CMD47

2025/9/3　Lecture 7 (15:00-16:30)

Functional Oxide Spintronics and the material design

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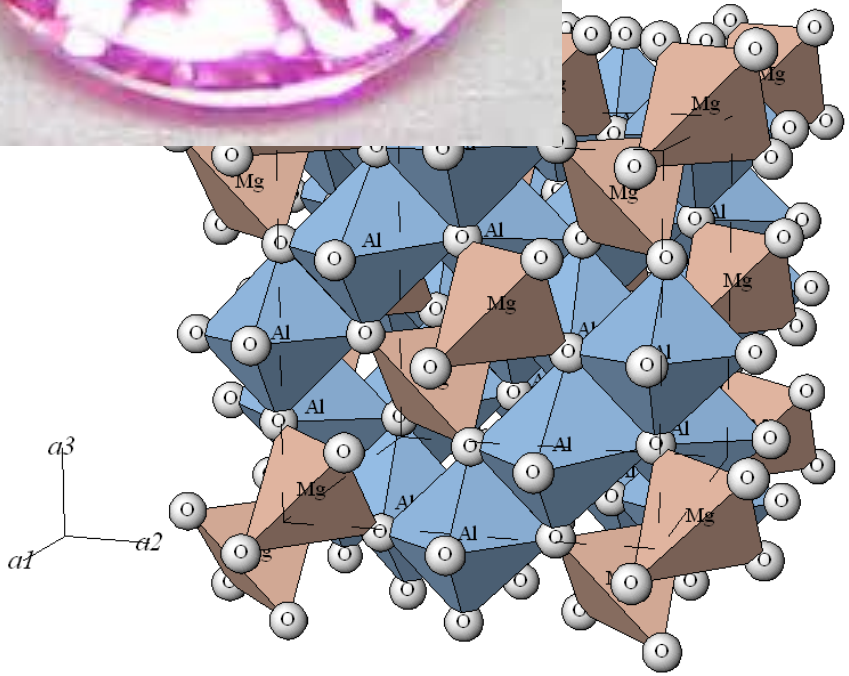
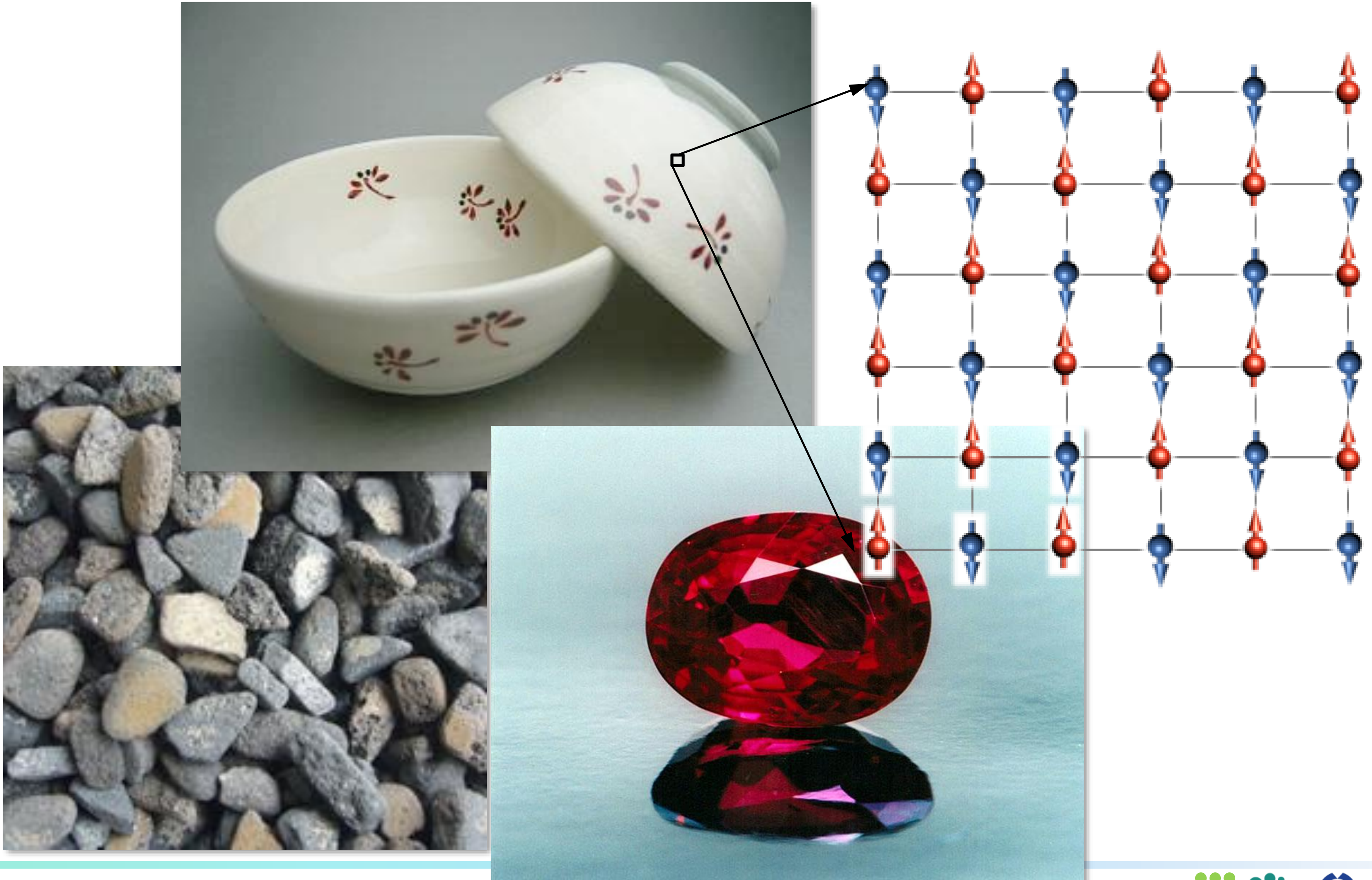
Ceramics

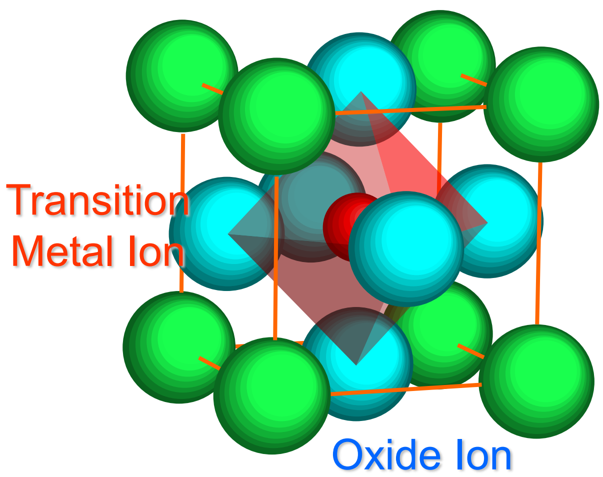
Jewelry (Spinel, Garnet)



Functional Oxides



Transition Metal Oxides



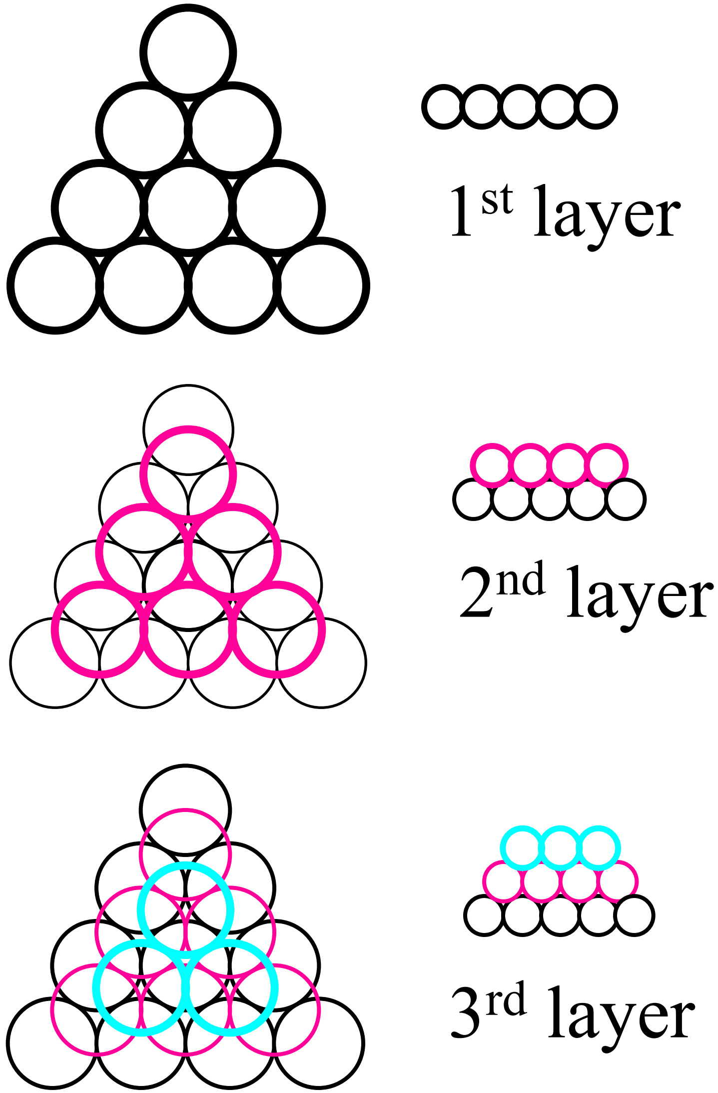
22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu
47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55
チタン	バナジウム	クロム	マンガン	鉄	コバルト	ニッケル	銅
Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper

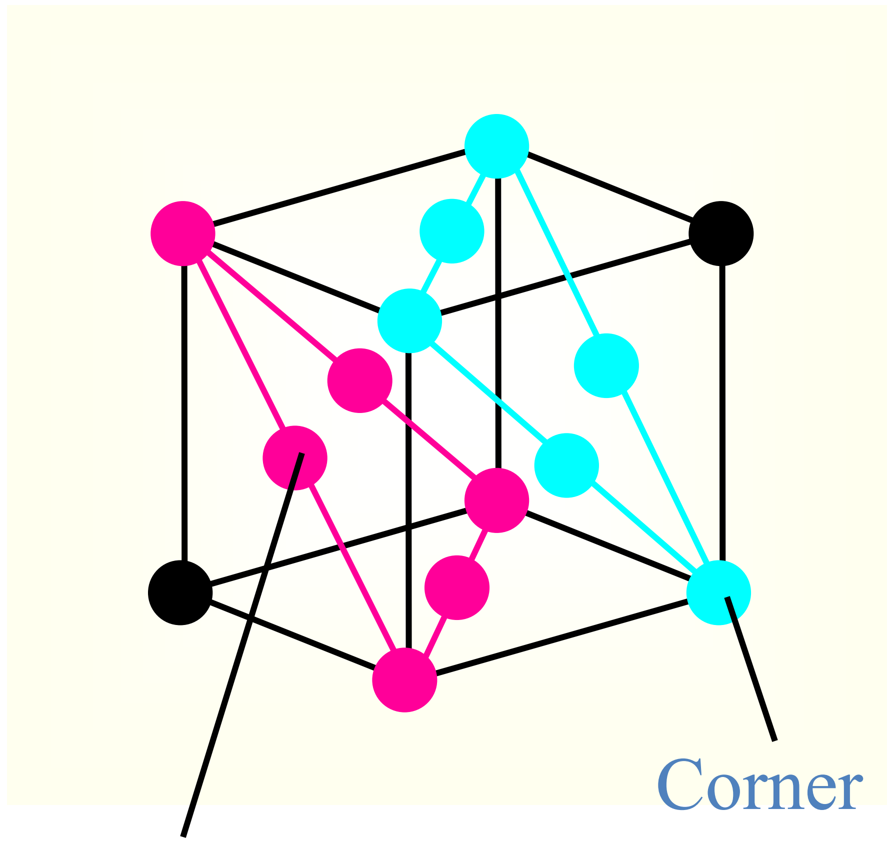
Ferro dielectrics
Anti-/Ferro magnetics
High temperature superconductors
Piezoelectrics
Colossal MR
Conductors

Memory (DRAM, FRAM、RRAM)
Magnetic head
Magnetic recorder
Josephson junction
Memory (MRAM)
electrode
SQUID
Piezoelectric devices
Bolometer

Information processing and data storage materials related with our daily life

Face-centered cubic => Closed pack structure





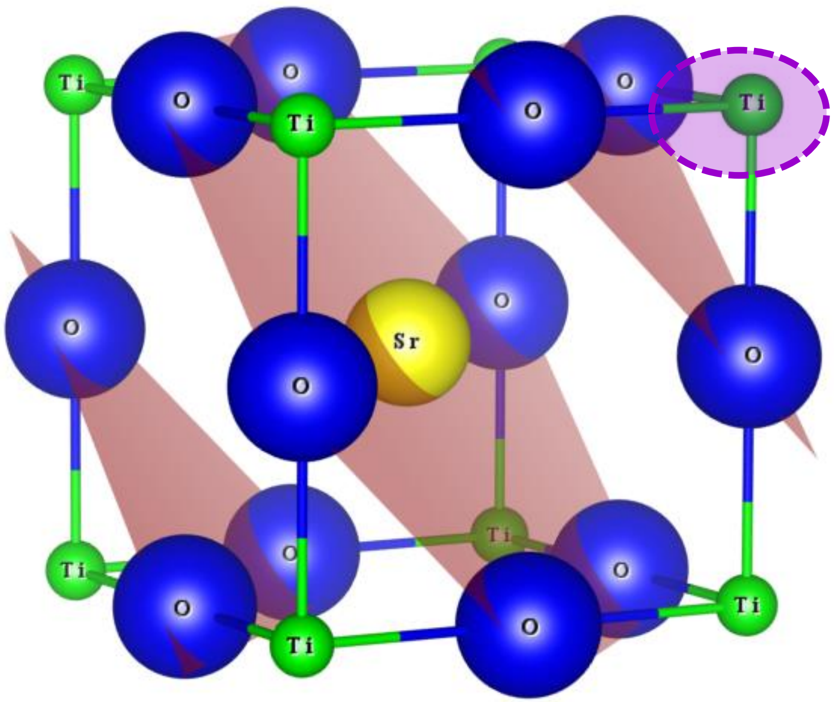
Perovskite structure：ABO_3 *e.g.* $SrTiO_3$

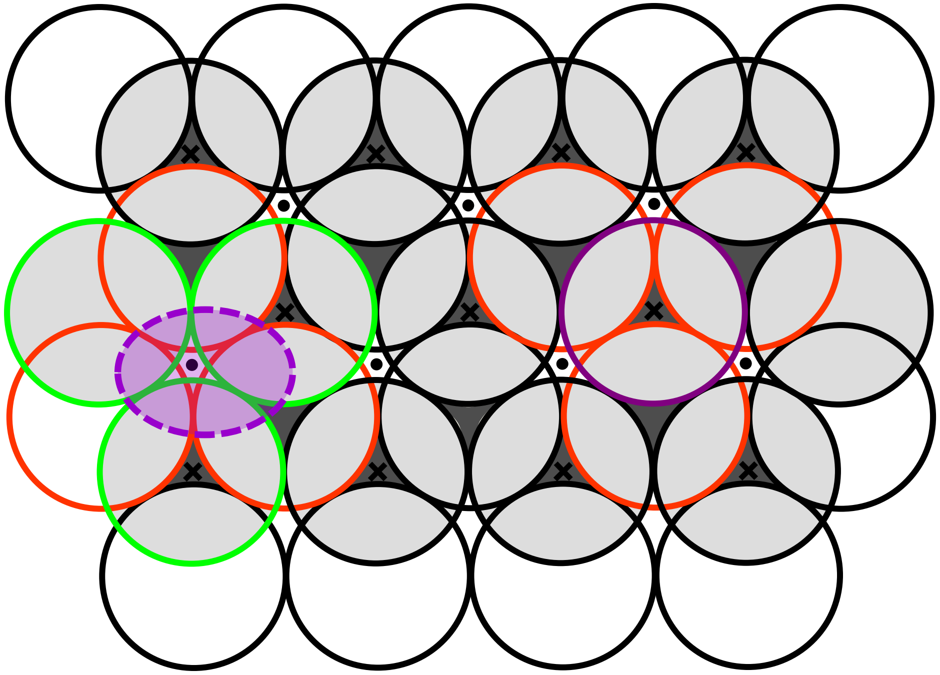
Interspace of close packed oxide ions：Octahedral interspace

O^{2-}=1.40 Å ,

Sr^{2+}=1.44 Å (12 coordination),

≥0.414r Ti^{4+}=0.42 Å (6 coordination)





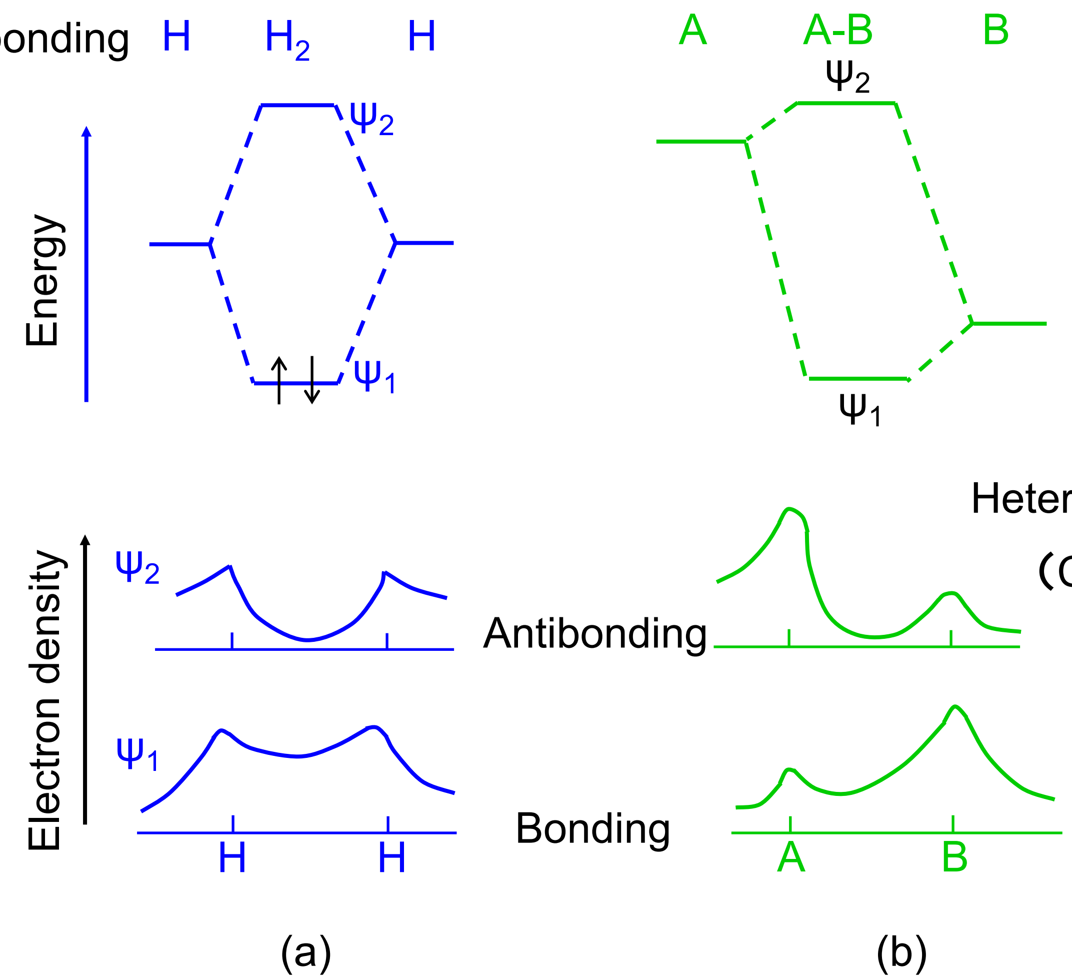
Orbital bonding

Bonding and Antibonding states ⇨ Valence and Conduction band

Covalent bonding

$\psi_2 = \chi_A - \chi_B$

$\psi_1 = \chi_A + \chi_B$



Ion bonding

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

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

Heteronuclear diatomic molecule

(Covalent or Ionic characters)

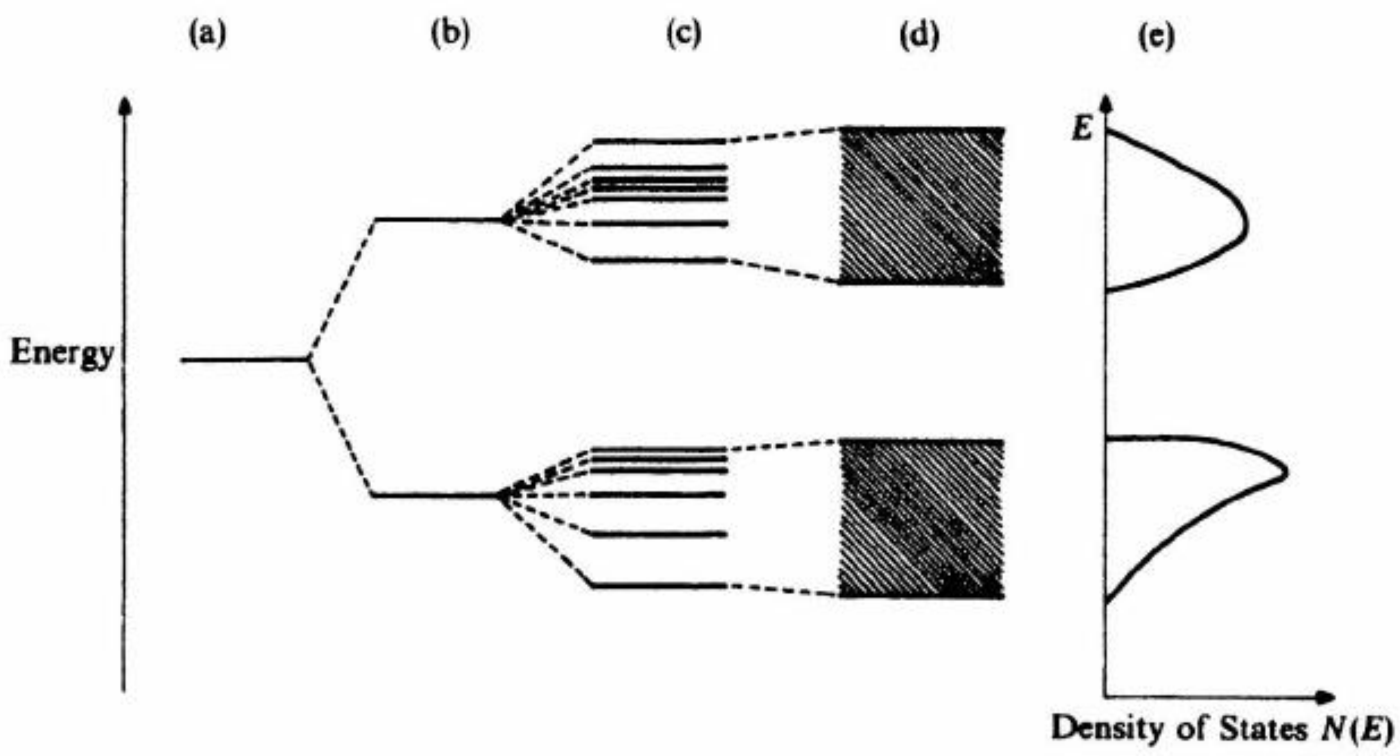
↓

Different orbital level

Electronegativity
Ionization potential

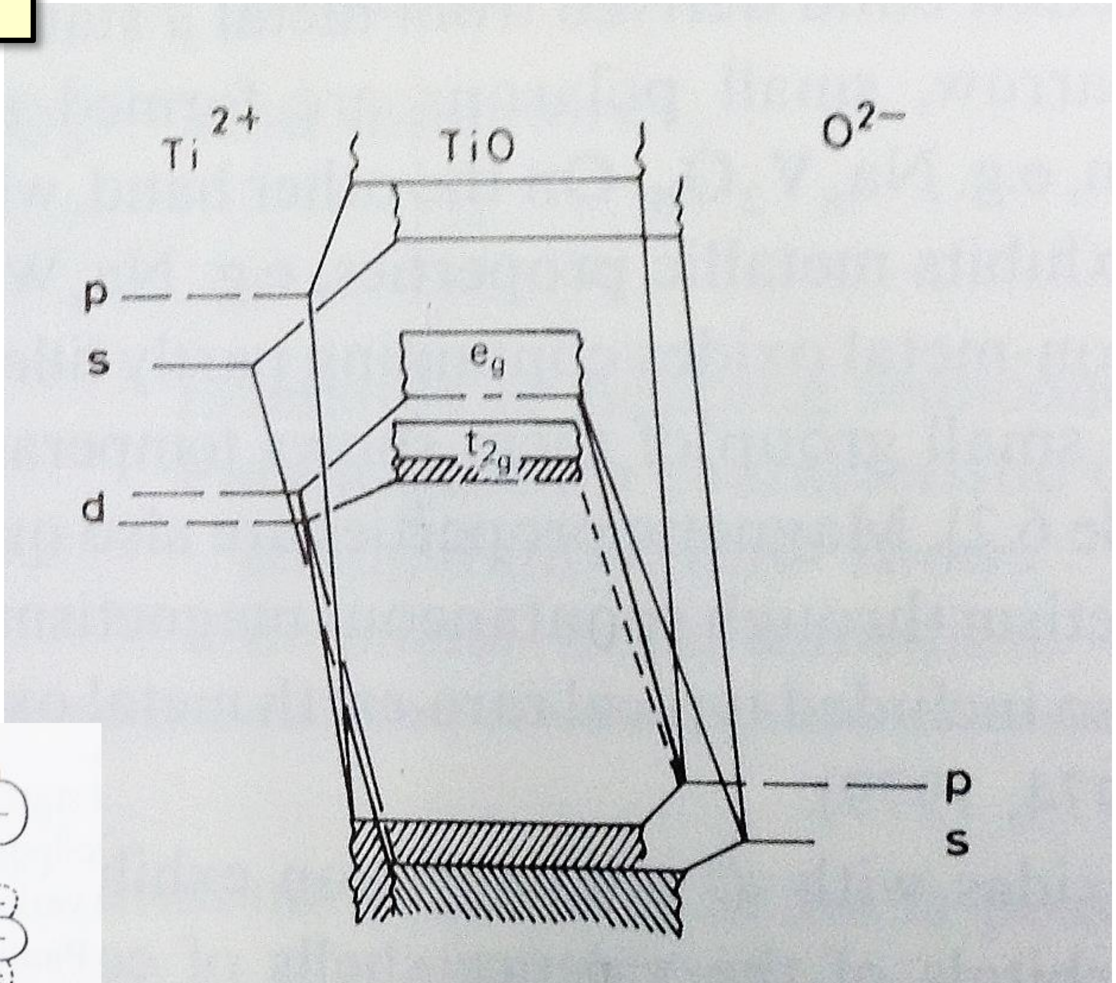
Electron distributions and energies of molecular orbitals in (a) H_2 and a heteronuclear molecule AB

From orbital to band formation

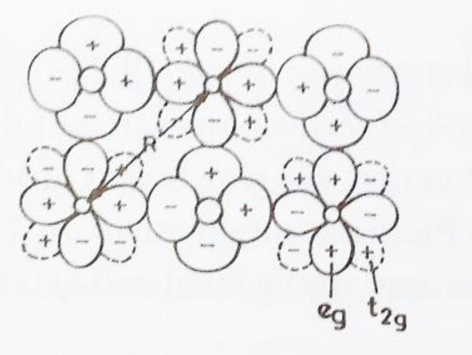


Orbital energies of (a) atom, (b) small molecule, (c) large molecule, (d) solid, and (e) density of states corresponding to (d)

TiO

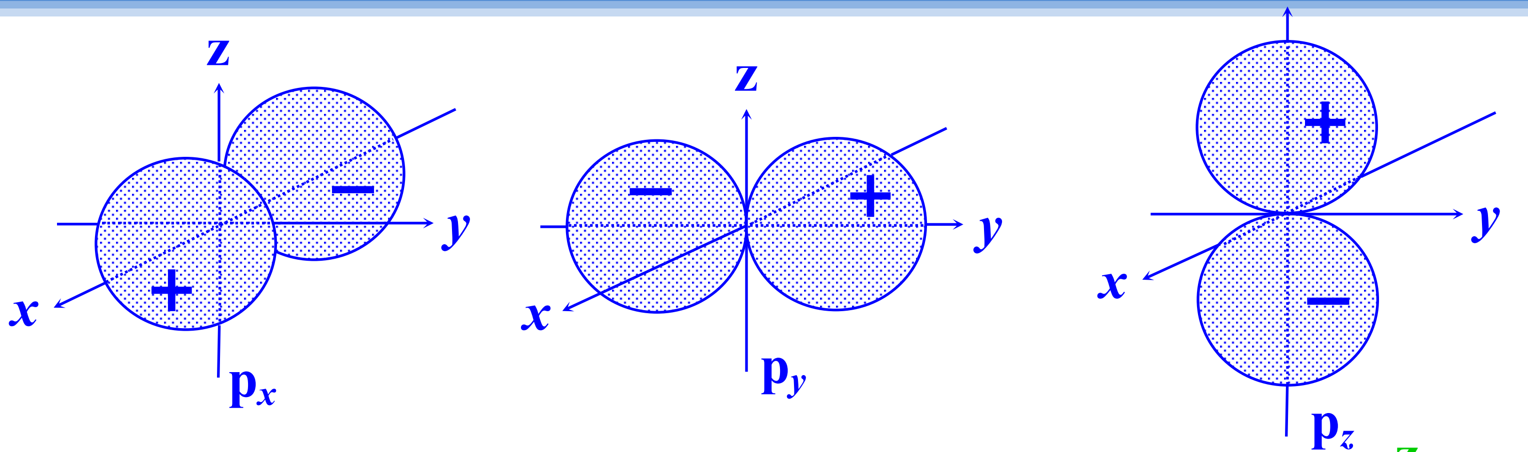


(b)

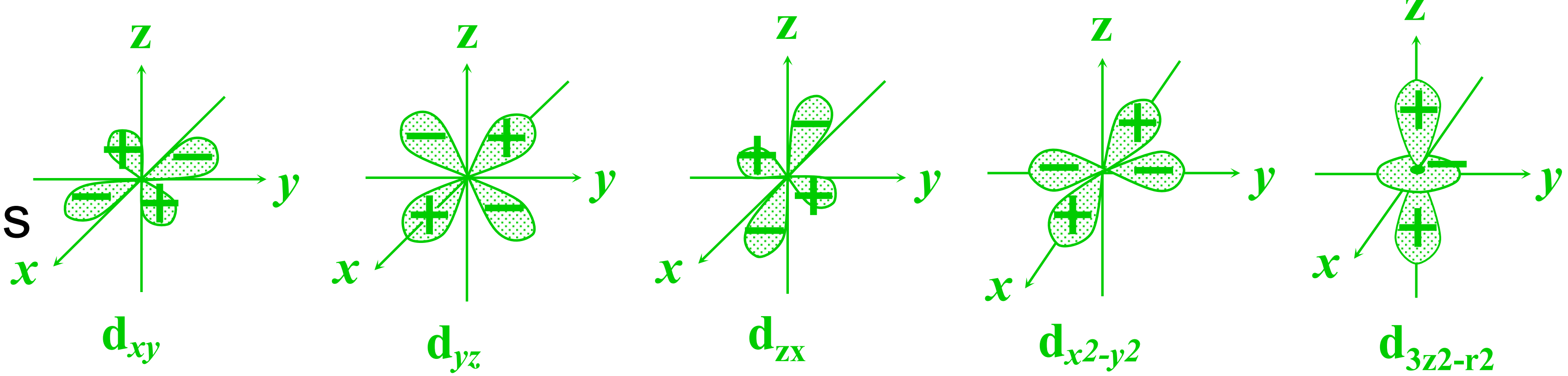


Existence of electrons・Orbital shape

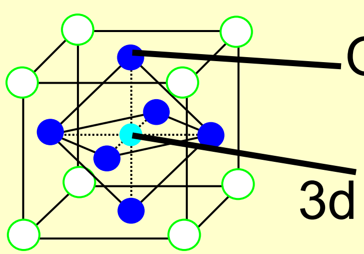
p orbitals



d orbitals



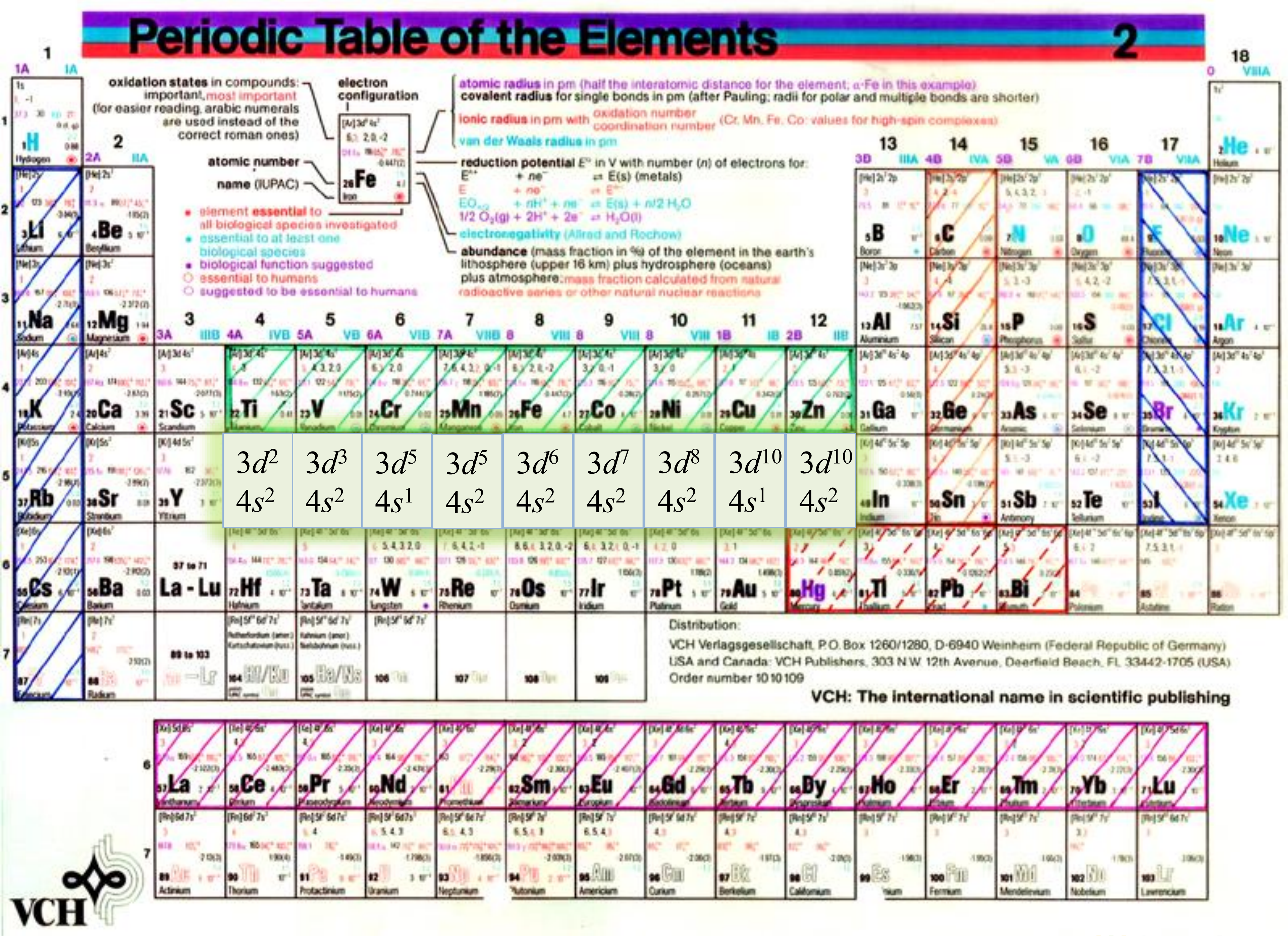
Perovskite structure



Ligand field splitting
(Crystal field splitting)

e_g — x^2-y^2, $3z^2$-r^2

t_{2g} — xy, yz, zx


Periodic Table of the Elements
2
oxidation states in compounds: important, most important
(for easier reading, arabic numerals are used instead of the correct roman ones)
electron configuration
atomic number
name (IUPAC)
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 oxidation number coordination number (Cr, Mn, Fe, Co: values for high-spin complexes)
van der Waals radius in pm
reduction potential E° in V with number (n) of electrons for:
electronegativity (Allred and Rochow)
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
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
Ti V Cr Mn Fe Co Ni Cu Zn
$3d^2$ $4s^2$
$3d^3$ $4s^2$
$3d^5$ $4s^1$
$3d^5$ $4s^2$
$3d^6$ $4s^2$
$3d^7$ $4s^2$
$3d^8$ $4s^2$
$3d^{10}$ $4s^1$
$3d^{10}$ $4s^2$
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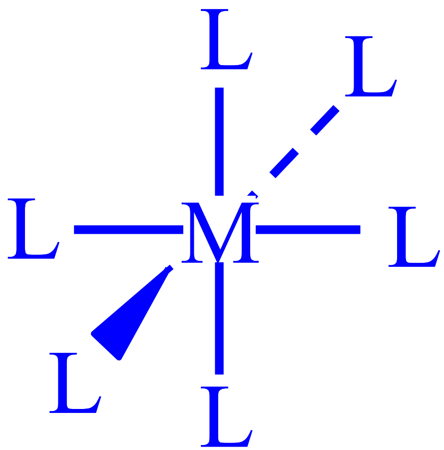
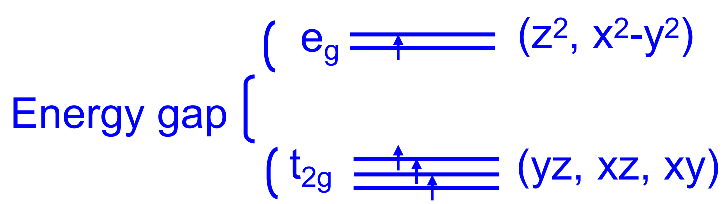
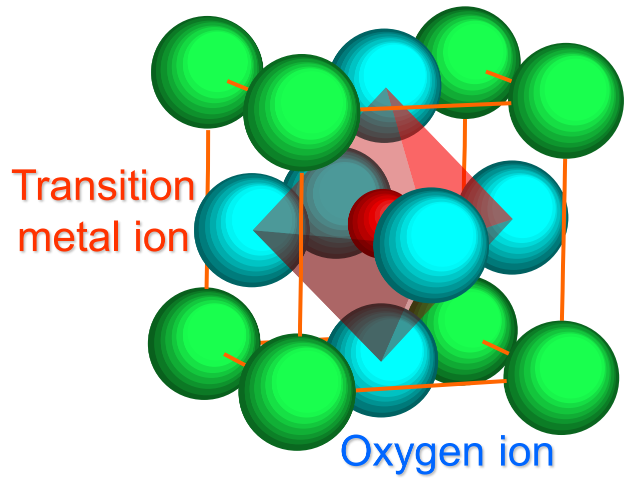
Crystal field splitting of perovskite structure

Octahedral ligands





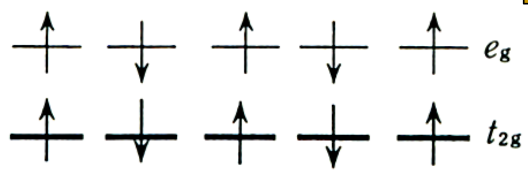


$La^{3+}Mn^{3+}O_3$

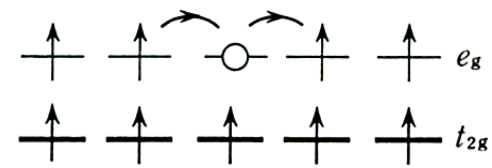
Required interaction for material design

Superexchange interaction | **Double exchange interaction**

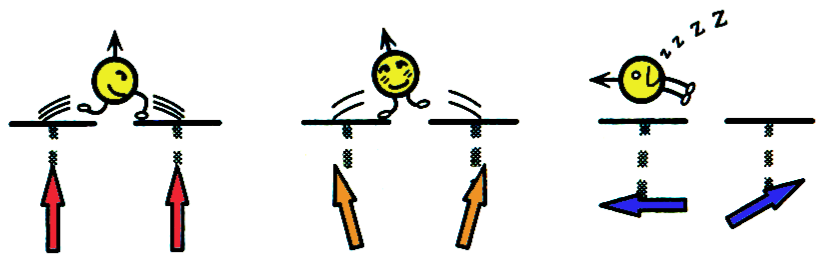
$LaMnO_3$ → Carrier doping → **$(La,Sr)MnO_3$**



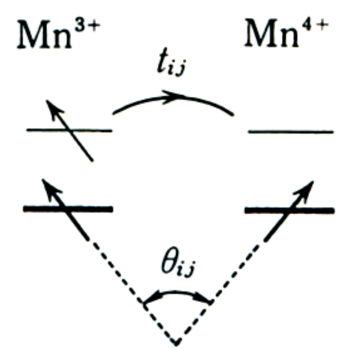
(a) $LaMnO_3$



(b) $La_{1-x}Sr_xMnO_3$ ($T \ll T_c$)



(a) (b) (c)

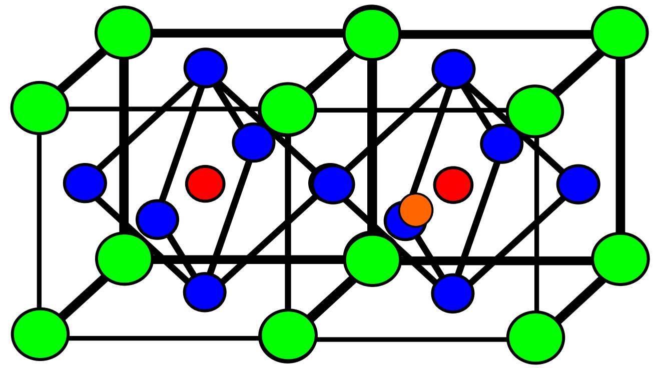


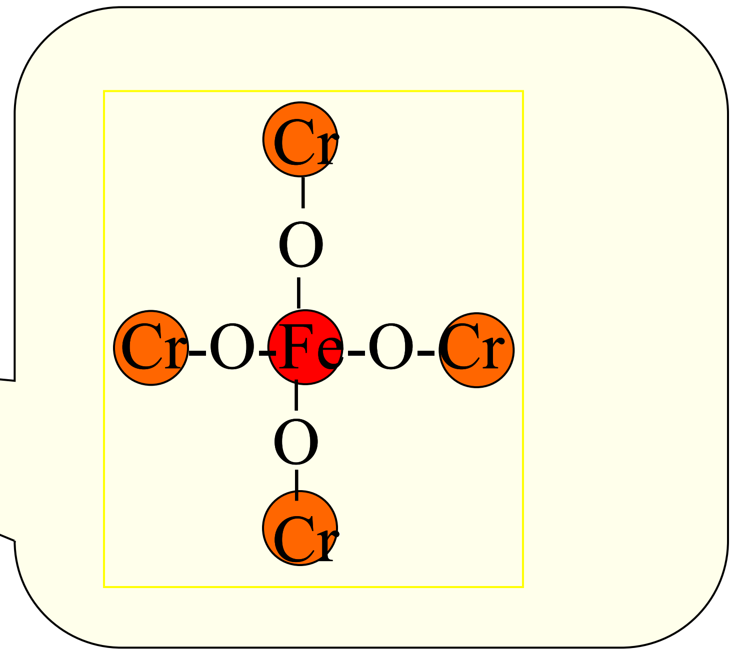
$t_{ij} = t\cos(\theta_{ij}/2)$

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

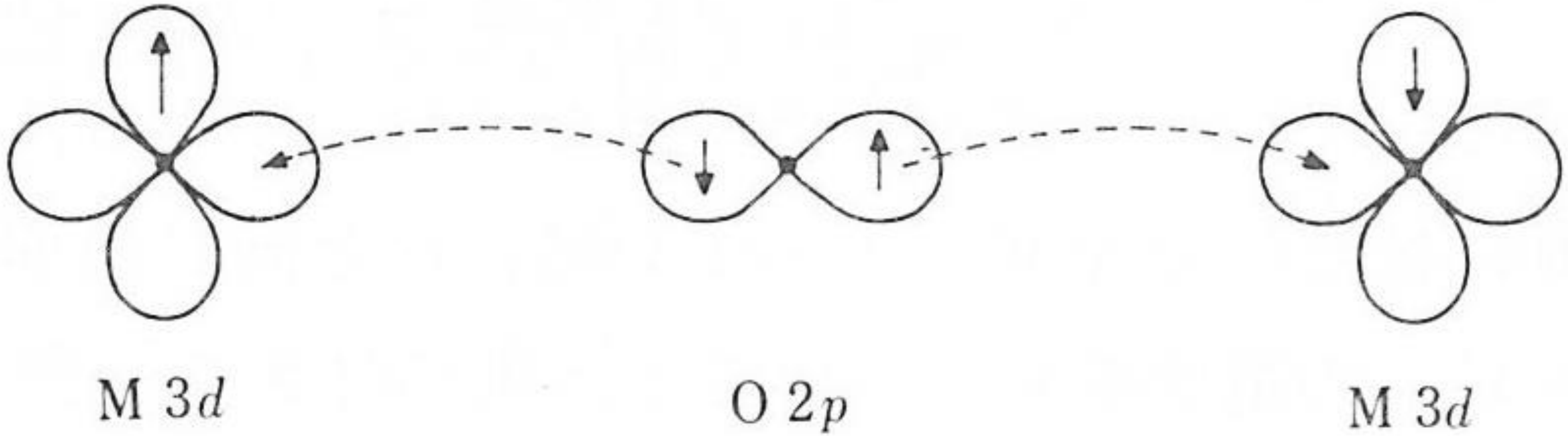
Kanamori-Goodenough rules

Kanamori former
president of Osaka Univ.





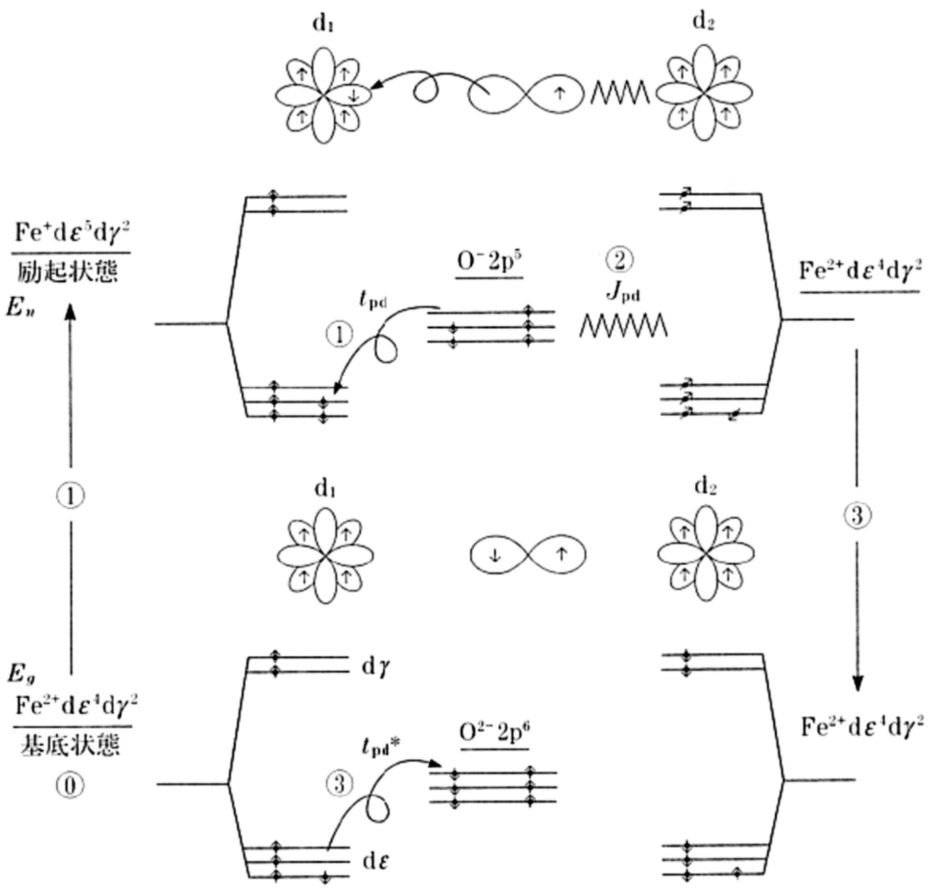
Superexchange interaction



Superexchange interaction

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

Superexchange interaction



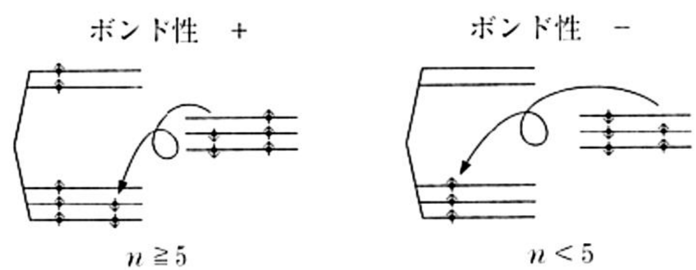
(a) Fe^{2+} - O^{2-} - Fe^{2+} 間の超交換相互作用模型

($3d^6$-$2p^6$-$3d^6$)

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

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

■bonding rule

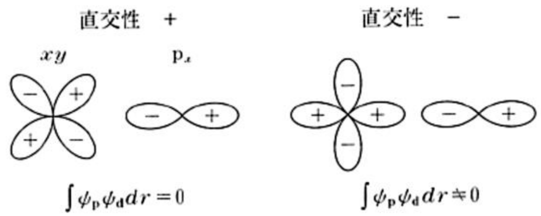


Considering a direct exchange interaction (J_{pd}) between 2p spin and 3d spin

Superexchange interaction

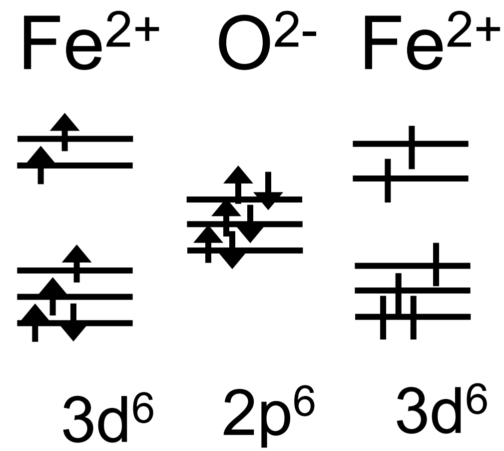
Sign of J_{pd} Ferromagnetic $J_{pd} > 0$、Antiferromagnetic $J_{pd} < 0$

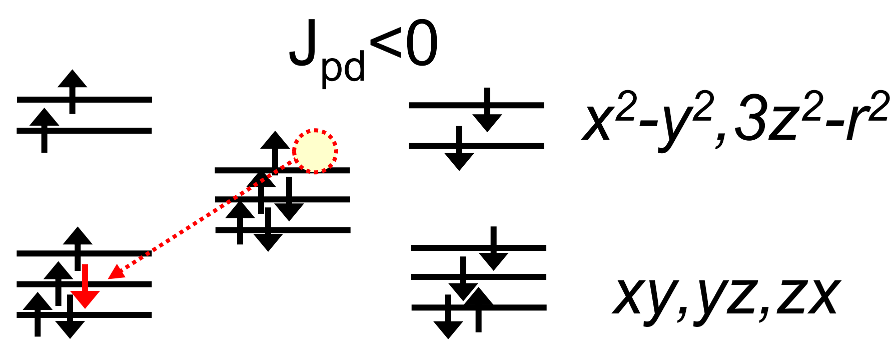
・・・ Orthogonal character of J_{pd}



(+：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	−(σ)	+	+	−(σ)
	Y	+	−(σ)	+	−(σ)
	Z	+	+	−(σ)	−(σ)
x^2-y^2	X	−(σ)	+	+	−(σ)
	Y	+	−(σ)	+	−(σ)
	Z	+	+	+	+
xy	X	+	−(π)	+	+
	Y	−(π)	+	+	+
	Z	+	+	+	+
yz	X	+	+	+	+
	Y	+	+	−(π)	+
	Z	+	−(π)	+	+
zx	X	+	+	−(π)	+
	Y	+	+	+	+
	Z	−(π)	+	+	+



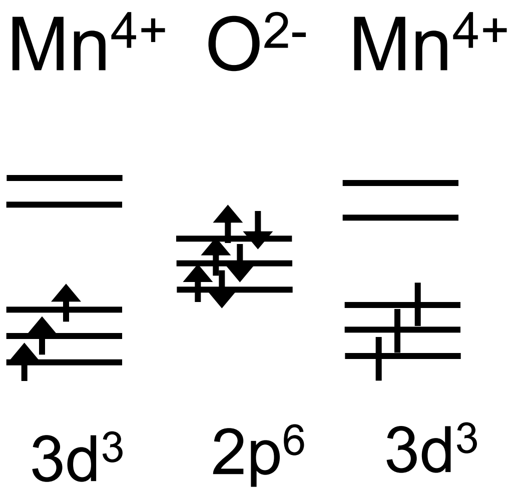


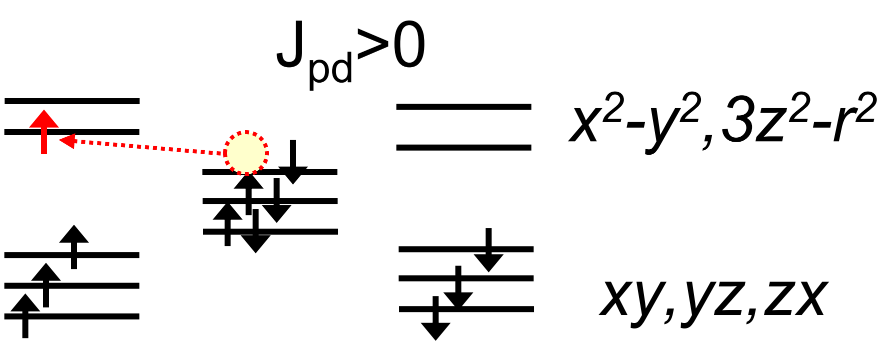
Orthogonal character table in case that d orbital function locates the origin and s and p orbitals arrange Orthogonal coordinates of X,Y and Z axes

FeO is an antiferromagnetic material

Superexchange interaction

Ex.） Mn^{4+} -Mn^{4+} : Antiferromagnetic





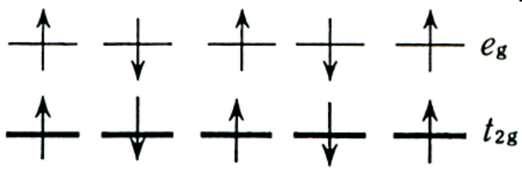
(＋：直交, －：非直交, (σ), (π) は σ および π 結合)

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	$-(\pi)$	+	+	+

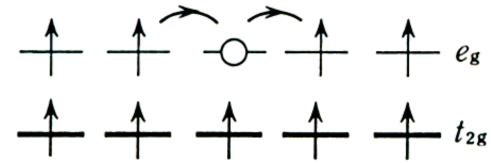
Double exchange interaction

Superexchange interaction | Double exchange interaction

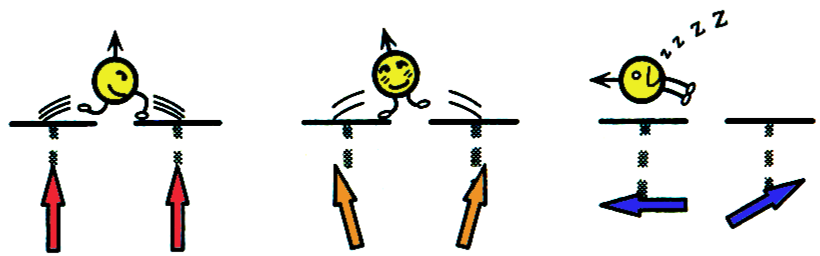
$LaMnO_3$ → Carrier doping → **$(La,Sr)MnO_3$**

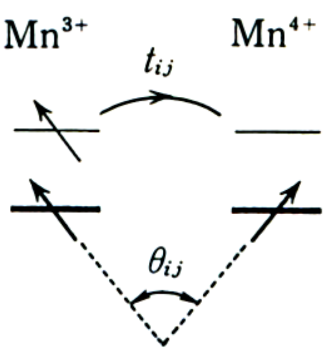


(a) $LaMnO_3$



(b) $La_{1-x}Sr_xMnO_3$ $(T \ll T_c)$


(a) (b) (c)

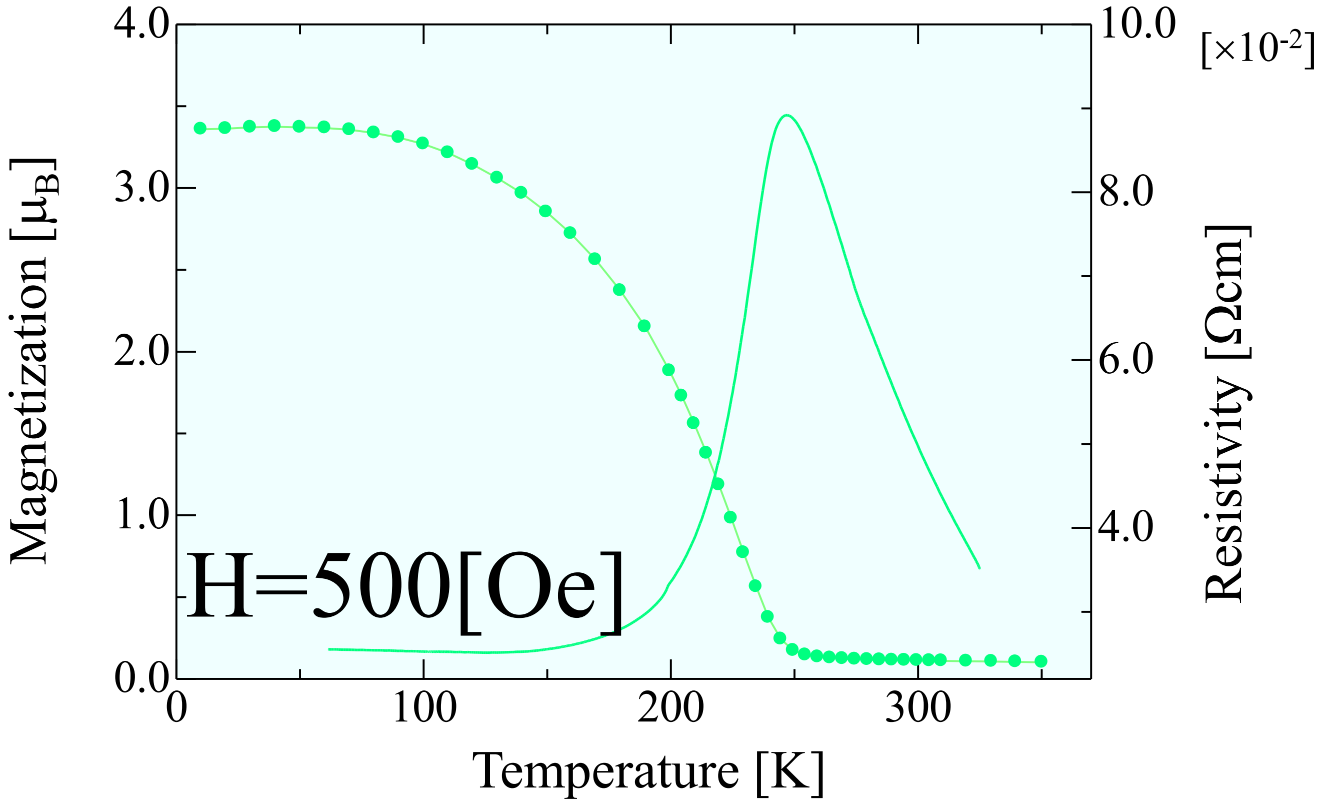


$t_{ij} = t\cos(\theta_{ij}/2)$

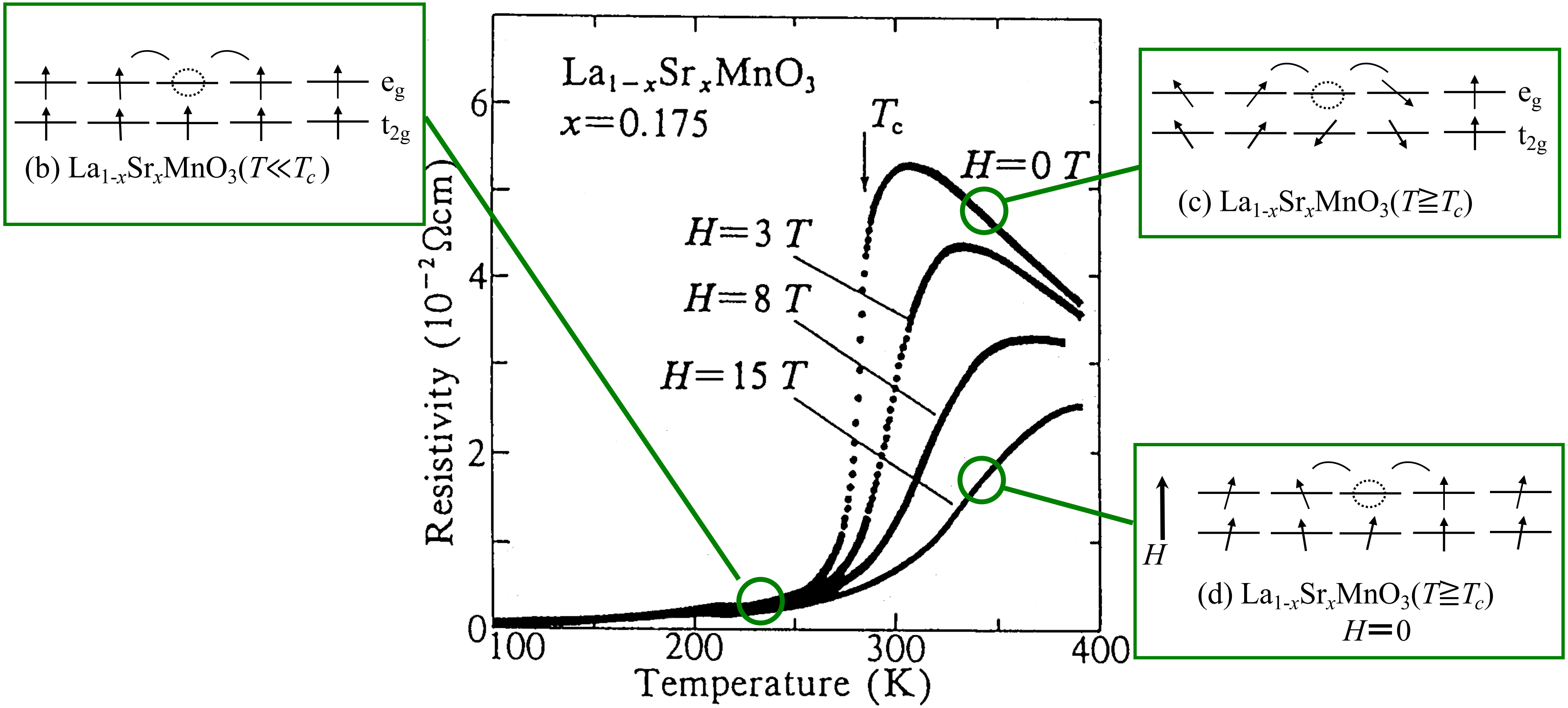
$$\boldsymbol{H} = -\boldsymbol{t}_{\mathrm{Mn-Mn}}\cos\left(\frac{\boldsymbol{\theta}}{2}\right) - K_{Hund}\boldsymbol{\sigma}\boldsymbol{S}_{\mathbf{Mn}} - J_{\mathrm{t2g}}\sum_{LMnO}\boldsymbol{S}_{\mathbf{Mn}}^{t2g}\boldsymbol{S}_{\mathbf{Mn}}^{t2g}$$

Magnetism modulation due to change of electron transfer integral

$$\boldsymbol{H} = -\boldsymbol{t}_{\mathrm{Mn-Mn}} \cos\left(\frac{\theta}{2}\right) - K_{Hund}\,\sigma \boldsymbol{S}_{\mathbf{Mn}} - J_{\mathrm{t2g}} \sum_{LMnO} \boldsymbol{S}_{\mathbf{Mn}}^{t2g} \boldsymbol{S}_{\mathbf{Mn}}^{t2g}$$

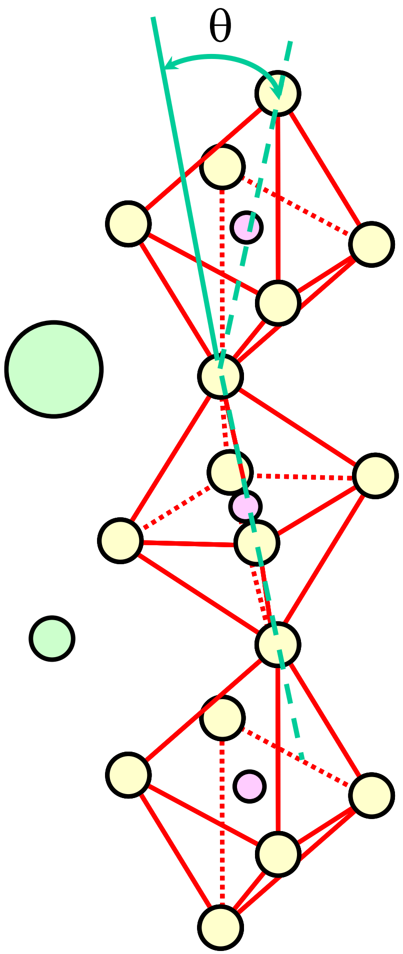


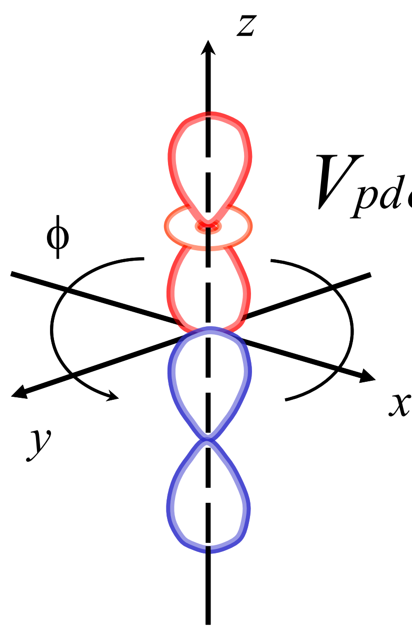
Colossal magneto resistance (CMR)



Temperature dependence of resistivity with a variety of magnetic fields in $La_{1-x}Sr_xMnO_3$ crystal（negative CMR）.
T_c indicates the Curie temperature at H=0 T.

Main parameters of transfer integral changes





Harrison's equation

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

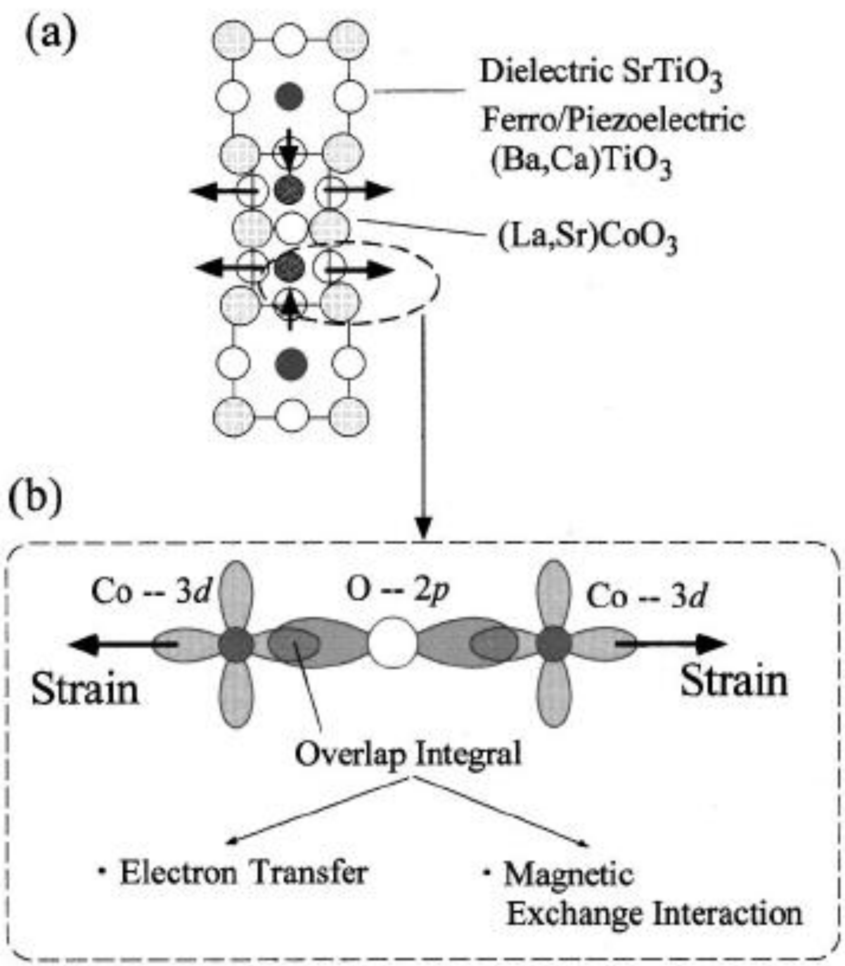
d: the distance between orbitals

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

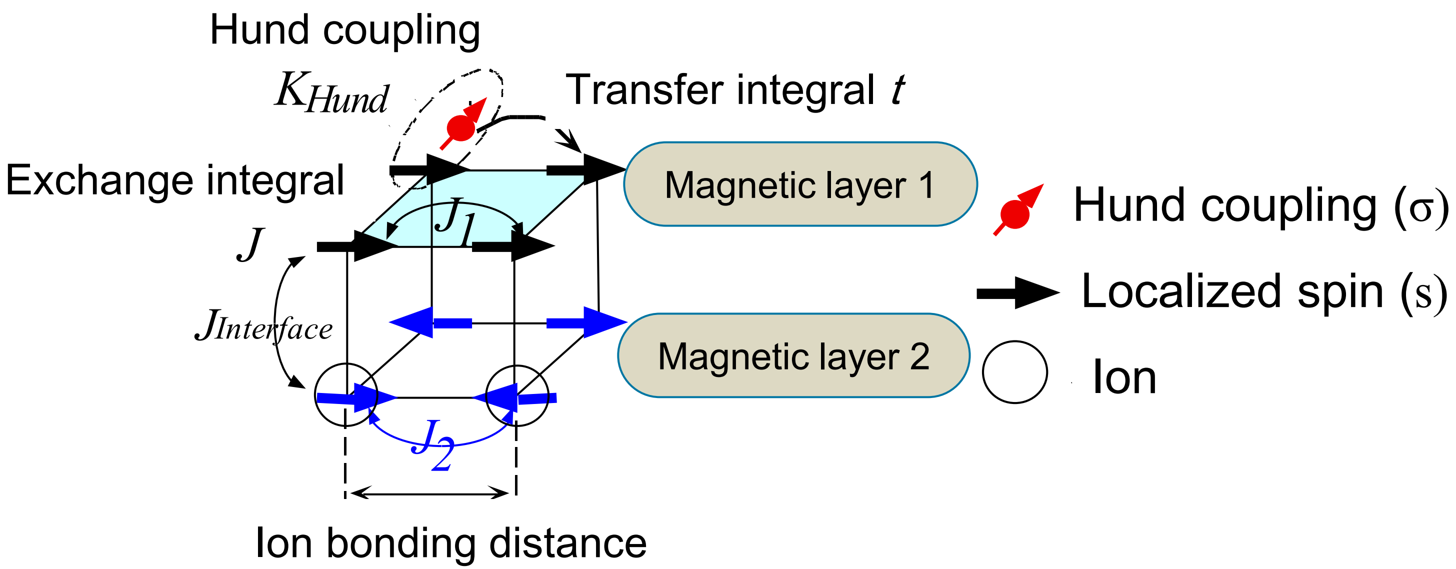
$$V_{pd\sigma} \sim d^{-7/2}$$

Compressive strain

Band width　W＝2zV

z：Coordination number

Material design for oxide spintronics



d electron energy | Coulomb integral | Hund coupling | Exchange integral

$$H_{electron} = \sum E_d + \frac{1}{2}\sum U + K_{Hund}\sum_i \sigma S_i + \sum_{i,j} J_{ij} S_i S_j$$

$$+ \sum E_p + \sum t + A\sum_i dQd$$

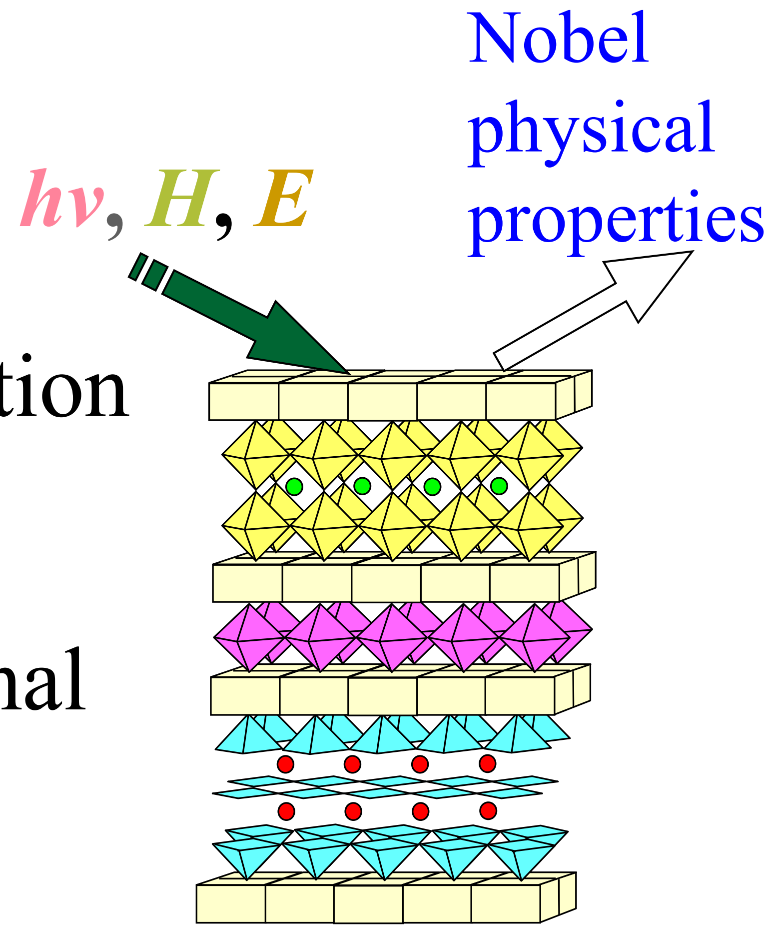
Transfer integral

Material design for oxide spintronics

(1) Introduce strain effect

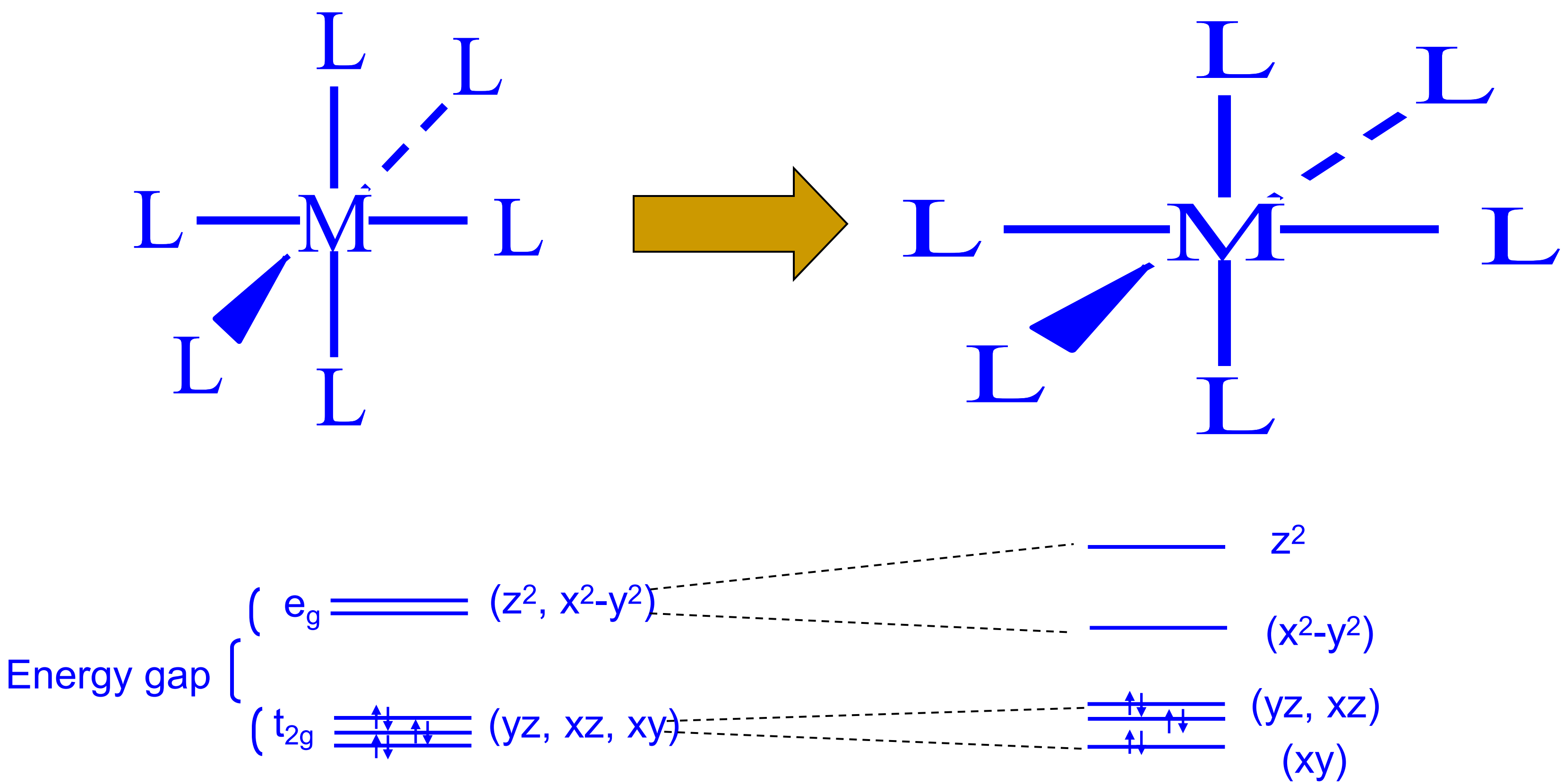
(2)Introduce magnetic interaction between different layers

(3) Integrate different functional materials

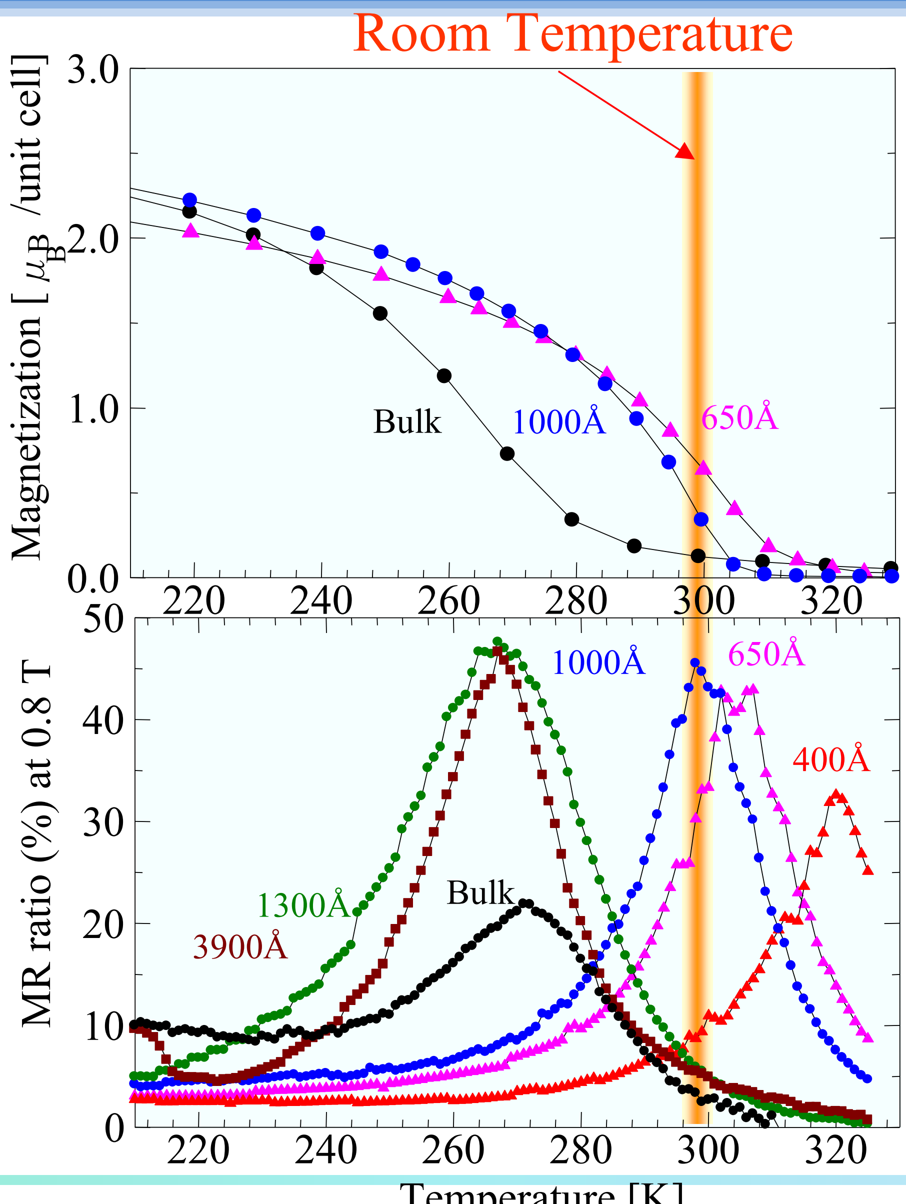


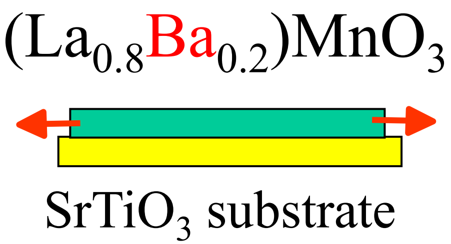
Control of crystal field splitting due to strain effect

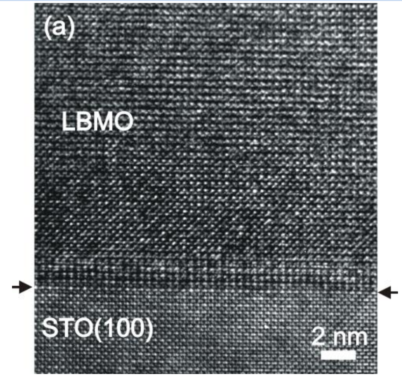
Octahedral coordination　　In-plane tensile strain



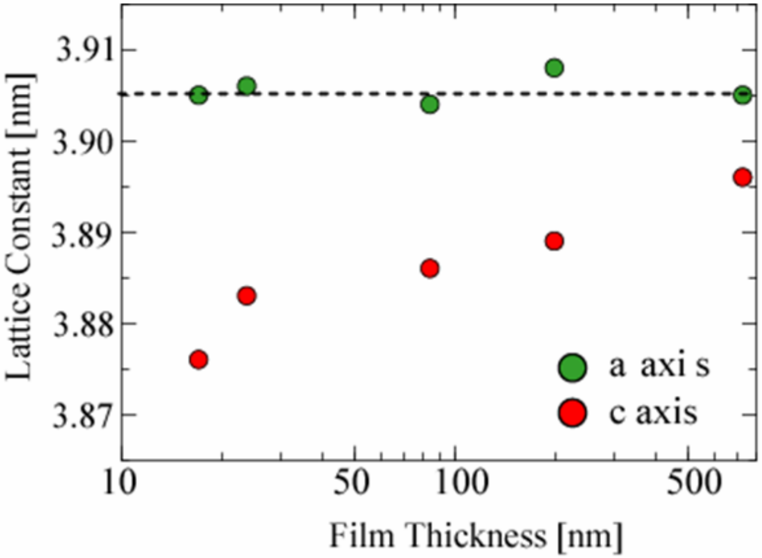
Design of room temperature CMR materials





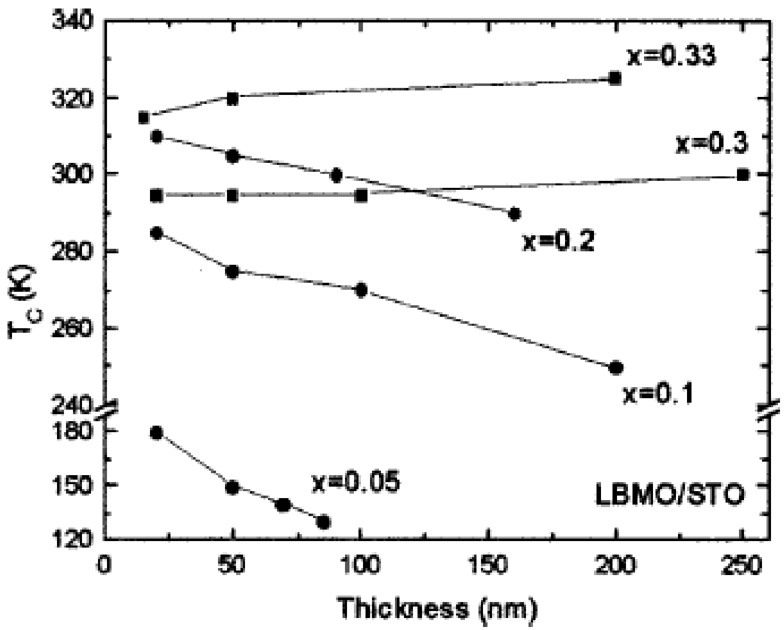


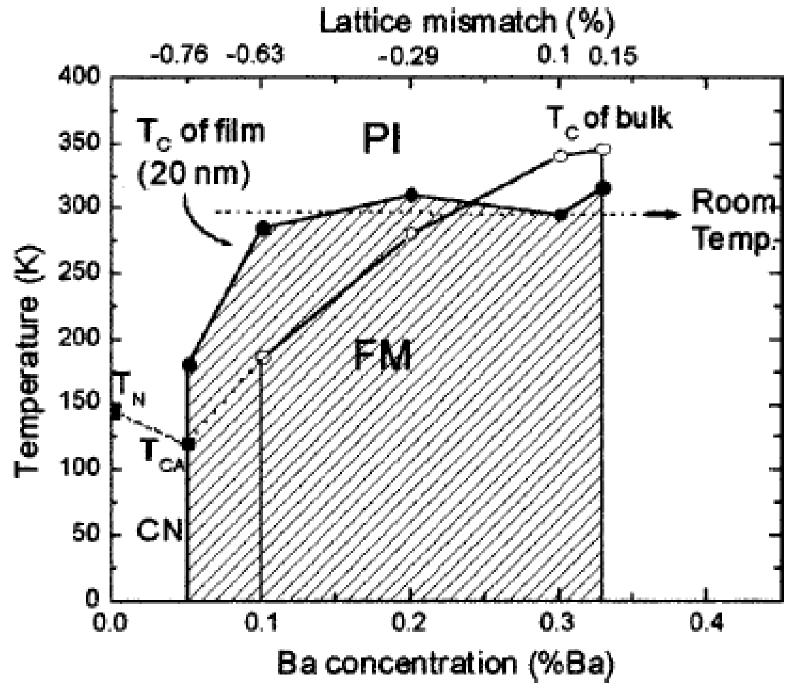
Tensile strain (0.3%)



Phys. Rev. B ***64****, 224418(2001)*

Strain effect vs T_C in LBMO films





Tensile strain ⇦ ⇨ 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

[a]For $x = 0.05$, spin canting transition temperature $T_{CA} = 120$ K.

Tensile strain

Increase in T_C

Compressive strain

decrease in T_C

Phys. Rev. B ***64***, *184404(2001)*

Stability of double exchange magnetism

Stability of magnetism induced by double exchange interaction

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

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

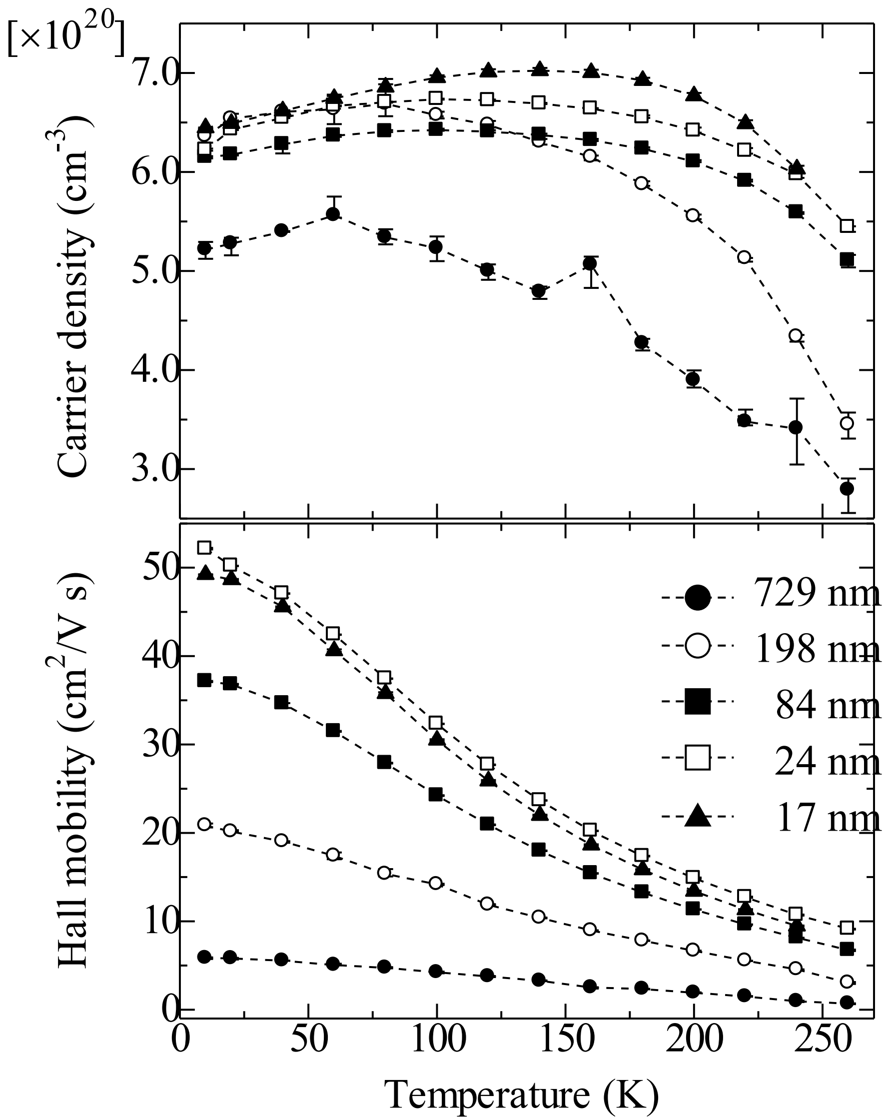
C. Zener: Phys. Rev. **82** (1951) 403
P. W. Anderson and H. Hasegawa: Phys. Rev. **100** (1955) 675
P. G. de Gennes:Phys. Rev. **118** (1960) 141

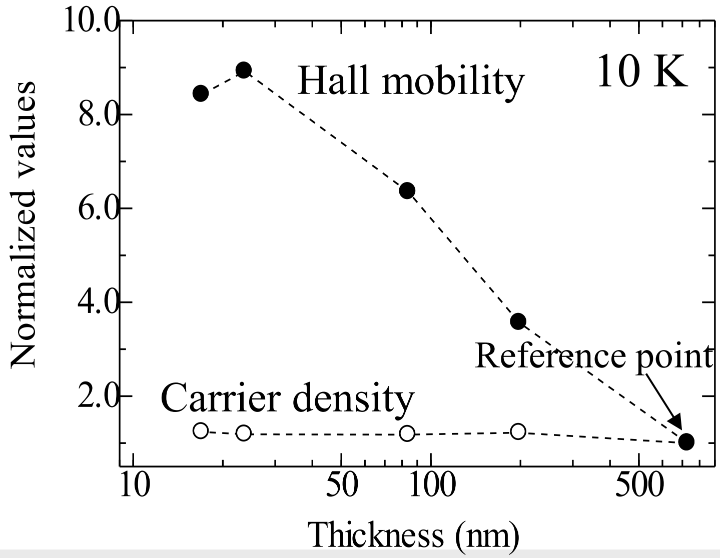
Main parameters indicating the stability of double exchange magnetism

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**

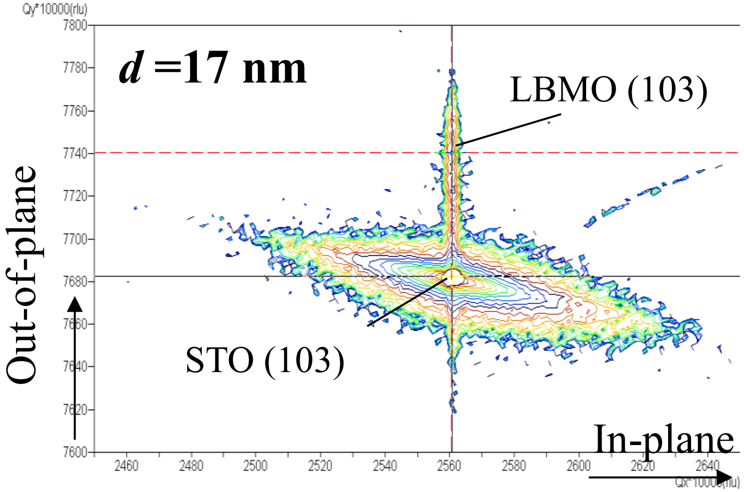
Hall mobility : Increase

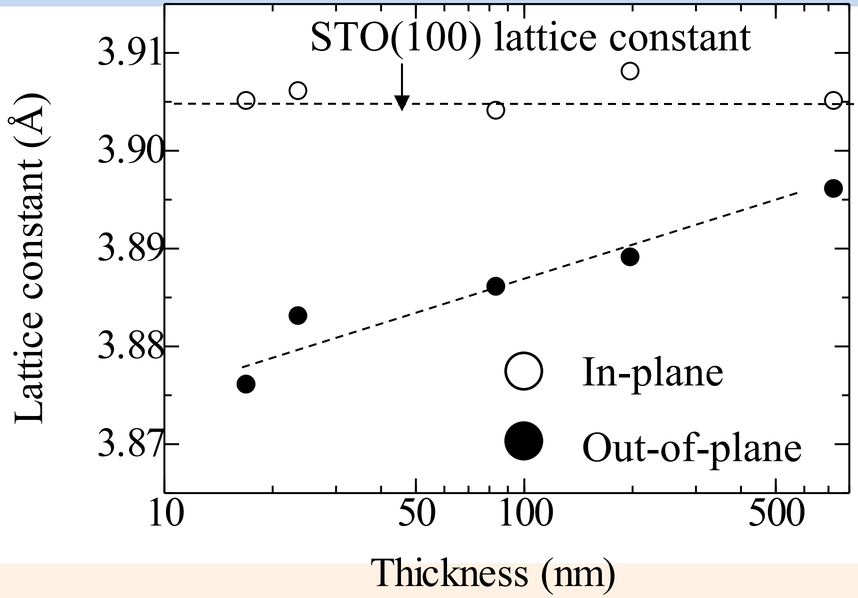
➡ Increase in transfer integral

➡ **change in orbital overlap state due to lattice strain effect**

Phys. Rev. B ***71***, *012403(2005)*

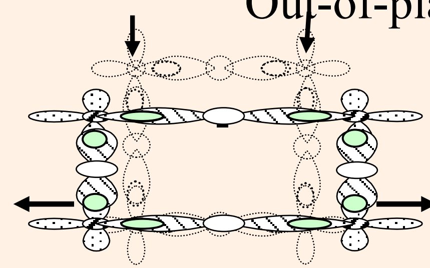
Stability of transfer integral due to lattice strain effect





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

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

b_{σ}: Spin-independent components

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

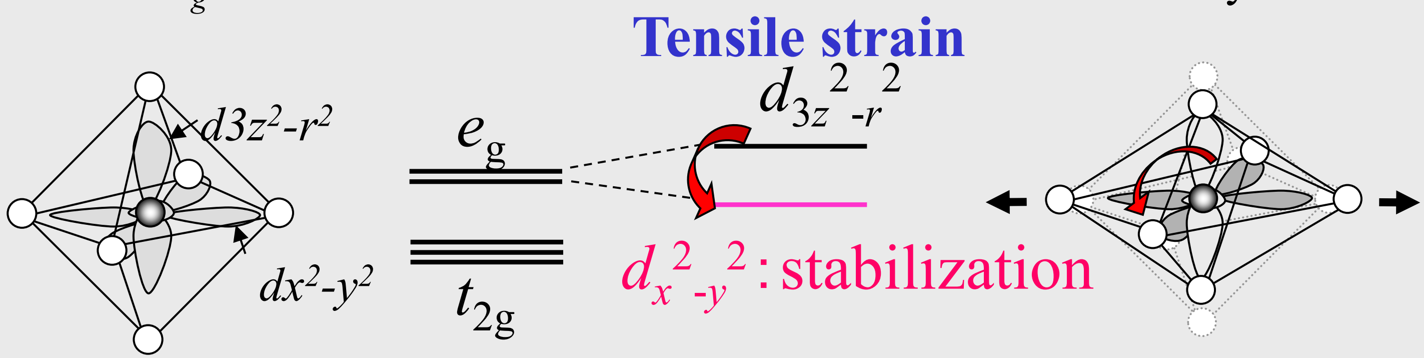
Contribution elements of stability in double exchange interaction

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

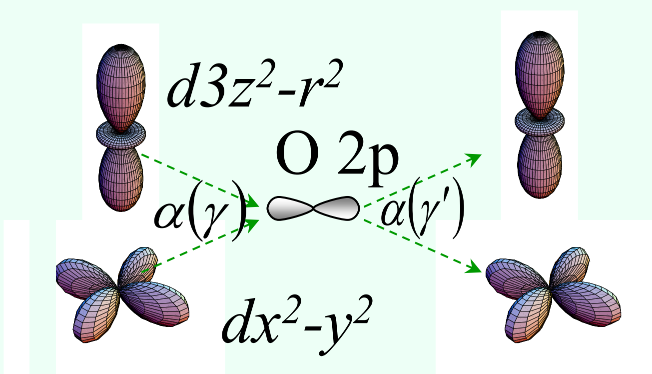
→ determination from lattice constants obtained by experiments

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	Out-of-plane		In-plane	
γ \ γ'	$\lvert x^2-y^2\rangle$	$\lvert 3z^2-r^2\rangle$	$\lvert x^2-y^2\rangle$	$\lvert 3z^2-r^2\rangle$
$\lvert x^2-y^2\rangle$	0	0	3/4	√3/4
$\lvert 3z^2-r^2\rangle$	0	1	√3/4	1/4

Phys. Rev. B ***64***, *224418(2001)*

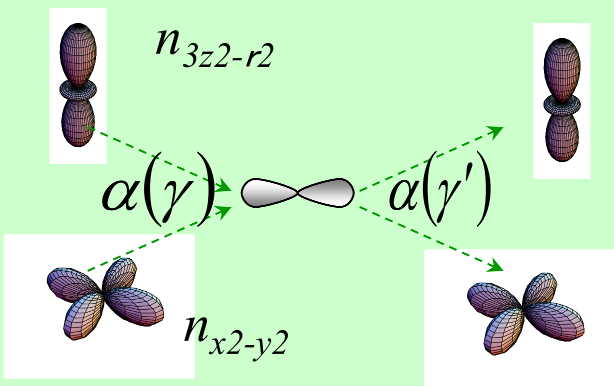
Contribution elements of stability in double exchange interaction

Stability of averaged double exchange interaction

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

Transfer strength from Mn3*d* orbital to O2*p* orbital $\alpha(\gamma)$

Transfer strength from O2*p* orbital to Mn3*d* orbital $\alpha(\gamma')$



In-plane: 4 directions
Out-of-plane : 2 directions

- d_{in} : the in-plane Mn-O length
- d_{out} : the out-of-plane Mn-O length

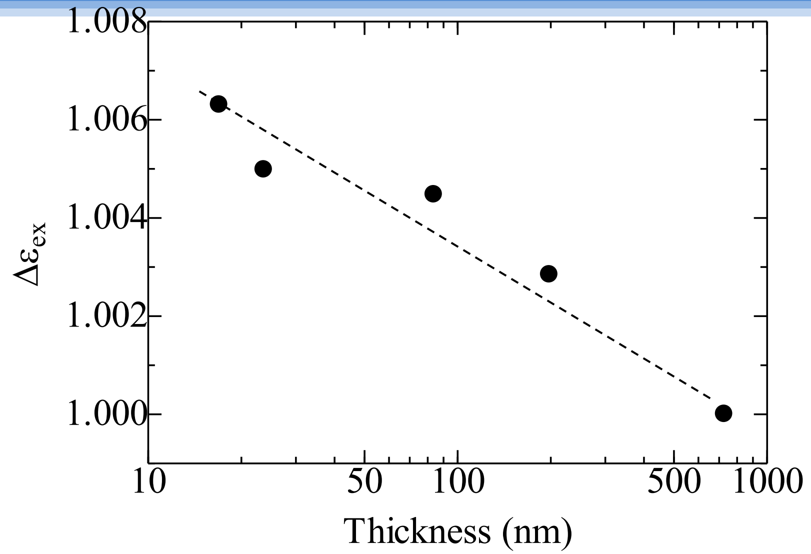
➡ derived by XRD measurement

- n_{x2-y2} : the ration of occupied electrons in d_{x2-y2} orbital
- n_{3Z2-r2} : the ration of occupied electrons in d_{3z2-r2} orbital

➡calculation by the DV-*Xα* method using experimental lattice constants

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

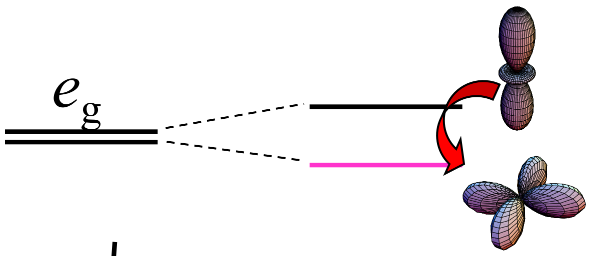
Stability of double exchange magnetism



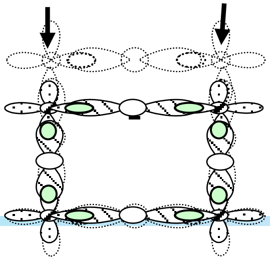
Stabilization of double exchange interaction with decreasing film thickness

What is main factors of T_C increase in strained (La,Ba)MnO_3 thin films

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



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

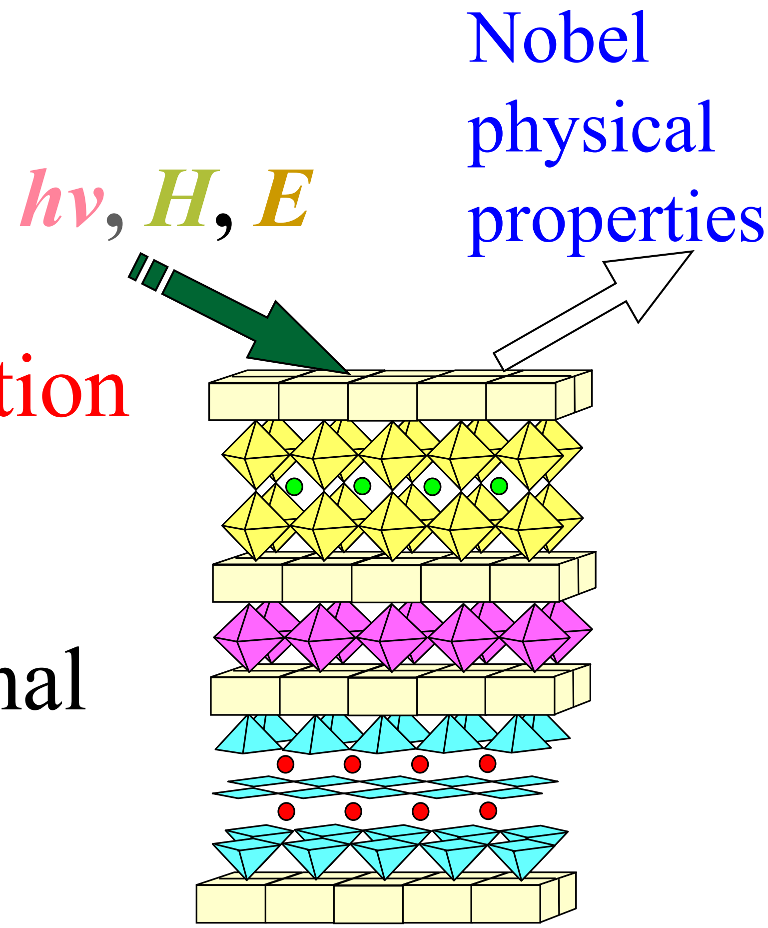


Function of interface

(1) Introduce strain effect

(2)Introduce magnetic interaction between different layers

(3) Integrate different functional materials



Control of interface magnetic interaction

Conductive electron | Localized spin

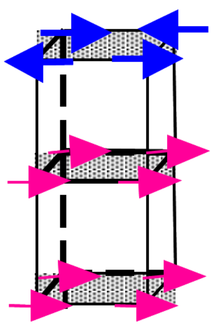
Hund coupling

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

$$-J_{\mathrm{Fe-Mn}} S_{\mathrm{Mn}}^{t2g} S_{\mathrm{Fe}} - \sum_{LFeO} J_{\mathrm{Fe-Fe}} S_{\mathrm{Fe}} S_{\mathrm{Fe}}$$

Interface magnetic interaction

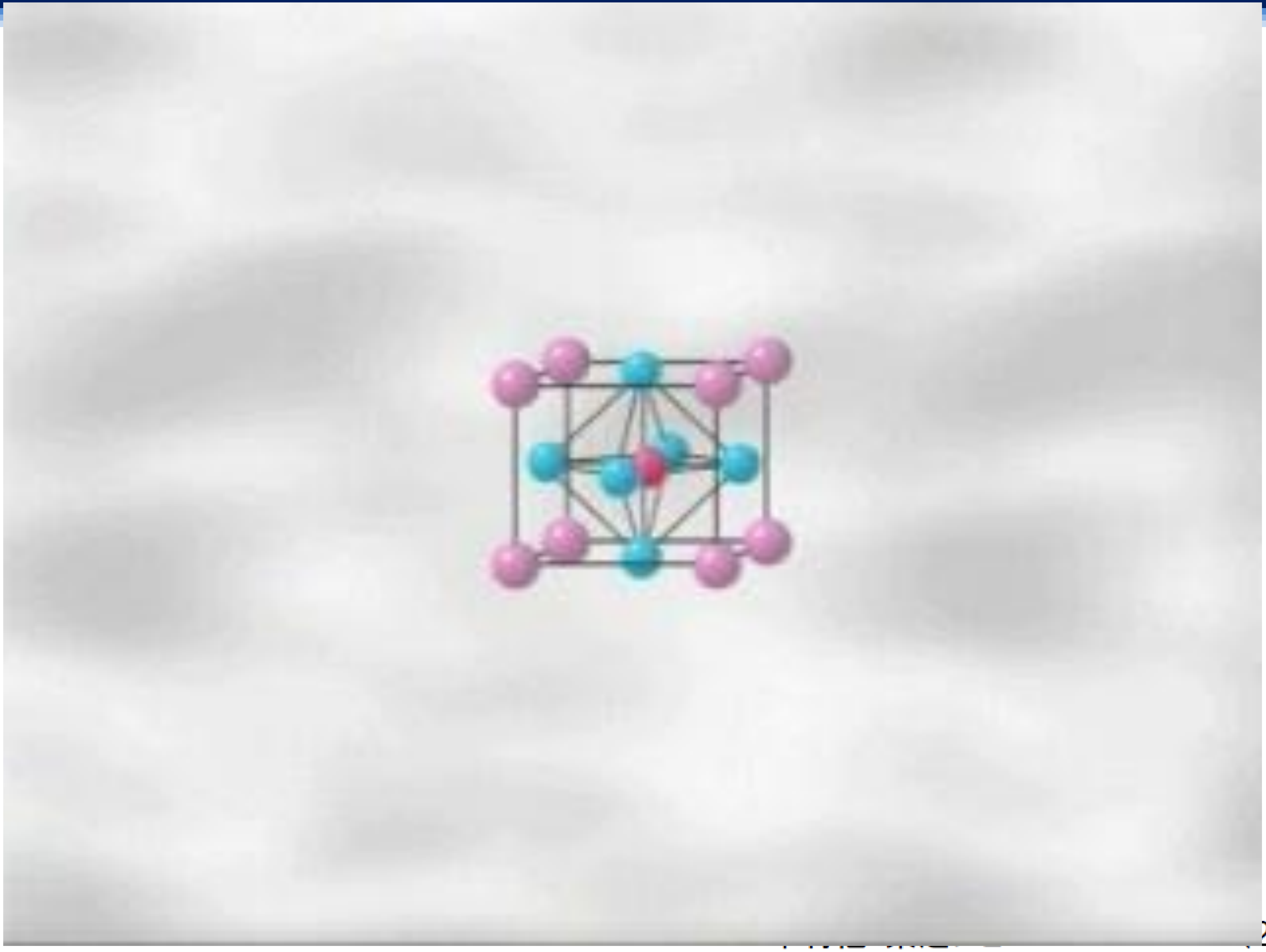
Antiferromagnet $LaFeO_3$



Ferromagnet $(La,Sr)MnO_3$

Combined with two materials
⇒ Magnetic susceptibility increases

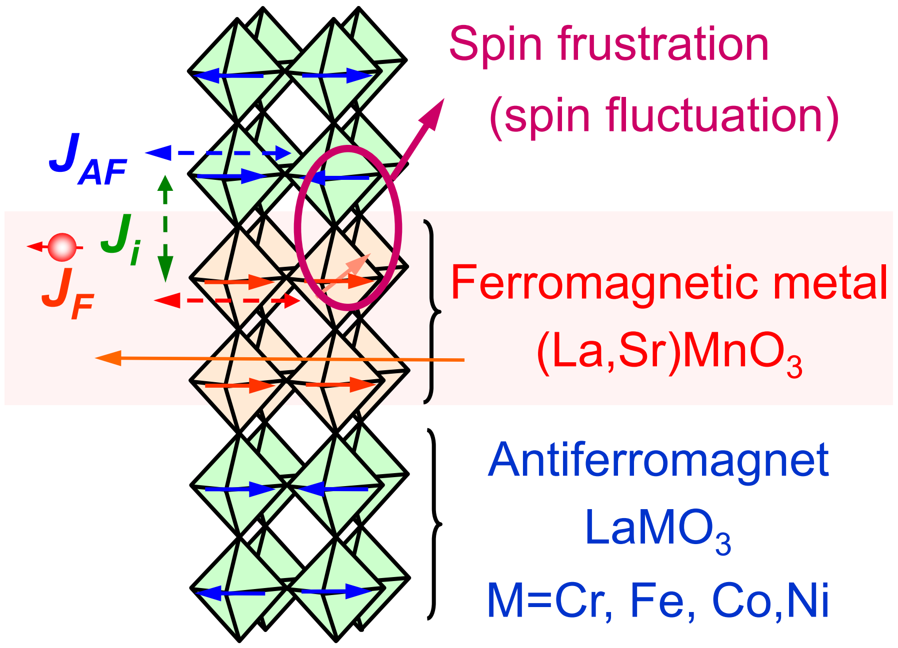
Spin frustration superlattice

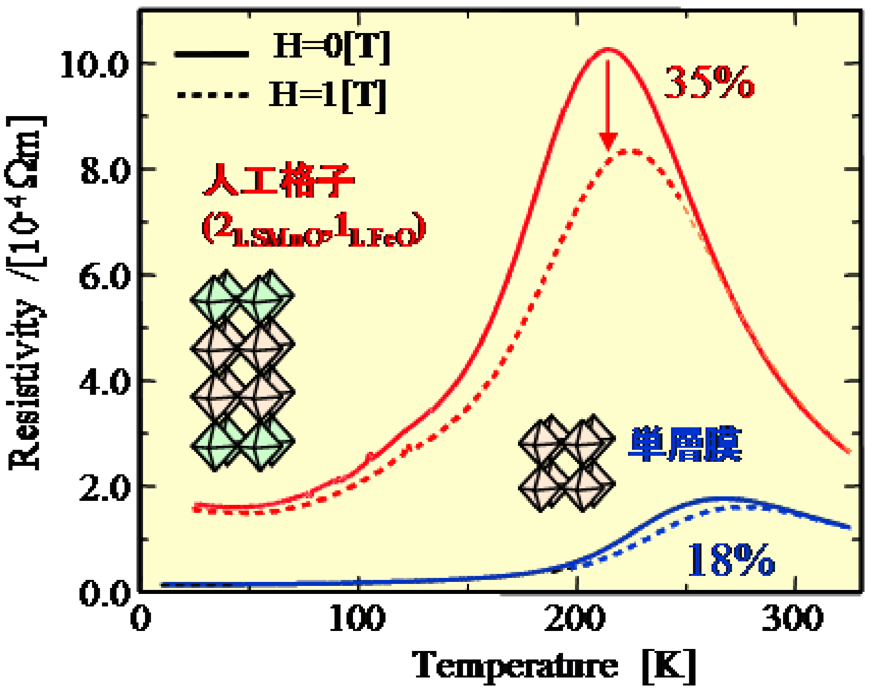


2006)

High sensitive response by magnetic field

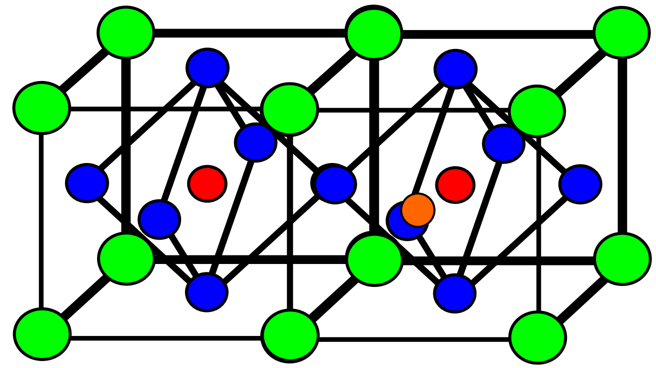
Spin frustration superlattice

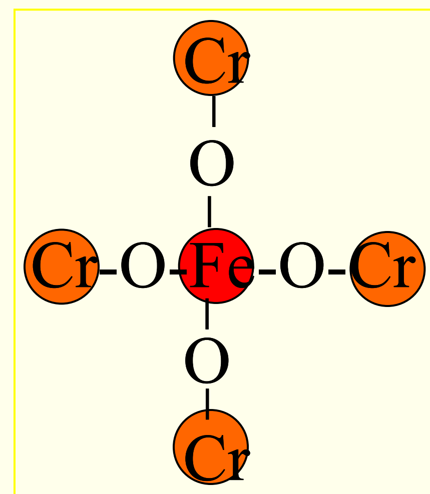




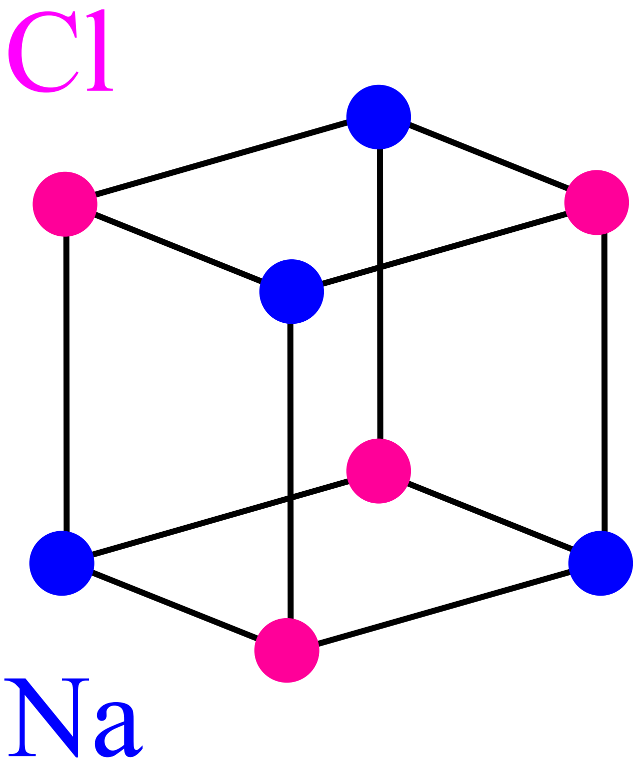
Theoretical prediction：New ferromagnet

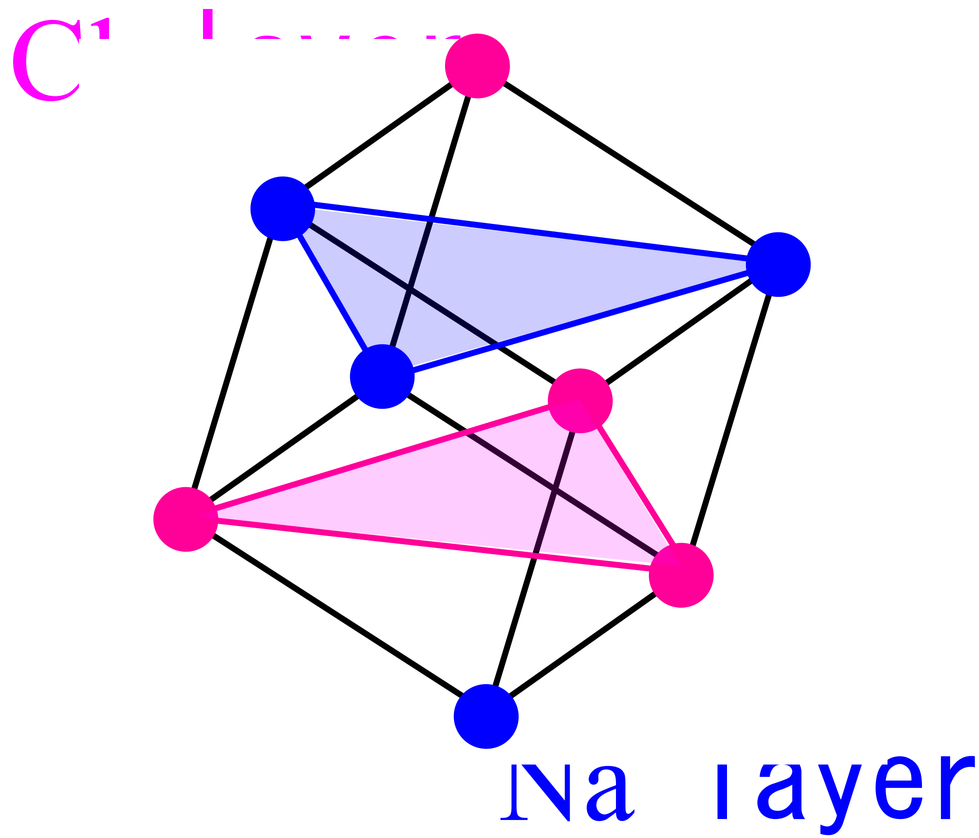
Kanamori former
president of Osaka Univ.



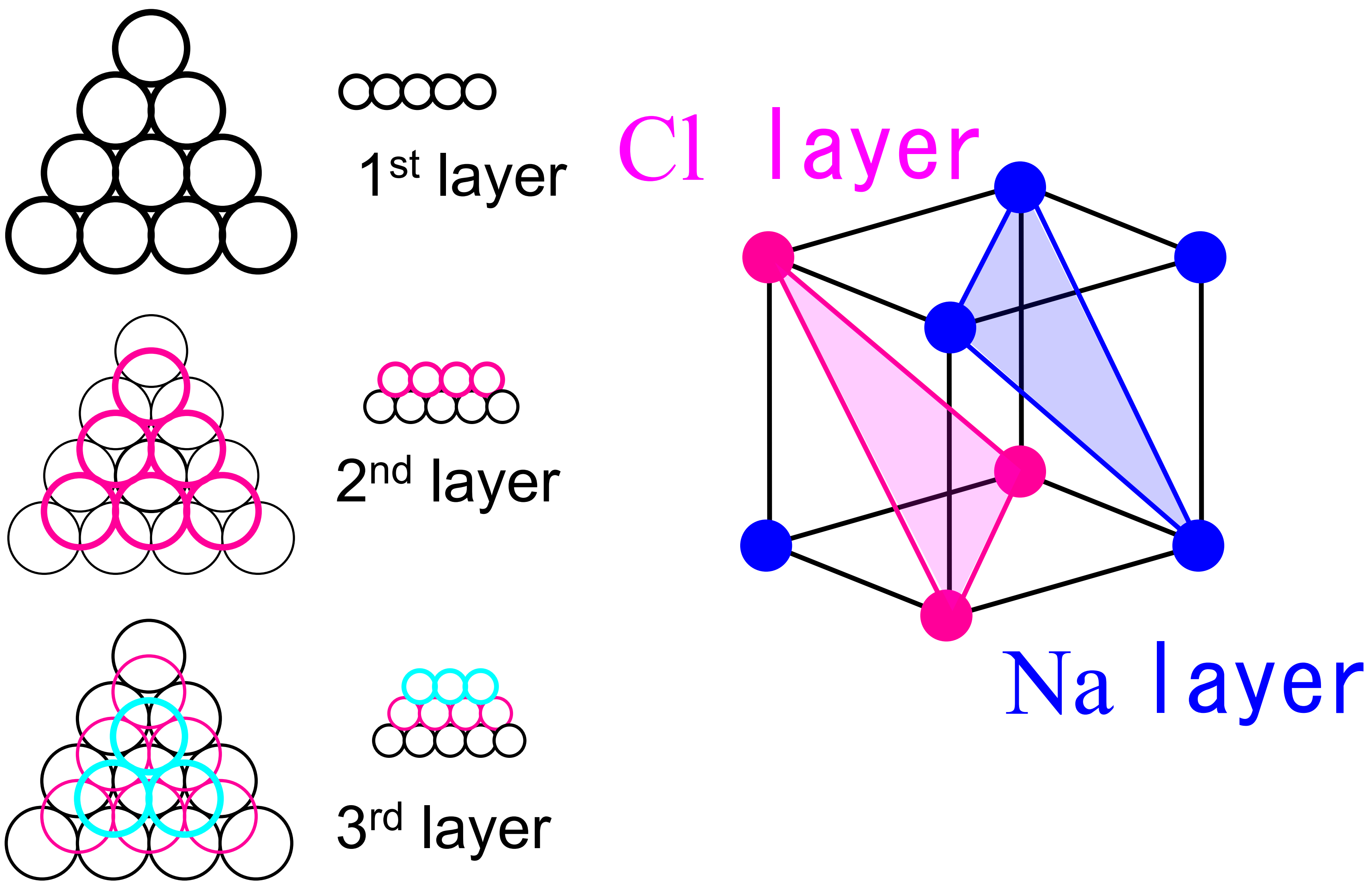


NaCl structure

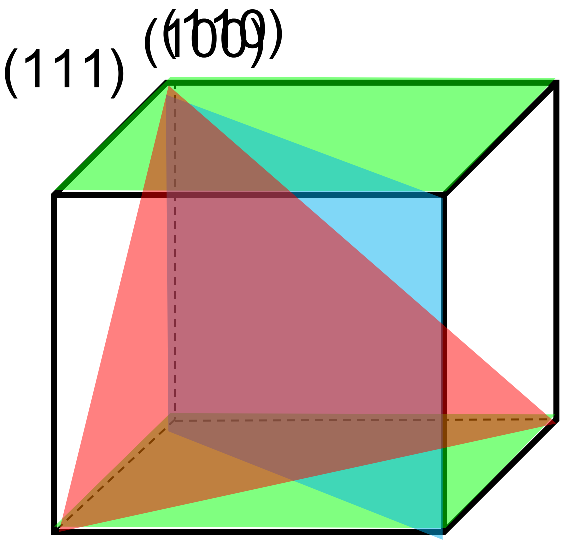


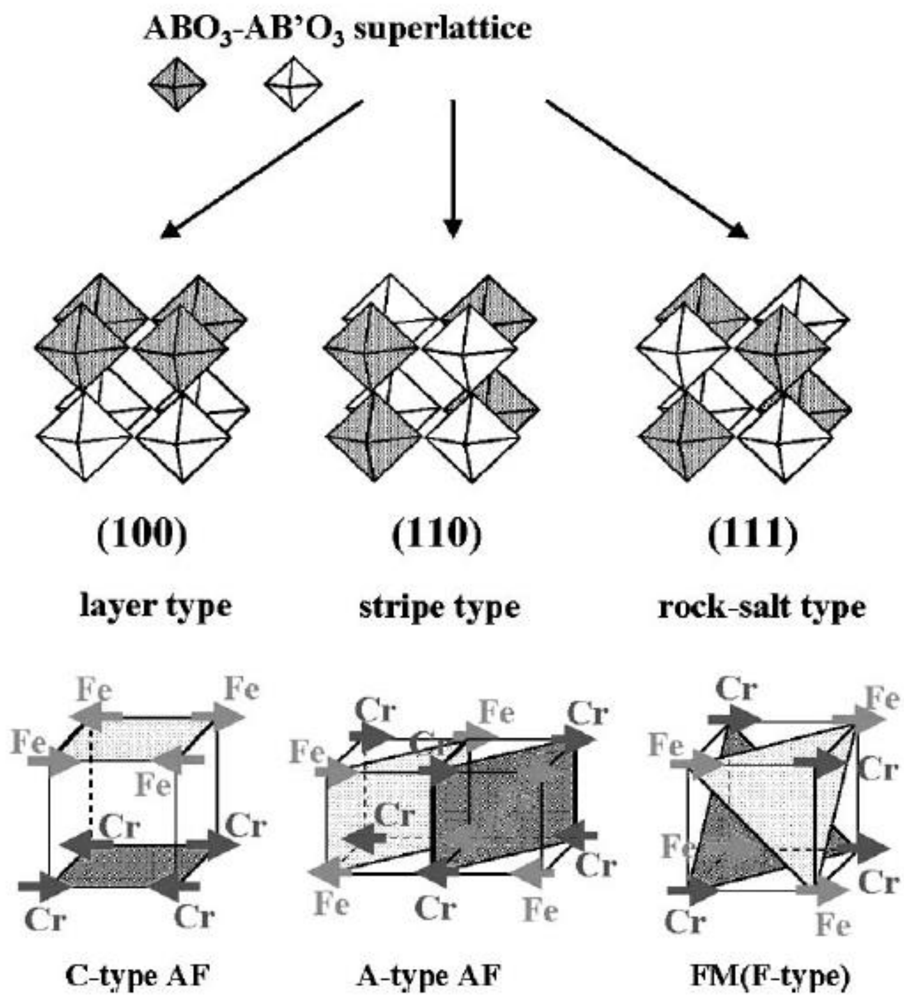


Lattice-direction control superlattice



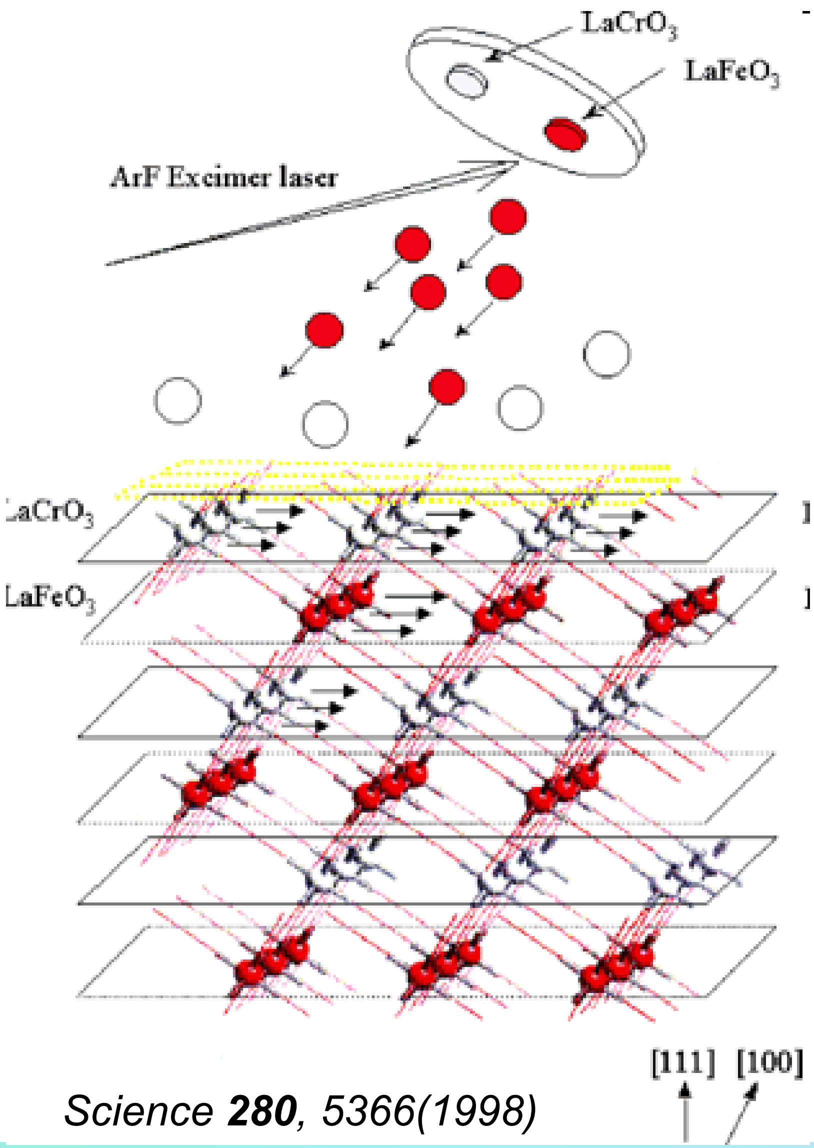
Lattice-direction control superlattice



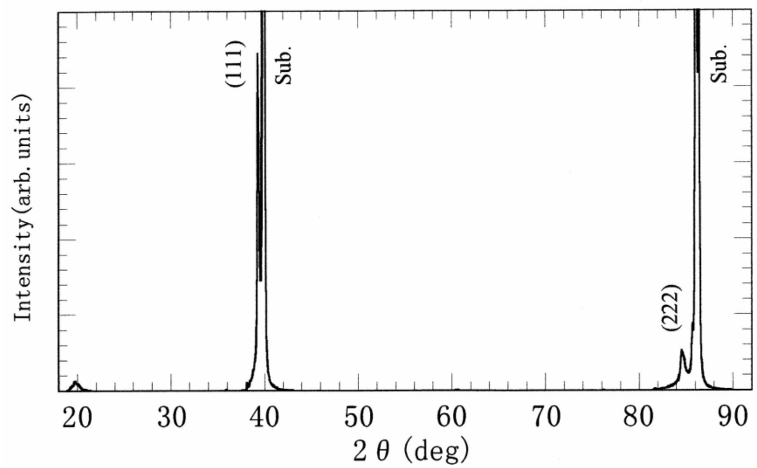


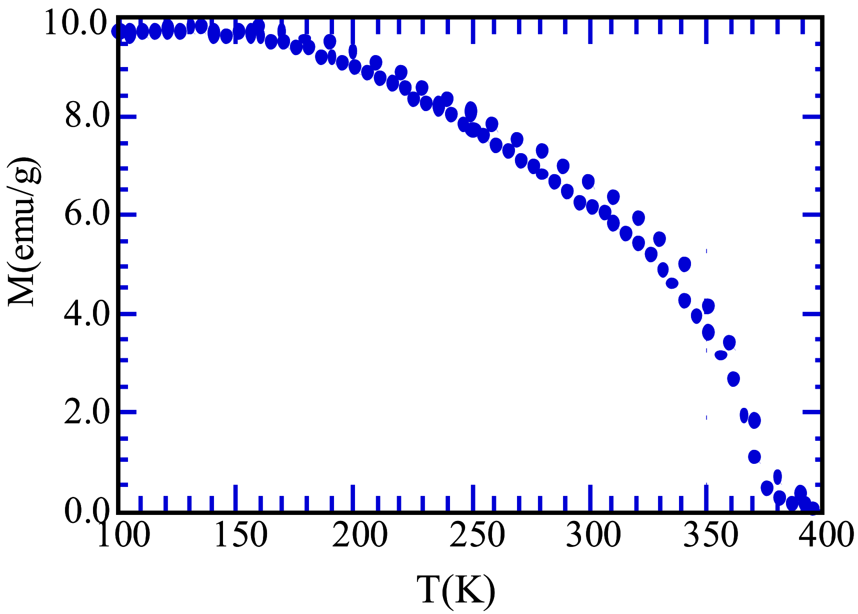
J. Appl. Phys. ***89***, *2847(2001)*

Lattice-direction control superlattice



Science ***280****, 5366(1998)*





Integration of different functional materials

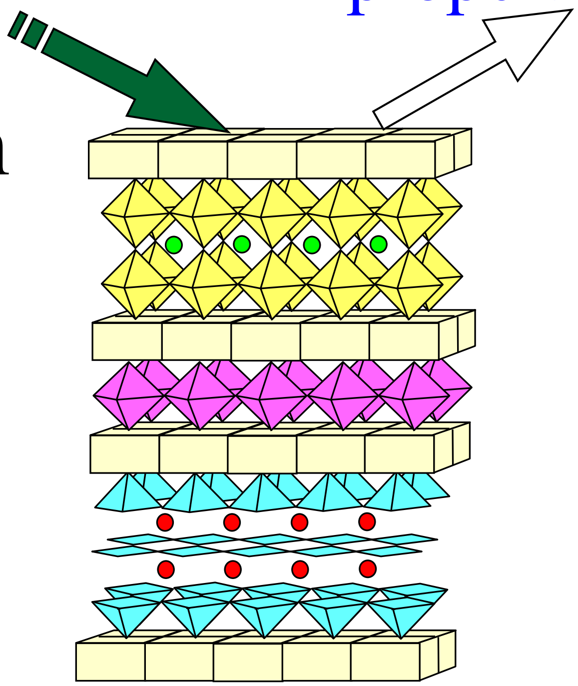
(1) Introduce strain effect

(2)Introduce magnetic interaction between different layers

(3) Integrate different functional materials

hν, *H*, *E*

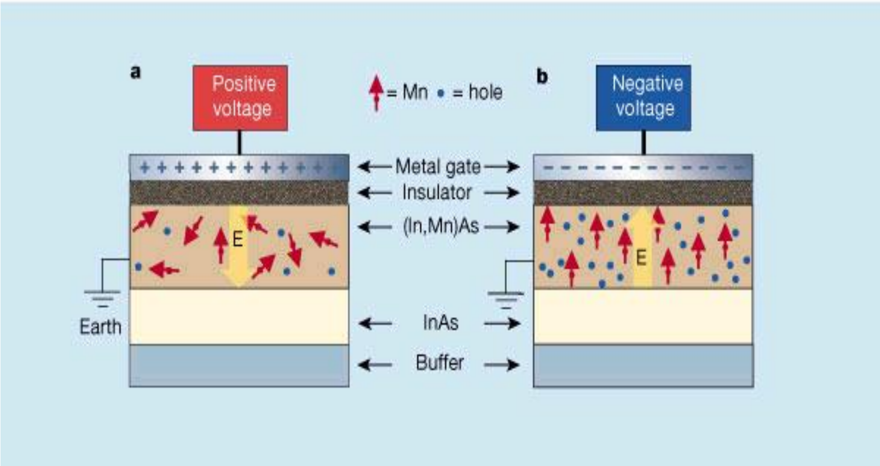
Nobel physical properties

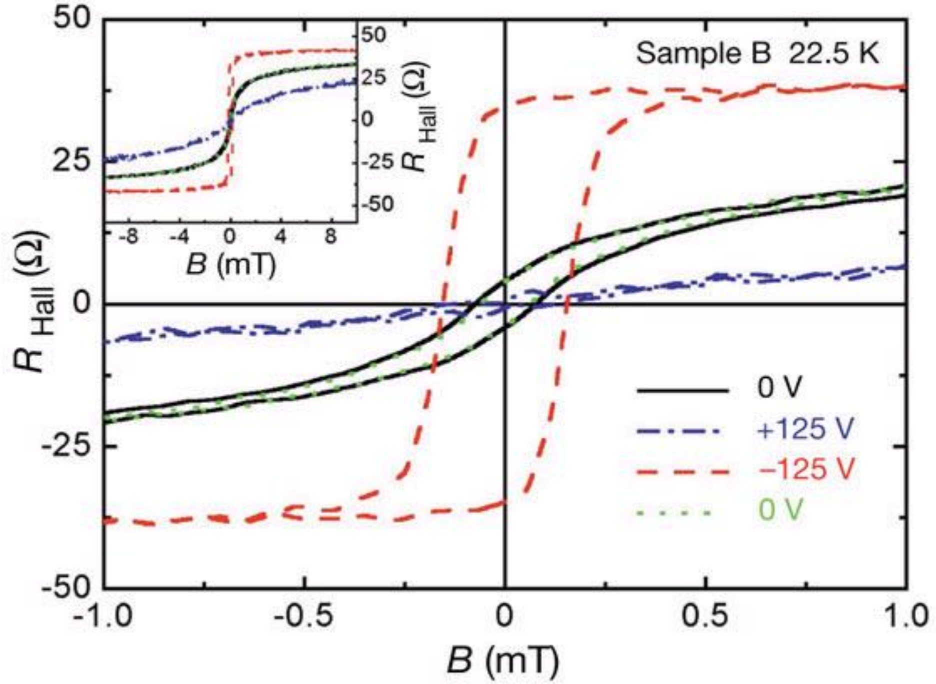


Ferromagnet/Ferroelectric material combination

Diluted magnetic semiconductor-- (In,Mn)As

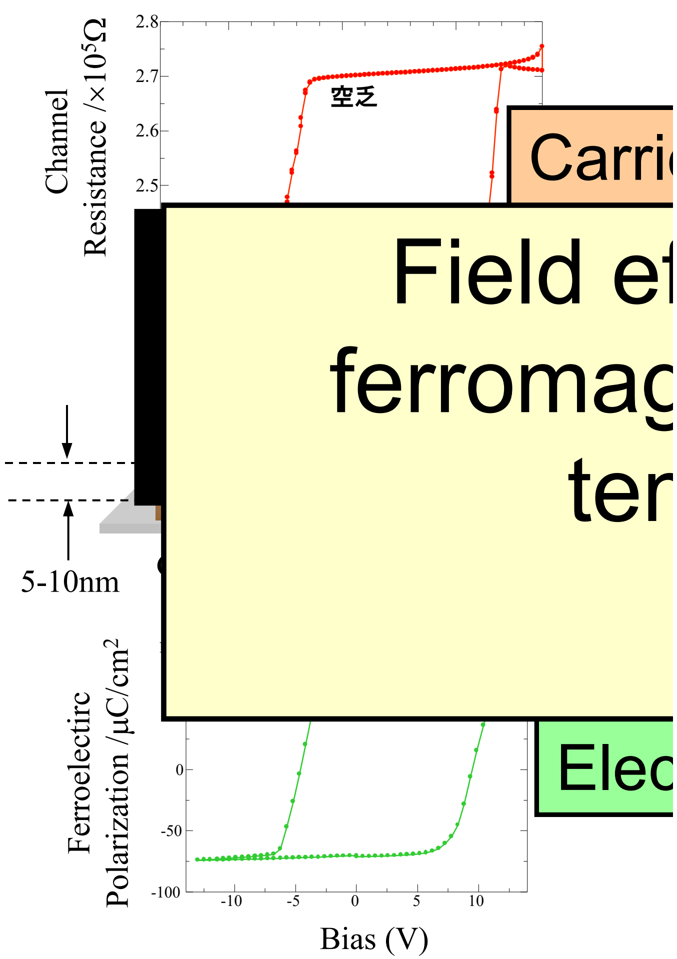
Field effect transistor

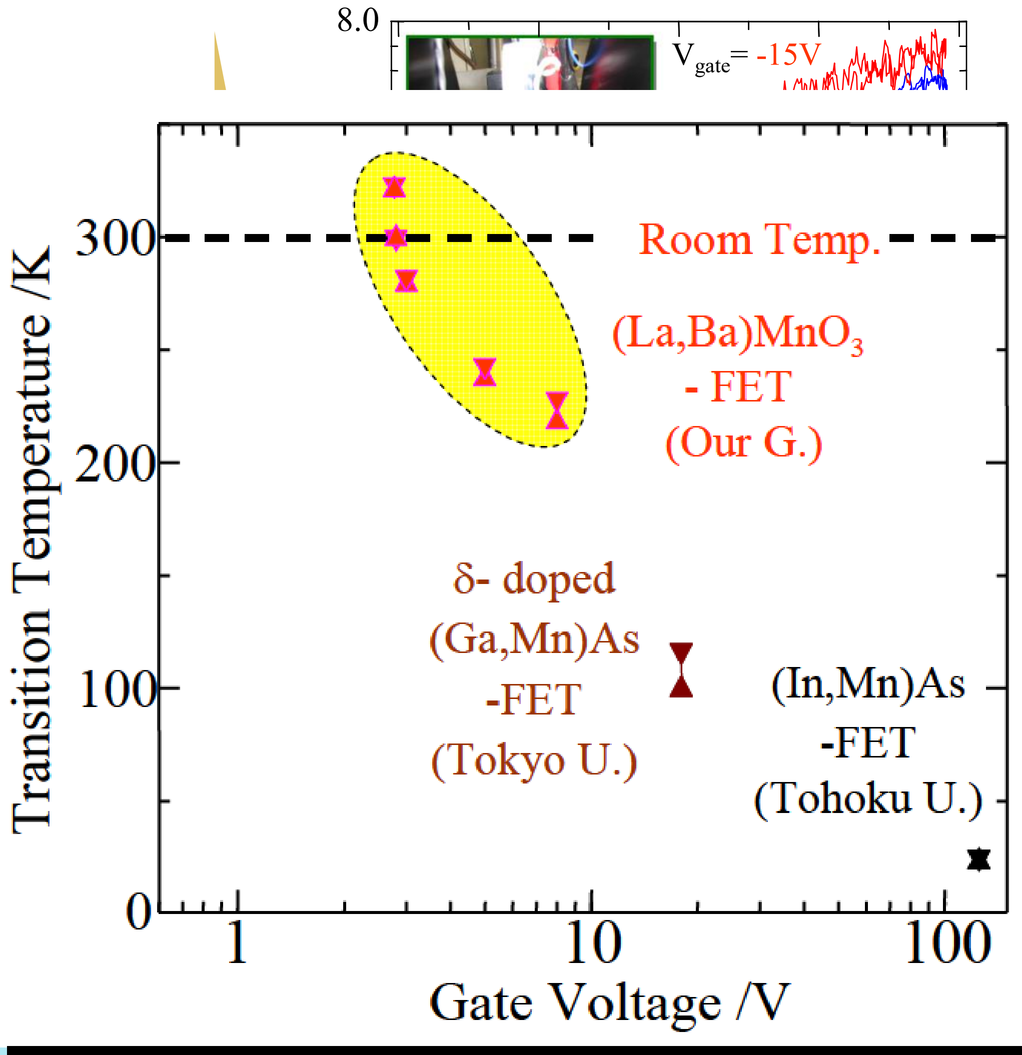




Nature ***408***, *944(2000)*

Ferromagnet/Ferroelectric material combination





Ferromagnet/Ferroelectric material combination

Conductive electron

Hund coupling

Localized spin

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

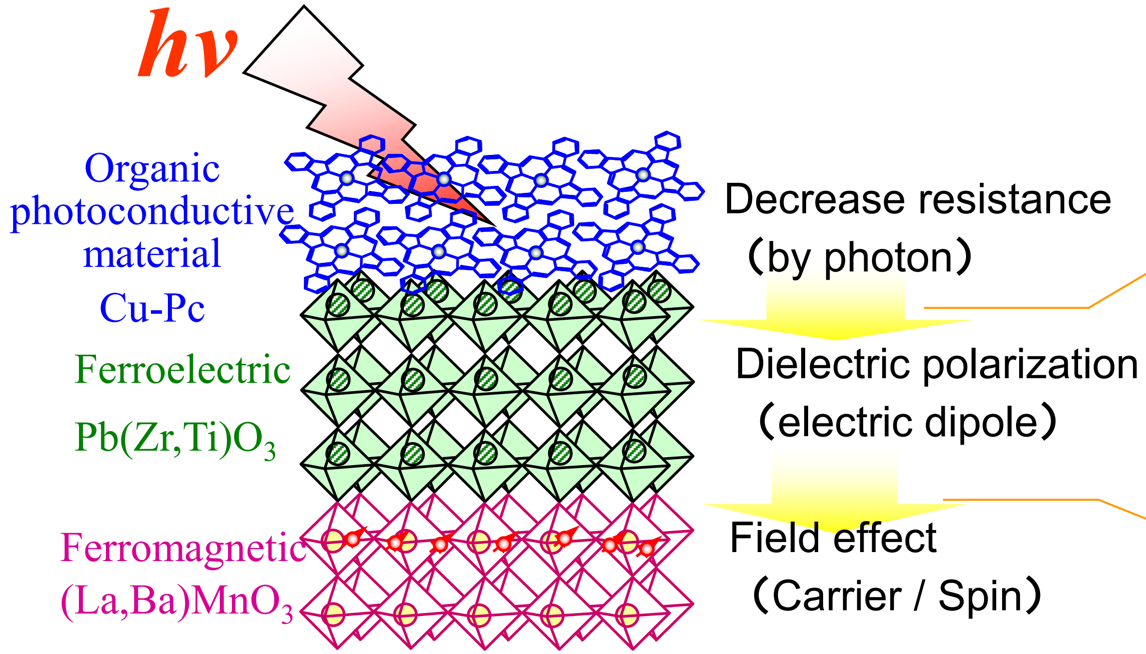
$\times$

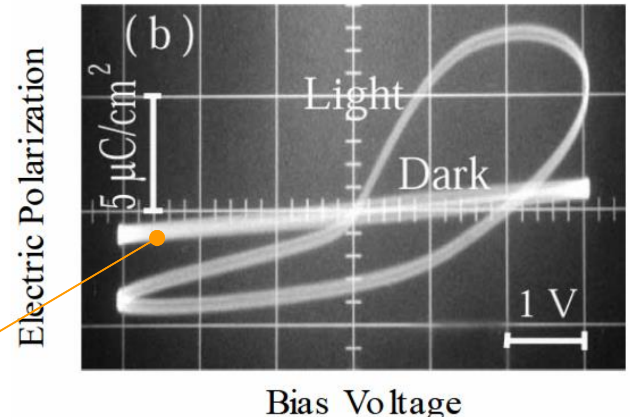
N (The number of carriers)

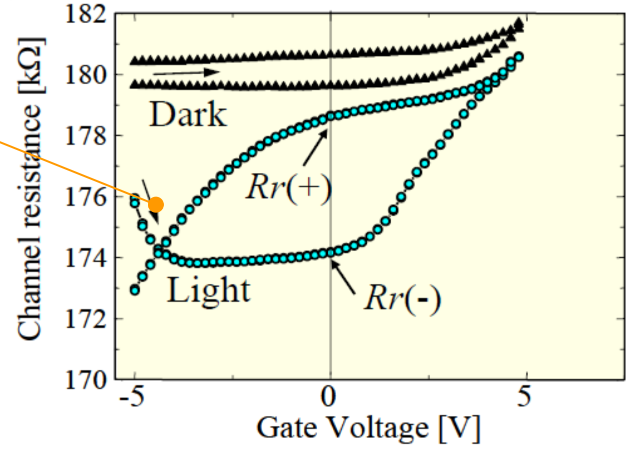
Electric field

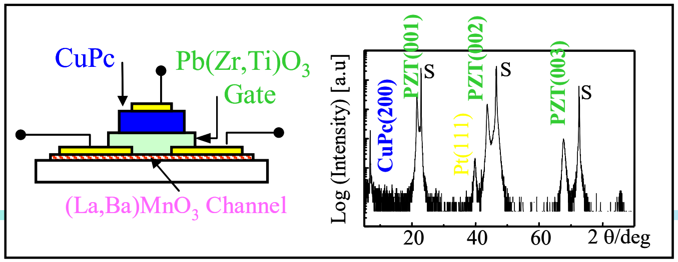
Photonic/Ferroelectric/magnetic material combination

Photon→Electric dipole → Carrier spin









Summary: Oxide spintronics

(1) Introduce strain effect --------- Room temperature CMR

(2) Introduce magnetic interaction between different layers --- Magnetic superlattice
Design of magnetic susceptibility

(3) Integrate different functional materials ------ Ferromagnetism + Ferroelectric