KITP-05

Strong Electron Correlation and Fermi Surface Topology of Na_xCoO_2

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Phys. Rev. Lett. 94, 206401 (2005)

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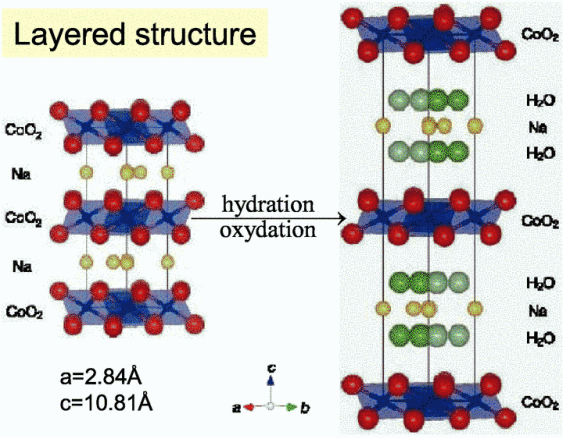
Outline: "Standard model"

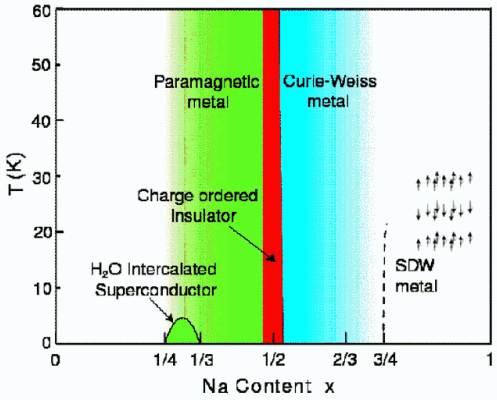
- The material and the electronic structure (LDA)
- How important are correlations? Specific heat data
- Fermi surface and band dispersion observed by ARPES
  - Discrepancies between LDA and ARPES
  - Importance of electron correlations
- Basic effects of local electron correlation (U)
  - Multi-band Hubbard model for Co t_{2g} orbitals
  - Weak-coupling, LDA+U, orbital Hartree-Fock
  - Strong-coupling, Gutzwiller
- Emergence of FM order at large sodium doping x

The cobaltate Na_xCoO_2, $Na_xCoO_2 \cdot yH_2O$

Layered structure

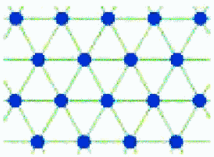


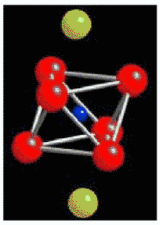
Phase diagram



Co: hexagonal layers

CoO_6: Octahedral tilt

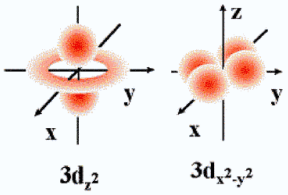




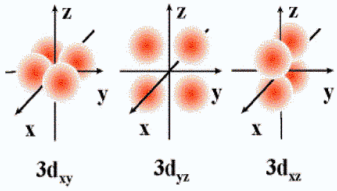
- Mott Insulator (?!) at x=0
- Charge ordered insulator at x=0.5
- High thermoelectric performance at x~0.7
- Magnetic order at larger x
- Unconventional superconductivity with hydration for x=1/4 ~ 1/3

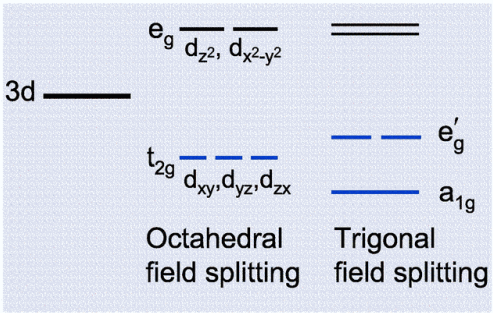
Co 3d atomic orbitals in the crystal lattice field

e_g



t_{2g}

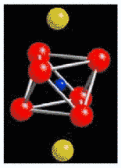




$$|a_{1g}\rangle = \frac{1}{\sqrt{3}}(|xy\rangle + |yz\rangle + |xz\rangle)$$

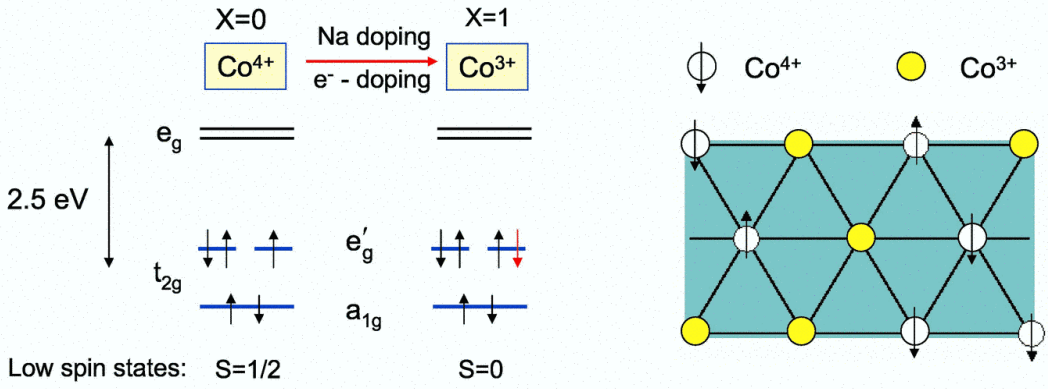
$$|e'_{g,1}\rangle = \frac{1}{\sqrt{2}}(|xz\rangle - |yz\rangle)$$

$$|e'_{g,2}\rangle = \frac{1}{\sqrt{6}}(2|xy\rangle - |yz\rangle - |xz\rangle)$$



- t_{2g} orbitals point to midpoint of O-O bond
- Direct exchange b/w t_{2g} orbitals on Co

Sodium doping in Na_xCoO_2



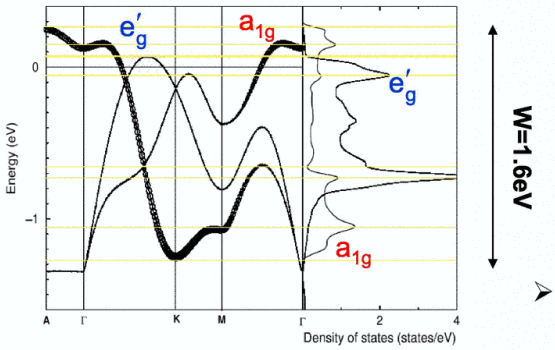
"Spin liquid" on a triangular lattice → Sodium (electron) doping → Band insulator

X=0 — X=1

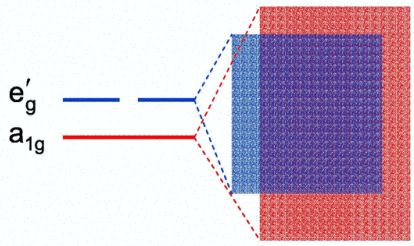
Moderate to large doping

☆ Na doping x → (5+x) electrons/Co(site) (1-x) holes/Co(site)

Band structure of Na_xCoO_2 – t_{2g} complex (LDA)



W=1.6eV

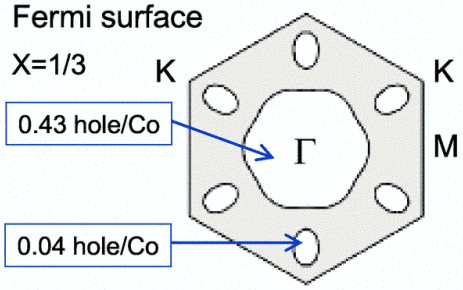


K.-W. Lee, et al, PRB **70**, 045104 (2004)

- a_{1g} band has lower center of gravity, but larger bandwidth t ~ -0.13eV, e'_g band (W=1.3eV) lies within a_{1g}.

Fermi surface

X=1/3



- Na_xCoO_2 is a multi-band system
- central hole FS around Γ (most a_{1g}), six hole FS pockets near K (mostly e'_g)
- density of states enhanced due to the six FS pockets

- U~5-8 eV. U>>W strongly correlated.
- narrow band system, direct Co-Co coupling, small AF exchange J ~ 12 meV

Basic effects of strong correlation

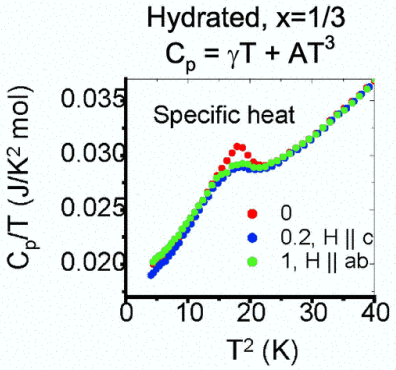
★ Specific heat : Chou, et. al. PRL 92, 157004 (2004)

DOS at Fermi level: 7.1 states/eV

Effective mass of a single tight-binding a_{1g} orbital on triangular lattice:

t_{eff}=–23meV

Mass enhancement: $t/t_{eff} \sim 6$

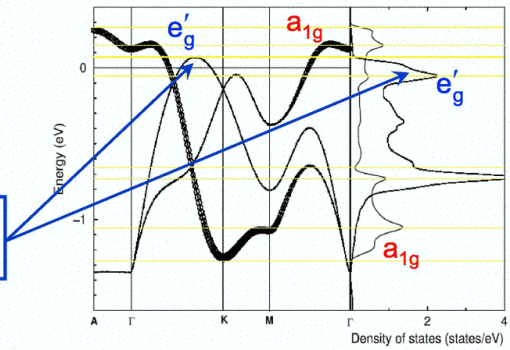


★ Band effects or correlation:

LDA Fermi level DOS: ~ 5 states/eV

However

DOS enhancement due to six hole pockets associated with e'$_g$ band



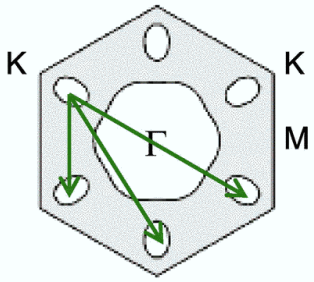
More wonders of the e'$_g$ pockets

★ Nearly perfect nesting:

- tendency to charge order
- enhanced spin fluctuations
- unconventional superconductivity

Johannes, et. al. PRL, 93, 097005 (2004)

Odd gap, triplet s-wave …



★ Superconductivity due to e'$_g$ band

Kuroki, et. al. PRL, 93, 077001 (2004)

Eliashberg, spin triplet f-wave ….

Yansase, et. al. J. Phys. Soc. Jpn, 74, 430 (2005); Mochizuki, et. al. cond-mat/0503233

Flex-Eliashberg, spin triplet p-wave and f-wave …

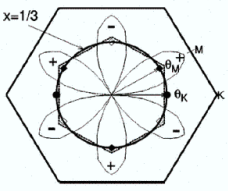
★ Superconductivity with a single a_{1g} band + correlation

Q.H. Wang, D.-H. Lee, and P.A. Lee, PRB, 69, 092504 (2004).
Baskaran, PRL (2003), Kumar and Shastry, PRB (2003), Ogata (2003)

One-band t-J model, RVB, spin singlet d+id wave…

Motrunich and P.A. Lee, PRB, 69, 214516 (2004)

t-V model, GW-Jastrow, near charge-order at x=1/3, f-wave ….



Absence of FS Pockets: ARPES experiments

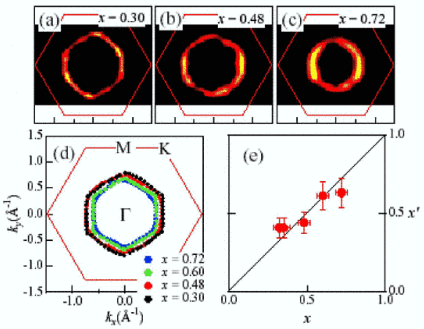
- Two groups:
  Boston College: Hong Ding …
  Princeton: M.Z. Hasan, …

  Yang, et. al., cond-mat/0501403, PRL (2005);
  Hasan, et. al, PRL 92, 246402 (2004),

- Three sample souces:
  Oakridge National Lab,
  MIT, and Princeton

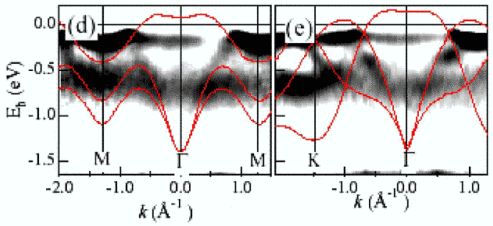
  Hasan et. al., cond-mat/0501530
  Yang, et. al. , PRL 92, 246403 (2004).

★ A single hole-FS around Γ at all x



Yang, et. al. cond-mat/0501403, PRL (2005)

★ e'_g bands fail to cross Fermi level



★ Significant band-narrowing

★ Bulk x-ray PE → same results

★ Discrepancy b/w ARPES and LDA → Important correlation effects, U>>W

Correlation effects on electronic structure of t_{2g} complex

★ Multi-orbital Hubbard model for t_{2g} complex on triangular lattice

Castellani, Natoli, and Ranninger, PRB 18, 4945 (1978). Magnetic structure of V_2O_3

$$H = H_0(\text{LDA-band structure}) + H_I(\text{correlations})$$

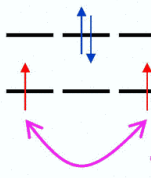
$$H_I = U\sum_i\sum_\alpha n_{i\alpha\uparrow}n_{i\alpha\downarrow} + U'\sum_i\sum_{\alpha>\beta} n_{i\alpha}n_{i\beta}$$

$$- J_H\sum_i\sum_{\alpha>\beta}(S_{i\alpha}\cdot S_{i\beta} - \frac{1}{4}n_{i\alpha}n_{i\beta}) + J_H\sum_i\sum_{\alpha\neq\beta} d^+_{i\alpha\uparrow}d^+_{i\alpha\downarrow}d_{i\beta\downarrow}d_{i\beta\uparrow}$$

$\alpha,\beta = 1,2,3$ orbital index of the t_{2g} band,

$$n_{i\alpha\sigma} = d^+_{i\alpha\sigma}d_{i\alpha\sigma},\ n_{i\alpha} = \sum_\sigma d^+_{i\alpha\sigma}d_{i\alpha\sigma},$$

$$S_{i\alpha} = \frac{1}{2}d^+_{i\alpha\sigma}\vec{\tau}_{\sigma\sigma'}d_{i\alpha\sigma}$$



U intra-orbital Coulomb

U' inter-orbital Coulomb

J_H inter-orbital Hund's rule coupling

On-Site

$$U = U' + 2J_H$$

$$U > U' > J_H > 0$$

Tight binding fit of the LDA band structure: H_0

★ Particle-hole transformation: t_{2g} orbitals with 1-x holes

$$H_0 = \sum_{ij,\sigma}\sum_{\alpha\beta} t_{ij}^{\alpha\beta} d_{i\alpha\sigma}^{+} d_{j\beta\sigma} + \frac{\Delta}{3}\sum_{i,\sigma}\sum_{\alpha\neq\beta} d_{i\alpha\sigma}^{+} d_{i\beta\sigma}$$

- ignore oxygen 2p orbitals
- keep hexagonal symmetry
- degenerate $t_{2g} = \{d_{xy}, d_{yz}, d_{zx}\}$

$t_{ij}^{\alpha\beta}$ hopping matrix on triangular lattice.
Δ trigonal crystal field splitting

$$H_0 = \sum_{k\sigma}\sum_{\alpha\beta} \mathbf{K}_{\alpha\beta}^{d}(k) d_{k\alpha\sigma}^{+} d_{k\beta\sigma} + \frac{\Delta}{3}\sum_{k\sigma}\sum_{\alpha\neq\beta} d_{k\alpha\sigma}^{+} d_{k\beta\sigma}$$

$$\mathbf{K}^{d}(k) = \begin{pmatrix} \varepsilon(t,k_1,k_2,k_3) & \varepsilon(t',k_3,k_1,k_2) & \varepsilon(t',k_2,k_3,k_1) \\ \varepsilon(t',k_3,k_1,k_2) & \varepsilon(t,k_2,k_3,k_1) & \varepsilon(t',k_1,k_2,k_3) \\ \varepsilon(t',k_2,k_3,k_1) & \varepsilon(t',k_1,k_2,k_3) & \varepsilon(t,k_3,k_1,k_2) \end{pmatrix}$$

$$k_1 = \frac{\sqrt{3}}{2}k_x - \frac{1}{2}k_y,\ k_2 = k_y,$$
$$k_3 = -\frac{\sqrt{3}}{2}k_x - \frac{1}{2}k_y$$

- $t,\ t'$: (intra, inter)-orbital hopping integral
- $\varepsilon(t,k_1,k_2,k_3) = 2t_1\cos k_1 + 2t_2(\cos k_2 + \cos k_3) + 2t_3\cos(k_2 - k_3)$
  $+ 2t_4[\cos(k_3 - k_1) + \cos(k_1 - k_2)] + 2t_5\cos(2k_1) + 2t_6[\cos(2k_2) + \cos(2k_3)] + \cdots\cdots$

Crystal field splitting and orbital basis

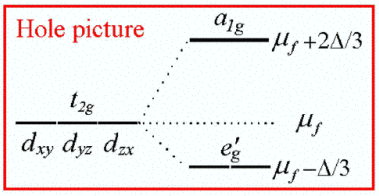
★ Rotate basis:

a-basis

$$\begin{pmatrix} e'_{g1} \\ e'_{g2} \\ a_{1g} \end{pmatrix} = \mathbf{O}\begin{pmatrix} d_{xy} \\ d_{yz} \\ d_{zx} \end{pmatrix}, \qquad \mathbf{O} = \begin{pmatrix} 0 & -1/\sqrt{2} & 1/\sqrt{2} \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \end{pmatrix}$$

$$H_0 = \sum_{k\sigma}\sum_{\alpha\beta} \mathbf{K}_{\alpha\beta}^{a}(k) a_{k\alpha\sigma}^{+} a_{k\beta\sigma} + \sum_{k\sigma}\sum_{\alpha\neq\beta} \Delta_{\alpha} a_{k\alpha\sigma}^{+} a_{k\beta\sigma}$$

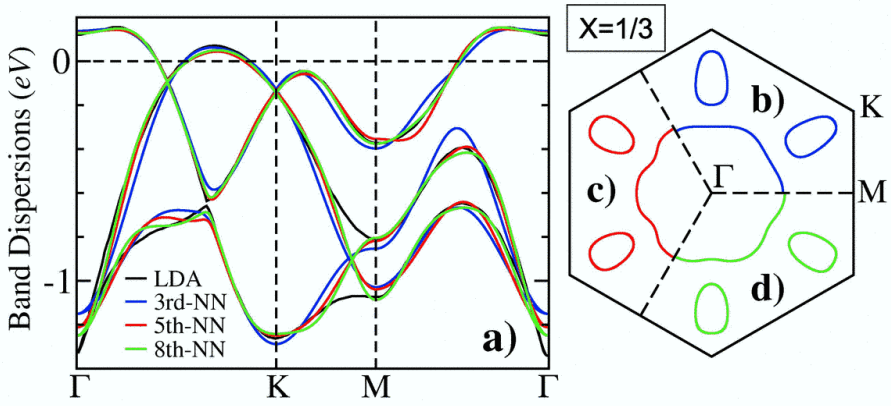
- $\Delta_{\alpha} = (-\Delta/3,\ -\Delta/3,\ 2\Delta/3)$
- $\mathbf{K}^{a}(k) = \mathbf{O}^{\mathrm{T}}\mathbf{K}^{d}(k)\mathbf{O}$
- holes prefer e'_g band (pockets)



★ Interaction part is basis independent

$$H_I = U\sum_{i}\sum_{\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + U'\sum_{i}\sum_{\alpha>\beta} n_{i\alpha} n_{i\beta}$$
$$- J_H\sum_{i}\sum_{\alpha>\beta}(S_{i\alpha}\cdot S_{i\beta} - \frac{1}{4}n_{i\alpha}n_{i\beta}) + J_H\sum_{i}\sum_{\alpha\neq\beta} a_{i\alpha\uparrow}^{+} a_{i\alpha\downarrow}^{+} a_{i\beta\downarrow} a_{i\beta\uparrow}$$

Tight binding fit to LDA t_{2g} band dispersions



- fit well at low energies beyond 3rd-NN hopping
- bandwidths → hole occupations: (a_{1g}= 0.421), (e'_g=0.123)
- discrepancies at high energies due to oxygen not included
  - Co-O and O-O hopping
  - no reflection symmetry along z

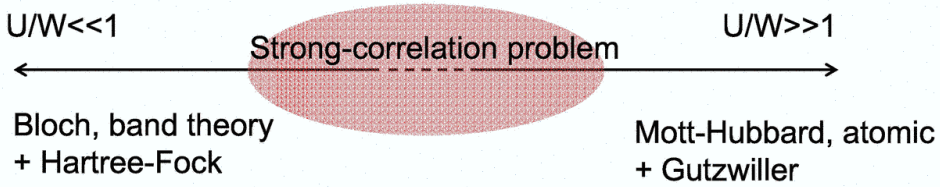
H_0(3rd NN hopping): $t = (-44.6, -9.0, 36.2, 5.9, 57.9, 36.7)$meV,
$t' = (-157.8, -30.2, 37.1, 9.2, -11.9, -21.0)$meV, $\Delta = 10$meV

Effects of local electronic correlations

$$H = H_0 + U\sum_i\sum_\alpha n_{i\alpha\uparrow}n_{i\alpha\downarrow} + U'\sum_i\sum_{\alpha>\beta} n_{i\alpha}n_{i\beta}$$

$$-J_H\sum_i\sum_{\alpha>\beta}(S_{i\alpha}\cdot S_{i\beta} - \frac{1}{4}n_{i\alpha}n_{i\beta}) + J_H\sum_i\sum_{\alpha\neq\beta} a^+_{i\alpha\uparrow}a^+_{i\alpha\downarrow}a_{i\beta\downarrow}a_{i\beta\uparrow}$$

Can correlations lead to
- carrier transfer and orbital polarization?
- band-narrowing ?



Study *H* in both LDA+Hartree-Fock and LDA+Gutzwiller approx.

Weak-coupling: LDA + orbital Hartree-Fock

$$H_I^{HF} = \sum_{k,\sigma}\sum_{\alpha}\left(\frac{1}{2}Un_\alpha + U'_{\text{eff}}\sum_{\beta\neq\alpha} n_\beta\right)a^+_{k\alpha\sigma}a_{k\alpha\sigma} - \frac{1}{4}U\sum_{k,\alpha} n_\alpha^2 - \frac{1}{2}U'_{\text{eff}}\sum_{k,\alpha\neq\beta} n_\alpha n_\beta$$

$$+\left(U-2U'_{\text{eff}}\right)\sum_{k,\sigma}\sum_{\alpha\neq\beta}\left(n_{\alpha\beta}a^+_{k\alpha\sigma}a_{k\beta\sigma} - \frac{1}{2}n^2_{\alpha\beta}\right), \qquad U'_{\text{eff}} = U' - J_H/2$$

- Double-counting in LDA+U depends only on total density
- In $\{e'_g, a_{1g}\}$-basis, HF theory diagonal in orbital space, $n_{\alpha\neq\beta} = 0$

Hartree-Fock self energy corrections

$$\Sigma^{HF}_{e'_g} = \frac{5}{2}\bar{n}\frac{U'}{U} + \frac{5}{4}\delta U\left(\frac{U'}{U} - \frac{3}{5}\right) \qquad \bar{n} = \frac{1}{3}(n_{a_{1g}} + 2n_{e'_g}) = \frac{1}{3}(1-x)$$

$$\Sigma^{HF}_{a_{1g}} = \frac{5}{2}\bar{n}\frac{U'}{U} - \frac{5}{2}\delta U\left(\frac{U'}{U} - \frac{3}{5}\right) \qquad \delta = \frac{1}{3}(n_{a_{1g}} - n_{e'_g}) > 0$$

Renormalized band center separation

$$\Delta^* = \Sigma^{HF}_{a_{1g}} - \Sigma^{HF}_{e'_g} = -\frac{15}{4}\delta U\left(\frac{U'}{U} - \frac{3}{5}\right)$$

sign of $\Delta^* \Rightarrow$ direction of charge transfer b/w orbitals

Orbital carrier transfer in Hartree-Fock

$U'/U < 3/5,\ \Delta^* > 0$

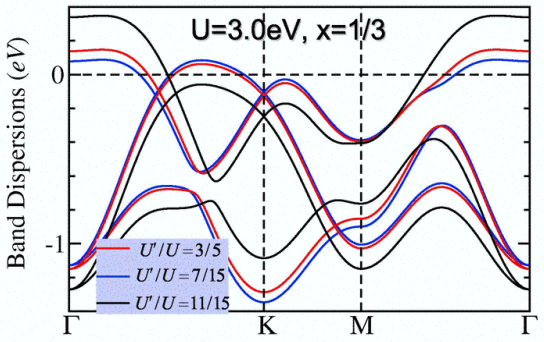
Holes $a_{1g} \rightarrow e'_g$, Pockets grow!

$U'/U = 3/5,\ \Delta^* = 0$

Band theory (LDA) unrenormalized!

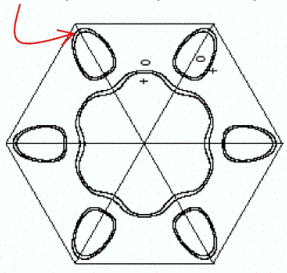
$1 \geq U'/U > 3/5,\ \Delta^* < 0$

Holes $e'_g \rightarrow a_{1g}$, Pockets shrink and disappear!



- For U'<(3/5)U, multiorbital occupation favored to reduce the cost of double occupation.
- Orbital polarization (sinking pockets) results from strong correlation
- Hartree-Fock becomes unphysical for large local Coulomb repulsion

DMFT, U=2eV, U'=1eV, x=0.3



Ishida, Johannes, Liebsch, PRL 94, 196401 (05)

Strong Coupling limit – LDA + Gutzwiller

- $U, U' >> J_H$, Infinite-(U,U') Hubbard model $\rightarrow \sum_{\alpha\sigma} a^+_{i\alpha\sigma} a_{i\alpha\sigma} = 0,1$

$H = H_0 +$ no double occupancy constraints

- Gutzwiller projection:

$$|\Psi\rangle = P_G |\Psi_0\rangle, \quad P_G: \text{ projection operator}, \quad H_0 |\Psi_0\rangle = E_0 |\Psi_0\rangle$$

Multi-orbital Gutzwiller approximation:

$$P_G a^+_{i\alpha\sigma} a_{j\beta\sigma} P_G \Rightarrow g_t^{\alpha\beta} a^+_{i\alpha\sigma} a_{j\beta\sigma} \qquad g_t^{\alpha\beta} = \frac{W\langle\Psi| a^+_{i\alpha\sigma} a_{j\beta\sigma} |\Psi\rangle}{W\langle\Psi_0| a^+_{i\alpha\sigma} a_{j\beta\sigma} |\Psi_0\rangle}$$

- Uniform paramagnetic phase:

$$g_t^{\alpha\beta} = \frac{x}{\sqrt{(1-n_\alpha/2)(1-n_\beta/2)}}$$

← Coulomb blocking

← Compensate Pauli blocking

Pauli blocking depends on occupations of orbitals connected by hopping!

Strong coupling – GW for paramagnetic state

$$H_{GW} = \sum_{k\sigma}\sum_{\alpha\beta} g_t^{\alpha\beta} \mathbf{K}^a_{\alpha\beta}(k) a^+_{k\alpha\sigma} a_{k\beta\sigma} + \sum_{k,\alpha,\sigma} \Delta_\alpha a^+_{k\alpha\sigma} a_{k\alpha\sigma} + \sum_\alpha \varepsilon_\alpha \left(\sum_{k\sigma} a^+_{k\alpha\sigma} a_{k\alpha\sigma} - n_\alpha \right)$$

$$\varepsilon_\alpha = \frac{1}{2-n_\alpha} \frac{1}{N_s} \sum_{k\beta\sigma} g_t^{\alpha\beta} \mathbf{K}^a_{\alpha\beta} \langle a^+_{k\alpha\sigma} a_{k\beta\sigma} \rangle \qquad n_\alpha = \sum_{k\sigma} \langle a^+_{k\alpha\sigma} a_{k\alpha\sigma} \rangle$$

- Physics in the strong coupling limit

No energy cost of order U
in contrast to HF theory

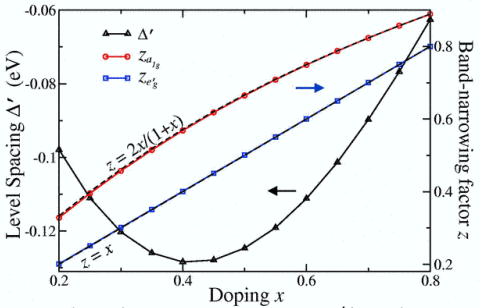
Charge transfer governed by

- Renormalized level spacing:

$$\Delta' = \varepsilon_{a_{1g}} - \varepsilon_{e'_g}$$

- Band-narrowing factor:

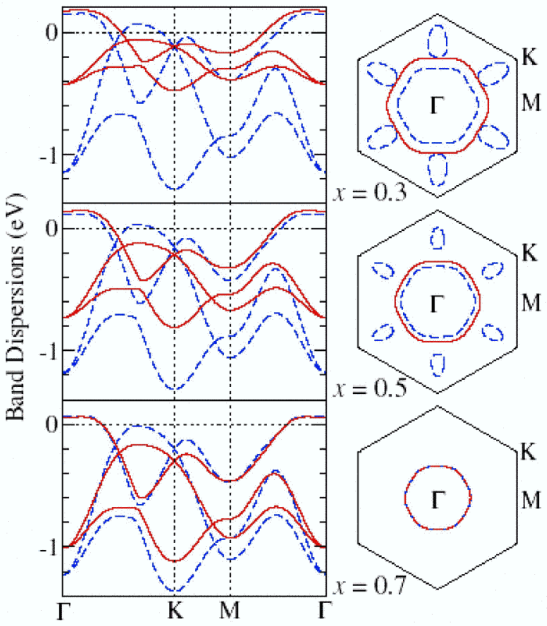
$$z_\alpha = g_t^{\alpha\alpha} = 2x/(2-n_\alpha)$$



$n_{a_{1g}} \approx (1-x)/2,\ n_{e'_g} \approx 0,\ z_{a_{1g}} \approx 2x/(1+x),\ z_{e'_g} \approx x$

Orbital with more hole occupation: smaller bandwidth reduction + lower band center
→ charge transfer of more holes: holes move out of e'_g band into the a_{1g} band.

Electronic structure in strong coupling limit



Noninteracting (LDA)

LDA + Gutzwiller

- e_g' band is pushed below the Fermi level
- Small FS pockets are absent due to strong correlation
- Renormalized bandwidth band-narrowing
- Large dos in specific heat due to strong correlation

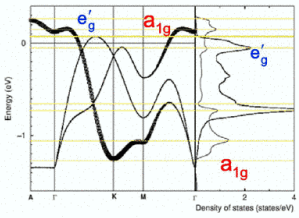
Zhou, Gao, Ding, Lee, ZW, PRL 94, 206401 (2005)

Ferromagnetic order at large x in strong coupling

- Paramagnetic LDA is unstable to Ferromagnetic order for all x

  Singh, PRB 61, 13397 (2000); 68, 020503(R) 2003.

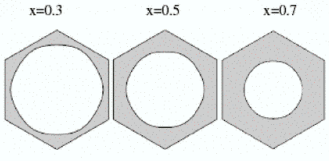
  - Dos is too large for the size of U/W, weak coupling approach is not reliable.

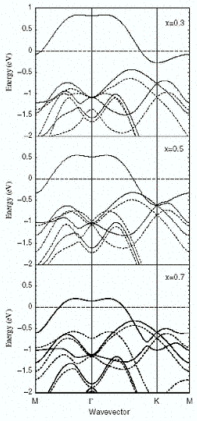


- LSDA+U leads to fully polarized FM metal for all x

  Zhang, Luo, Cohen, Louie, PRL 93, 236402 (2004)
  Zou, Wang, Zeng, PRB 69, 132505 (2004)

  - FM not seen in experiments for x < 0.75
  - Spin polarized FS and spin split bands
  - FS with twice the volume, not seen in ARPES
  - Enhanced bandwidth of t_{2g} complex inconsistent with experiments



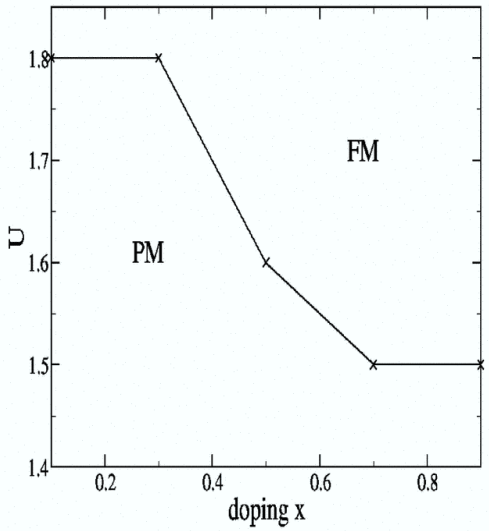


- How to explain the absence of ferromagnetism for x < 0.75?

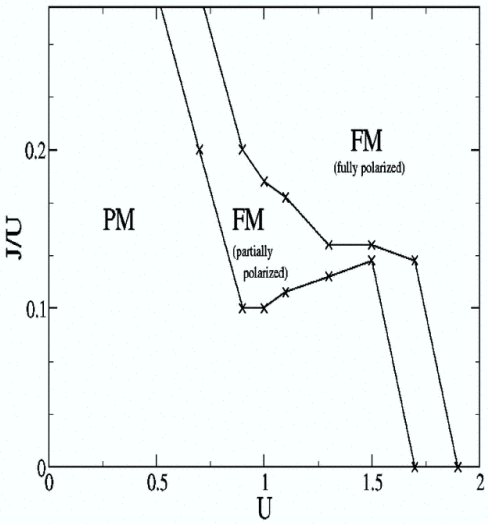
Zhang, Luo, Cohen, Louie, PRL 93, 236402 (2004)

Hartree-Fock Approximation

- Weak-Coupling/LDA +U



Phase diagram in Hartree-Fock approximation, with J=0, U=U'.



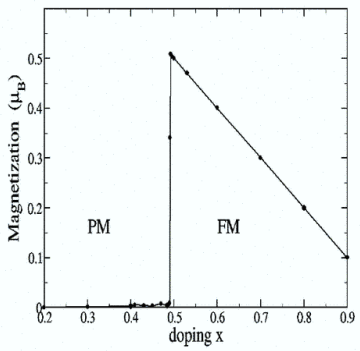
HF Phase diagram at x=0.5.
From left to right are para magnetism, partial and full ferromagnetism.

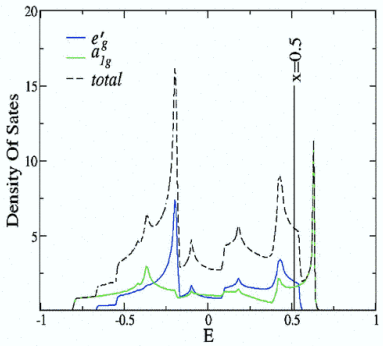
Strong correlation and Ferromagnetism at large x

Generalize GW approximation to allow FM

$$H_{GW} = \sum_{k\sigma}\sum_{\alpha\beta} g^{\alpha\beta}_{t,\sigma}\mathbf{K}^{a}_{\alpha\beta}(k)a^{+}_{k\alpha\sigma}a_{k\beta\sigma} + \sum_{k,\alpha,\sigma}\Delta_{\alpha}a^{+}_{k\alpha\sigma}a_{k\alpha\sigma} + \sum_{\alpha\sigma}\varepsilon_{\alpha\sigma}\left(\sum_{k}a^{+}_{k\alpha\sigma}a_{k\alpha\sigma} - n_{\alpha\sigma}\right)$$

$$g^{\alpha\beta}_{t,\sigma} = \frac{x}{\sqrt{(1-n_{\alpha\sigma})(1-n_{\beta\sigma})}}, \qquad \varepsilon_{\alpha\sigma} = \frac{1}{2-n_{\alpha}}\frac{1}{N_s}\sum_{k\beta} g^{\alpha\beta}_{t\sigma}\mathbf{K}^{a}_{\alpha\beta}\left\langle a^{+}_{k\alpha\sigma}a_{k\beta\sigma}\right\rangle$$





- Paramagnetic state for x <0.48
- Polarized FM for x>0.48
- Ordered moment/Co=1-x for x>0.5

Gao, et.al, to be published (2005).

Ferromagnetic order at large x – strong coupling

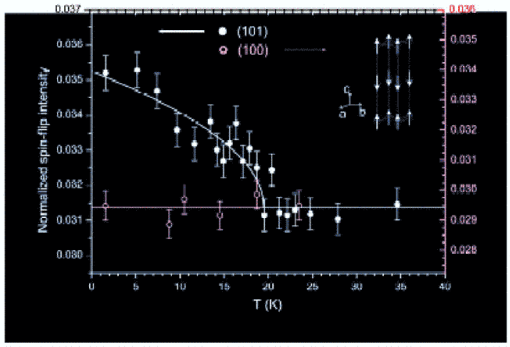
- Neutron scattering at x=0.82

A-type magnetic order T < 20K

- Ferromagnetic within layer
  Antiferromagnetic b/w layers
- More 3D-like exchange couplings

Ordered moment: $0.13\mu_B$ / Co

- Density of Co^{4+}=1-x=0.18
- Amounts to an ordered moment of 0.32 μ_B/Co^{4+} if all Co ions are in the low spin state.



Bayrakei, et. al. PRL (2005).

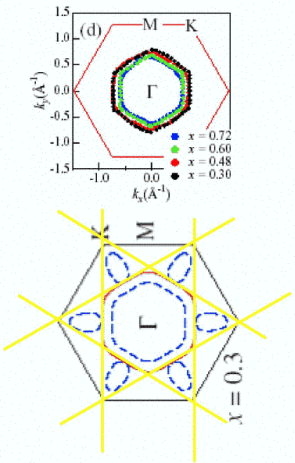
- Summary:

Strong correlation drives the e'$_g$ band below Fermi level:
(1) Absence of FS pockets (2) Band narrowing of the t_{2g} complex
(3) Stability of PM phase for small x (4) Emergence of FM at large x

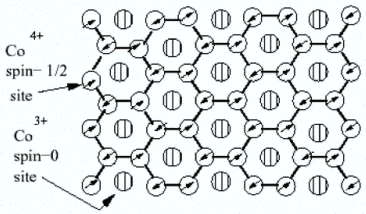
Questions and outlook

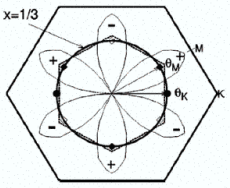
- Effects of crystal field splitting and role of hydration
- If and how the Mott insulator emerges at x=0 (?!)
- Finite-U, charge transfer, orbital order (polarization) at critical U_c(?!)

- Charge order (fluctuations) and superconductivity near x=1/3



Hexagonal FS at $x = 1/3$ coincides with
zone boundary of $\sqrt{3} \times \sqrt{3}$ charge order





- Charge disproportionation
- CDW via jamming due to V

Pickett (2003), Baskaran (2003)
Motrunich and Lee (2004)