Double Exchange *IV*:
Ligand Field Effects

Detian Yang

09/25/2020

Ligand-Field Theory

Part I: A Simple Introduction(07/31/2020)

Part II: Molecular-orbital theory (Covalent Bond Theory)

II.I: Theoretical Frame for Exchange Interaction in Insulators (08/28/2020)

II.II: Superexchange

II.III: Goodenough-Kanamori Rule

II.IV: $3d^1$ Covalent Bond Method

Part III: Crystal Field theory (Electrostatic Theory)

III.I: $3d^1$ Model-Based Method (07/03/2020)

III.II: $3d^1$ Symmetry-Based Method

III.III: $3d^N, \mathrm{N} \geq 2$ Model-Based Method

III.IV: $3d^1$ Model-Based Method: Phillips-Cohen-Heine Theorem

Part II.III: Goodenough-Kanamori Rules I.

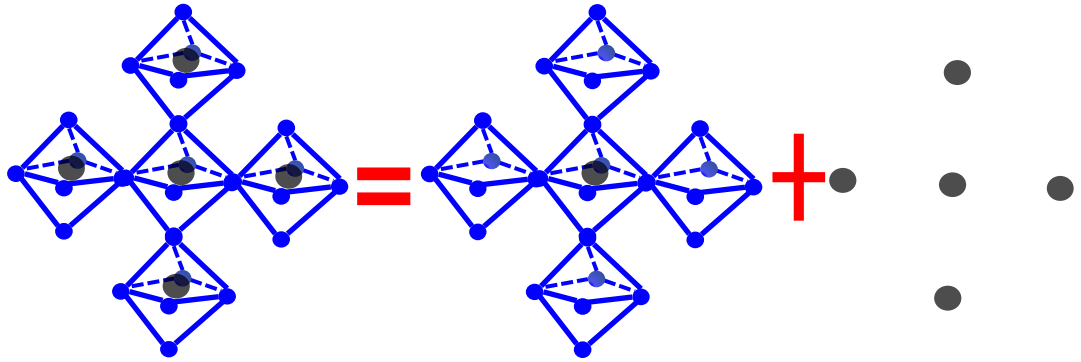
J. B. Goodenough, Phys. Rev. 100, 564 (1955)

J. B. Goodenough, Phys. And Chem. Solids 6, 287 (1958)

J. Kanamori, Phys. and Chem. Solids 10,87 (1959)

P.W. Anderson, Ch.2: Exchange in Insulators: Superexchange, Direct Exchange, and Double Exchange; Magnetism Volume I Edited by G. T. Rado & H. Suhl

Exchange Interaction in Transition Metal Oxides Insulator



(1) (2)

Theoretical Approach

(1) Local quasi-particle including all the influence of diamagnetic lattice

(2) Exchange Interaction between quasi-particles as perturbation

Semiempirical Approach

(1) Nearest-neighbors approximation in Ligand field theory: molecular orbitals or covalent bond

(2) Semiempirical rules to determine exchange type between two neighbor magnetic ions:

Goodenough-Kanamori Rules

Semiempirical Approach

Step 1:

Ligand Field Theory → **d Energy Level splitting**

→ **3d Spin Configuration**

↓

Step 2:

Local symmetry(Goodenough-Kanamori rules)

→ **Partial Bonds between Cations** → **Spin Order(Magnetism)**

Early Empirical 180° Rule: MnO, FeO, CoO, NiO, CuO…

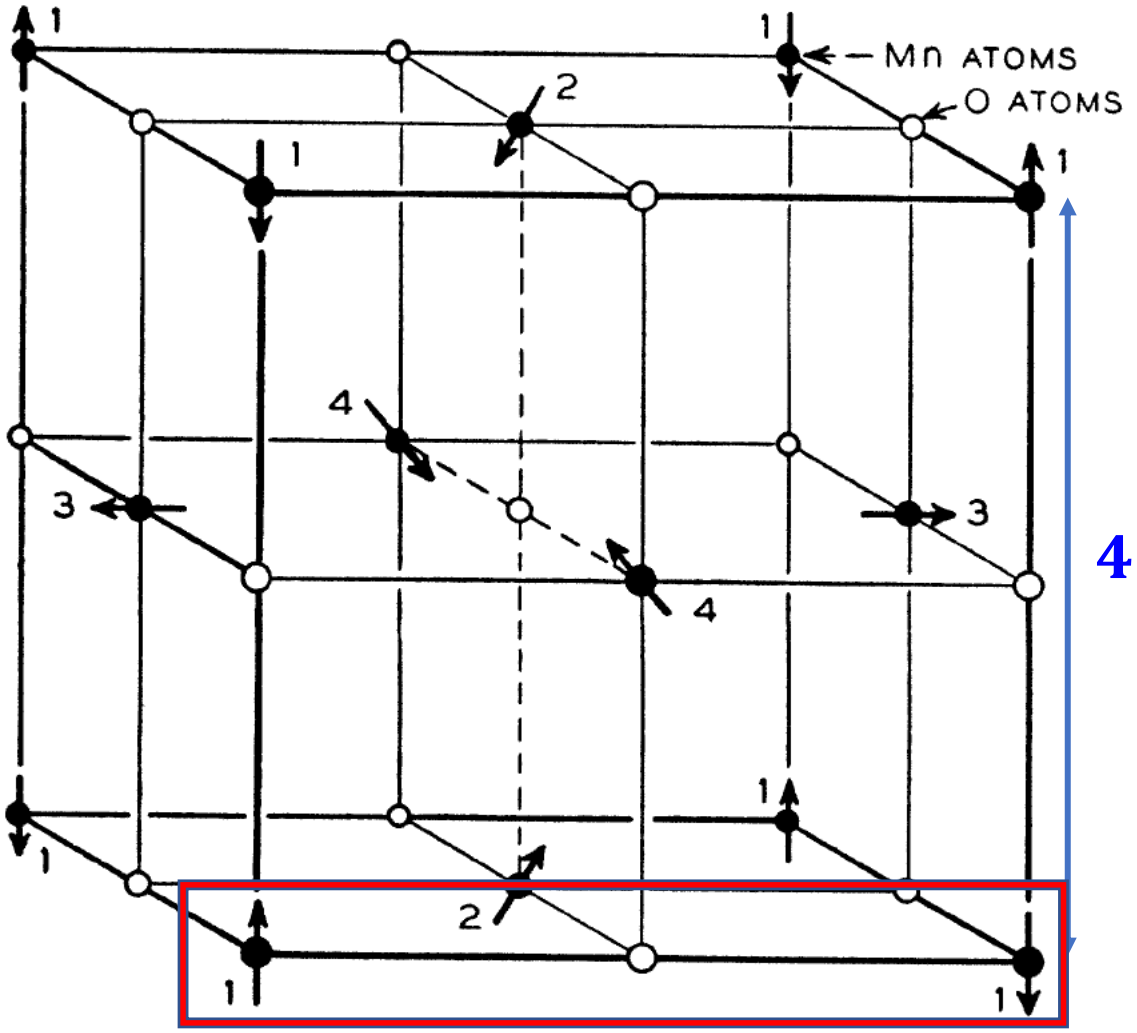
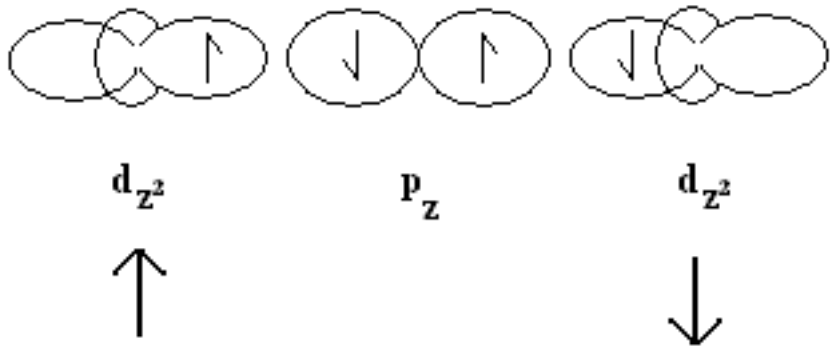


FIG. 1. Pattern for the MnO structure.

180° $d_{z^2} - p_\sigma$ bond



Kramers Formula: $H_{tt'} = \sum_{u,u'} \frac{\langle t|H^{tr}|u\rangle\langle u|H^{ex}|u'\rangle\langle u'|H^{tr}|t\rangle}{(E_u - E_t)(E_{u'} - E_t)}$

t, t': spin ground states; u, u': spin excited states;
H^{tr}: transition term; H^{ex}: exchange term

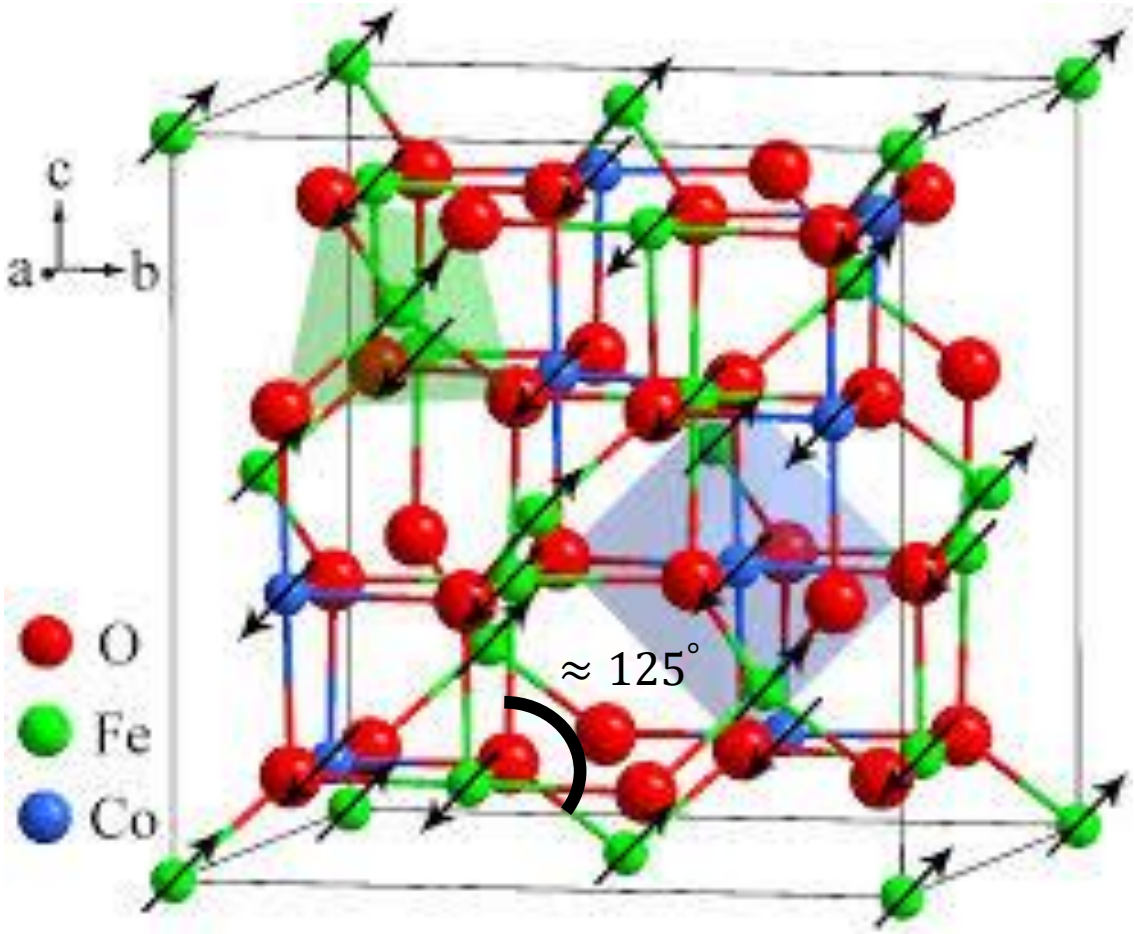
$$\Delta\hat{H}_{4;ex} = -\sum_{\vec{R}\neq\vec{R}',\sigma,\sigma'} \frac{b^2_{\vec{R}-\vec{R}'}}{\Delta V} \hat{S}^{\dagger}(\vec{R}',\sigma)\hat{S}(\vec{R},\sigma)\hat{S}^{\dagger}(\vec{R},\sigma')\hat{S}(\vec{R}',\sigma')$$

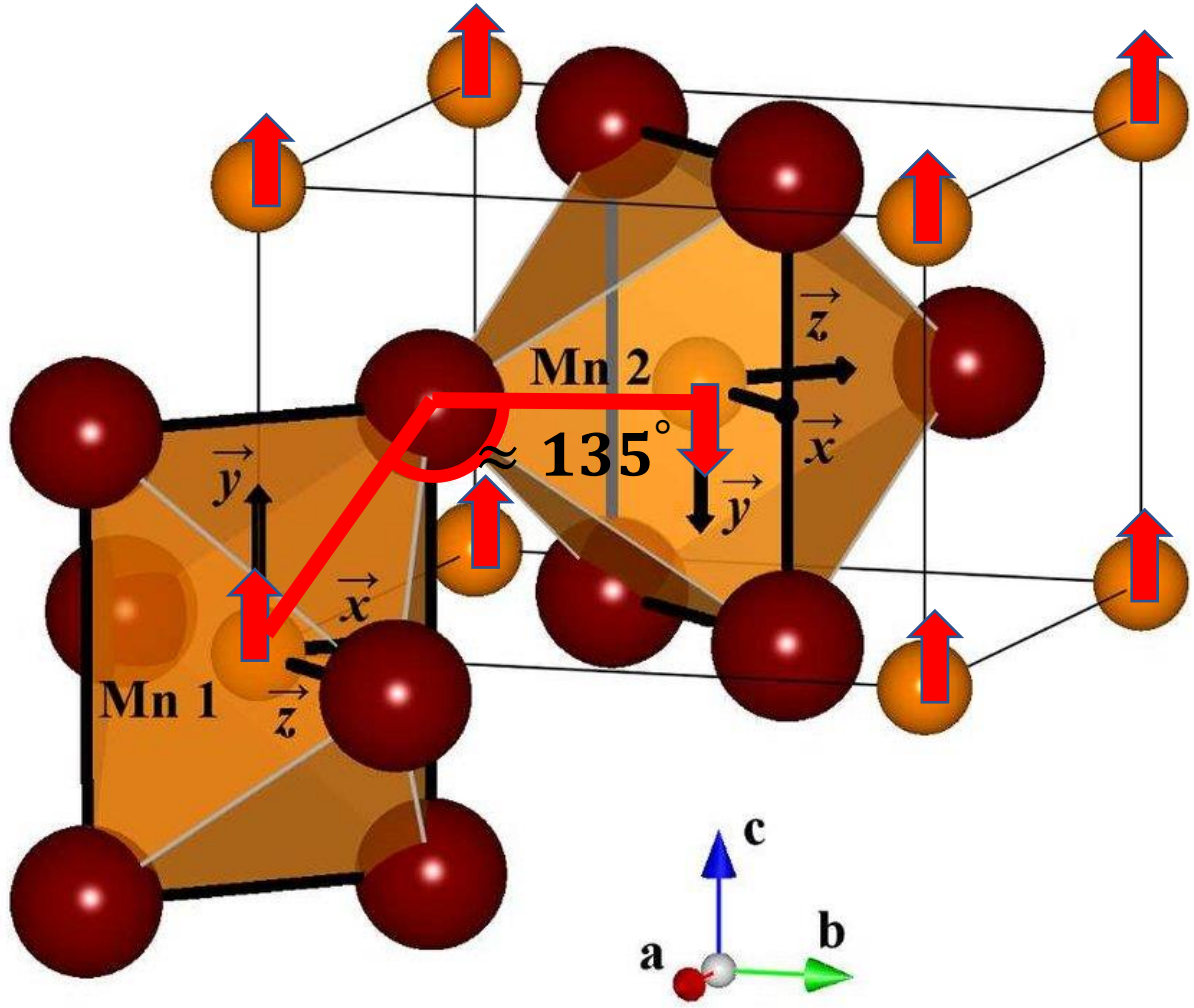
ΔV: Coulomb interaction between d spins on the same site

H. A. Kramers, Physica 1, 182 (1934)

P. W. Anderson, Phys. Rev. 79, 350 (1950)

Early Empirical 180° Rule: Spinel Ferrites AB_2O_4, Difluorides MF_2





$(Fe^{3+})_O d_{z^2} - (O^{2-})sp^3{}_\sigma - (Fe^{3+})_T sp^3$

$(Mn^{2+})_O d_{z^2} - (O^{2-})p_\sigma - (Mn^{2+})_O d_{x^2-y^2}$

Crystal Field Splitting: Ionic + Covalent

$$V_L = V_L^{\text{point}} + V_L^K + V_L^E.$$

Hartree-Fock Equation $h\Psi = E\Psi$;

$$h = h_0 + h',$$

$$h_0 = -\tfrac{1}{2}\Delta + V_M + V_L,$$

$$V_M = V_{\text{core}} + V_d^{\text{Coul}} + V_d^{\text{ex}};$$

$$E^a = \frac{1}{1-\lambda S}[(\varphi|h|\varphi) - \lambda(\varphi|h|\chi)], \qquad E^b = \frac{1}{1+\gamma S}[(\chi|h|\chi) + \gamma(\varphi|h|\chi)],$$

$$= \frac{1}{1-\lambda^2}[(\varphi|h|\varphi) - \lambda^2(\chi|h|\chi)], \qquad = \frac{1}{1-\gamma^2}[(\chi|h|\chi) - \gamma^2(\varphi|h|\varphi)].$$

$$\chi_e = \mu_s\chi_s + \mu_\sigma\chi_\sigma,$$

$$S_e = \mu_s S_s + \mu_\sigma S_\sigma, \qquad \mu_s^2 + \mu_\sigma^2 = 1.$$

$$\lambda_e = \lambda_s/\mu_s = \lambda_\sigma/\mu_\sigma,$$

$$\begin{aligned}\Delta = E_e^a - E_t^a = &[(\varphi_e|h|\varphi_e) - (\varphi_t|h|\varphi_t)] \\ &+ [(\lambda_s S_s + \lambda_\sigma S_\sigma - \lambda_\pi S_\pi)(\varphi_e|h|\varphi_e)] \\ &- [S_s(\varphi_e|h|\chi_s) + S_\sigma(\varphi_e|h|\chi_\sigma) - S_\pi(\varphi_t|h|\chi_\pi)] \\ &- [\gamma_s(\varphi_e|h|\chi_s) + \gamma_\sigma(\varphi_e|h|\chi_\sigma) \\ &\qquad - \gamma_\pi(\varphi_t|h|\chi_\pi)].\end{aligned}$$

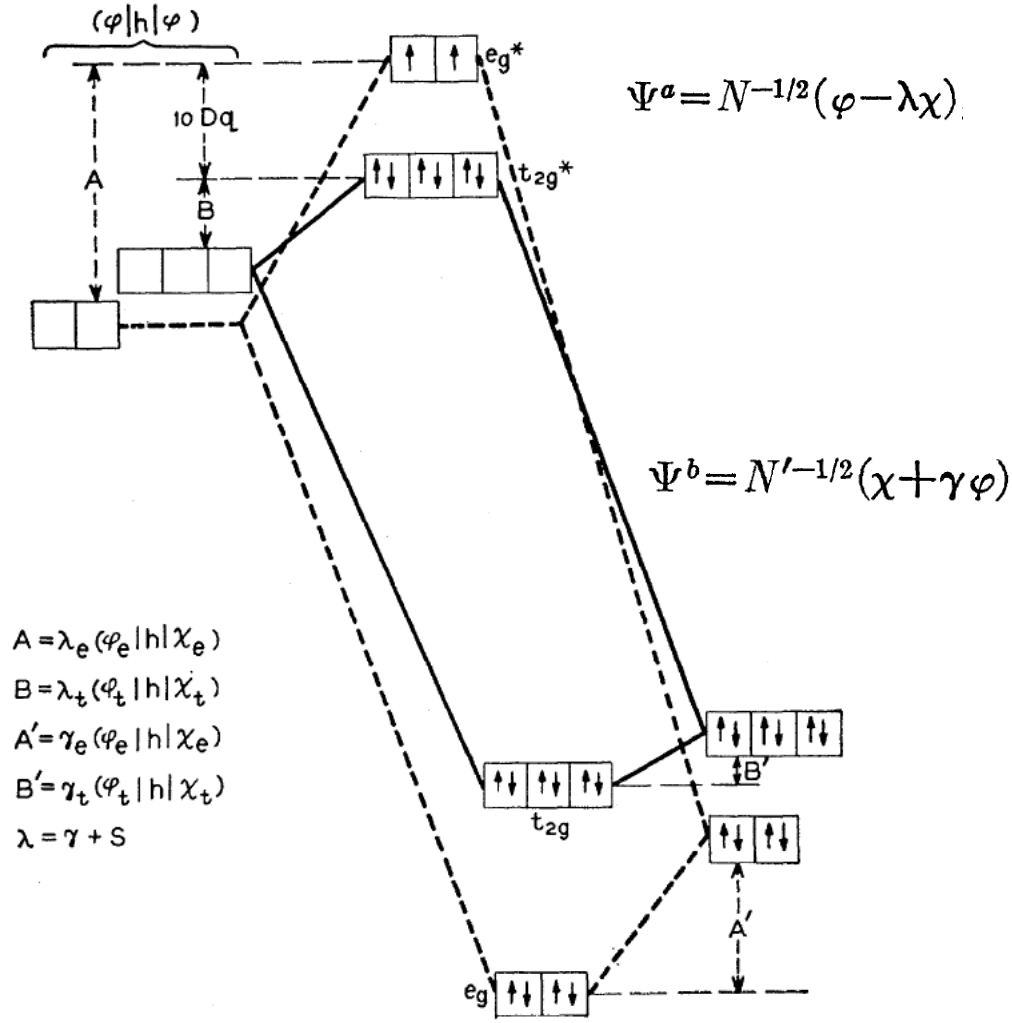


FIG. 5. Energy-level diagram for the molecular orbitals formed between Ni^{2+} d electrons and the F^- ligands.

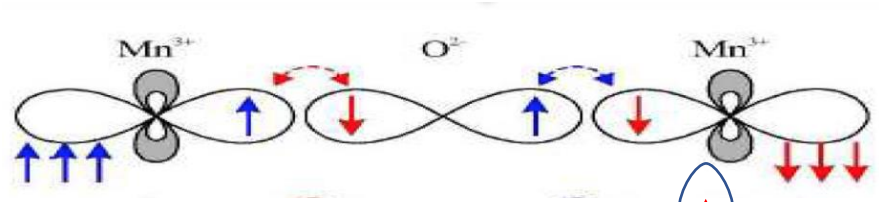
K. Knox, R. G. Shulman and S. Sugano, Phys. Rev. 130, 512(1963)

Goodenough-Kanamori Rules

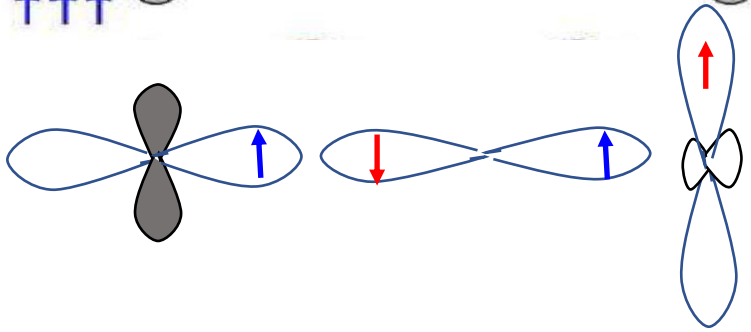
Assumptions:

1. The conservation of spin angular momentum
In the process of electron transfer, virtual or real.
2. The Pauli exclusion principle
3. Intraatomic spin-spin exchange is ferromagnetic
4. Double exchange

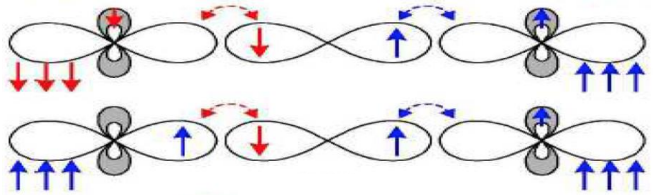
A



B



C



A. When the two ions have lobes of magnetic orbitals pointing to each other in such a way that the orbitals would have a reasonably large overlap integral, the exchange is **antiferromagnetic**.

(a) When the lobes are $\boldsymbol{d_{z^2}}$-type orbitals in the octahedral case, particularly in the "180° position" in which these lobes point directly to a ligand and each other, a particularly large superexchange is obtained

(b) When $\boldsymbol{d_{xy}}$ orbitals are in the 180° position to each other, so that they can interact via $p\pi$ orbitals on the ligands, antiferro-magnetism is obtained

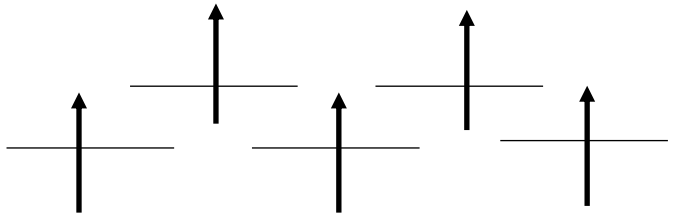
(c) In a 90° ligand situation, when one ion has a $\boldsymbol{d_{z^2}}$ occupied and the other a $\boldsymbol{d_{xy}}$, the $p\pi$ for one is the $p\sigma$ for the other and strong overlap and thus antiferromagnetic exchange are expected

B. When the orbitals are arranged in such a way that they are expected to be in contact but to have no overlap integral-most notably, a $\boldsymbol{d_{z^2}}$ and a $\boldsymbol{d_{xy}}$ in 180° position, where the overlap is zero by symmetry-the rule gives ferromagnetic interaction which usually is not as strong as antiferromagnetic one.

C. Electrons of anions can transfer into empty $\boldsymbol{d}$ orbitals of cations. The spins of transferred electron is parallel with the spin of the less-than-half full cation.

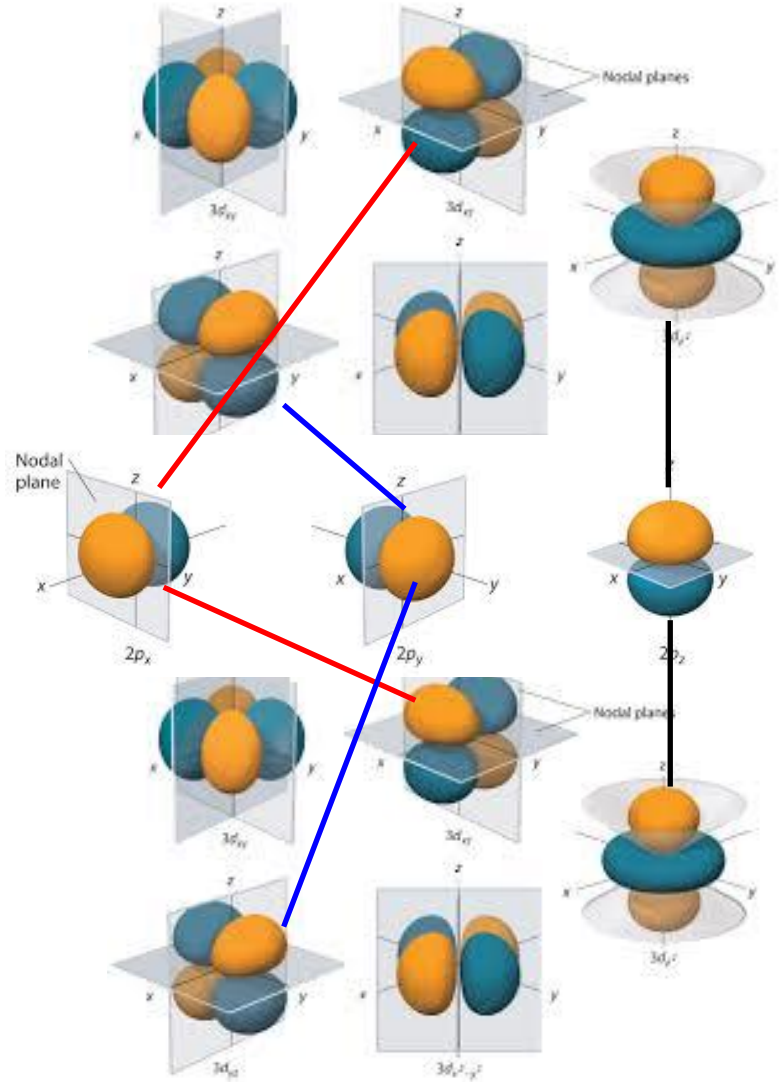
Goodenough-Kanamori Rules A.(a)&(b)&B: $LaFeO_3$, d^5

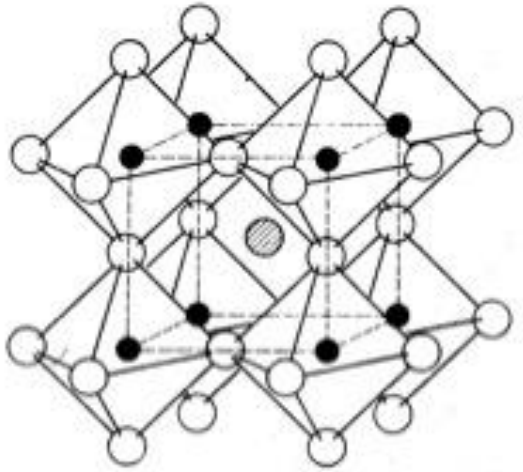
Fe^{3+},weak field

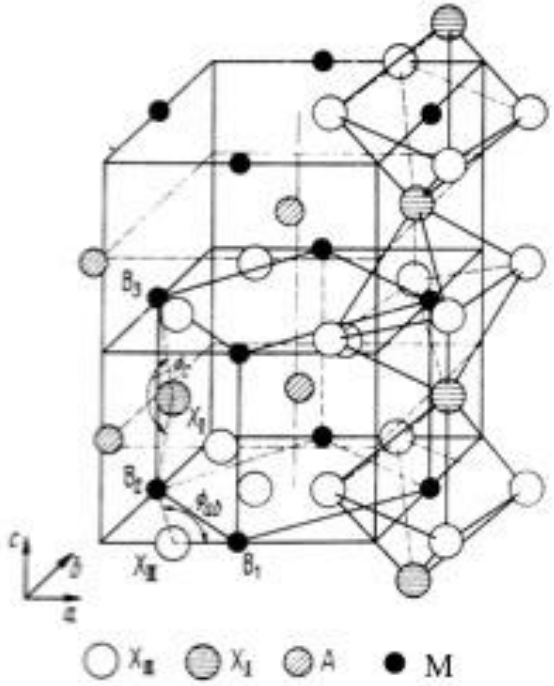


e_g γ

t_{2g} ϵ

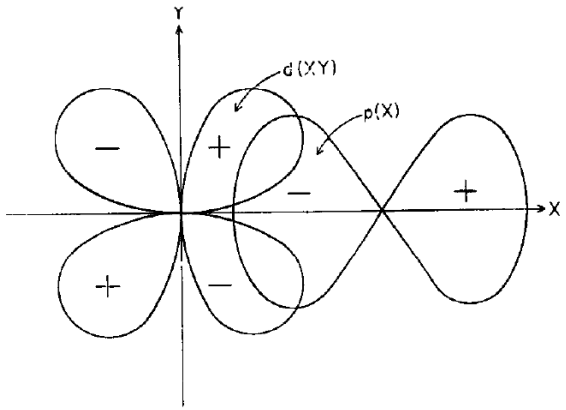


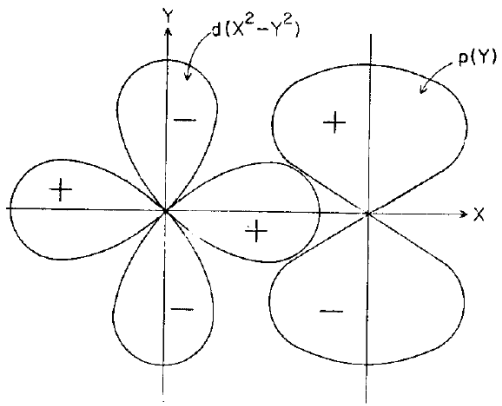




Cubic

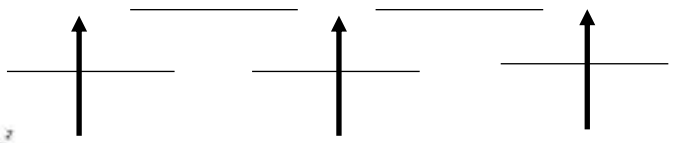
Orthorhombic

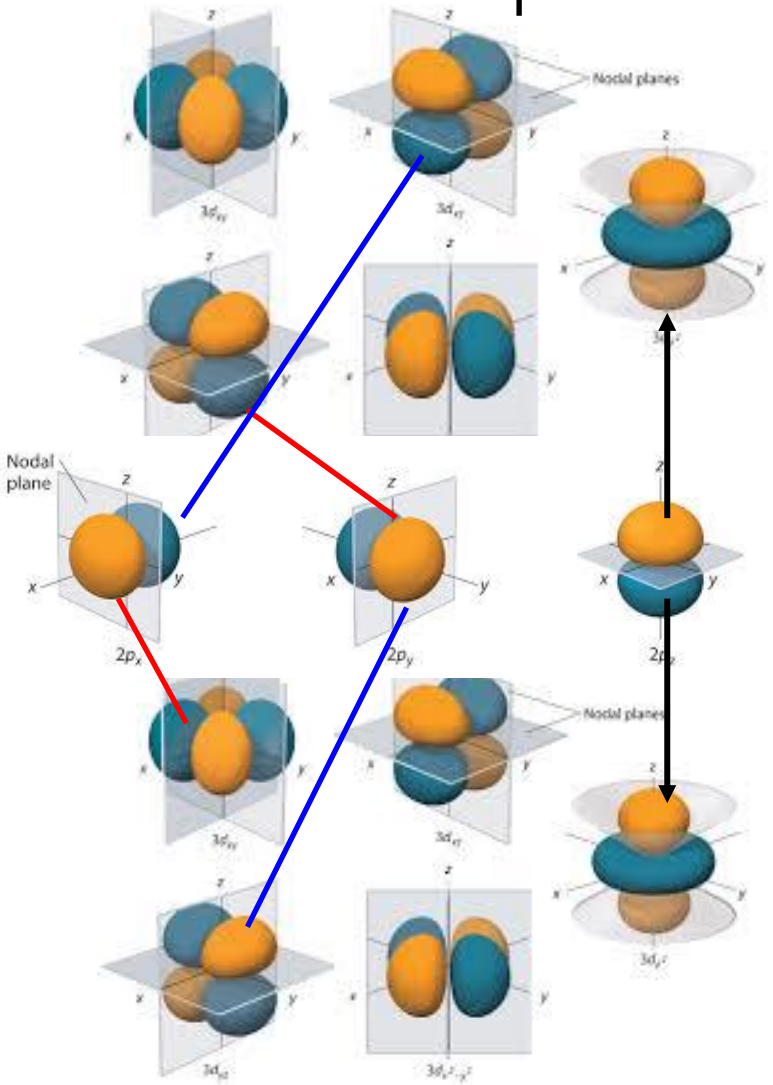




Goodenough-Kanamori Rules A.(b)&B&C: $LaCrO_3$, $SrMnO_3$, d^3

Cr^{3+}, weak field

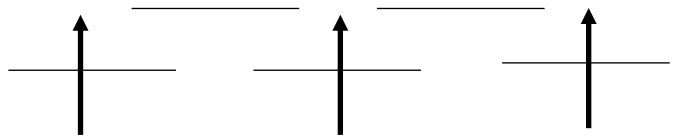




d^2sp^3

d^2sp^3

Mn^{4+}, weak field



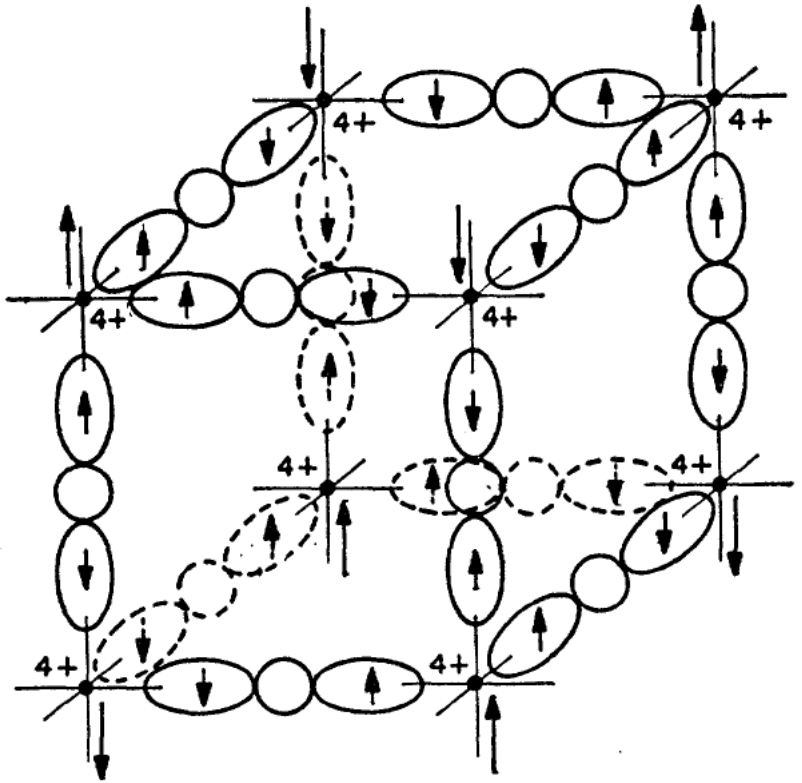
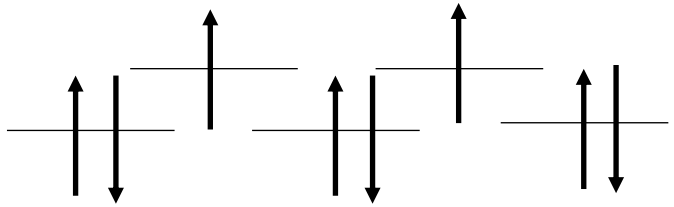
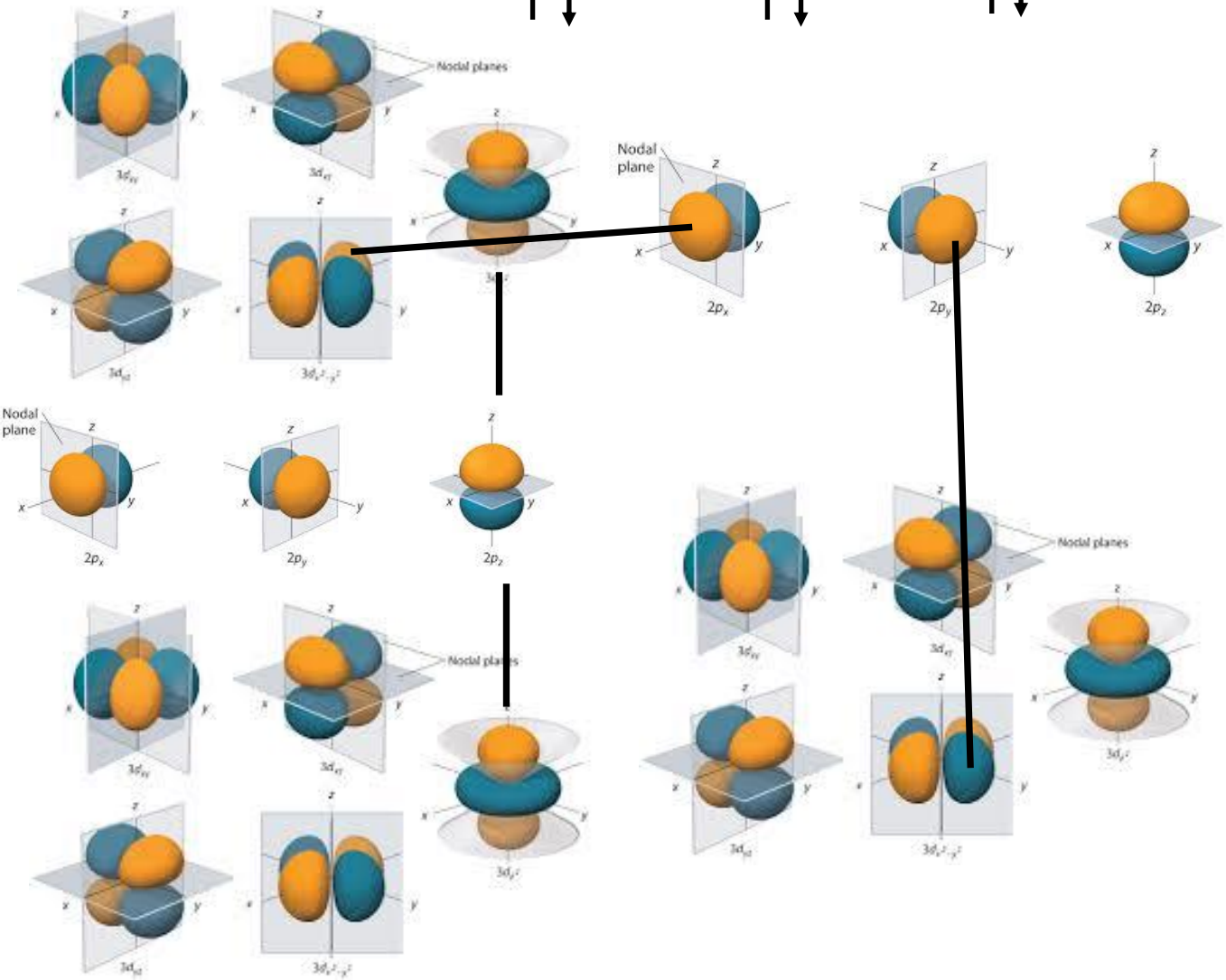


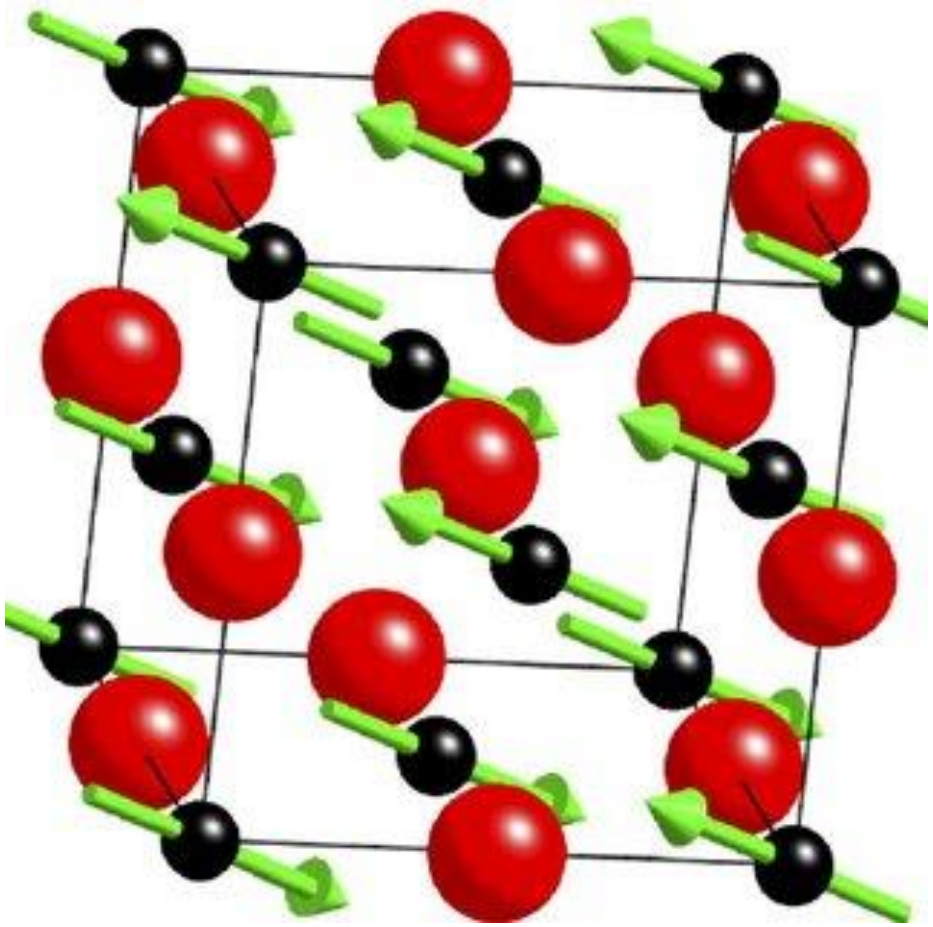
FIG. 1. Magnetic lattice for $x=1$; type G.

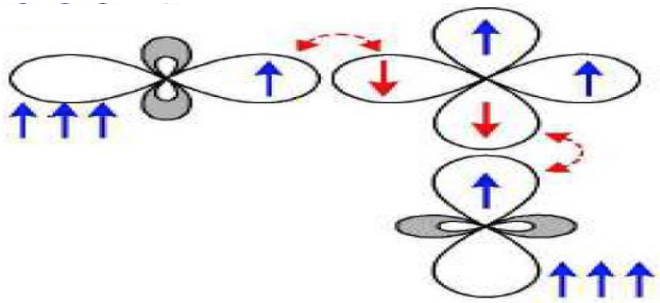
Goodenough-Kanamori Rules A.(a)&(c): NiO, d^8

Ni^{2+}, weak field









Study about Mixed-Valence Hexagonal Mangnites

$La_{1-x}Sr_xMnO_3$

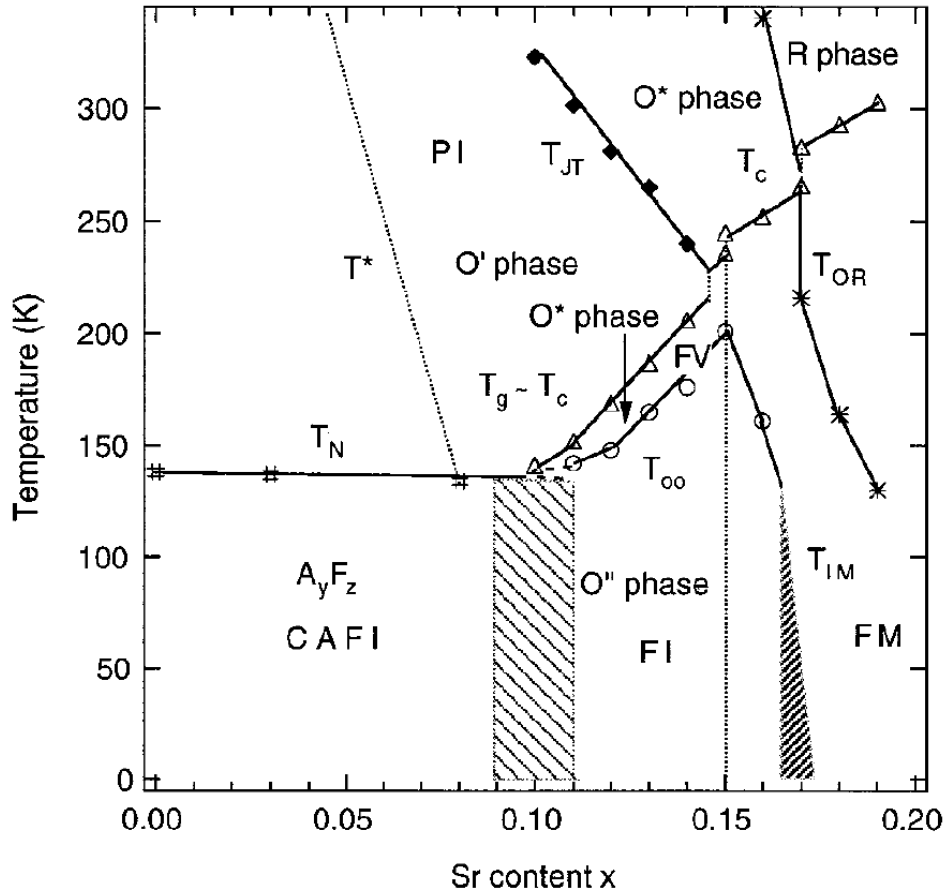


FIG. 1. Phase diagram for $La_{1-x}Sr_xMnO_3$, $0 \leqslant x \leqslant 0.20$. Experimental points above 310 K taken from the literature; T_N and two values of T_c for $x=0.17$ taken from $M(T)$; two values of T_c for $x=0.15$ taken from $C_p(T)$; all other points taken from Fig. 2.

Goodenough & Zhou, et al. PHYSICAL REVIEW B, VOLUME 64, 144414

$Y_{1-x}Sr_xMnO_3$

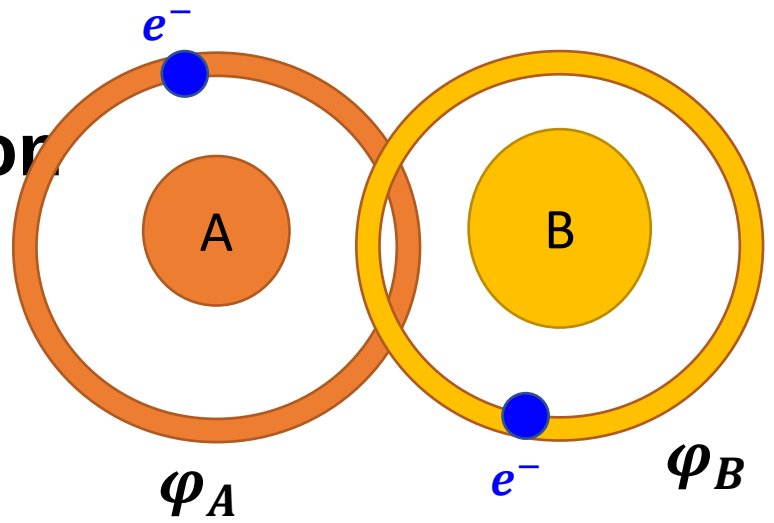
?????

Supplementary

Molecular Orbital, Bond and Hybridization

Molecular-orbital Theory

Molecular Orbital, Bond and Hybridization



MO: In molecules, a single electron moves in an averaged field of the nuclei and other electrons and its motion is described by a MO.

Hartree-Fock Method: Self-consistent Field Theory

Assumptions:

1. Heitler-London Method

LCAO: $|\psi\rangle = C_A|\varphi_A\rangle + C_B|\varphi_B\rangle$

$\hat{H}|\psi\rangle = \epsilon|\psi\rangle$ $\langle\varphi_A|\hat{H}|\psi\rangle = \langle\varphi_A|\epsilon|\psi\rangle$ $\langle\varphi_B|\hat{H}|\psi\rangle = \langle\varphi_B|\epsilon|\psi\rangle$

2. NO degeneracy

$$\begin{bmatrix} \epsilon_A - \epsilon & \beta - S\epsilon \\ \beta - S\epsilon & \epsilon_B - \epsilon \end{bmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = 0$$

3. $\epsilon_B > \epsilon_A$; $\frac{\beta}{\epsilon_B - \epsilon_A}, S \ll 1$

$$(\epsilon_A - \epsilon)(\epsilon_B - \epsilon) - (\beta - S\epsilon)^2 = 0$$

$$\epsilon^a \approx \epsilon_A + \frac{(\beta - S\epsilon_B)^2}{\epsilon_B - \epsilon_A} \quad \psi^a = \frac{1}{\sqrt{N_a}}(\varphi_B - \lambda\varphi_A)$$

$$\epsilon^b \approx \epsilon_A - \frac{(\beta - S\epsilon_A)^2}{\epsilon_B - \epsilon_A} \quad \psi^b = \frac{1}{\sqrt{N_b}}(\varphi_A + \gamma\varphi_B)$$

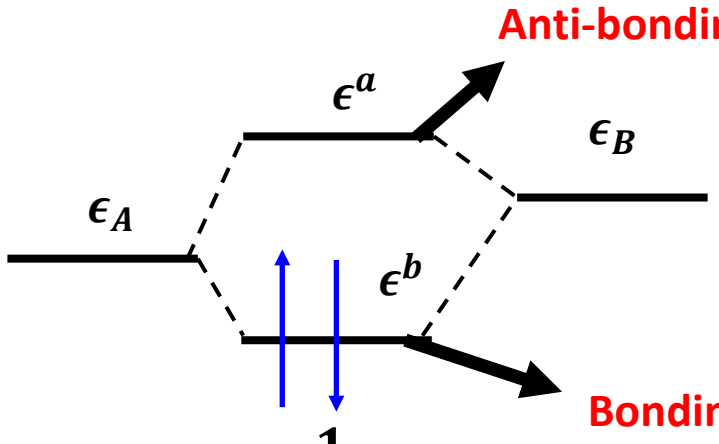
$\epsilon_A \equiv \langle\varphi_A|\hat{H}|\varphi_A\rangle$ $\epsilon_B \equiv \langle\varphi_B|\hat{H}|\varphi_B\rangle$

$S \equiv \langle\varphi_A|\varphi_B\rangle$ $\beta \equiv \langle\varphi_A|\hat{H}|\varphi_B\rangle = \langle\varphi_B|\hat{H}|\varphi_A\rangle$

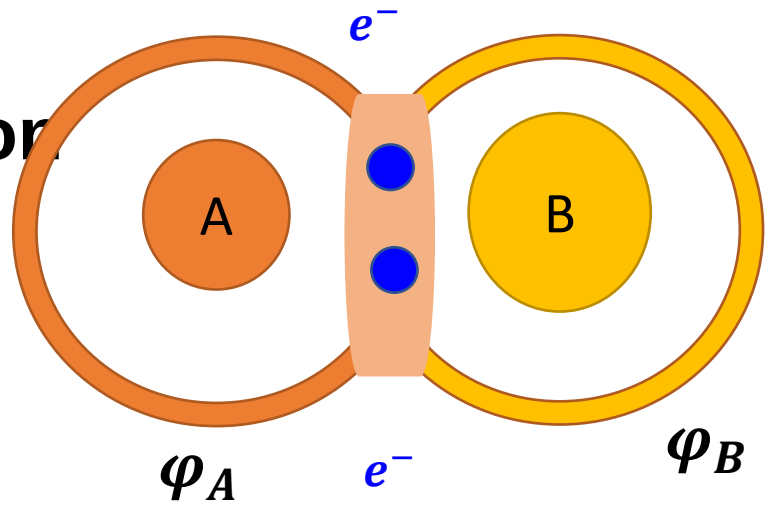
Covalency Parameter $\gamma \approx -\frac{\beta - S\epsilon_A}{\epsilon_B - \epsilon_A}$ $\lambda \approx \gamma + S$

Molecular-orbital Theory

Molecular Orbital, Bond and Hybridization

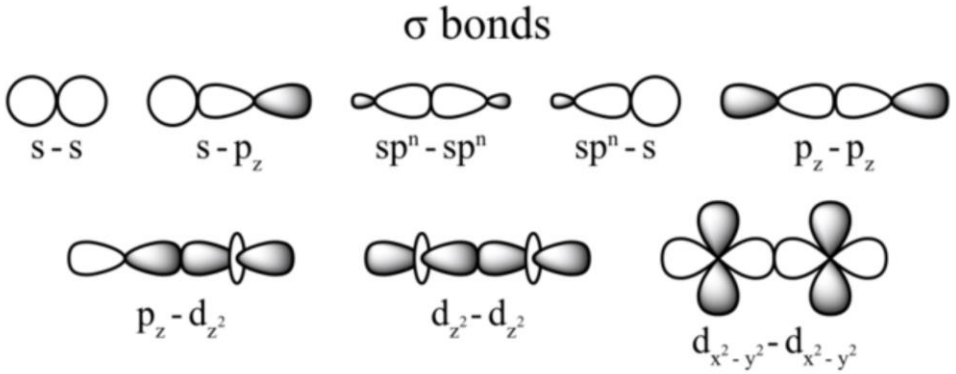


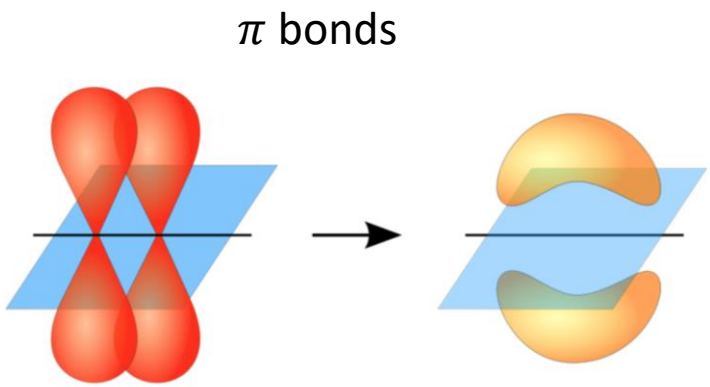
$$\chi \equiv \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$



$$\Psi = \psi_1^b \psi_2^b \chi = \frac{1}{N_b}(\varphi_{1A} + \gamma\varphi_{1B})(\varphi_{2A} + \gamma\varphi_{2B})\chi$$

$$\approx \frac{1}{N_b}[\varphi_{1A}\varphi_{2A} + \gamma(\varphi_{1A}\varphi_{2B} + \varphi_{2A}\varphi_{1B})]\chi = \Psi_{ion}\chi + \gamma\Psi_{cov}\chi$$





Hybrid Orbitals and Geometry			
Atomic Orbitals Used	Hybrid Orbitals Formed	Geometry	Example Compound
s,p	Two sp orbitals	180° Linear	CO_2
s,p,p	Three sp^2 orbitals	120° Trigonal Planar	SO_3
s,p,p,p	Four sp^3 orbitals	109.5° Tetrahedral	$GeCl_4$
s,p,p,p,d	Five dsp^3 orbitals	90°, 120° Trigonal Bipyramidal	PCl_5
s,p,p,p,d,d	Six d^2sp^3 orbitals	90°, 90° Octahedral	$Mo(CO)_6$

Molecular-orbital Theory

A Naive Bond Model of $MX_6(O_h)$: σ bon

n d electrons + 12 ligand electrons $= n + 12$

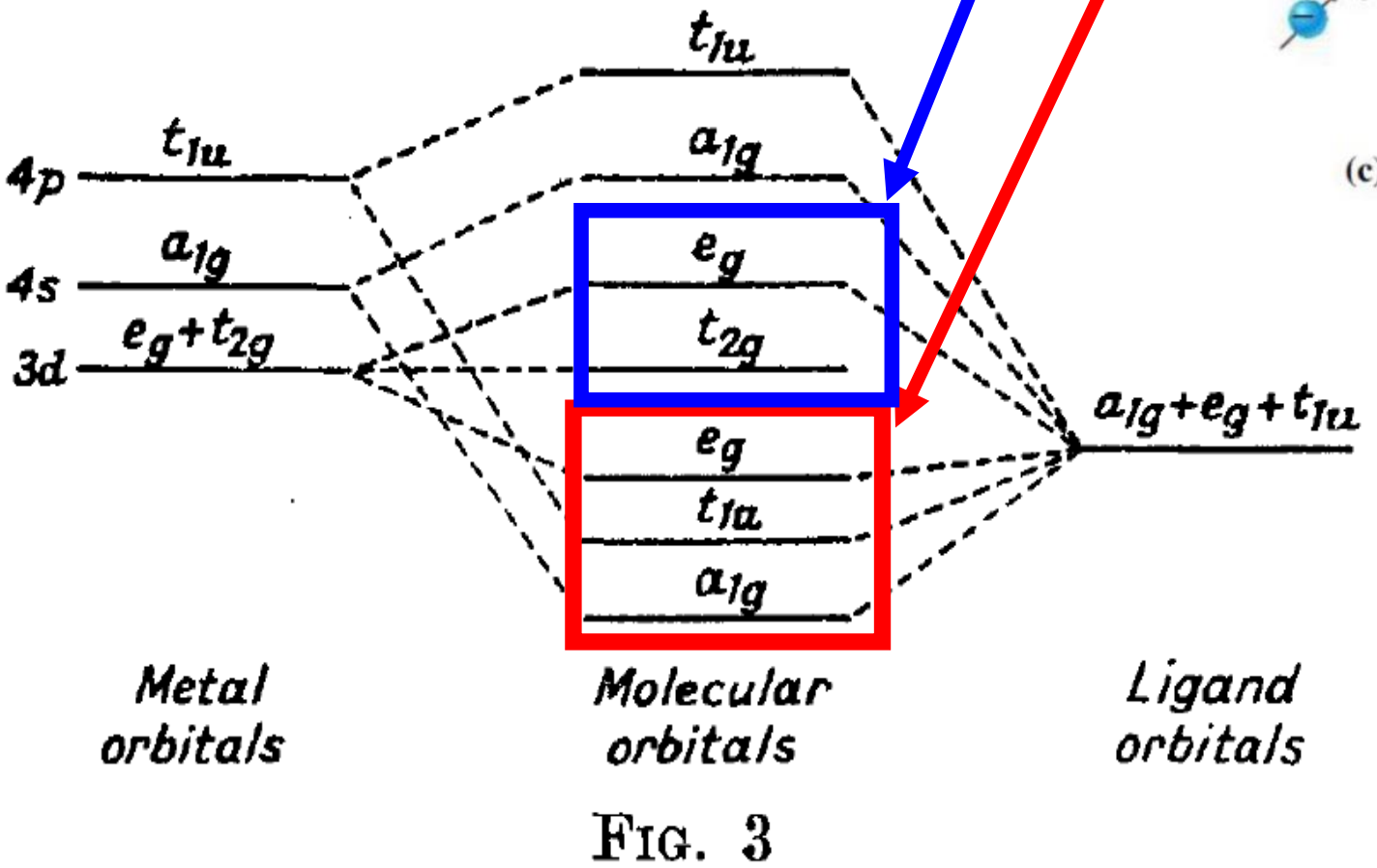
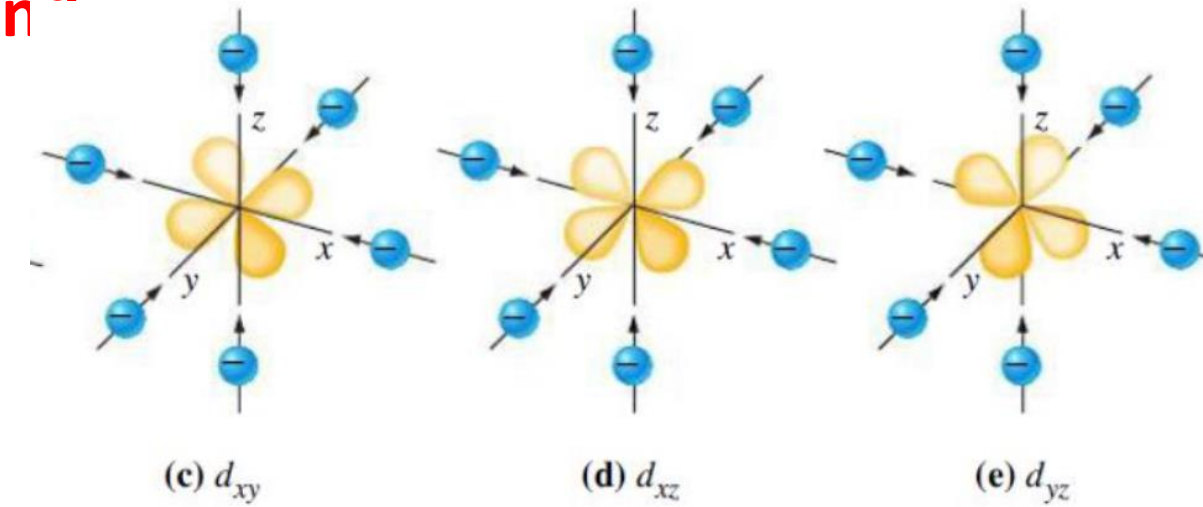
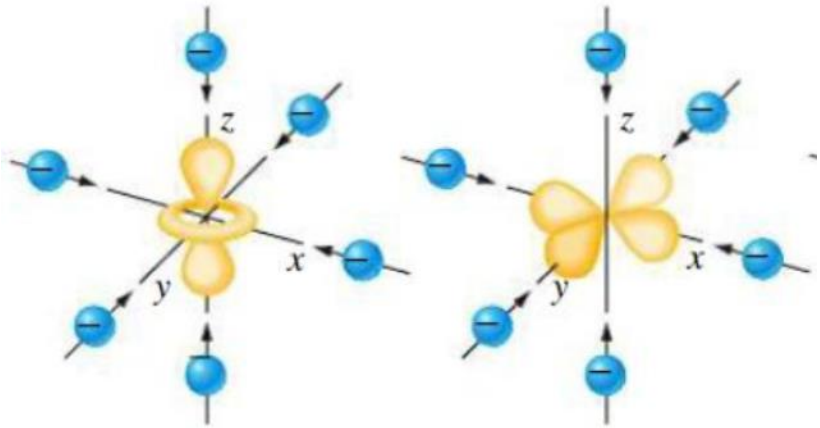


FIG. 3



(c) d_{xy} (d) d_{xz} (e) d_{yz}



(a) d_{z^2} (b) $d_{x^2-y^2}$

Kanamori’s Summary

Kanamori's Summary

Table 2. The 180° interaction between cations in octahedral sites

Number of 3*d*-electrons of interacting cations	Species of interacting cations	Relevant bond and mechanism	Resultant superexchange interaction	Total superexchange interaction
d^3–d^3	Mn^{4+}–Mn^{4+} Cr^{3+}–Cr^{3+}	σ-bond and π-bond A, G, A–H, S	Antiferro.	Antiferro.
d^8–d^8	Ni^{2+}–Ni^{2+}	σ-bond A, G, A–H, S	Antiferro.	Antiferro.
d^5–d^5	Mn^{2+}–Mn^{2+} Fe^{3+}–Fe^{3+}	σ-bond A, G, A–H, S π-bond G, A–H, S π-bond A	Antiferro. Antiferro. (weak) Uncertain (weak)	Antiferro.
d^8–d^3	Ni^{2+}–V^{2+}	σ-bond and π-bond A, G, A–H, S	Ferro.	Ferro.
d^5–d^3	Fe^{3+}–Cr^{3+}	σ-bond A, G, A–H, S π-bond G, A–H π-bond A, S	Ferro. Antiferro. (weak) Uncertain (weak)	Ferro.
d^4–d^4	Mn^{3+}–Mn^{3+}	*		
d^6–d^6	FeO	σ-bond A, G, A–H, S π-bond	Antiferro. Uncertain (weak)	Antiferro.
d^7–d^7	CoO	σ-bond A, G, A–H, S π-bond	Antiferro. †	Antiferro.

* Depends on the direction of the line of superexchange.
† Weak, but dependent on the direction of the line of superexchange.
A = Anderson's mechanism, G = Goodenough's mechanism, A-H = Anderson and Hasegawa's mechanism, S = Slater's mechanism.

Table 5. The 90° interaction between cations in octahedral sites

Number of 3*d*-electrons of interacting cations	Species of interacting cations	Relevant bond and mechanism	Resultant superexchange interaction	Total superexchange interaction
d^8–d^8	Ni^{2+}–Ni^{2+}	$p\sigma$–$d\gamma$ bond A, G S s–$d\gamma$ bond A, G, A–H, S	Ferro. Uncertain Antiferro.	Ferro.
d^5–d^5	Mn^{2+}–Mn^{2+} Fe^{3+}–Fe^{3+}		Uncertain	*
d^3–d^3	Cr^{3+}–Cr^{3+}	$p\sigma$–$d\gamma$ and $p\sigma$–$d\epsilon'$ A, G, A–H, S $p\pi$–$d\epsilon$ and s–$d\gamma$ A, G, A–H, S	Ferro. Antiferro. (weak)	Ferro.
d^8–d^3	Ni^{2+}–V^{2+}	$p\sigma$–$d\gamma$ and $p\sigma$–$d\epsilon'$ A, G, A–H S $p\pi$–$d\epsilon'$ and s–$d\gamma$, s–$d\gamma'$ A, G, A–H	Antiferro. Uncertain (weak) Ferro. (weak)	Antiferro.

* Tendency towards antiferromagnetic interaction with decreasing number of 3*d*-electrons.

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