Theory of Ferromagnetism in Double Perosvkites.

Luis Brey CSIC-Madrid

F. Guinea CSIC-Madrid

S.Das Sarma Univ.Maryland

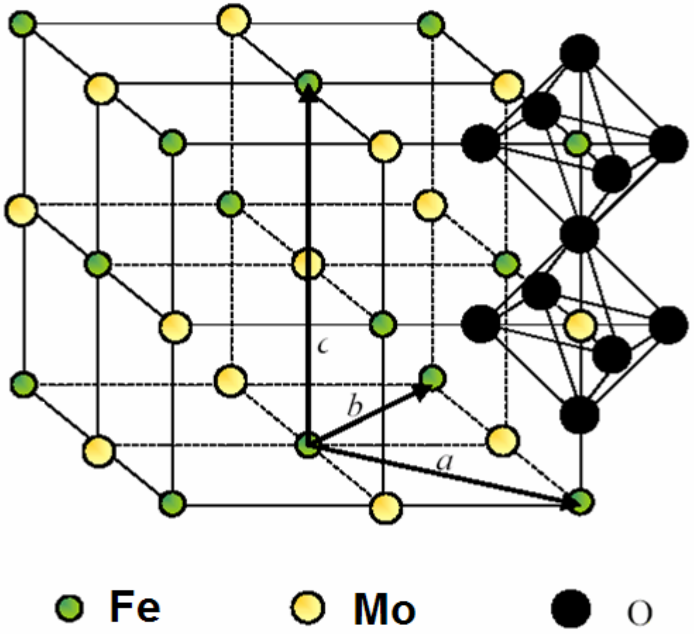
OUTLINE

- Introduction to Fe based double perovskites.
    - Chemistry
    - Band structure
- Ferromagnetism induced by carriers.
- Paramagnetic Phase of Doubles Perovskites.
- Mean Field Theory.
- Heisenberg like Hamiltonian.
- Effect of the Electron-Electron interaction.
- Summary

Sr_2FeMoO_6

Sr	$5s^2$		2+ (4+)
Fe	$3d^6\, 4s^2 \rightarrow 3d^5$		3+
Mo	$4d^5 5s^1 \rightarrow 4d^1$		5+
O	$2s^2\, 2p^4 \rightarrow 2s^2\, 2p^6$		2- (12-)

Two interpenetrating FCC sublattices (Fe and Mo)



Ideal double perovskite structure.

Magnetic active orbitals, Fe (5/2)

Distance Fe-Fe is larger than 5.5Å no direct interaction

Electrons live in Mo (1 electron per Fe)

Sr →$Sr_{1-x}La_x$	1+x electrons per Fe (trivalent)
Sr →$Sr_{1-x}K_x$	1-x electrons per Fe (monovalent)
Mo → Re	2 electrons per Fe (Re: $5d^5 6s^2$)

$\boxed{0.5<x<1.5}$

Interest of Fe-based Double Perovskites.

- **High Ferromagnetic T_c (more than 450K)**
- **Half metallic ferromagnet. Electrical current is 100% spin polarized.**
- **The T_c can be raised by electron doping.**
- **No clear the origin of the ferromagnetism.**

Attractive both in terms of basic investigations and technological applications.

Some names (not all).

Theory:

•D.D.Sarma et al.	Band structure.
•Y.Tokura et al.	Band structure.
•I.V.Solovyev.	Band structure.
•F. Guinea et al.	Monte Carlo.
•A.Millis et al.	DMFT (CPA)

Experiments:

- Y.Tokura et al.
- D.D.Sarma et al.
- Ogale et al.
- Mar García et al.
- Fontcuberta et al.
- Ibarra et al.

•Tc is lower than observed.

•Tc decreases with electron doping!!

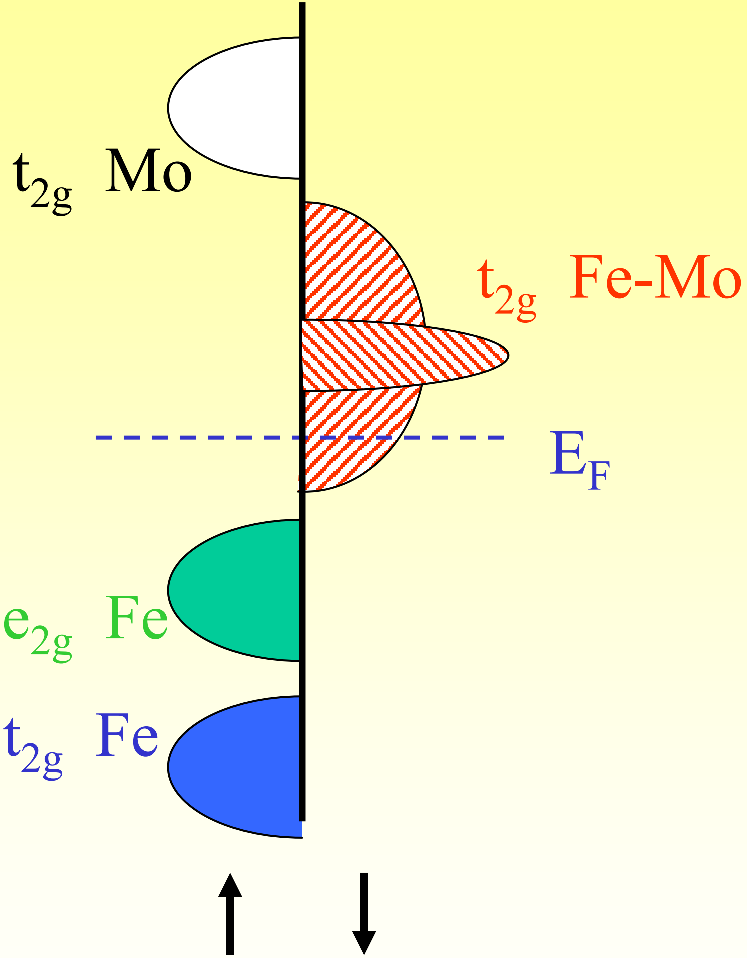
•Make a mean field theory and compute Tc.

•Compare with DMFT and MC.

•Try to improve the model. (what other ingredients are needed.)

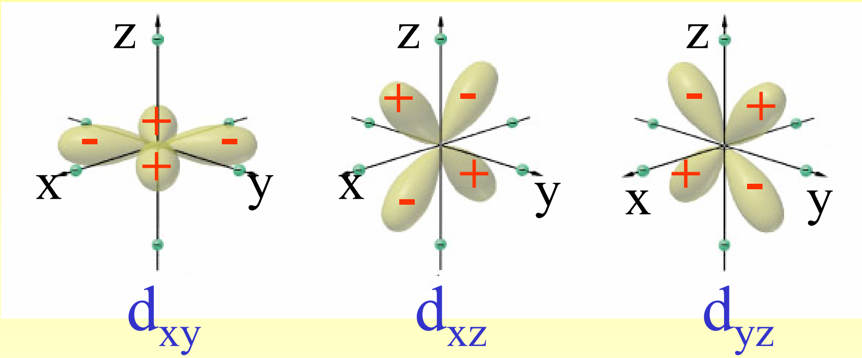
•Are the experimental findings intrinsic or extrinsic properties?

Ferromagnetic Band structure



T=0, ferromagnetic DOS.

t_{2g} orbitals

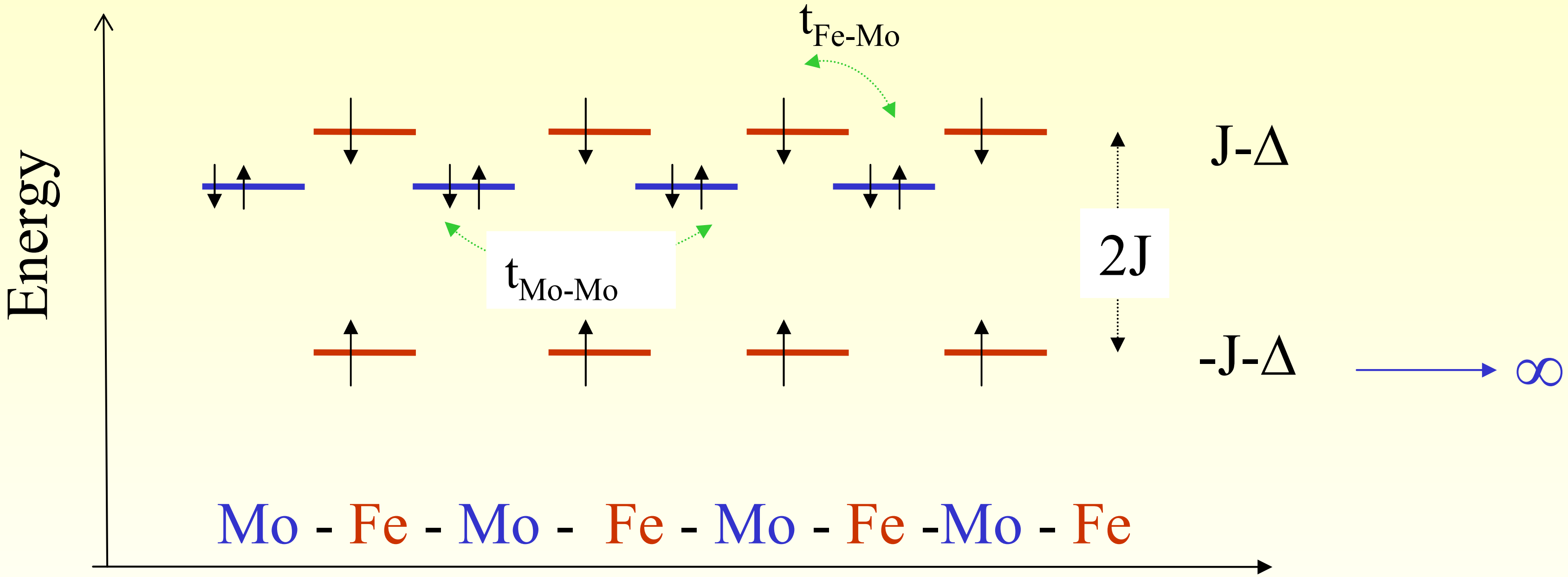


The symmetry of the t_{2g} orbitals implies that a given orbital can mix only orbitals of the same symmetry and only with orbitals in the corresponding plane. $d_{\alpha\beta}$ in the plane **αβ**

The band structure is the sum of three two dimensional tight binding systems.

$$\boxed{t_{\text{Mo-Fe}}\ ,\ t_{\text{Mo-Mo}}\ ,J\ ,\Delta}$$

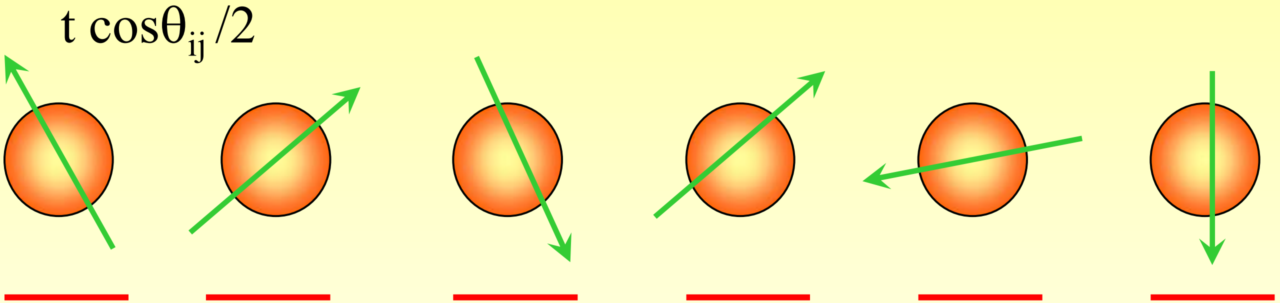
Ferromagnetic GS scheme.



The motion of the electrons is through Fe (↓) and for minimizing KE the carriers become polarized ↓ . The effective AF coupling between the carriers and the core Fe (↑) produces ferromagnetic order.

FERROMAGNETIC ORDER INDUCED BY THE CARRIERS

Double Exchange ($LaCaMnO_3$)



$$\boxed{T_C \sim t\langle C^{+}{}_{i} C_{i+1}\rangle}$$

Increases with carriers doping.

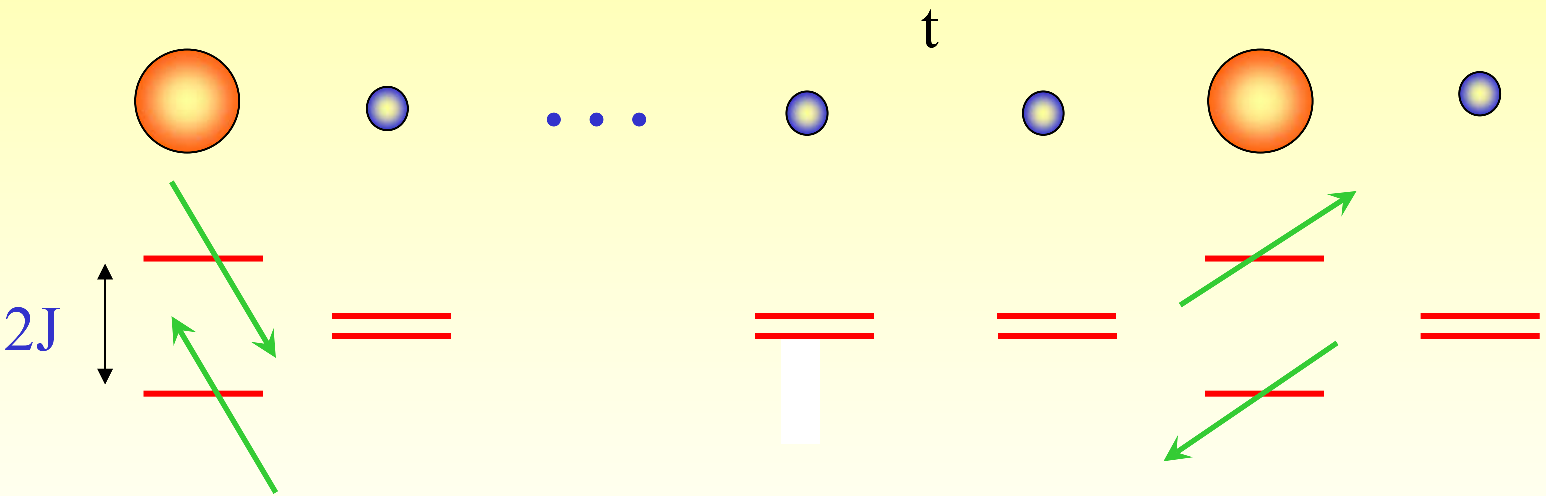
de Gennes ‘60

FERROMAGNETIC ORDER INDUCED BY THE CARRIERS

Double Exchange (LaCaMnO$_3$)

$T_C \sim t\langle C^+_i C_{i+1} \rangle$

Diluted Magnetic Semiconductors (GaMnAs)



$T_C \sim J^2 N(E_F)\, c$

- Perturbation theory
- Increases with electron doping

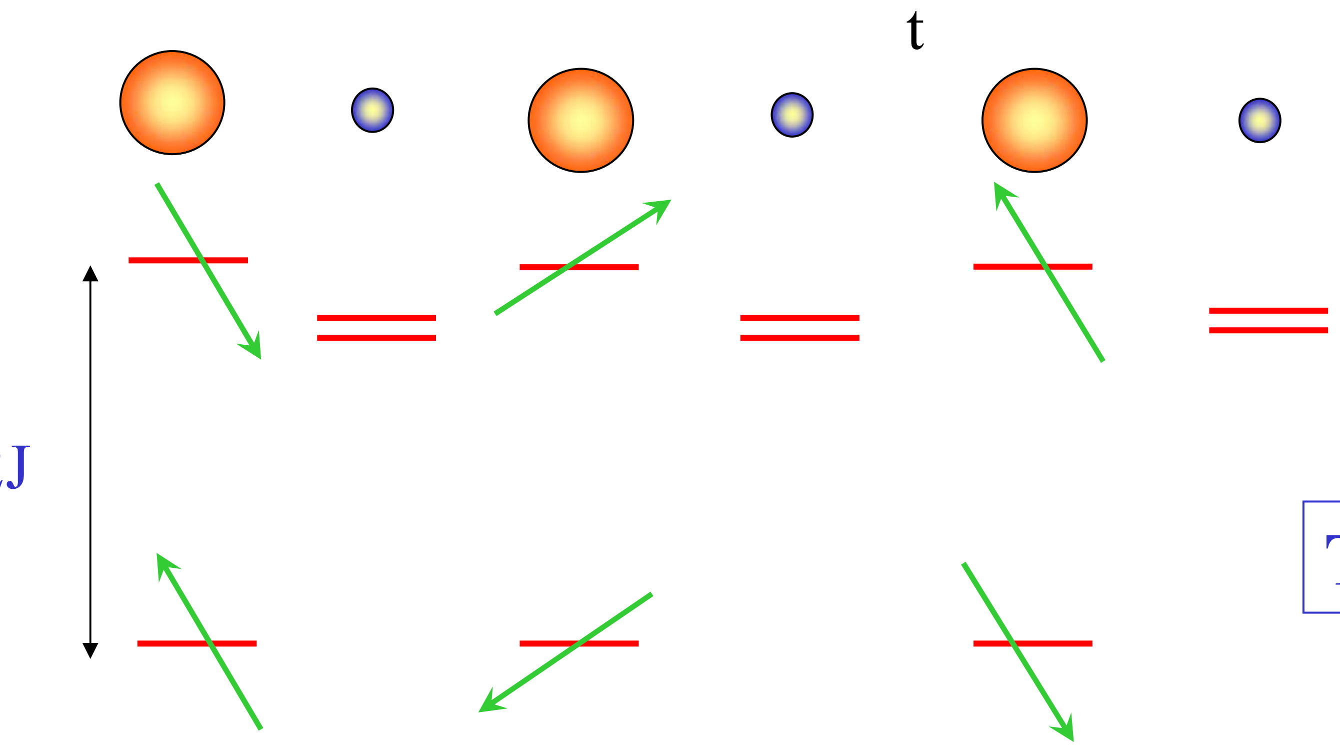
Vonsovky ('46) Zener ('51)

FERROMAGNETIC ORDER INDUCED BY THE CARRIERS

Double Exchange ($LaCaMnO_3$) $T_C \sim t<C^+_i C_{i+1}>$

Diluted Magnetic Semiconductors (GaMnAs) $T_C \sim J^2 N(E_F)\, x$

Double Perovskites $SrFeMoO_6$



- No diluted.
- J very large
- Paramagnetic atom

$T_C \sim ?$

STRATEGY: Mean Field Approximation

$$\boxed{F[m]= E_{KE}[m]+ F_{ions}[m]}$$

- m, magnetization order paramate
- Carriers at T=0, $E_F >> kT$

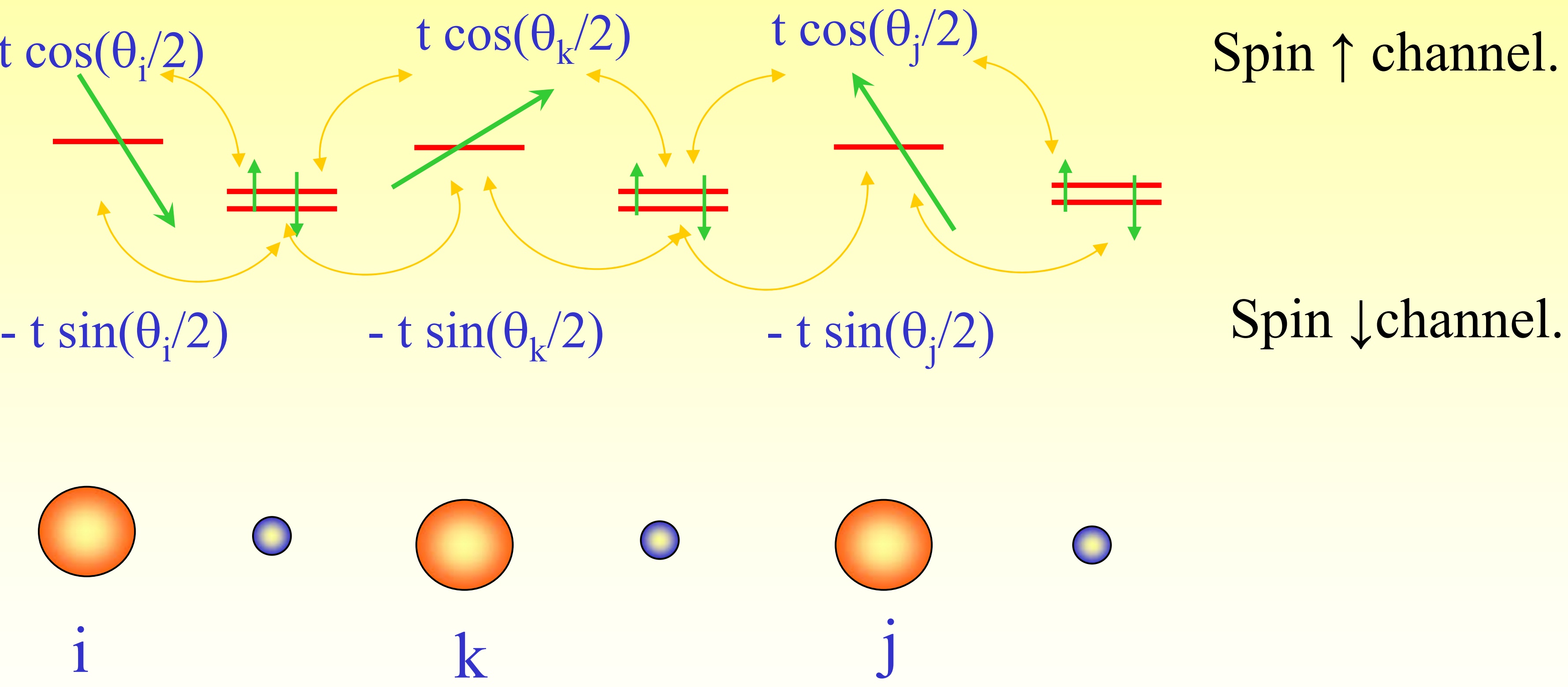
$m \rightarrow 0$

$$\frac{\partial^2 F}{\partial m^2} = 0 \quad \Rightarrow \quad \boxed{T_C = \frac{2}{3} \frac{\partial E_{KE}}{\partial (m^2)}}$$

We need to know the paramagnetic phase…

(*Ab initio* band structure calculation are done for ordered ferromagnetic phase)

PARAMAGNETIC PHASE



$t\ \cos(\theta_i/2)$

$t\ \cos(\theta_k/2)$

$t\ \cos(\theta_j/2)$

Spin ↑ channel.

$-\ t\ \sin(\theta_i/2)$

$-\ t\ \sin(\theta_k/2)$

$-\ t\ \sin(\theta_j/2)$

Spin ↓channel.

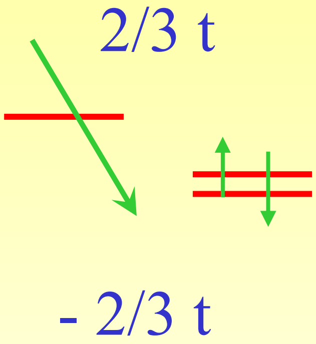
i

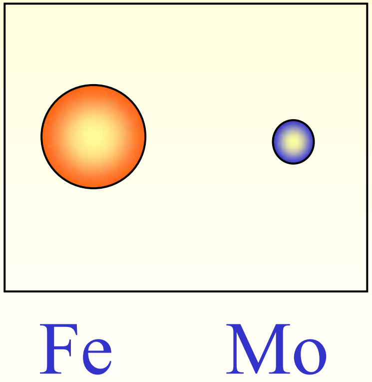
k

j

PARAMAGNETIC PHASE , VCA

$<\cos(\theta_i/2)>=<\sin(\theta_i/2)>= 2/3$

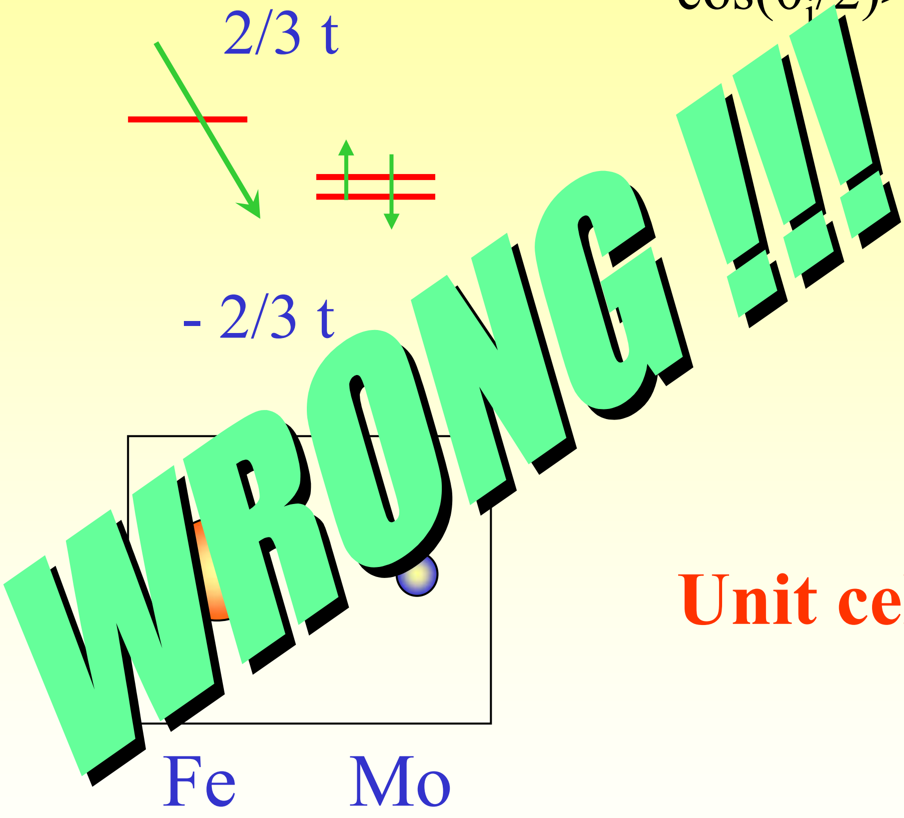




Unit cell

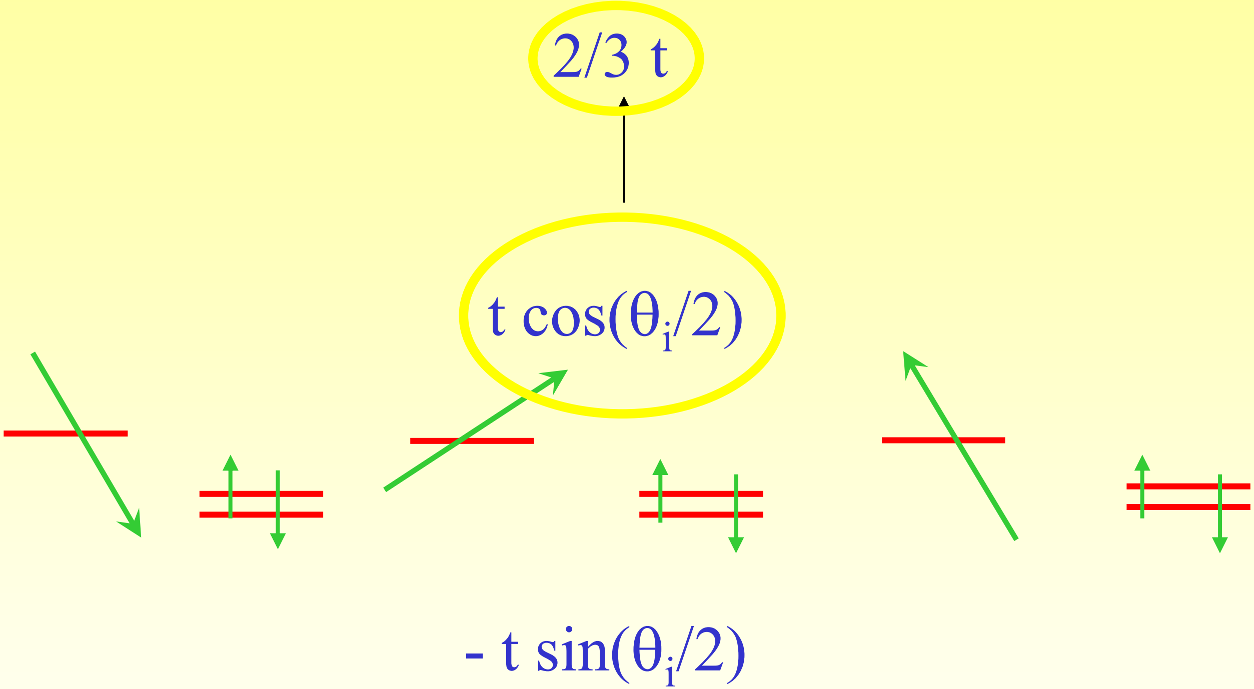
PARAMAGNETIC PHASE , VCA

$\cos(\theta_i/2)>=<\sin(\theta_i/2)>= 2/3$

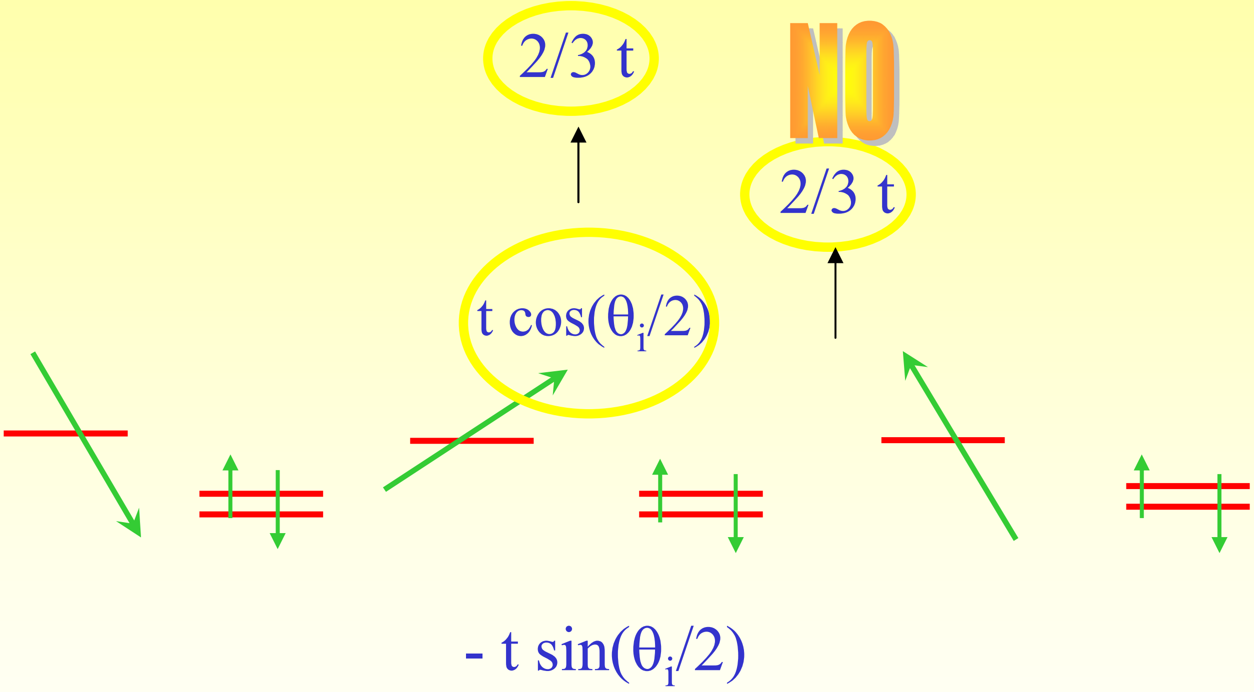


Unit cell

PARAMAGNETIC PHASE (3)



PARAMAGNETIC PHASE



$2/3\ t$

NO

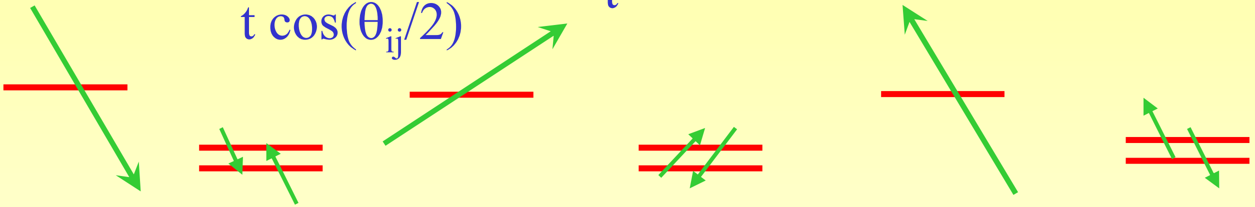
$2/3\ t$

$t \cos(\theta_i/2)$

$- t \sin(\theta_i/2)$

PARAMAGNETIC PHASE

We refer the spins of the Mo, to the Fe spin in the same unit cell.



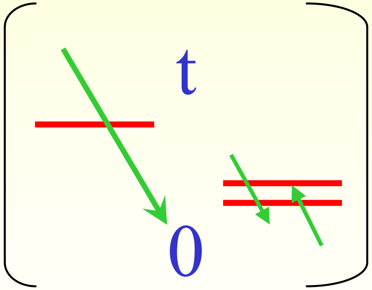
$t\cos(\theta_{ij}/2)$ t

Channel ∥

$-t\sin(\theta_{ij}/2)$ 0

Channel anti-∥

Virtual Crystal Approx.

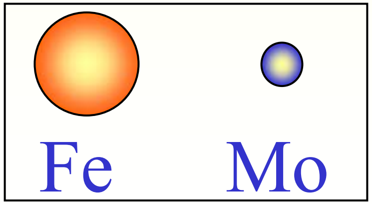


t

0

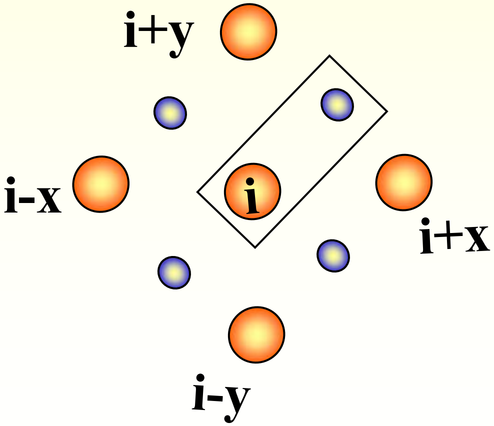
$t<\cos(\theta_{ij}/2)>$

$-t<\sin(\theta_{ij}/2)>$



VCA HAMILTONIAN

$$
\begin{aligned}
H = {} & (J-\Delta)\sum_i d_i^+ d_i \\
& + t_{Mo-Mo}\sum_{<i,j>}\left(<\cos\frac{\theta_{ij}}{2}>(c^+_{i,p}c_{j,p}+c^+_{i,ap}c_{j,ap}) - <\sin\frac{\theta_{ij}}{2}>(c^+_{i,ap}c_{j,p}+c^+_{i,p}c_{j,ap}) \right) \\
& + t_{Fe-Mo}\sum_i d_i^+\left[c_{i,p} + <\cos\frac{\theta_{ij}}{2}>\left(c_{i-x,p}+c_{i-x-y,p}+c_{i-y,p}\right)\right] \\
& + t_{Fe-Mo}\sum_i d_i^+\left[- <\sin\frac{\theta_{ij}}{2}>\left(c_{i-x,ap}+c_{i-x-y,ap}+c_{i-y,ap}\right)\right]
\end{aligned}
$$



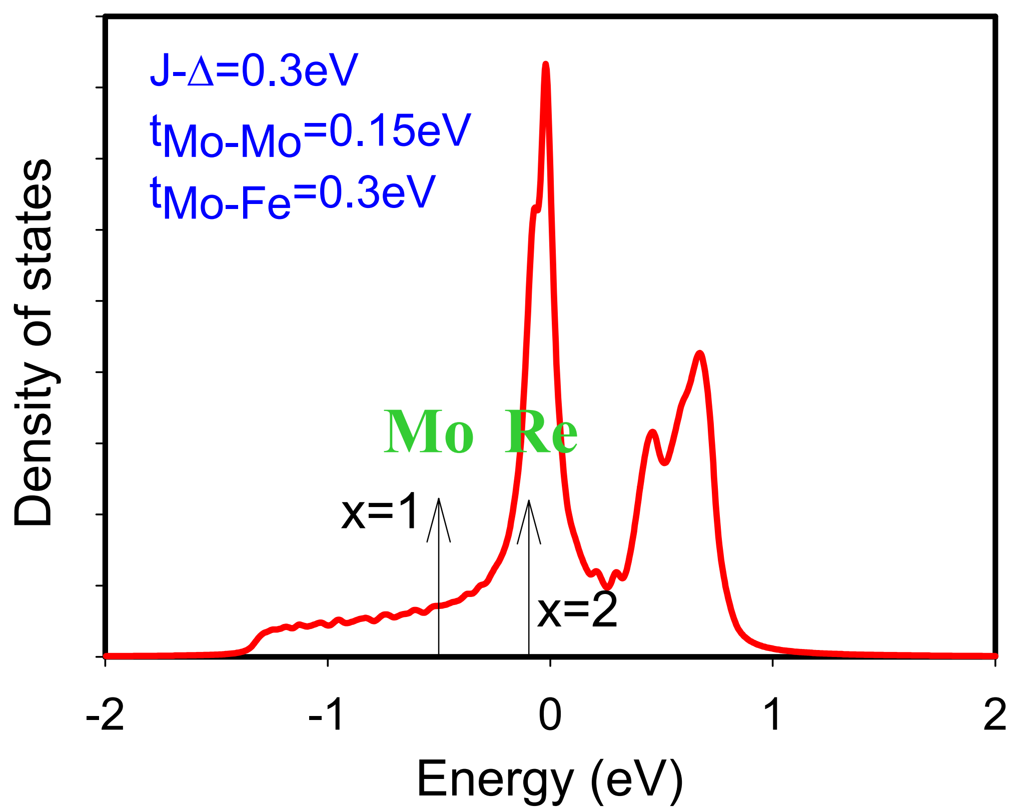
•$c_{i,p(ap)}$ destroys an electron in Mo at site i, with spin parallel (antiparallel) to the spin of the Fe spin.

•d_i destroys an electron in Fe at site i., with th spin parallel to the core spins.

PARAMAGNETIC PHASE

m=0

$<\cos \theta_{ij}/2>=<\sin \theta_{ij}/2>= 2/$



DOS at the Fermi Energy increases with doping and is rather smooth between x=0 and x=2. Tc smooth between these densities?.

Curie Temperature.

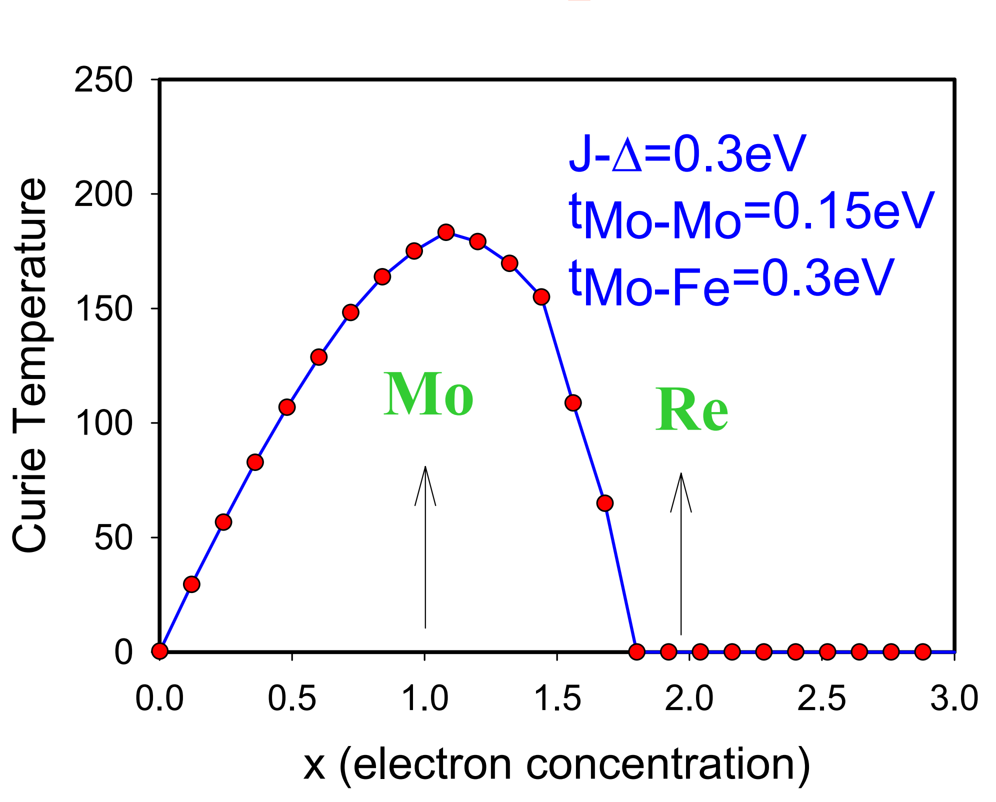
$$m = \langle \cos\theta_i \rangle \quad \Rightarrow \quad \begin{cases} \langle \cos\theta_{ij}/2 \rangle \approx 2/3 + 2/5\, m^2 \\ \langle \sin\theta_{ij}/2 \rangle \approx 2/3 - 2/5\, m^2 \end{cases}$$

Using the expectation values of $\langle c^+d \rangle$ obtained in the paramagnetic phase, we obtain $E_{KE}(m^2)$ and

$$\boxed{T_C = \frac{2}{3}\frac{\partial E_{KE}}{\partial (m^2)}}$$

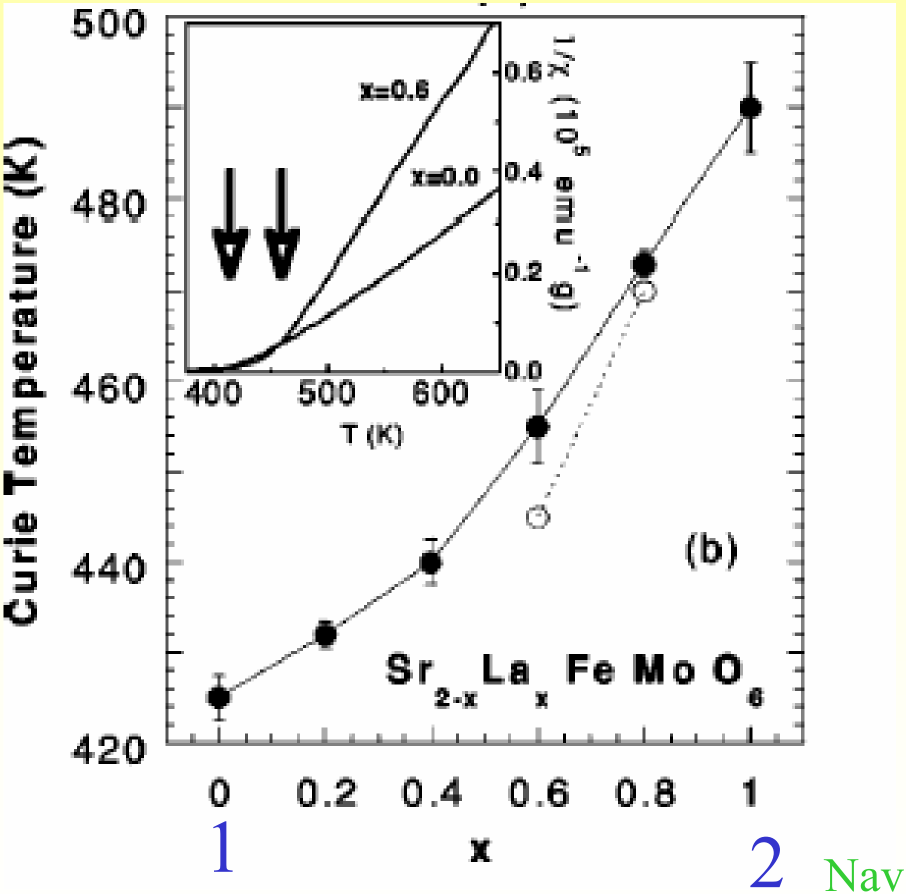
Perturbation Theory

Curie Temperature as function of x



- Low $T_{C.}$
- Maximum x ~1.
- T_C=0 for x ~2.
- Agreement with MC and DMFT
- Disagreement with experiments!

Experimental variation of Curie Temperature with electron density

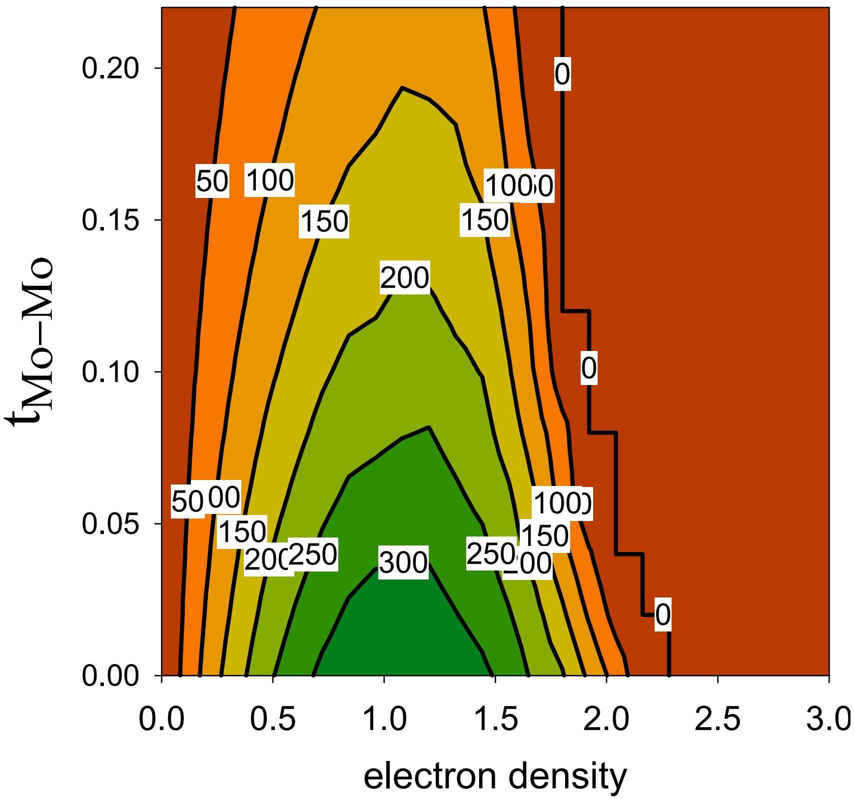


Navarro et al. PRB **64**, 092411 (2001)

Curie Temperature as function of x

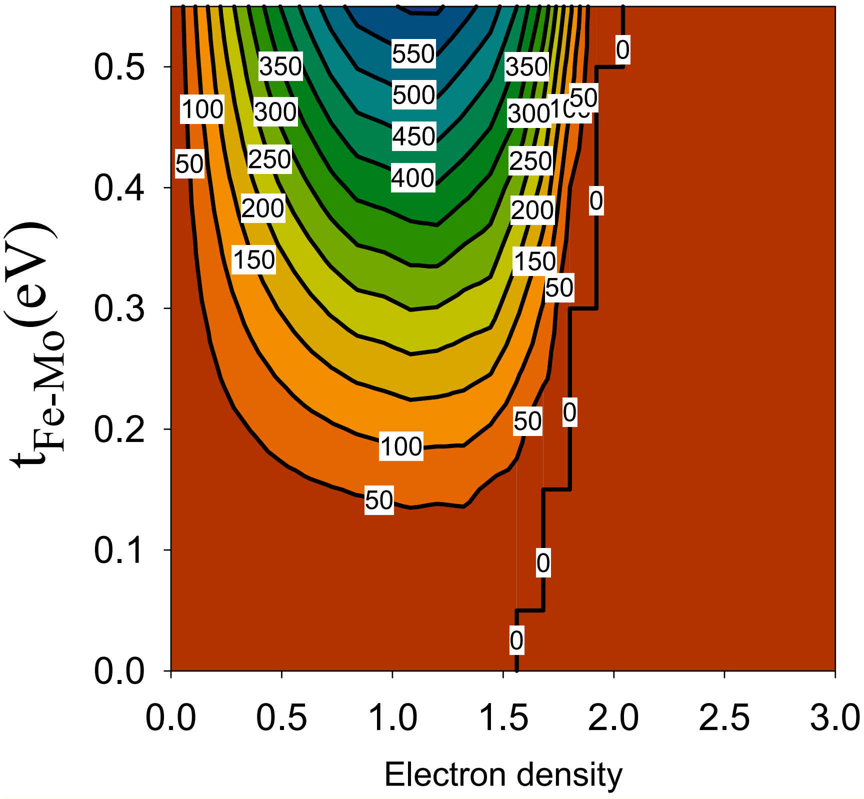
$t_{Fe\text{-}Mo}$=0.25 (eV)

J-Δ=0.3eV.



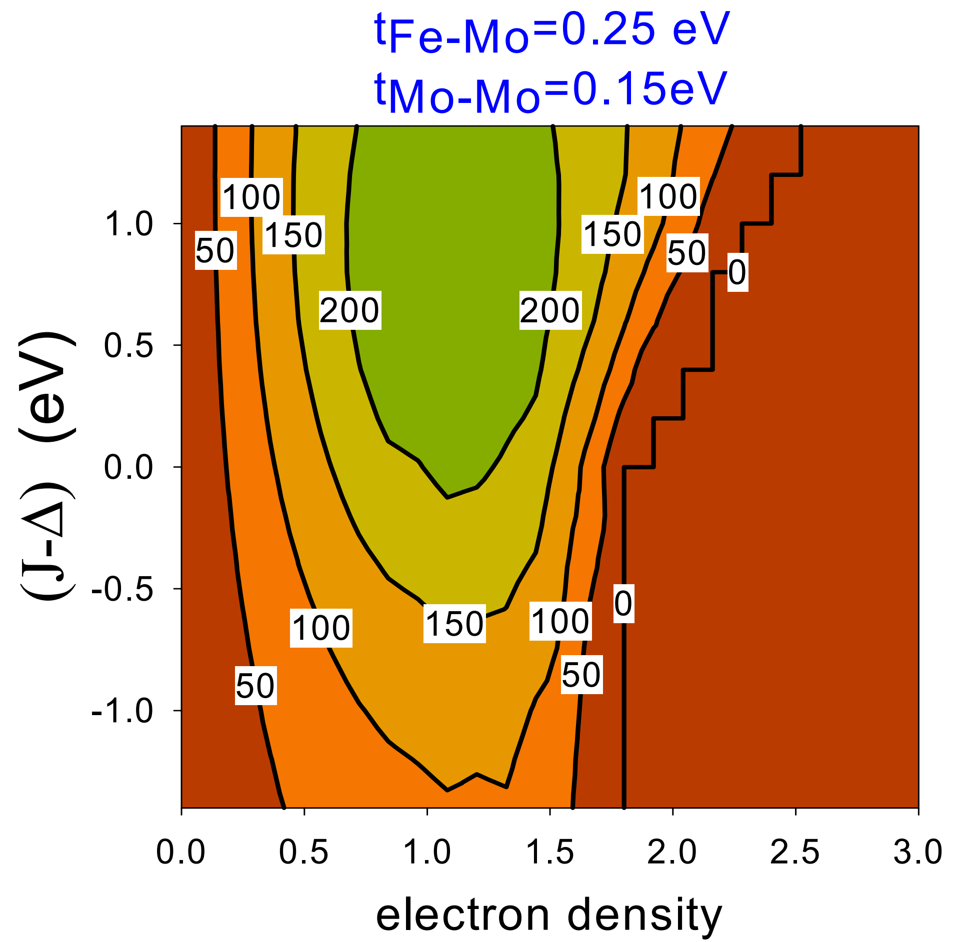
t_{Mo-Mo}=0.15 (eV)

J-Δ=0.3eV



- **Low $T_{C.}$**
- **Maximum x ~1. Increases with $t_{Fe\text{-}Mo}$**
- **T_C=0 for x ~2. Independent of $t_{Fe\text{-}Mo}$ and $t_{Mo\text{-}Mo}$**

Curie Temperature as function of x



- $\bullet$Low $T_{C.}$
- $\bullet$Maximum x ~1. T_c can be fitted
- $\bullet T_C$=0 for x ~2. Always.
- $\bullet$Agreement with MC and DMFT
- $\bullet$Disagreement with experiments

Why this behavior?

Let us rewrite the internal energy of the system in other way.

$$\begin{aligned} H = {} & (J-\Delta)\sum_i d_i^{+} d_i \\ & + t_{Mo-Mo}\sum_{<i,j>}\left(<\cos\frac{\theta_{ij}}{2}> (c^{+}_{i,p}c_{j,p} + c^{+}_{i,ap}c_{j,ap}) - <\sin\frac{\theta_{ij}}{2}> (c^{+}_{i,ap}c_{j,p} + c^{+}_{i,p}c_{j,ap}) \right) \\ & + t_{Fe-Mo}\sum_i d_i^{+}\left[c_{i,p} + <\cos\frac{\theta_{ij}}{2}> \left(c_{i-x,p} + c_{i-x-y,p} + c_{i-y,p} \right) \right] \\ & + t_{Fe-Mo}\sum_i d_i^{+}\left[- <\sin\frac{\theta_{ij}}{2}> \left(c_{i-x,ap} + c_{i-x-y,ap} + c_{i-y,ap} \right) \right] \end{aligned}$$

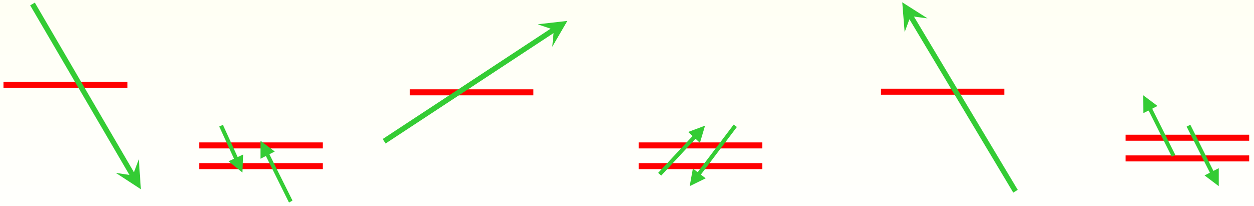
We write the energy as a function of the orientation of the Fe spins, $\{S_i\}$. $\Delta E(\cos\theta_{ij}/2, \ \sin\theta_{ij}/2)$. We use the expectation values of the paramagnetic phase.

Heisenberg-like description of Double Perovskites.(1)

$$\Delta E = -\sum_{<i,j>} \underbrace{J_C^{Fe-Mo}\cos\frac{\theta_{i,j}}{2}} + \underbrace{J_S^{Fe-Mo}\sin\frac{\theta_{i,j}}{2}} + \underbrace{J_C^{Mo-Mo}\cos\frac{\theta_{i,j}}{2}} + \underbrace{J_S^{Mo-Mo}\sin\frac{\theta_{i,j}}{2}}$$

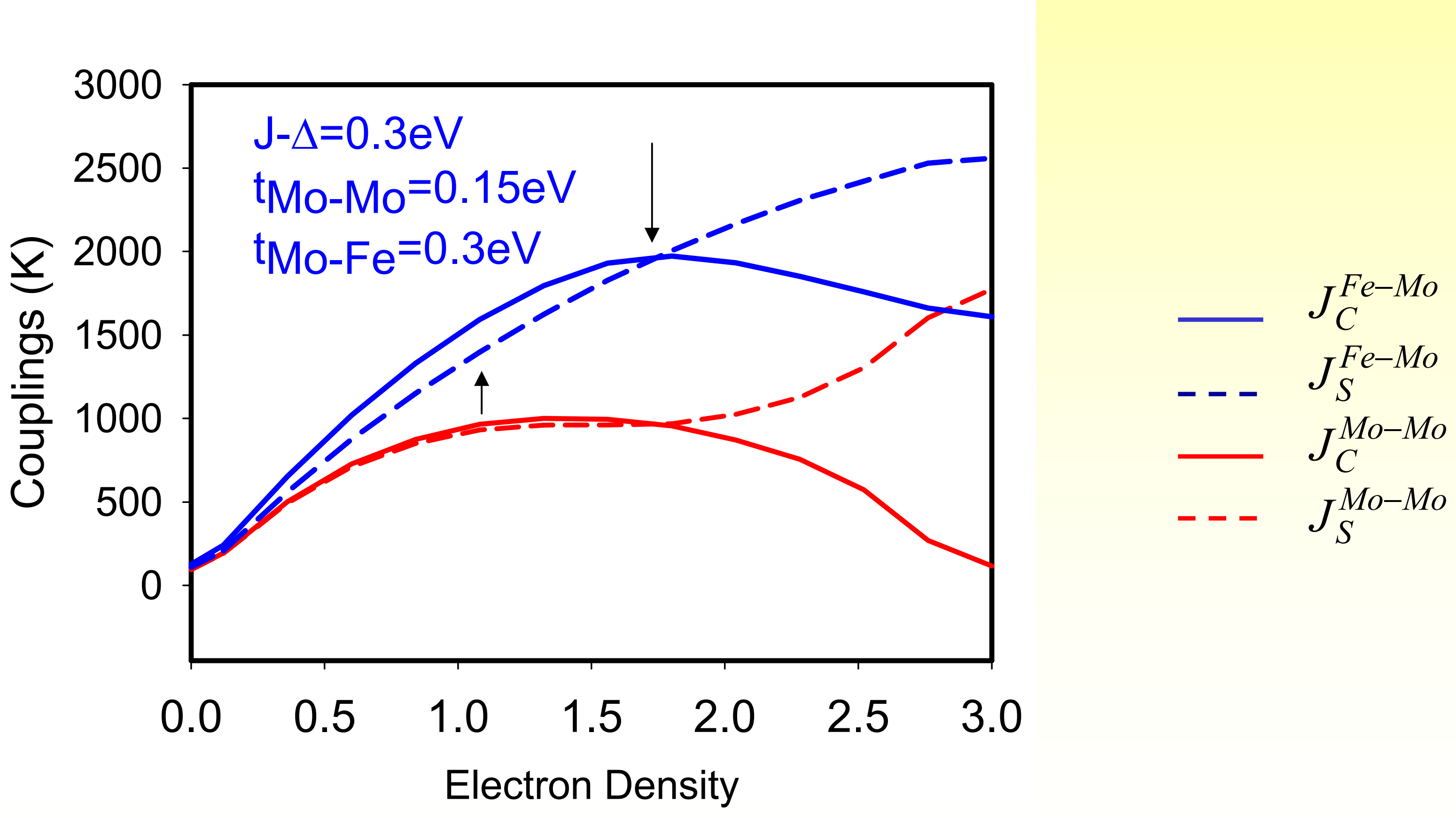
KE due to the motion of the carriers with spin locally parallel to the Fe ions.

KE due to the motion of the carriers with spin locally anti-parallel to the Fe ions



Heisenberg-like description of Double Perovskites(2).

$$\Delta E = -\sum_{<i,j>} J_C^{Fe-Mo} \cos\frac{\theta_{i,j}}{2} + J_S^{Fe-Mo} \sin\frac{\theta_{i,j}}{2} + J_C^{Mo-Mo} \cos\frac{\theta_{i,j}}{2} + J_S^{Mo-Mo} \sin\frac{\theta_{i,j}}{2}$$



Heisenberg-like description of Double Perovskites(3).

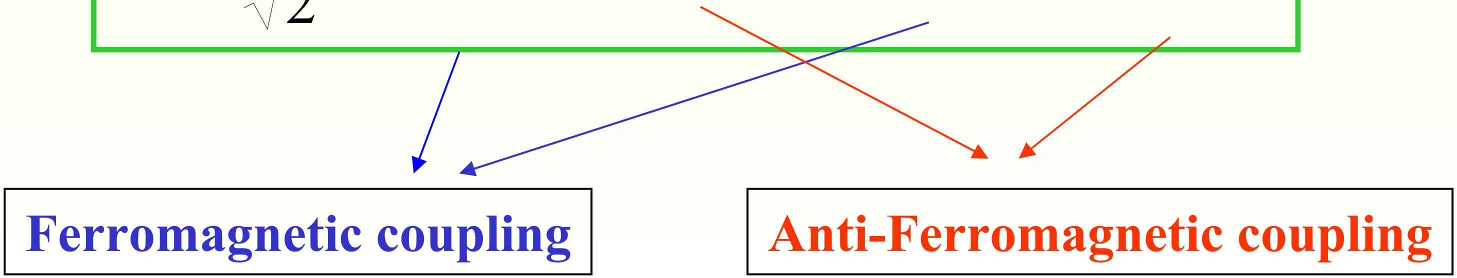
$$\Delta E = -\sum_{<i,j>} J_C^{Fe-Mo} \cos\frac{\theta_{i,j}}{2} + J_S^{Fe-Mo} \sin\frac{\theta_{i,j}}{2} + J_C^{Mo-Mo} \cos\frac{\theta_{i,j}}{2} + J_S^{Mo-Mo} \sin\frac{\theta_{i,j}}{2}$$

$$\Big\downarrow \quad m \to 0$$

$$\Delta E^{Heis.} = -\frac{1}{2\sqrt{2}} \sum_{<i,j>} \left(J_C^{Fe-Mo} - J_S^{Fe-Mo} + J_C^{Mo-Mo} - J_S^{Mo-Mo} \right) \cos\theta_{i,j}$$

$$\Big\downarrow$$

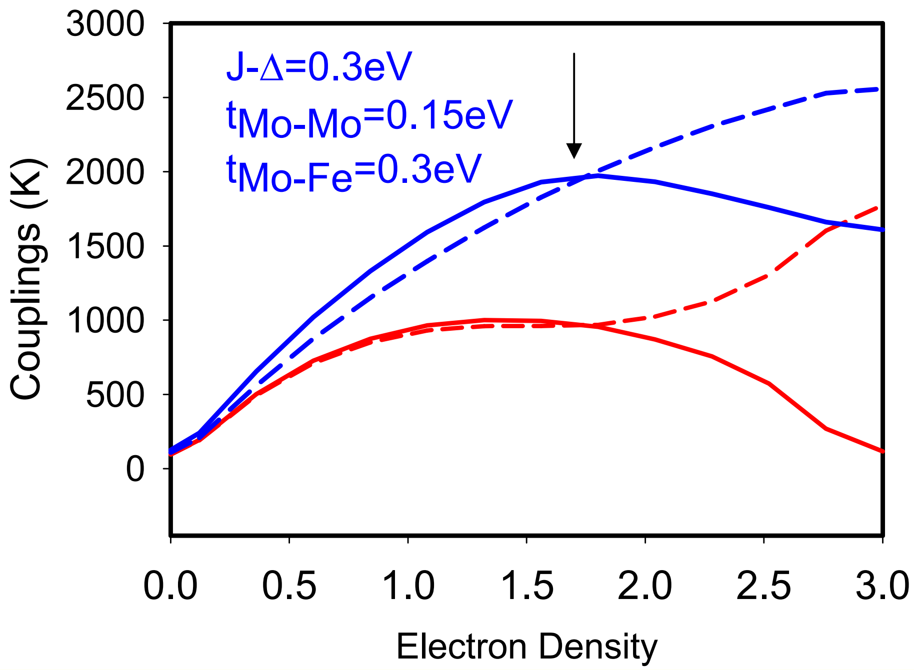
$$T_C = \frac{1}{\sqrt{2}} \left(\overbrace{J_C^{Fe-Mo} - J_S^{Fe-Mo}}^{t_{Mo\text{-}Fe}} + \overbrace{J_C^{Mo-Mo} - J_S^{Mo-Mo}}^{t_{Mo\text{-}Mo}} \right)$$

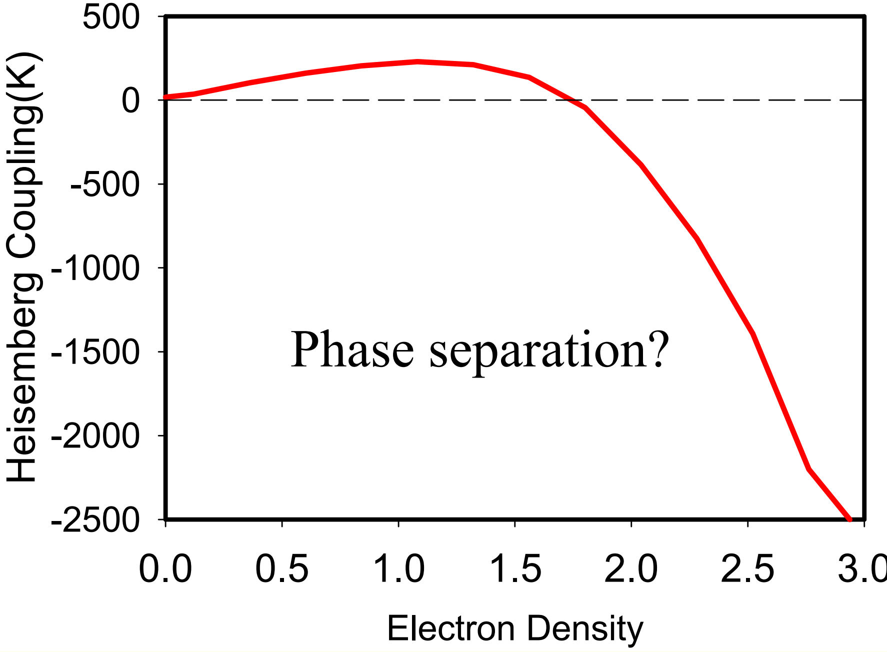


Ferromagnetic coupling

Anti-Ferromagnetic coupling

For x>1.2, T_C decreases with doping because the loose of KE in the antiparallel channel is bigger than the gain of KE in the parallel channel





Phase separation?

What ingredient in the problem will privilege a channel against the other?

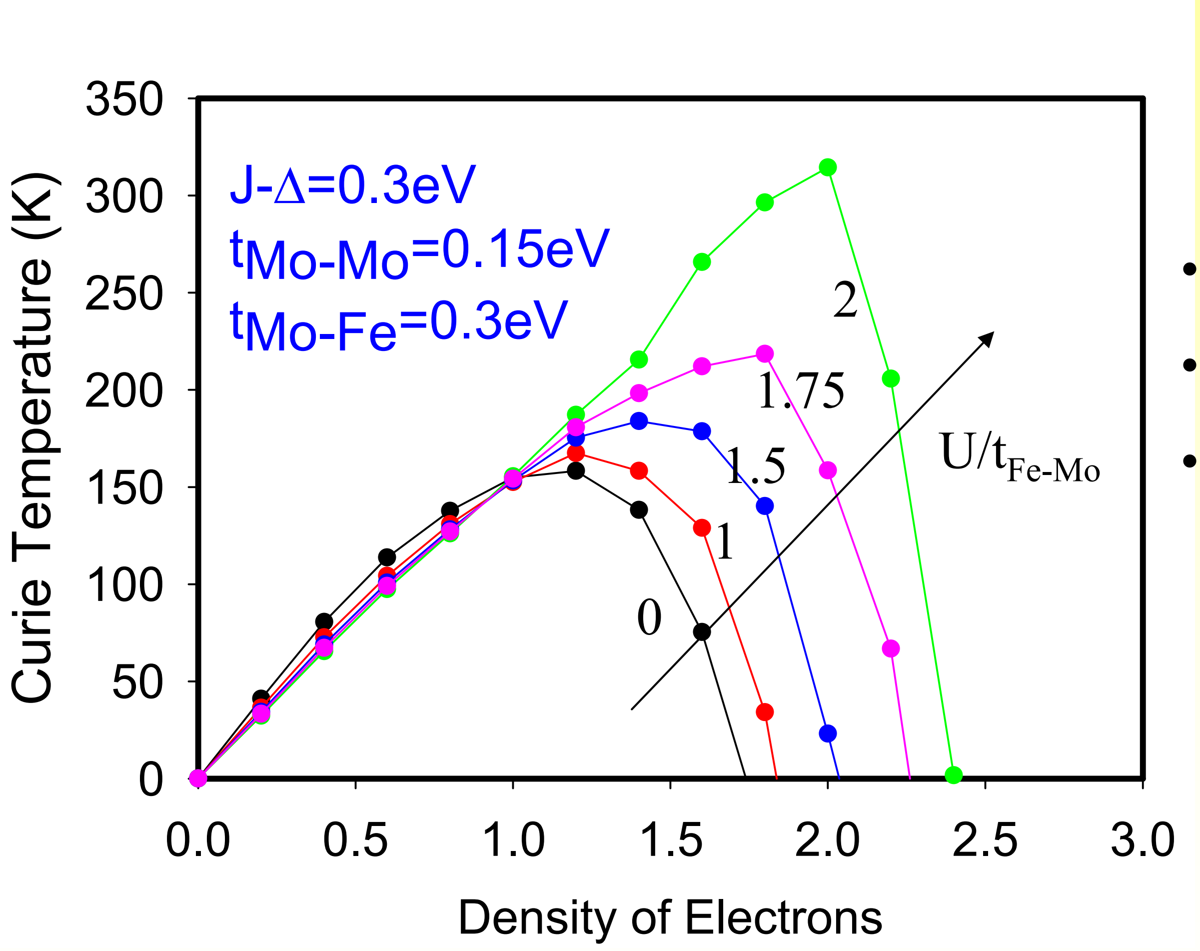
What ingredient in the problem will privilege a channel against the other?

Coulomb Interaction. Intraband Hubbard term, **U** , penalizes the occupation of two spin orientations at the same site.

$$\boxed{U\sum_{i} n_{i\uparrow} n_{i\downarrow}}$$

Interband Coulomb interactions, U’, are weaker than intreband. (Kanamori, Castellani, Tang…) No orbital ordering.

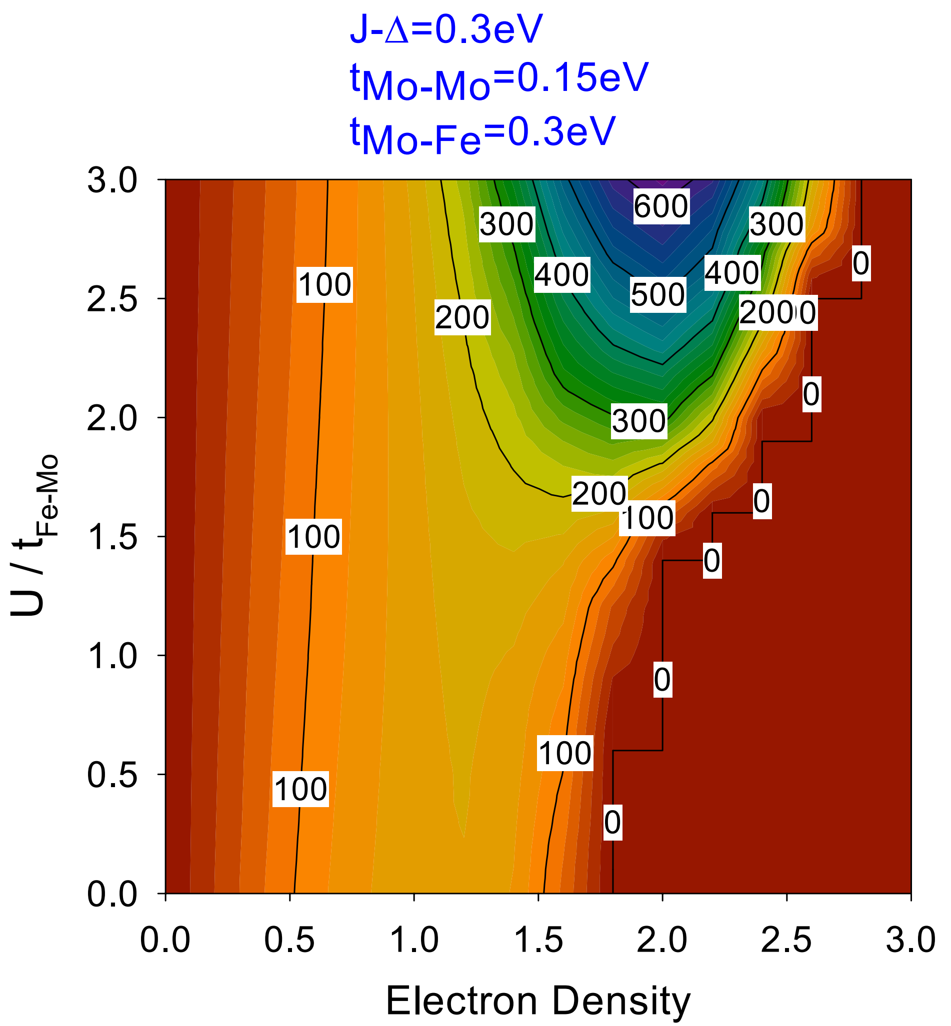
EFFECT OF THE ON-SITE COULOMB REPULSION ON T_C



- U, both in Fe and Mo.
- Mean field approx.
- $U<<W\approx8\ t_{Fe-Mo}$

EFFECT OF THE ON-SITE COULOMB REPULSION ON T_C

- **U, both in Fe and Mo.**
- **U<<W≈8 $t_{\text{Fe-Mo}}$**
- **Tc increases at x=1**
- **Tc finite at x=2.**



SUMMARY

- We have presented a Mean Field Theory for ferromagnetism in Fe-based Double Perovskites.
- Agreement with MC and DMFT.
  - Low T_c at x=1
  - No Ferromagnetism at x=2
- Disagreement with Experiments. T_c increases with doping.
- Inclusion of electron-electron interaction (moderate values of U) increases T_c and makes the x=2 case ferromagnetic.

Density of States T=0 Ferromagnetic Phase