Last time

Magnetic moments
Types of magnetism

Environment
    Rare earth's: 4f shell's small ('inner' electrons)
    Iron group: 3d shell's on the outside
        => decoupling of L and S, J no longer good Quantum number
        => splitting of the 2L+1 orbital states
        => Quenching of the orbital angular momentum ($L_z \rightarrow 0$)

        => High spin – Low spin transitions
        => Jahn-Teller distortions
        => Orbital excitations (orbitons)

    Anisotropy

Lectures

Lect. 1	Introduction	Ch.1; 2.1-2.5; 8.9
Lect. 2	Interactions, environment	3.1, Ch.4; 7.1-7.7
Lect. 3	Ordering, Domains	5.1-5.3; 6.7; 8.3, 8.7, 8.8
Lect. 4	Symmetry breaking	6.1-6.6
Lect. 5	Quantum magnetism	8.1-8.6

Interactions

- Dipole – Dipole

- Direct exchange (H_2 molecule)

- Indirect exchange

- Double exchange

- Anisotropic exchange

- Rudeman Kittel Kasuya Yoshida (RKKY)

- Stoner ("spontaneous Pauli")

- Ch. 4 & 7.2,7.3,7.7

Dipole-dipole interaction

Dipole-dipole interaction is an anisotropic interaction

$$E = \frac{\mu_0}{4\pi} \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \vec{e}_{12})(\vec{\mu}_2 \cdot \vec{e}_{12})}{r_{12}^3}$$

$$E \approx 10^{-23} \text{ J} \sim 1\text{K} \text{ for } r = 2 \overset{\text{o}}{\text{A}} \text{ and } \mu = \mu_B$$

In real materials: $T_c \sim 10^2 - 10^3$ K !!

→ Dipole-dipole interaction hardly ever dominates

H$_2$ molecule

- LCAO gives wrong solution (e.g. triplet ground state)
- Correlated picture (Heitler-London approach) is better
  - Starting point: two electron orbitals $\left|\phi_a(1)\phi_b(2)\right\rangle$ and $\left|\phi_a(2)\phi_b(1)\right\rangle$
  - Wavefunctions

$$\Psi_S = \frac{1}{\sqrt{2}}\left[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)\right]\chi_S$$

$$\Psi_T = \frac{1}{\sqrt{2}}\left[\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right]\chi_T$$

  - Spin parts:

$$\chi_S = \frac{1}{\sqrt{2}}\left(\left|\uparrow\downarrow\right\rangle - \left|\downarrow\uparrow\right\rangle\right)$$

$$\chi_T = \begin{cases} \left|\uparrow\uparrow\right\rangle \\ \frac{1}{\sqrt{2}}\left(\left|\uparrow\downarrow\right\rangle + \left|\downarrow\uparrow\right\rangle\right) \\ \left|\downarrow\downarrow\right\rangle \end{cases}$$

H₂ molecule

- ## Singlet ground state

- ## Exchange energy: Pauli + Coulomb

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1{}^2 + \nabla_2{}^2\right) + V_c(1,2)$$

$$V_c(1,2) = \frac{e^2}{|r_1 - r_2|} + \frac{e^2}{|R_1 - R_2|} - \frac{e^2}{|r_1 - R_2|} - \frac{e^2}{|r_2 - R_2|}$$

$$E_S - E_T = 2\langle \phi_a(1)\phi_b(2)|V_c|\phi_a(2)\phi_b(1)\rangle := 2J$$

$$H = -2J\vec{S}_1 \cdot \vec{S}_2 = \begin{cases} -2J \cdot -\dfrac{3}{4} & \text{for the spin singlet} \\ \\ -2J \cdot \dfrac{1}{4} & \text{for the spin tripl et} \end{cases}$$

Exchange interaction

- Heisenberg Hamiltonian

$$H = -2\sum_{i,j}{}' J_{ij} \vec{S}_i \cdot \vec{S}_j$$

- J>0: Ferro
- J<0: Antiferro

Direct exchange

- **Need direct wave function overlap**
  - Often ferromagnetic
  - Small in 4f, 5f elements
  - Can be important in 3d oxides (but see indirect!)
  - In 3d metals: electron delocalization

Oxide: ferro   'hopping': ferro   'hopping': antiferro
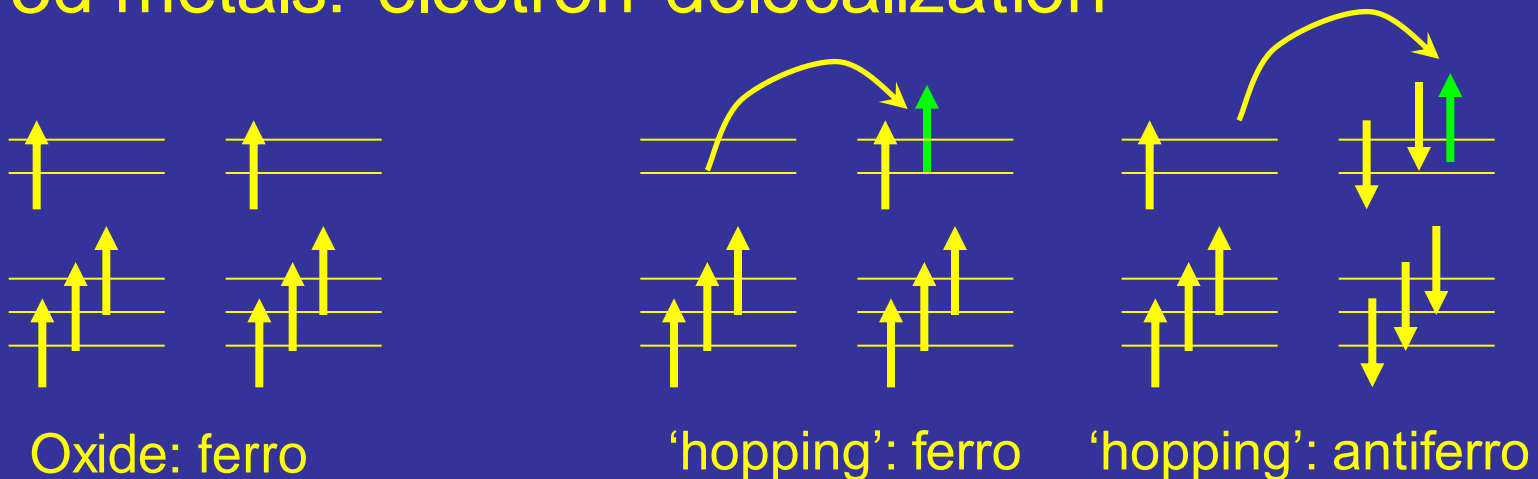
- Relatively small (but remember TiOX)
- Depends on orbital occupation and geometry

Indirect exchange
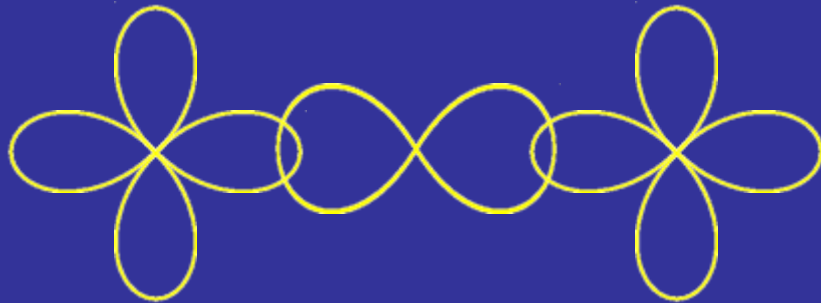
Ground state antiferro
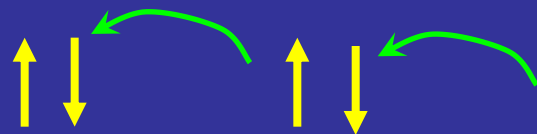
'2*hopping'
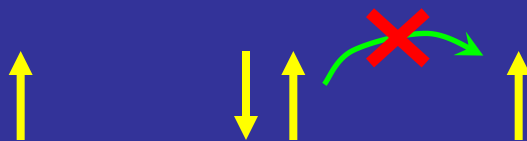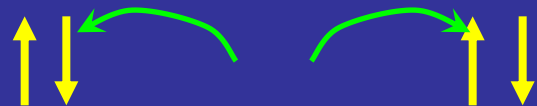
Pauli forbidden

Hopping →
        delocalization →
                energy gain

Energy: 2 hops = 2t; cost=U
                → $J \sim -t^2/U$

Examples: High Tc's; MnO; MnF_2

Indirect exchange
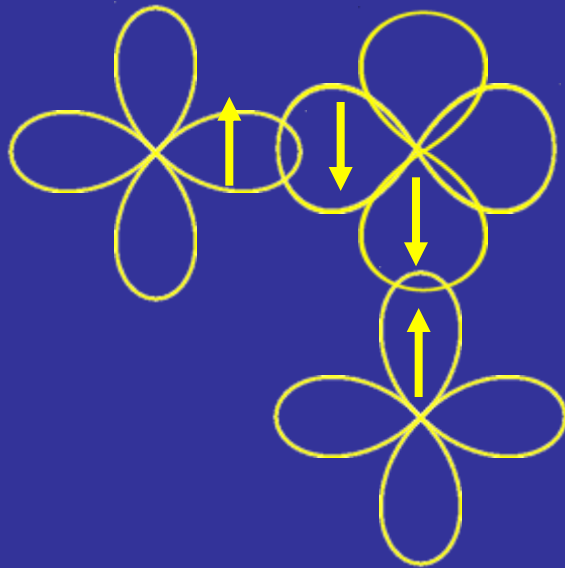
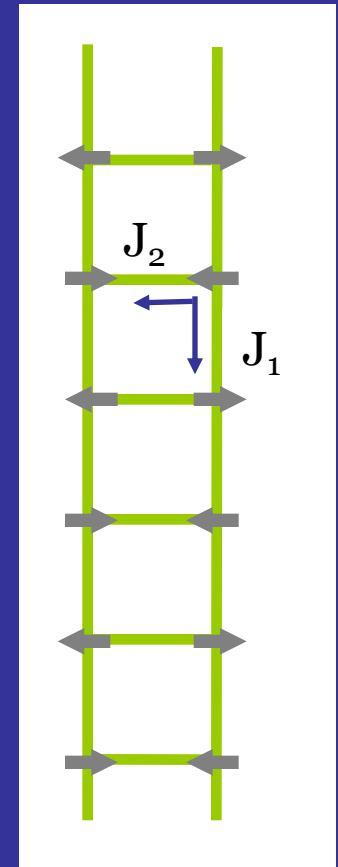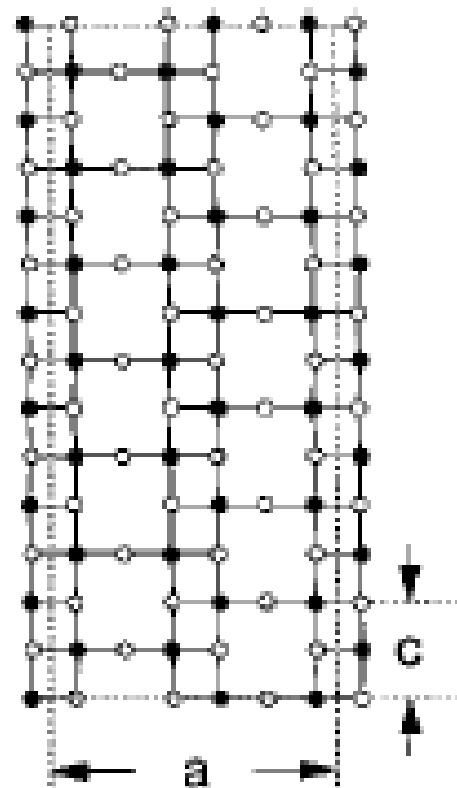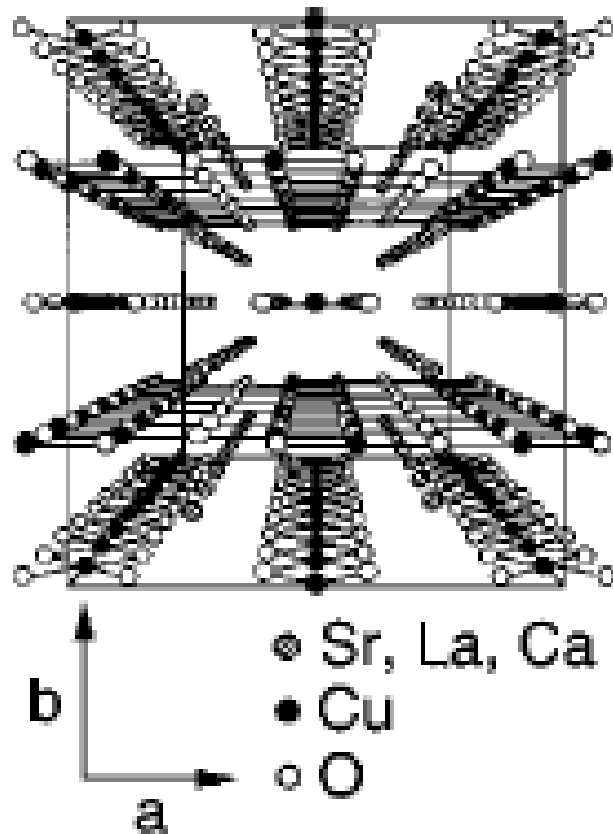Hopping → delocalization → energy gain
Energy: 2 hops = 2t; cost=U

$$\rightarrow J \sim -t^2/U$$

Examples: High Tc's; MnO; MnF_2;
          telephone number compound

Relatively strong (depends on U)
Usually AF (F when not same 3d, e.g.d^3-d^5)
Strongly dependent on angle of bonding
          at 180^0 strongly AF
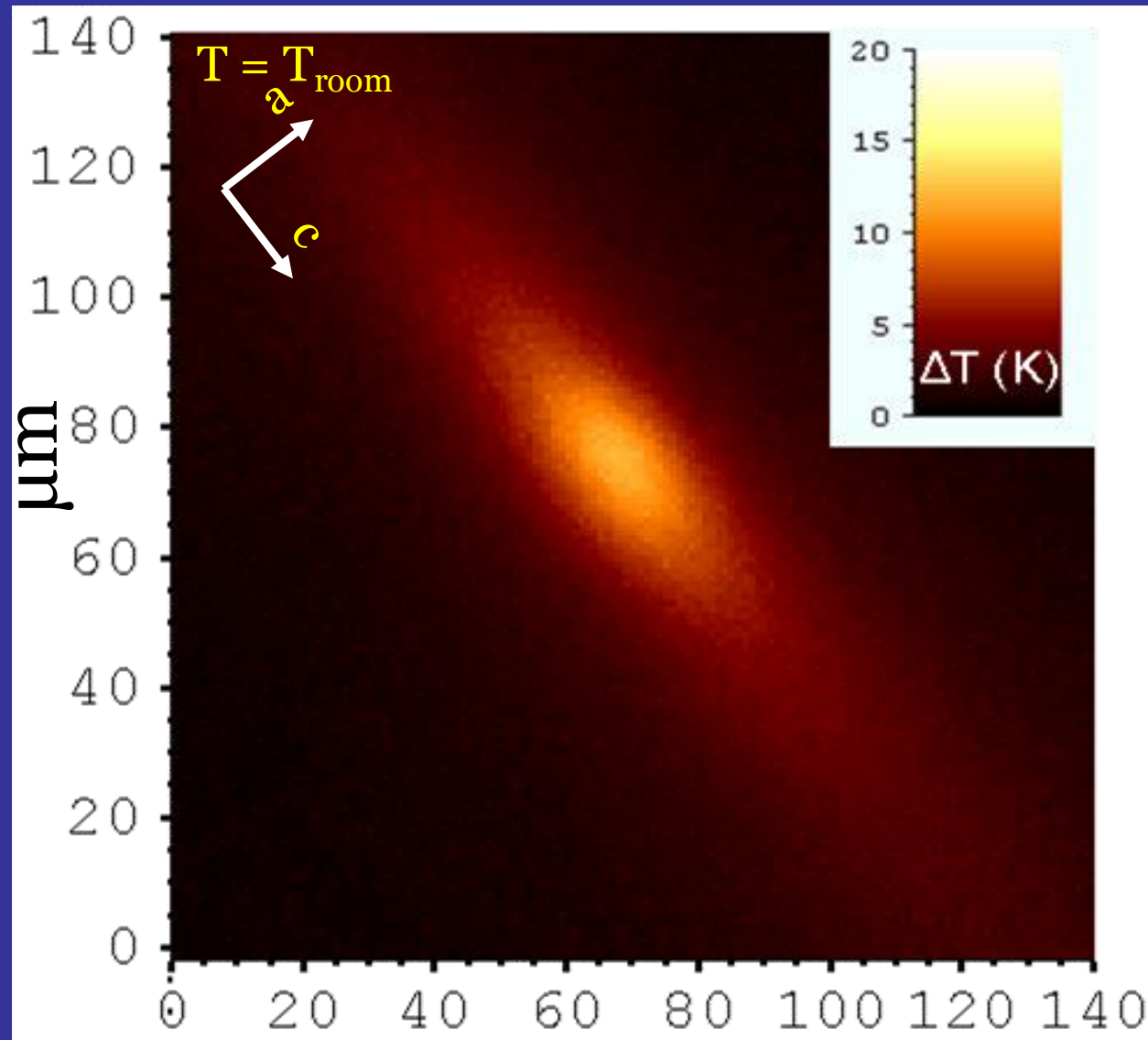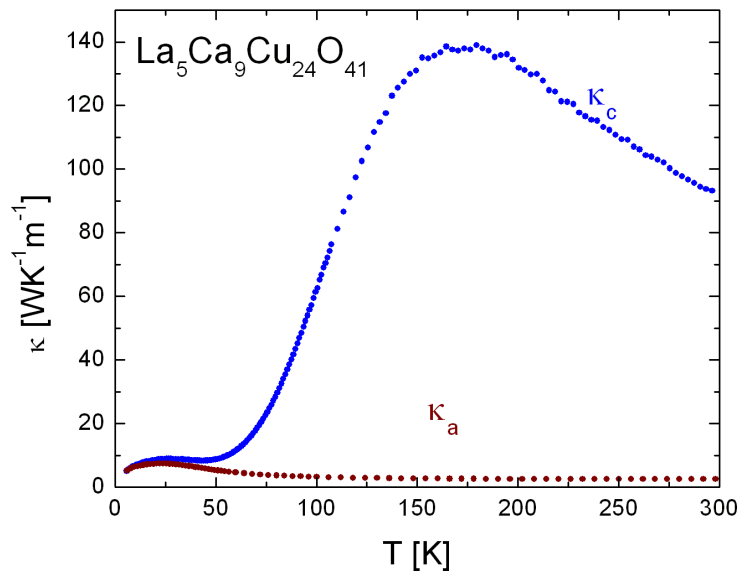   at zero weakly F
(goodenough kanamouri rules)

-J

90   180
angle
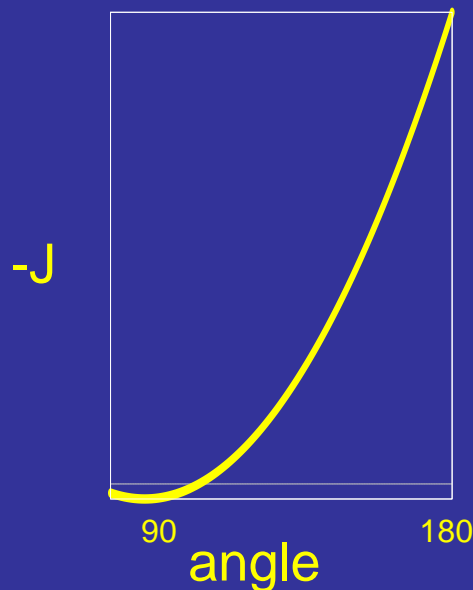
$(Sr,La,Ca)_{14}Cu_{24}O_{41}$

- Sr, La, Ca
- Cu
- O

J_1=130 meV
J_2= 70 meV
Δ=32 meV

Eccleston *et al.*, PRL **81**, 1702 (1998)

$La_9Ca_5Cu_{24}O_{41}$

La_5Ca_9Cu_24O_41

κ_c

κ_a

κ [WK^{-1}m^{-1}]

T [K]

T = T$_{room}$

a

c

ΔT (K)

μm

Double exchange

- Mixed valence
- Usually ferro metal
- Relatively strong
- $La_{1-x}Sr_xMnO_3$ (Mn^{3+}/Mn^{4+}) Fe_3O_4 (AB_2O_4, Fe^{2+}/Fe^{3+})
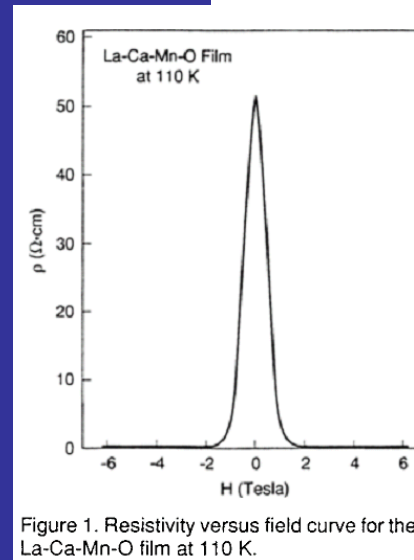
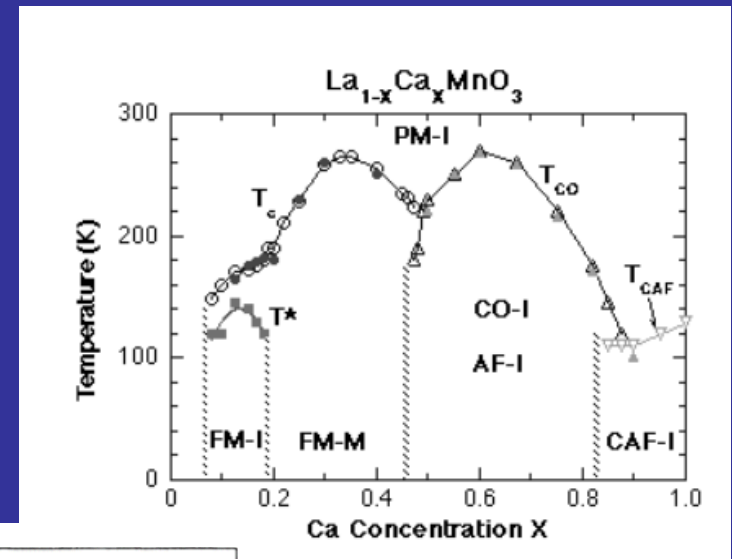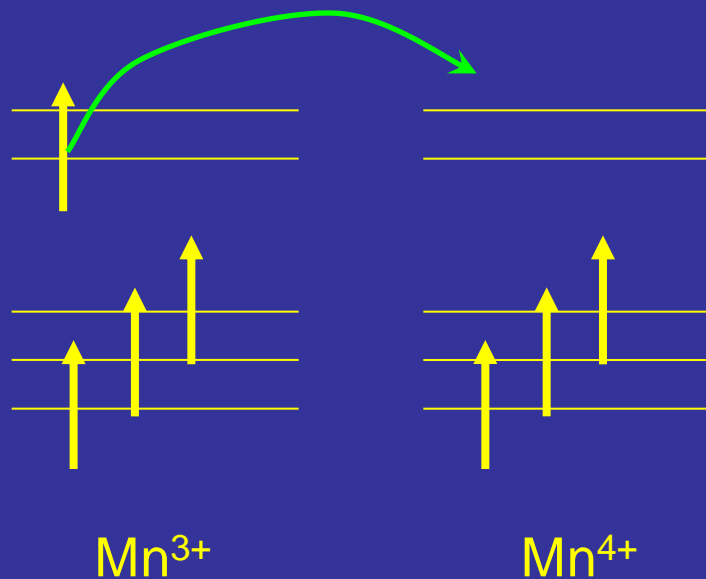Mn^{3+} Mn^{4+}

$La_{1-x}Ca_xMnO_3$

Figure 1. Resistivity versus field curve for the La-Ca-Mn-O film at 110 K.

PM-I paramagnetic insulator
FM-M ferromagnetic metal
FM-I ferromagnetic insulator
CO-I charge-ordered insulator
CAF-I canted antiferromagnetic insulator

Fujishiro and co-workers

CMR in para phase close to T_{curie}

Anisotropic exchange

- Dzyaloshinsky-Moriya interaction
- Mixing in of excited d-states
- LS coupling in excited state
- If spins inversion symm. related then 0
- Form different from Heisenberg: $\vec{D} \cdot \vec{S}_i \times \vec{S}_j$
- Favors perpendicular alignment
- Examples: α-Fe_2O_3, $MnCoO_3$
- In AF's leads to net moment $\rightarrow$ weak ferro (canted AF)
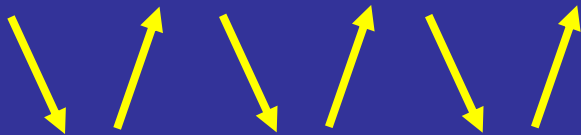
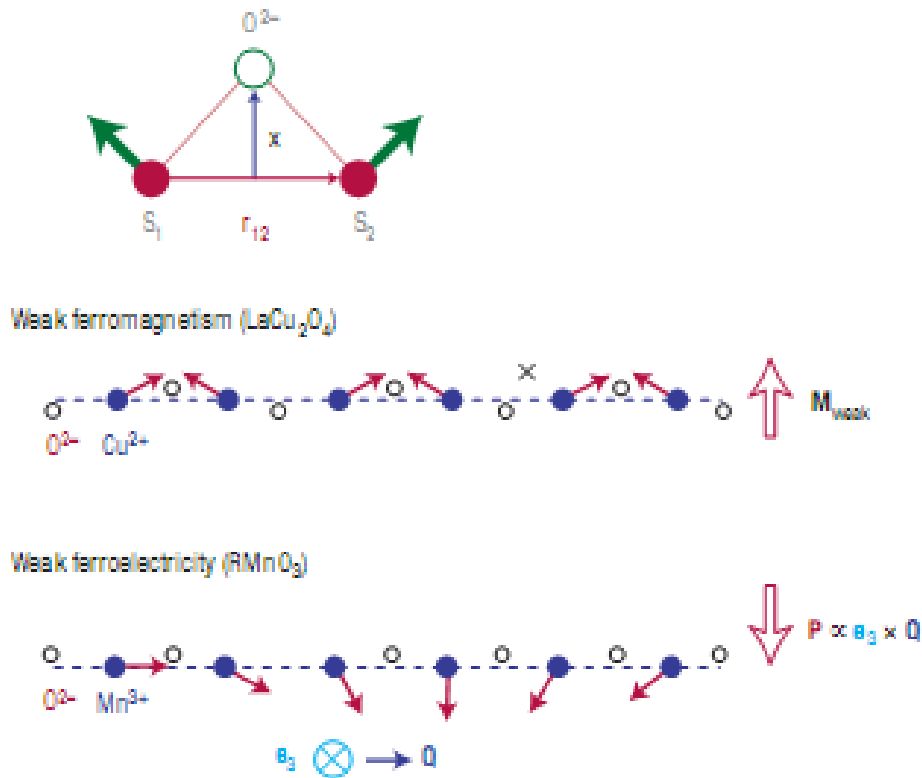# *Multiferroics*

Effects of Dzyaloshinskii–Moriya interaction

Figure 5 Effects of the antisymmetric Dzyaloshinskii–Moriya interaction. The interaction $H_{DM} = D_{12} \cdot [S_1 \times S_2]$. The Dzyaloshinskii vector D_{12} is proportional to spin-orbit coupling constant λ, and depends on the position of the oxygen ion (open circle) between two magnetic transition metal ions (filled circles), $D_{12} \propto \lambda x \times \hat{r}_{12}$. Weak ferromagnetism in antiferromagnets (for example, $LaCu_2O_4$ layers) results from the alternating Dzyaloshinskii vector, whereas (weak) ferroelectricity can be induced by the exchange striction in a magnetic spiral state, which pushes negative oxygen ions in one direction transverse to the spin chain formed by positive transition metal ions.
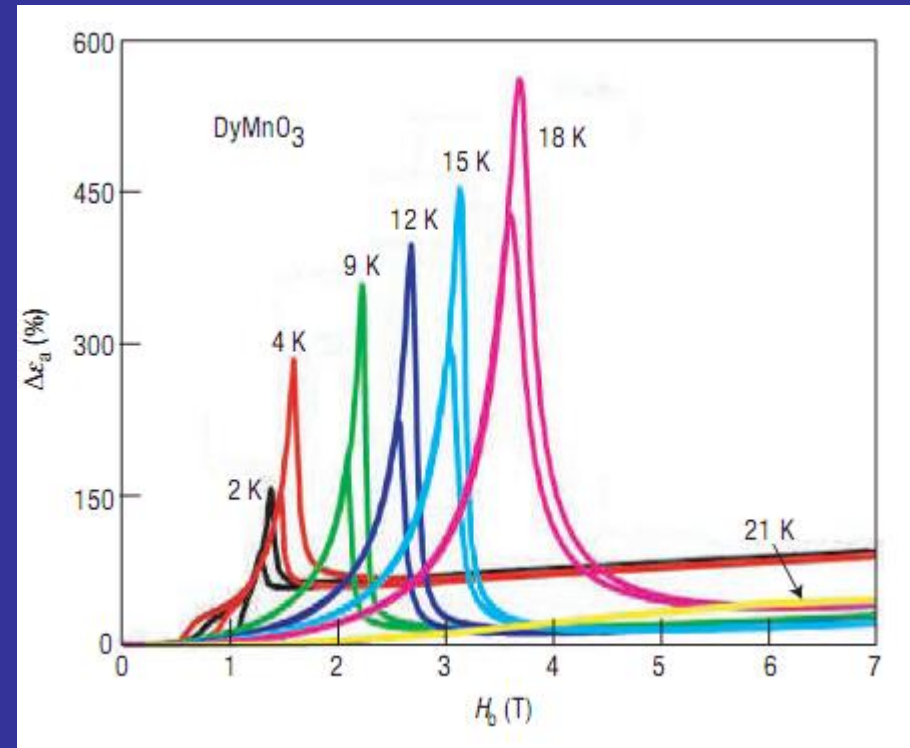
$$P \propto [(M \cdot \partial)M - M(\partial \cdot M)] .$$

Mostovoy & Cheong

Excercises

- 3.1; 3.5 ; 3.11
- Which 3d ions can be Jahn Teller active, what are the corresponding d-electron occupations ?
- The lowest 3d levels in an octahedral field are the t_{2g} triplet (states like d_{xy}). Can you predict the energy splitting in a tetrahedral environment
- 4.4; 4.5; 5.1; 6.13