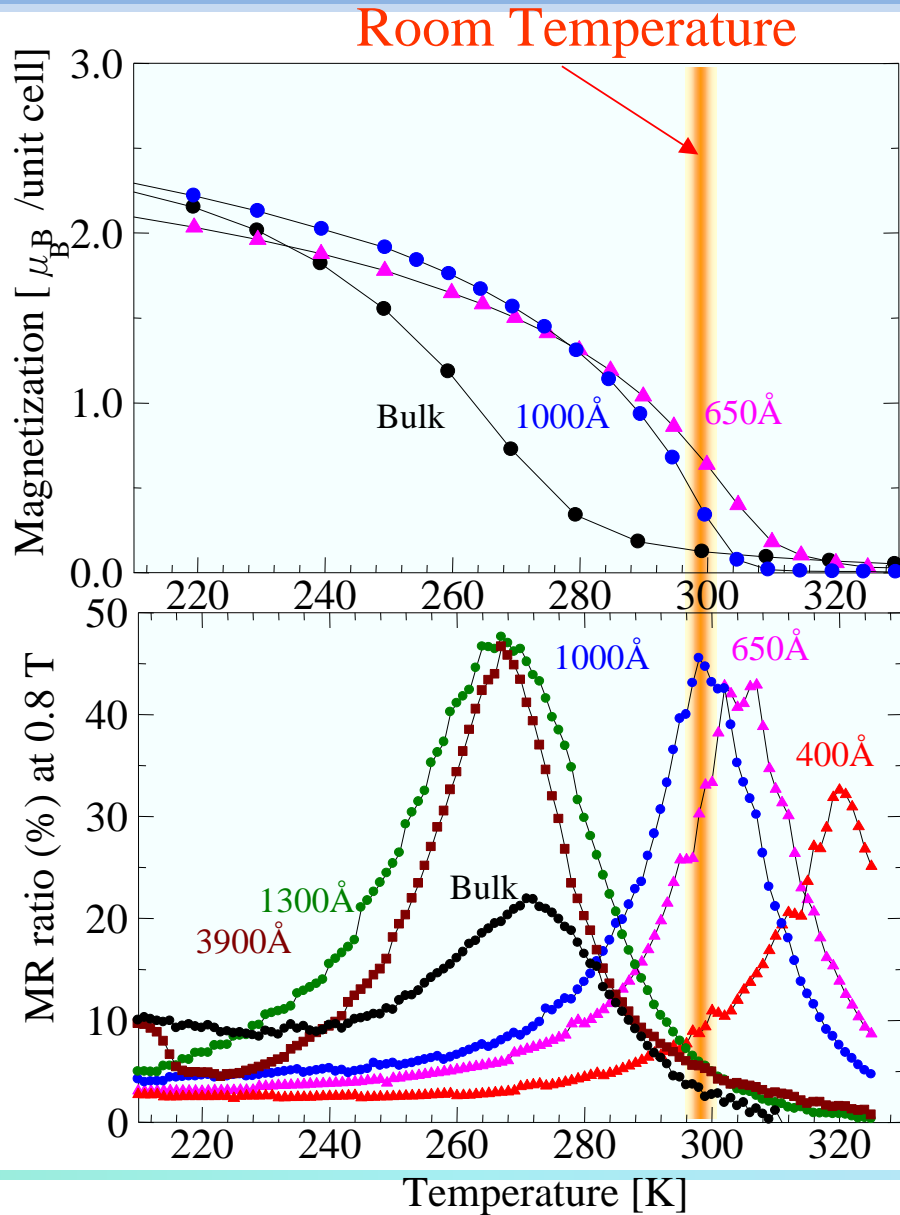
Octahedral coordination

In-plane tensile strain

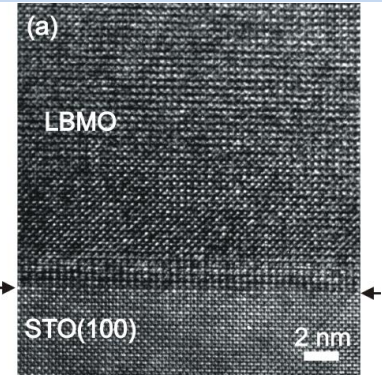




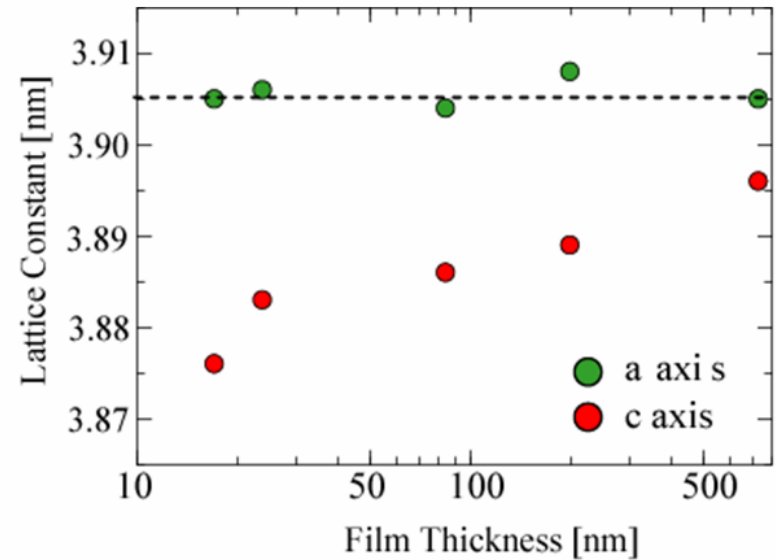
Design of room temperature CMR materials



SrTiO₃ substrate

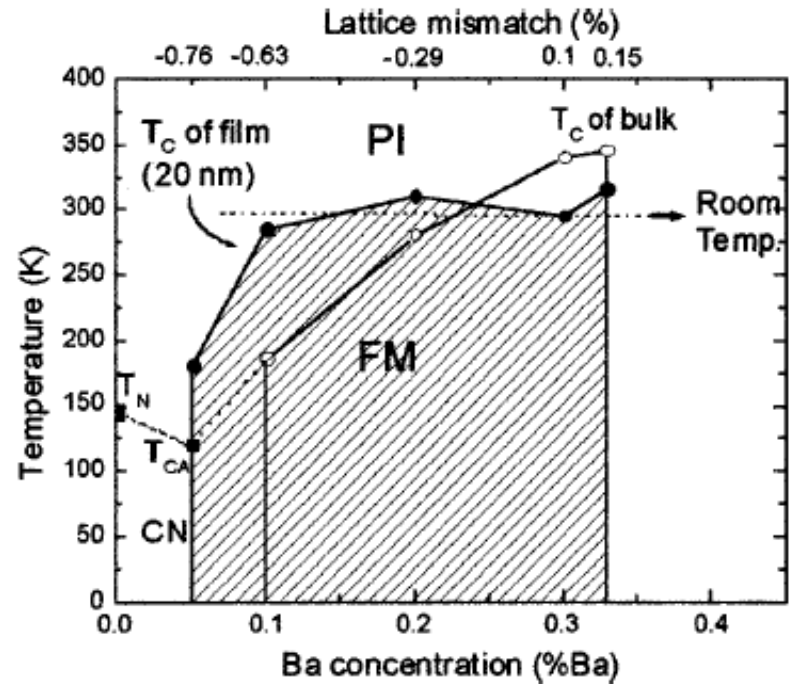
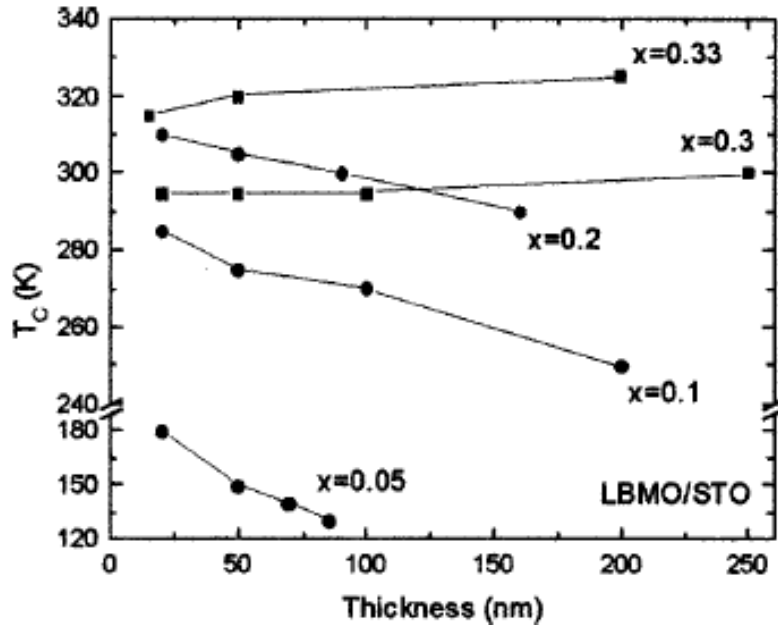


Tensile strain
(0.3%)



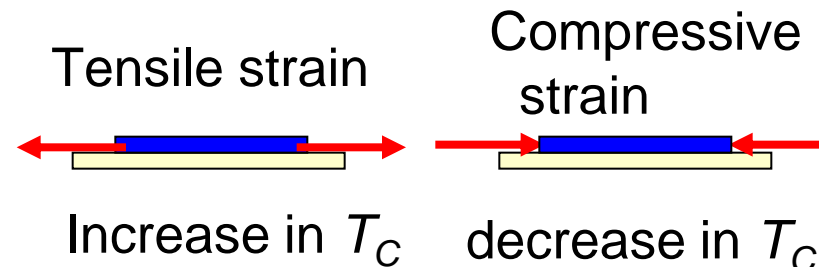


Strain effect vs T_C in LBMO films



Tensile strain \leftarrow \rightarrow Compressive strain

x	0.05	0.1	0.2	0.3	0.33
Lattice mismatch (%)	-0.76	-0.63	-0.29	0.1	0.15
Strain type	T	T	T	C	C
T_C of bulk (K)	120 ^a	185	280	340	345
T_C of film (20 nm) (K)	180	285	310	290	315



^aFor $x=0.05$, spin canting transition temperature $T_{CA}=120$ K.



Stability of double exchange magnetism

Stability of magnetism induced by double exchange interaction

$$\Delta\varepsilon_{ex}^D = zxt_{ij} = zxb_{\sigma} \langle \cos(\theta_{ij} / 2) \rangle$$

C. Zener: Phys. Rev. **82** (1951) 403

P. W. Anderson and H. Hasegawa: Phys. Rev. **100** (1955) 675

P. G. de Gennes: Phys. Rev. **118** (1960) 141

Z: the coordination number of nearest neighbor atoms ; Z=6

t_{ij} : the transfer energy

θ_{ij} : the spin angle between Mn_i and Mn_j

Main parameters indicating the stability of double exchange magnetism

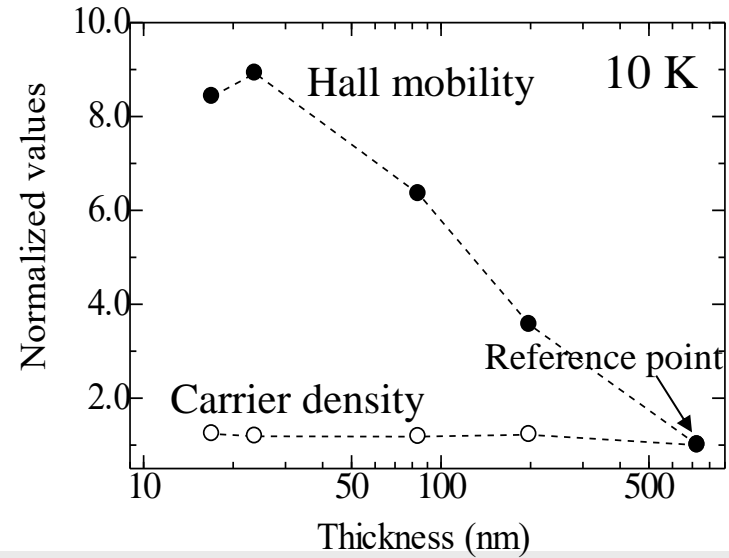
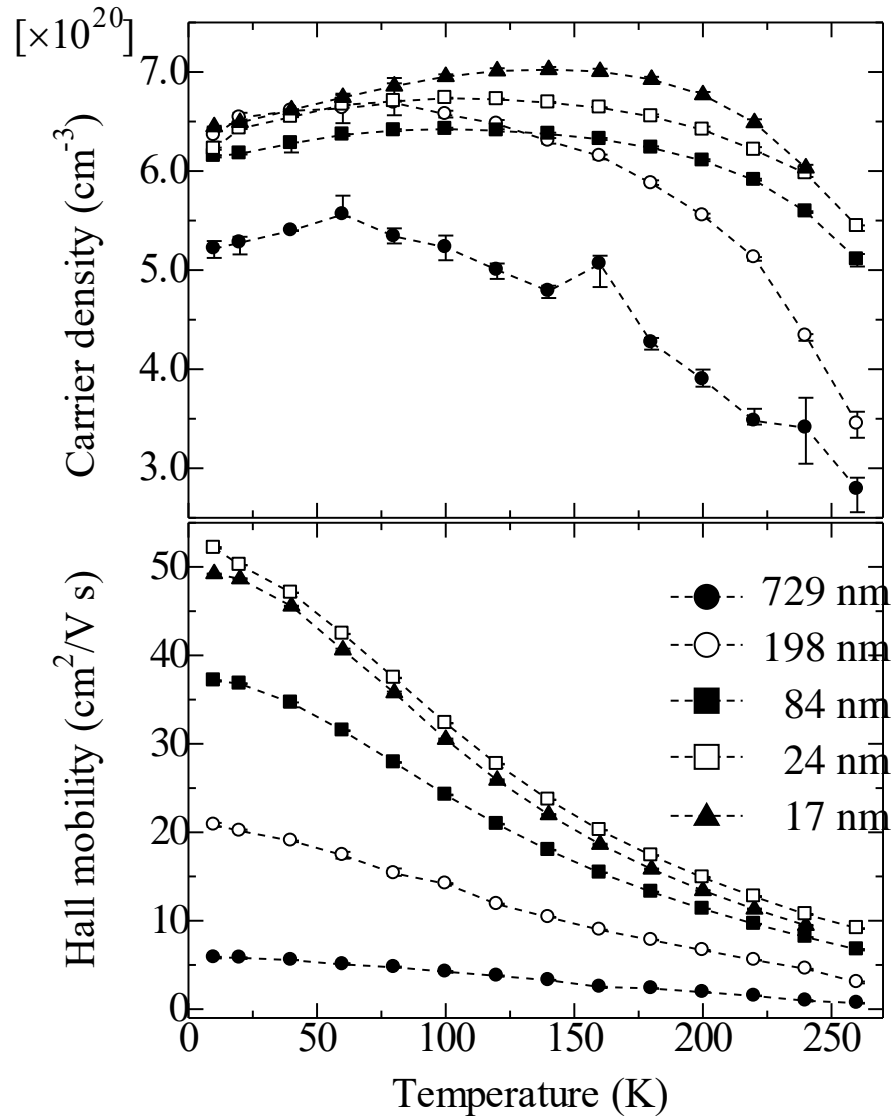
x : the number of carriers per a Mn site

b_{σ} : Spin-independent components

(dependence of orbital overlap and bond angle of Mn-O-Mn)



Carrier density and Hall mobility



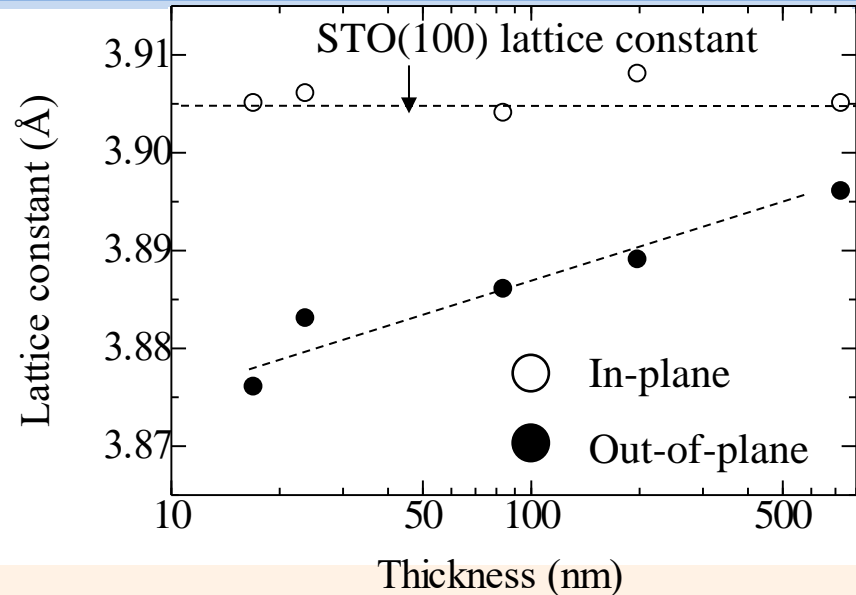
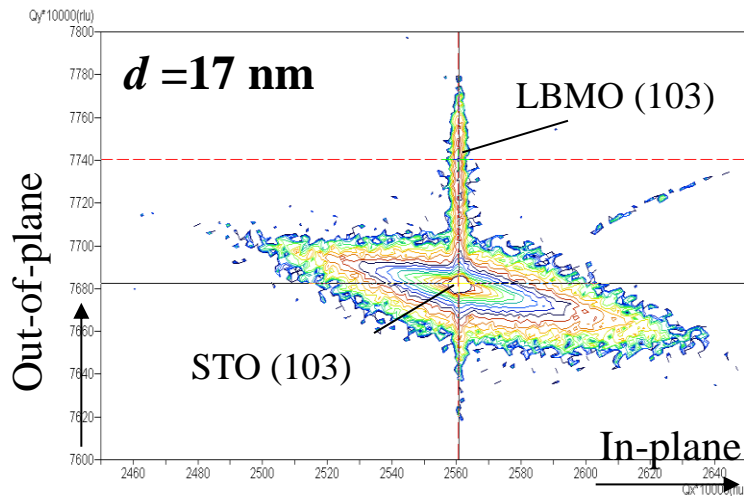
Carrier density : Constant

- ➔ the number of carrier x : constant
- ➔ **Not generating cation deficiency**

Hall mobility : Increase

- ➔ Increase in transfer integral
- ➔ **change in orbital overlap state due to lattice strain effect**

Stability of transfer integral due to lattice strain effect



Calculation of stability in double exchange interaction every thickness

◆ stability of double exchange interaction

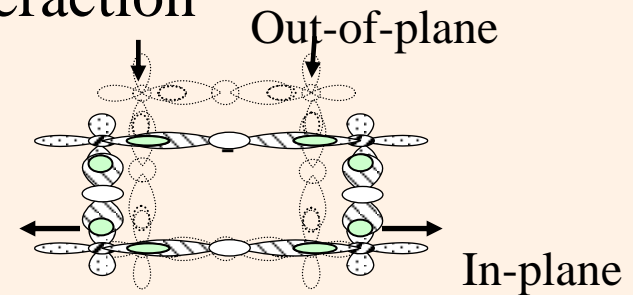
$$\Delta \varepsilon_{ex}^D = z \Delta x \Delta t_{ij} \propto \Delta x \Delta b_{\sigma} \propto \Delta b_{\sigma}$$

x : the number of carriers per a Mn site

b_{σ} : Spin-independent components

(dependence of orbital overlap and bond angle of Mn-O-Mn)

Z : the coordination number of nearest neighbor atoms ; $Z=6$





Contribution elements of stability in double exchange interaction

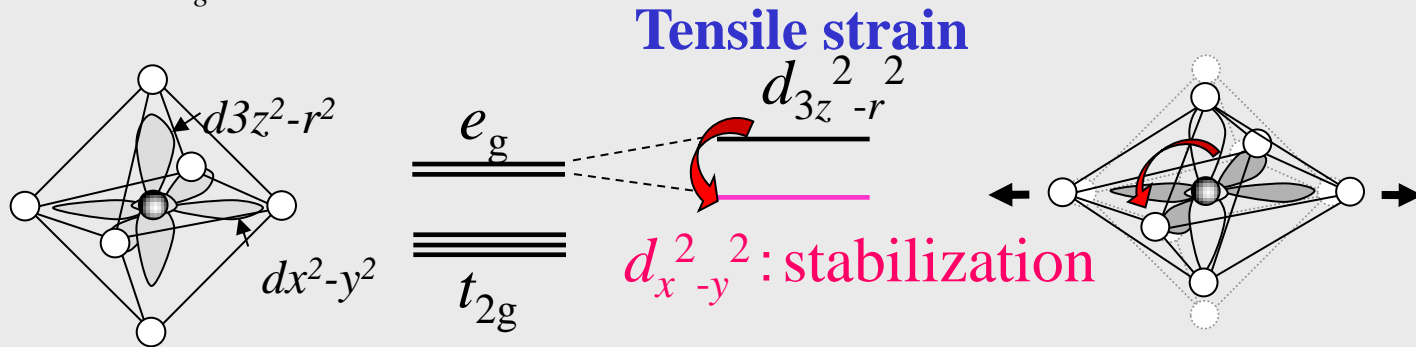
1. In-plane and Out-of-plane orbital overlap

→ determination from lattice constants obtained by experiments

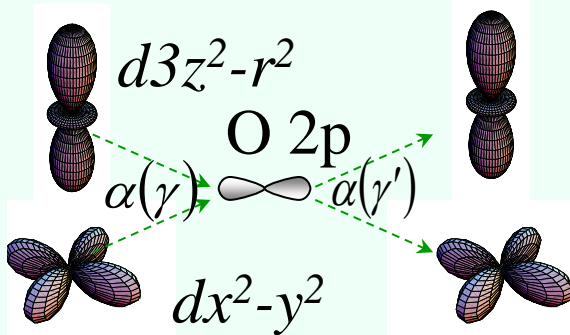
matrix element between p and d orbitals: $V_{pd} = d_{\text{Mn-O}}^{-7/2}$

Mn-O-Mn bond angle: 180°

2. Redistribution of e_g electrons due to lattice strain effect → calculation by the DV- $X\alpha$ method



3. Anisotropy of d orbital



Transfer strength $\gamma \setminus \gamma'$	Out-of-plane		In-plane	
	$ x^2 - y^2\rangle$	$ 3z^2 - r^2\rangle$	$ x^2 - y^2\rangle$	$ 3z^2 - r^2\rangle$
$ x^2 - y^2\rangle$	0	0	3/4	$\sqrt{3}/4$
$ 3z^2 - r^2\rangle$	0	1	$\sqrt{3}/4$	1/4



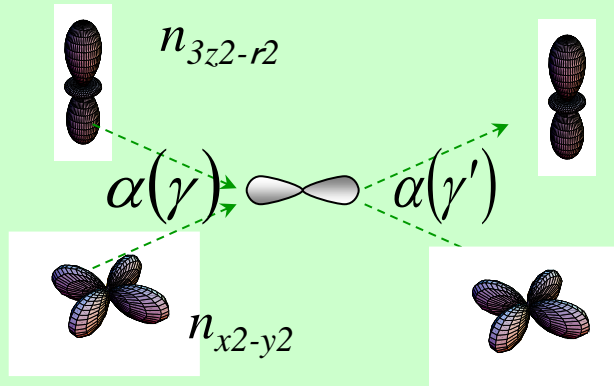
Contribution elements of stability in double exchange interaction

Stability of averaged double exchange interaction

$$\Delta \varepsilon_{ex}^D \propto \sum_{\langle i, j \rangle} (n_{x^2-y^2}, n_{3z^2-r^2}, \alpha(\gamma_i)\alpha(\gamma'_j), d_{in}^{-7}, d_{out}^{-7})$$

Transfer strength from Mn3d orbital to O2p orbital $\alpha(\gamma)$

Transfer strength from O2p orbital to Mn3d orbital $\alpha(\gamma')$



d_{in} : the in-plane Mn-O length
 d_{out} : the out-of-plane Mn-O length
 → derived by XRD measurement

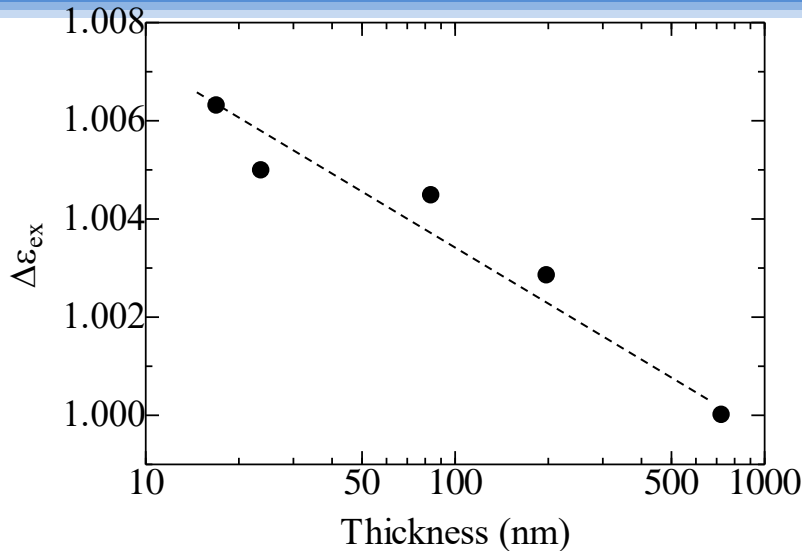
$n_{x^2-y^2}$: the ration of occupied electrons in $d_{x^2-y^2}$ orbital
 $n_{3z^2-r^2}$: the ration of occupied electrons in $d_{3z^2-r^2}$ orbital
 → calculation by the DV- $X\alpha$ method using experimental lattice constants

In-plane: 4 directions

Out-of-plane : 2 directions

$$\Delta \varepsilon_{ex}^D \propto \left((3 + \sqrt{3})n_{x^2-y^2} + (1 + \sqrt{3})n_{3z^2-r^2} \right) d_{in}^{-7} + 2n_{3z^2-r^2} d_{out}^{-7}$$

Stability of double exchange magnetism

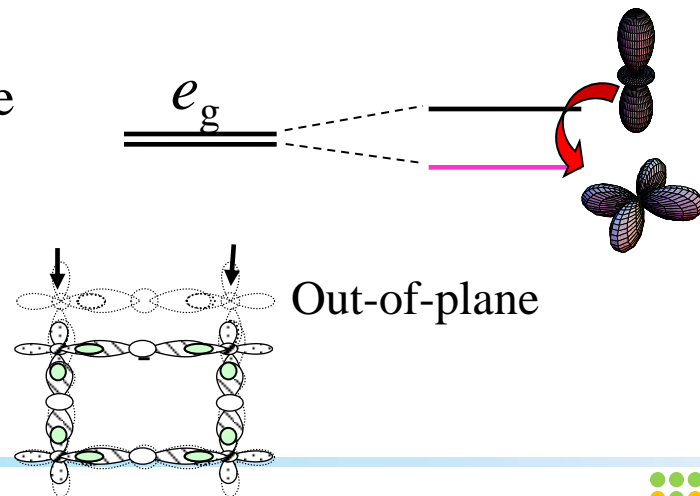


Stabilization of double exchange interaction with decreasing film thickness

What is main factors of T_C increase in strained (La,Ba)MnO₃ thin films

◆ redistribution effect by e_g electrons due to anisotropy d orbital.

◆ Orbital overlap of in-plane and out-of-plane





Function of interface

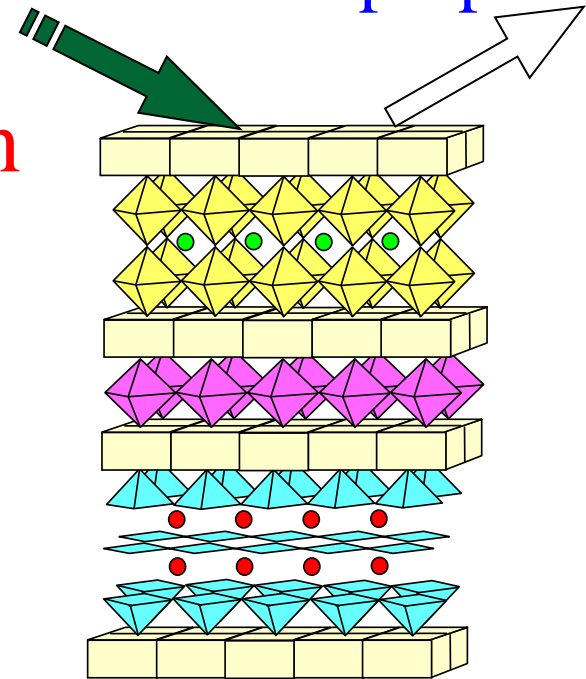
(1) Introduce strain effect

(2) Introduce magnetic interaction
between different layers

(3) Integrate different functional
materials

$h\nu$, H , E

Nobel
physical
properties



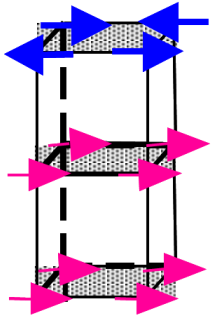
Control of interface magnetic interaction

Conductive electron

Localized spin

$$H = -t_{\text{Mn-Mn}} \cos\left(\frac{\theta}{2}\right) - K_{\text{Hund}} \sigma S_{\text{Mn}} - J_{\text{t2g}} \sum_{\text{LMnO}} S_{\text{Mn}}^{t2g} S_{\text{Mn}}^{t2g} - J_{\text{Fe-Mn}} S_{\text{Mn}}^{t2g} S_{\text{Fe}} - \sum_{\text{LFeO}} J_{\text{Fe-Fe}} S_{\text{Fe}} S_{\text{Fe}}$$

Antiferromagnet LaFeO_3 Interface magnetic interaction

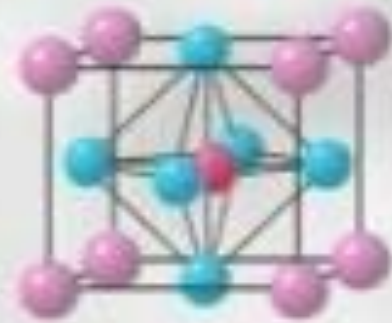


Combined with two materials

Ferromagnet $(\text{La,Sr})\text{MnO}_3$



Spin frustration superlattice

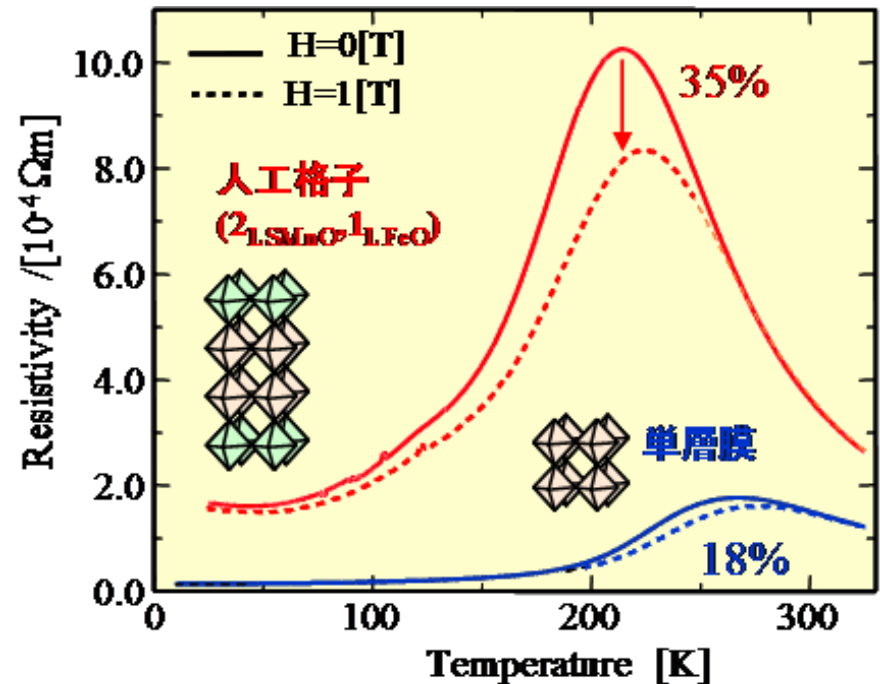
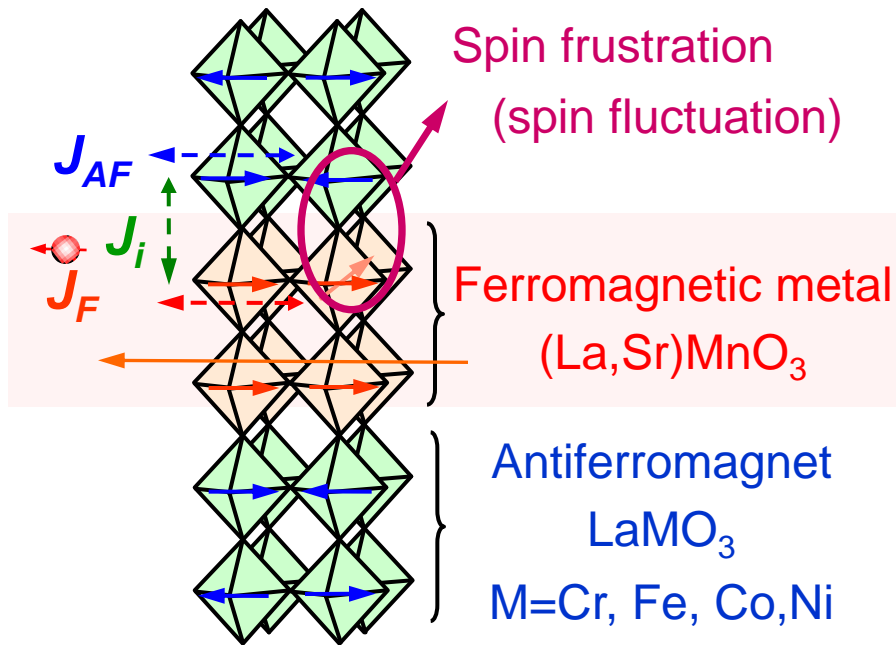


(2006)



High sensitive response by magnetic field

Spin frustration superlattice

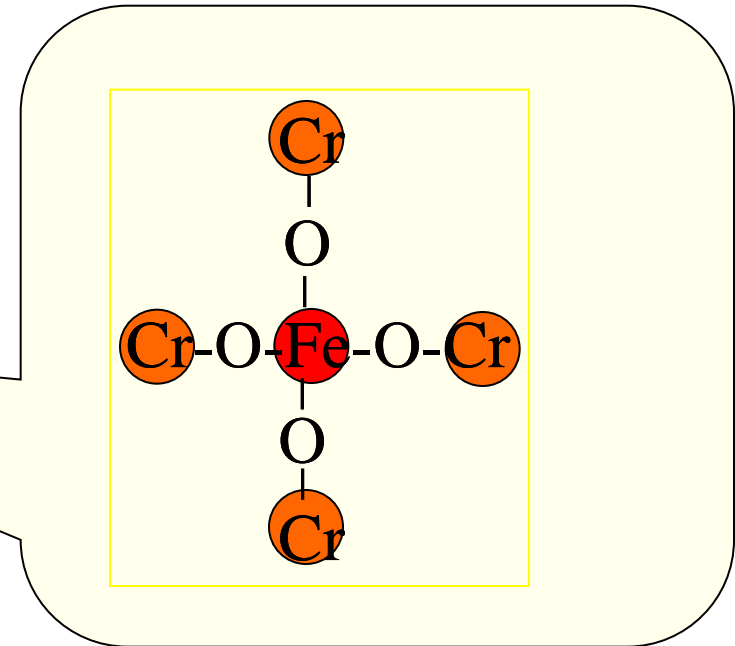
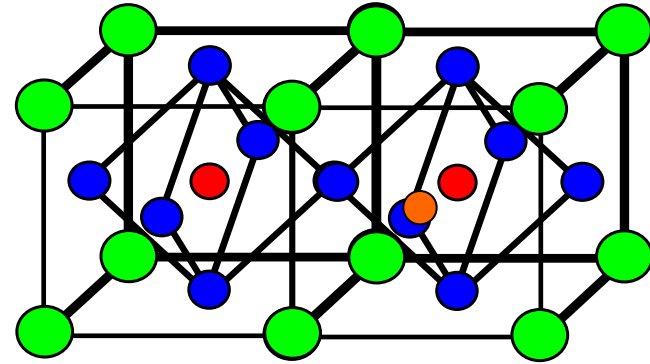




Theoretical prediction : New ferromagnet

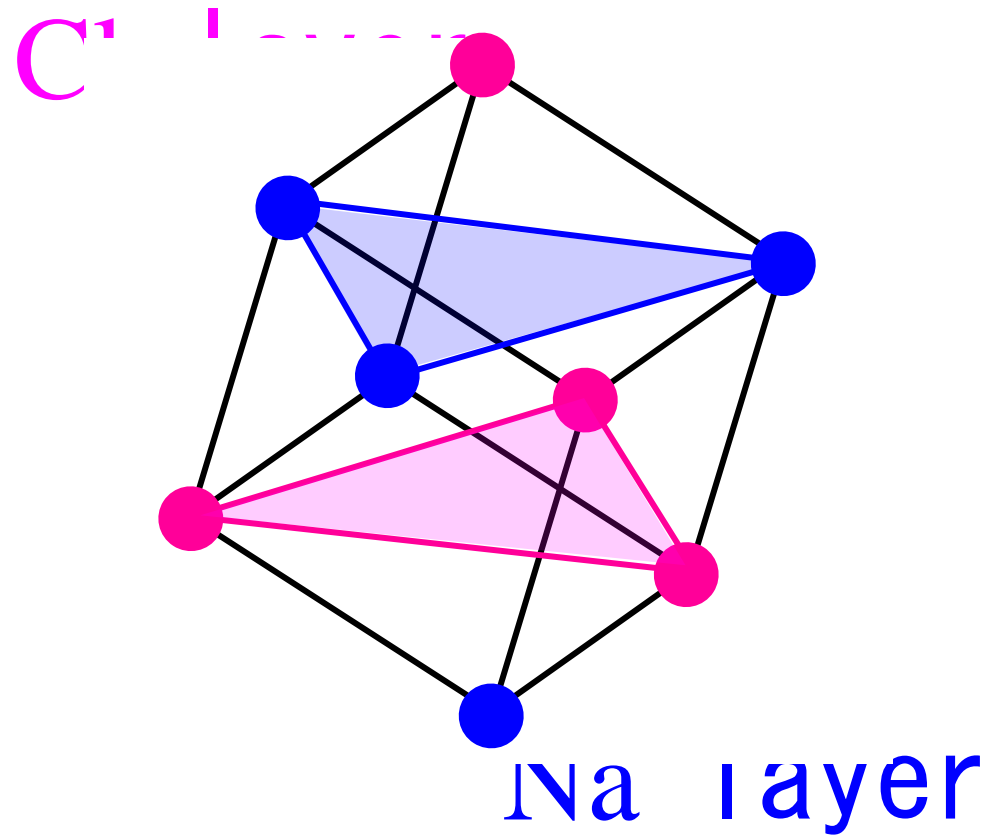
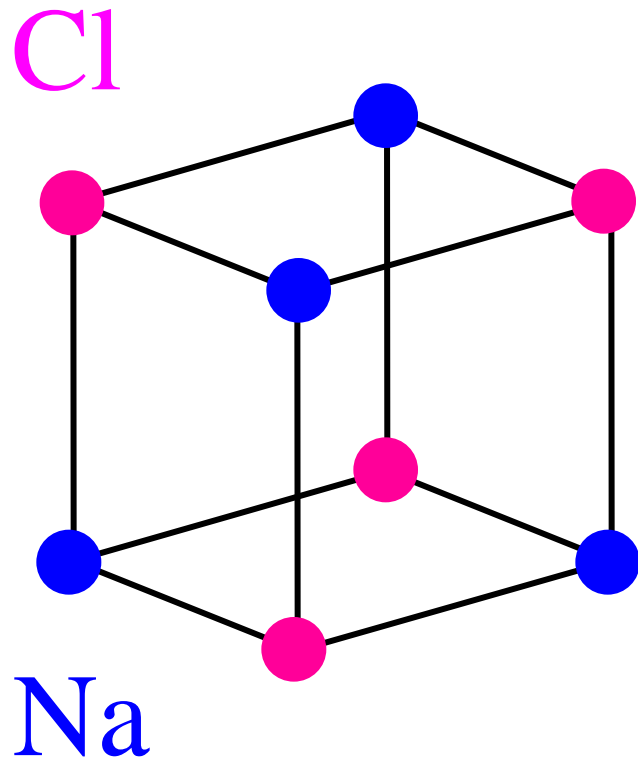
60 years ago

Kanamori former
president of Osaka Univ.

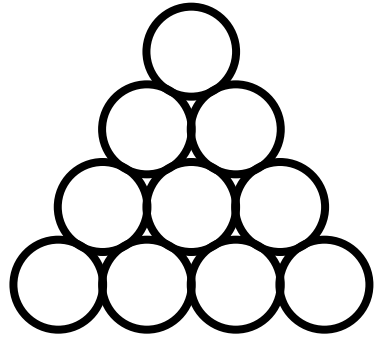




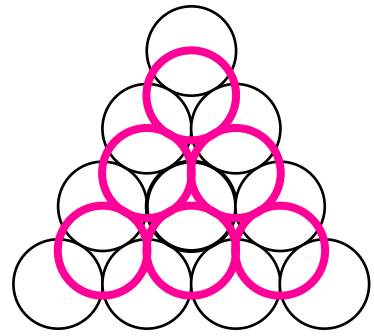
NaCl structure



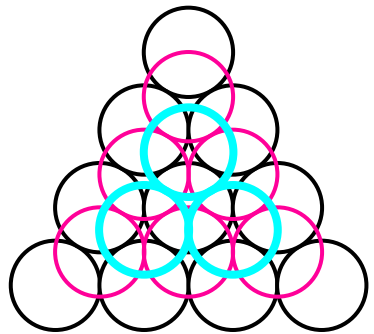
Lattice-direction control superlattice



○○○○○
1st layer

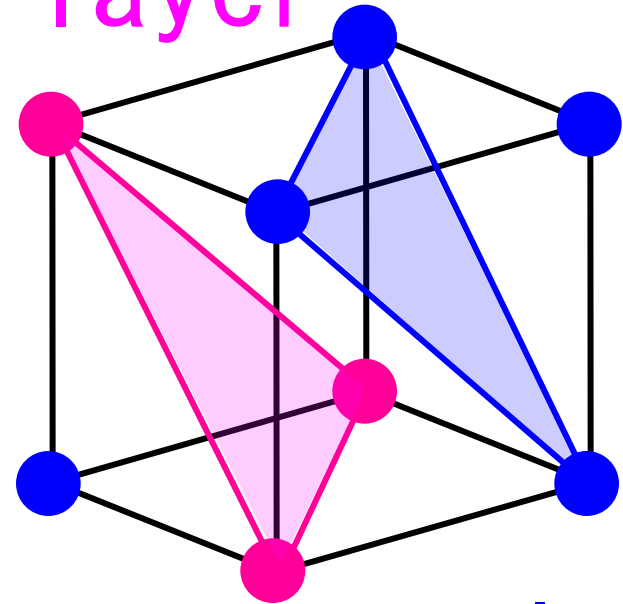


○○○○○
○○○○○
2nd layer



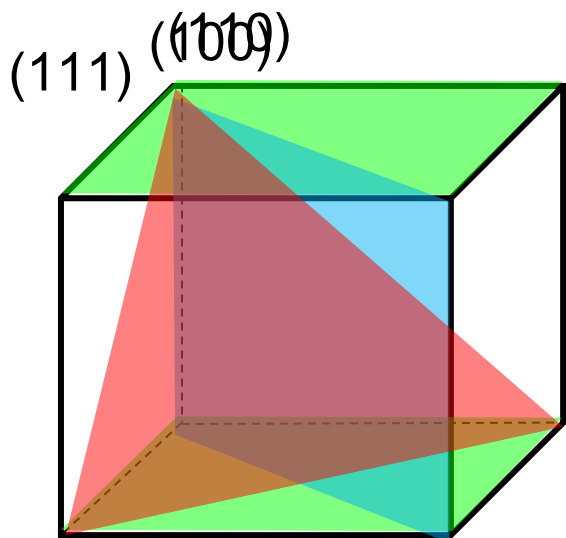
○○○○○
○○○○○
○○○○○
3rd layer

Cl layer

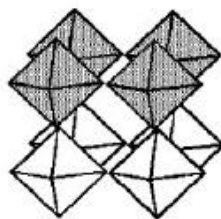


Na layer

Lattice-direction control superlattice

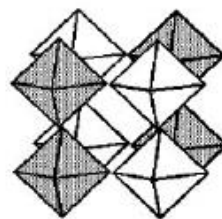


ABO₃-AB'O₃ superlattice



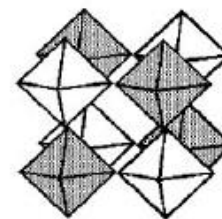
(100)

layer type



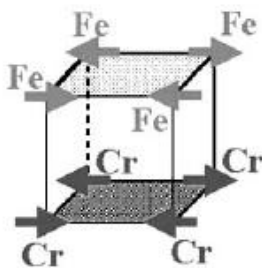
(110)

stripe type

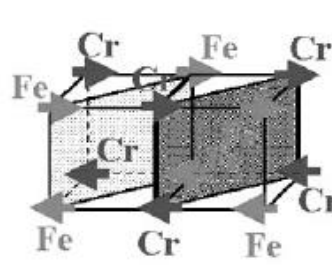


(111)

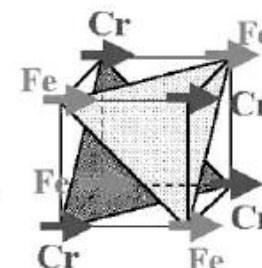
rock-salt type



C-type AF



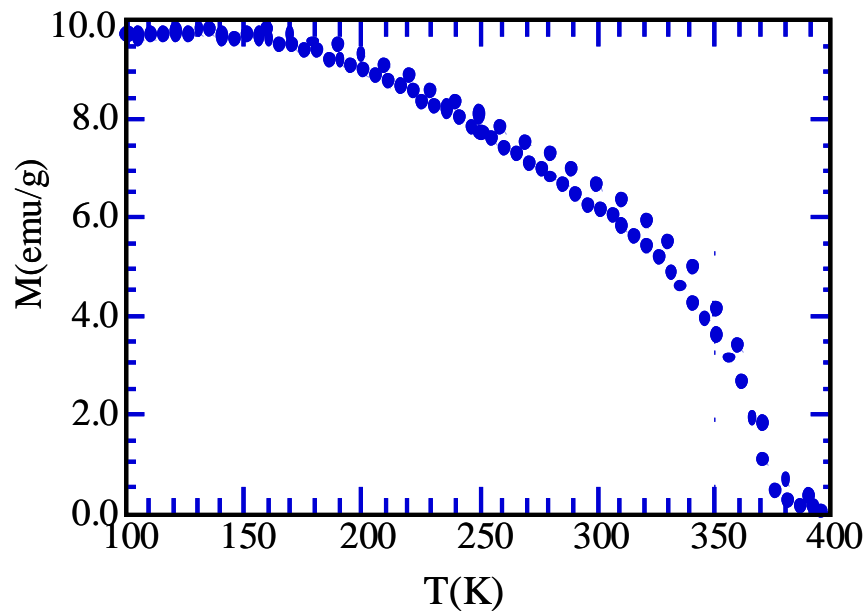
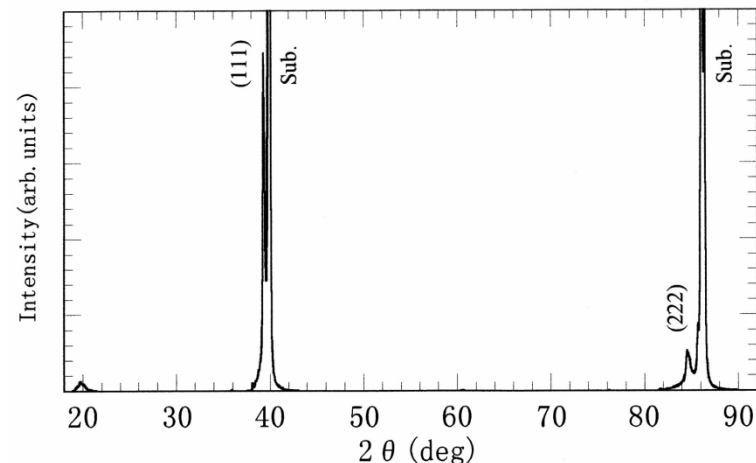
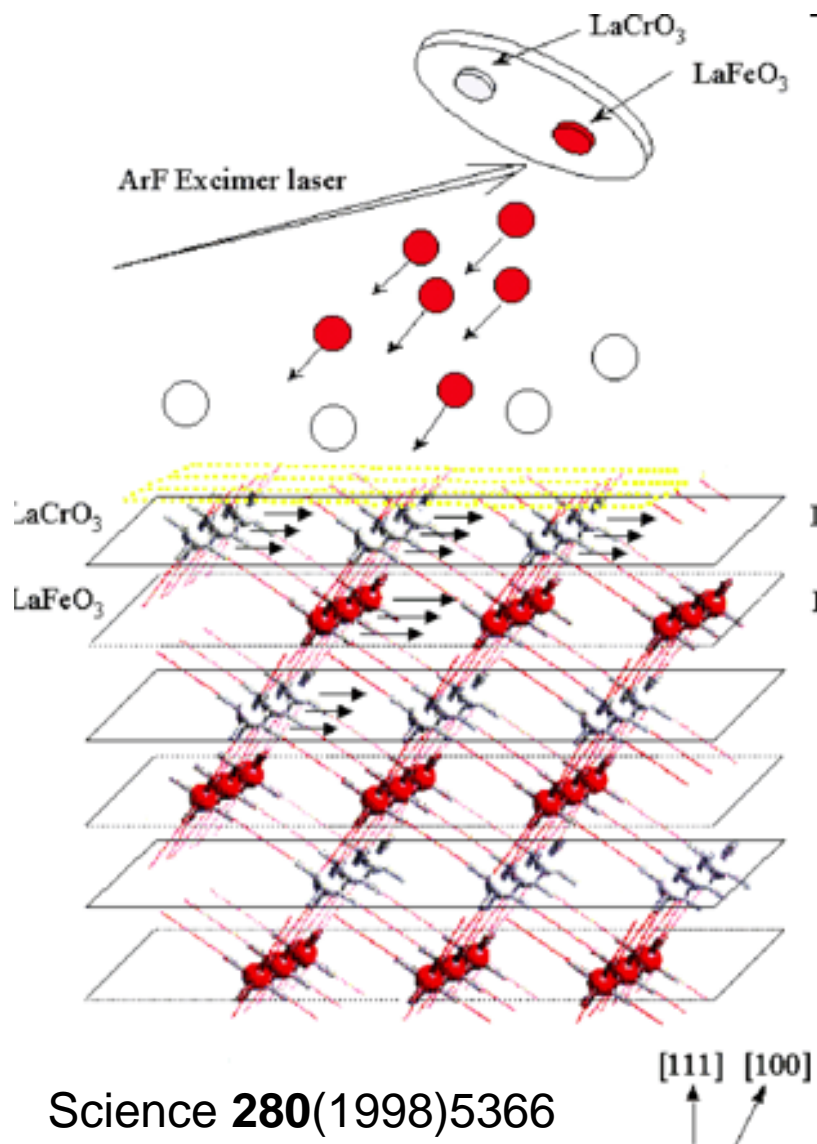
A-type AF



FM(F-type)

JAP89(2001)2847

Lattice-direction control superlattice





Integration of different functional materials

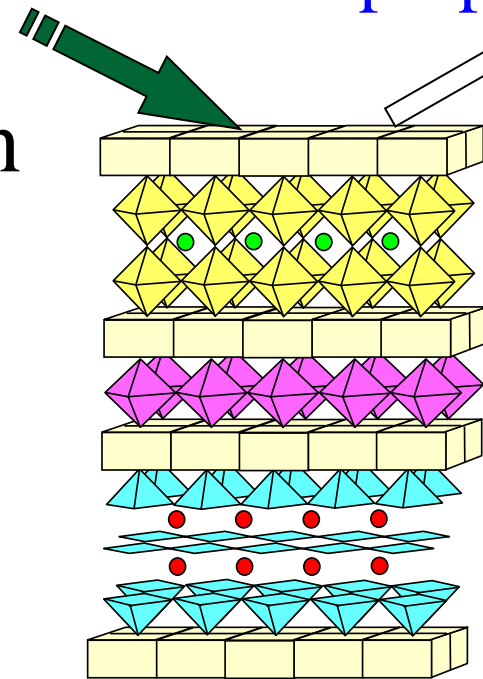
(1) Introduce strain effect

(2) Introduce magnetic interaction between different layers

(3) Integrate different functional materials

$h\nu$, H , E

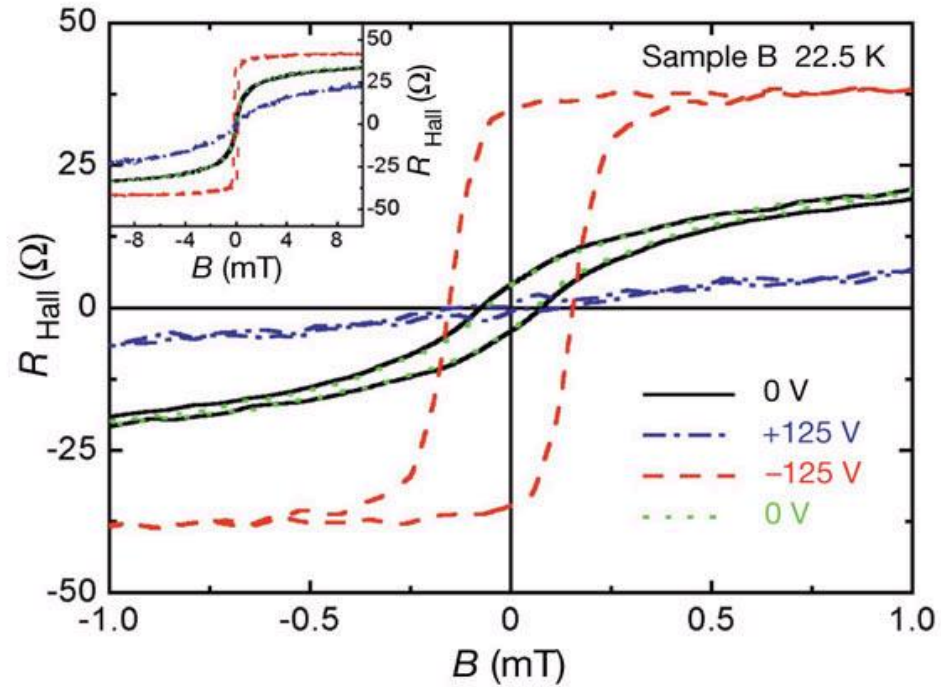
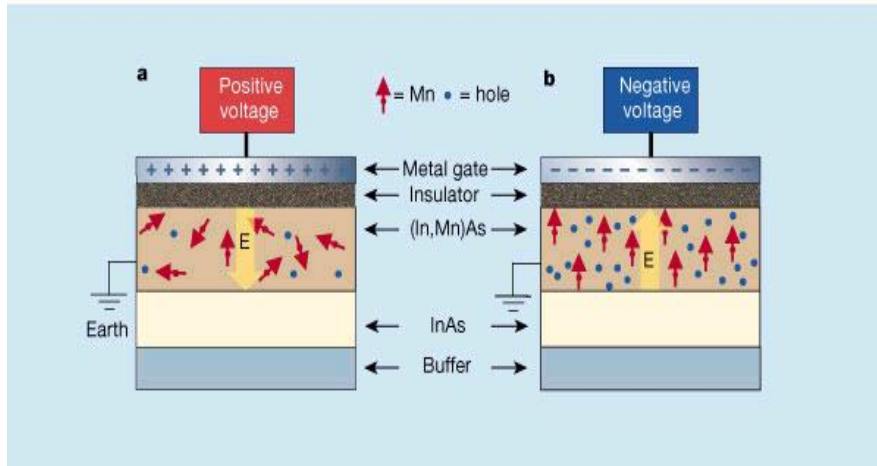
Nobel
physical
properties





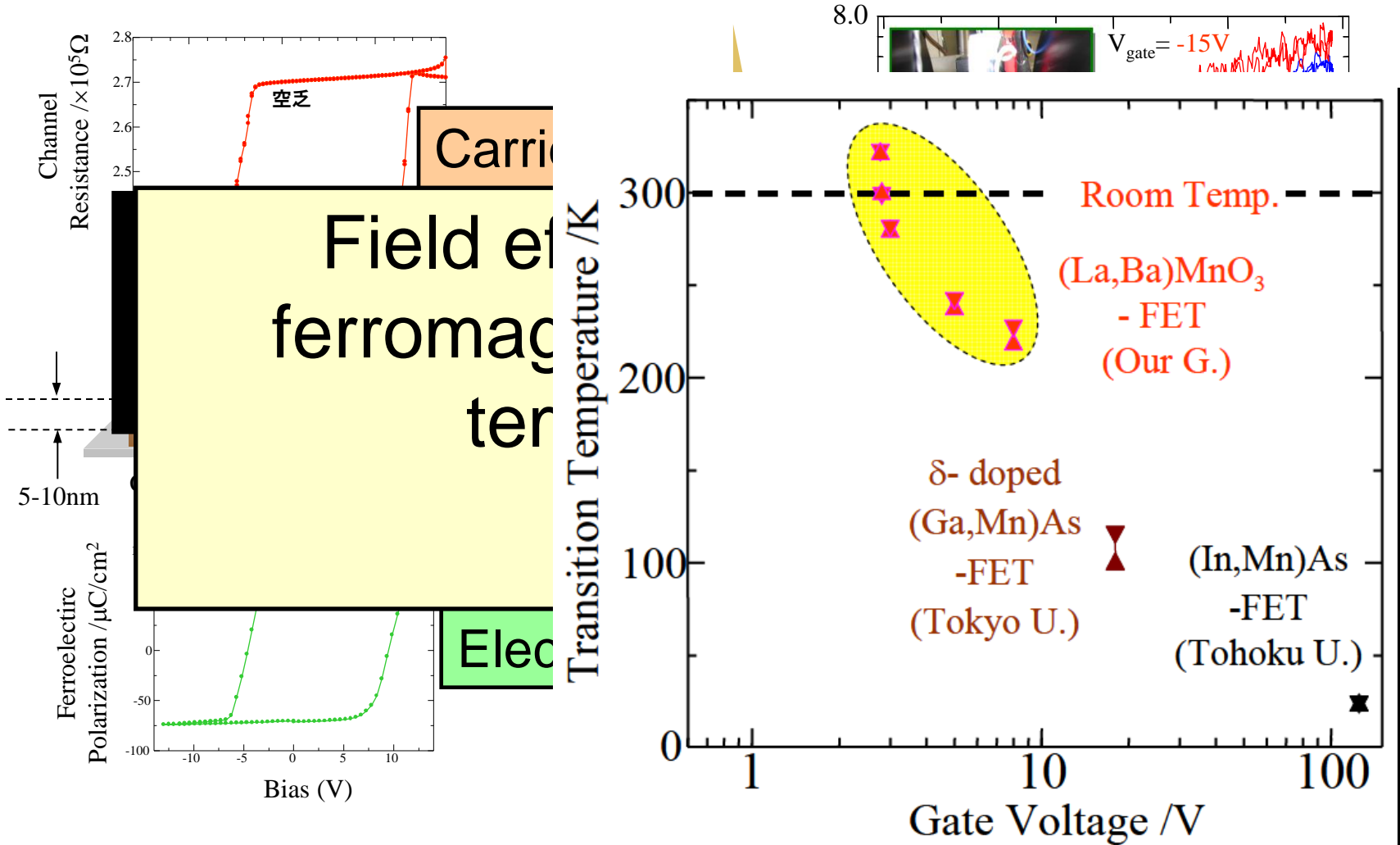
Diluted magnetic semiconductor-- (In,Mn)As

Field effect transistor





Ferromagnet/Ferroelectric material combination





Ferromagnet/Ferroelectric material combination

Conductive electron

$$H = -t_{\text{Mn-Mn}} \cos\left(\frac{\theta}{2}\right) - K_{\text{Hund}} \sigma \mathcal{S}_{\text{Mn}}$$

Localized spin

$$-J_{t2g} \sum_{LMnO} S_{\text{Mn}}^{t2g} S_{\text{Mn}}^{t2g}$$

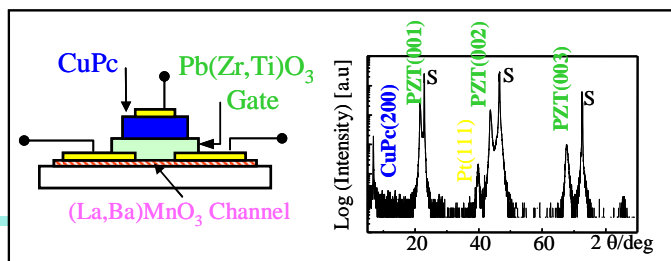
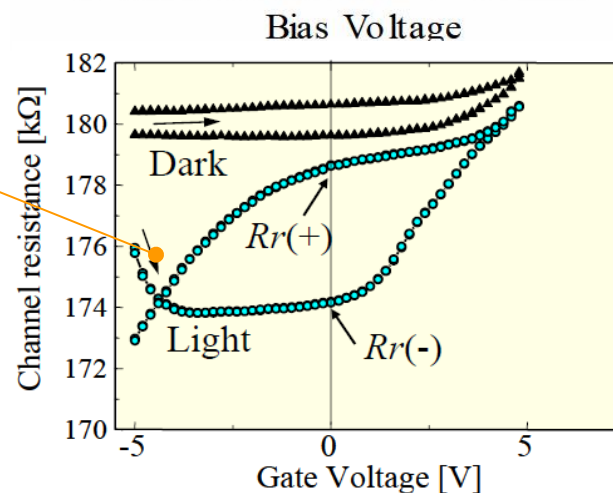
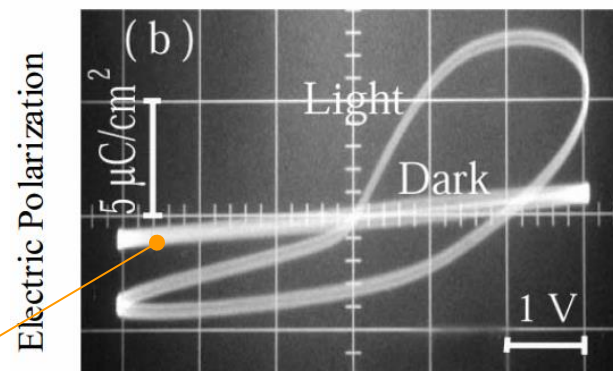
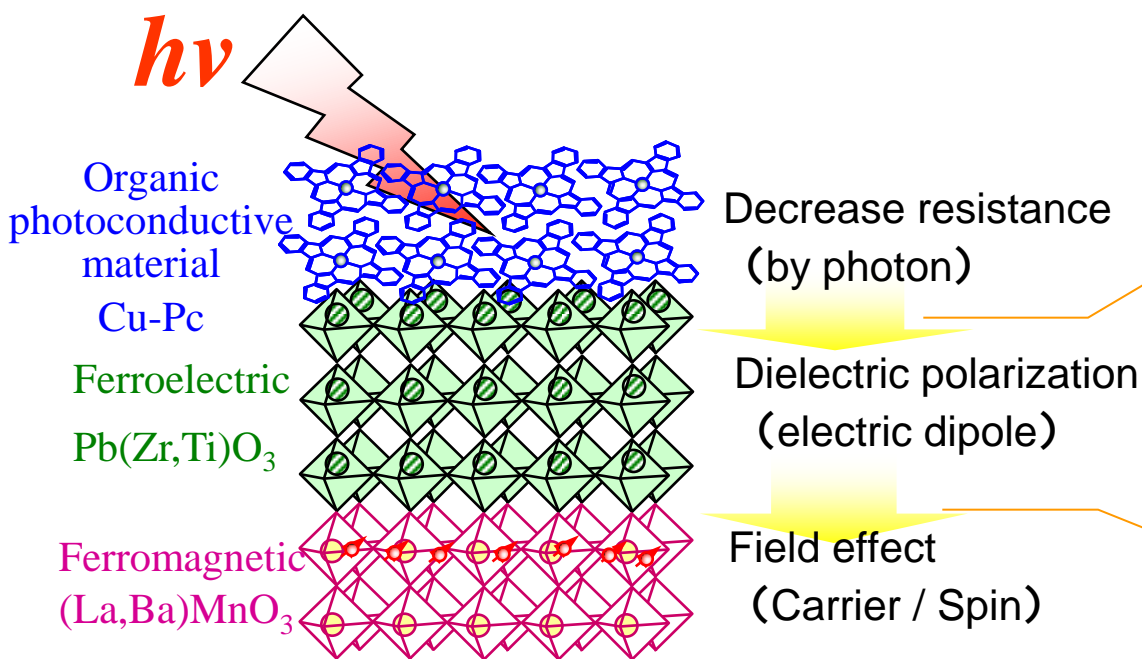
$$N \times$$

(The number of carriers)

Electric field

Photonic/Ferroelectric/magnetic material combination

Photon → Electric dipole → Carrier spin





Summary: Oxide spintronics

- (1) Introduce strain effect ----- Room temperature CMR
- (2) Introduce magnetic interaction --- Magnetic superlattice
between different layers Design of magnetic susceptibility
- (3) Integrate different functional ----- Ferromagnetism
materials + Ferroelectric