Instant superconductor: Just Add Water!

Electronic Structure, Magnetism and Superconductivity in Na_xCoO_2

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Nesting, spin fluctuations, and odd-gap superconductivity in $Na_xCoO_2 \cdot yH_2O$

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Acknowledgment:
Dan Agterberg

Outline

Introduction

-- What's interesting about Na_xCoO_2?

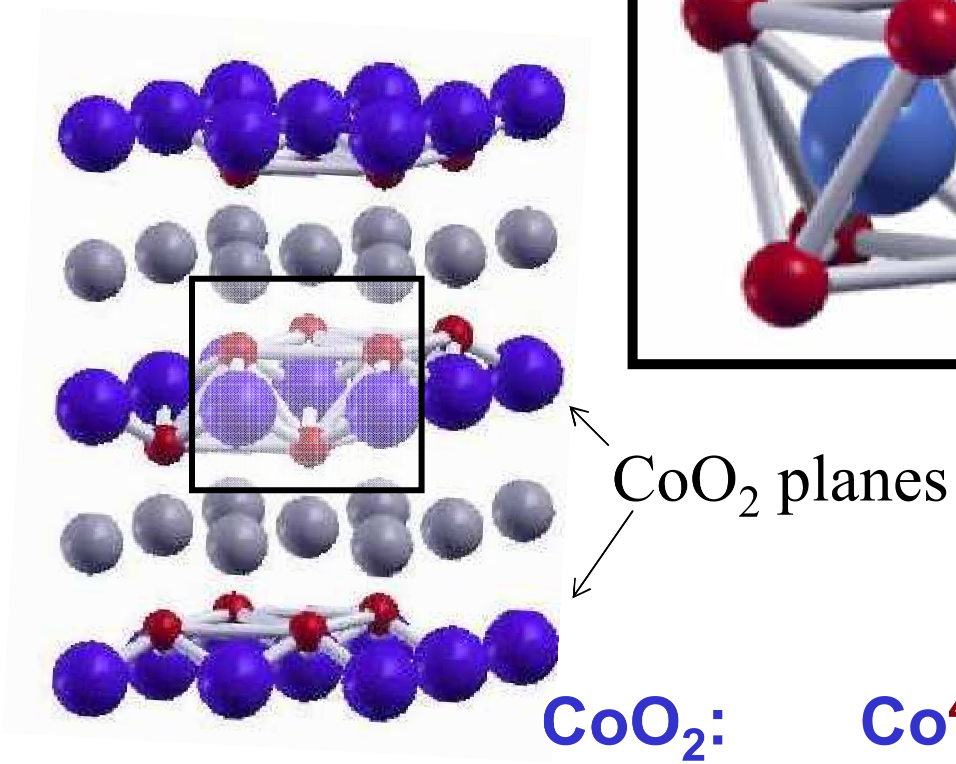
PART I

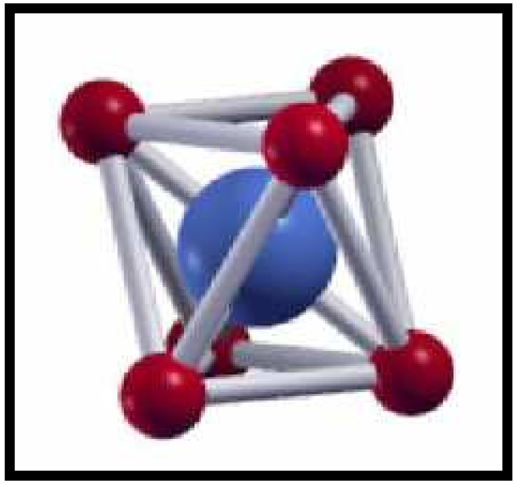
Electronic properties

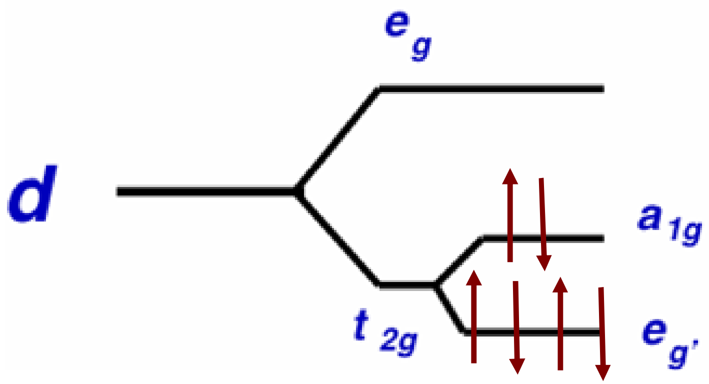
PART II

Spin fluctuations and superconductivity

The Distorted Octahedral Environment of Co Ions





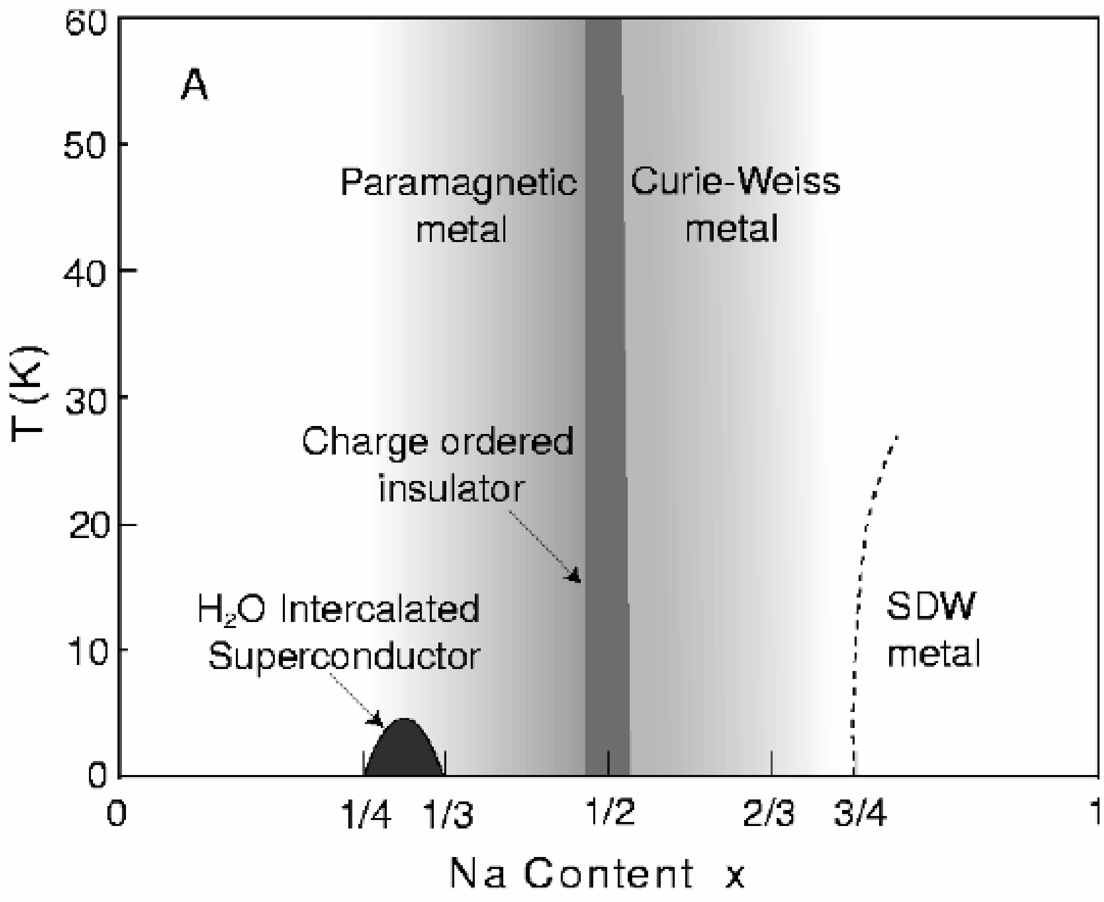


CoO_2: Co^{4+} ($3d^5$) => Mott insulator?

$NaCoO_2$: Co^{3+} ($3d^6$) => band insulator

But Na_xCoO_2 behaves almost *oppositely*…

Na content phase diagram



EXPECTED

- At x =0, system is a magnetic insulator
- At x=1, system is a band insulator
- For x < 0.5, system is a magnetic metal
- For x > 0.5, system is a simple metal

OBSERVED

- For x < 0.5, system is a simple metal
- For x > 0.5, system go through a sequence of magnetic metallic phases

- At x=0 system is a nonmagnetic metal
- At x=1 compound does not form
- At x=0.5 system is insulating

The calculated phase diagram of Na_xCoO_2

$x = 0.3$	$x = 0.5$	$x = 0.7$
LDA: FM	LDA: FM	LDA: FM
Exp: PM	Exp: AFM	Exp: PM
$\gamma_{th} = 11.8\ mJ/mol\ K^2$	$\gamma_{th} = 13.0\ mJ/mol\ K^2$	$\gamma_{th} = 9.1\ mJ/mol\ K^2$
$\gamma_{exp} \sim 15\ mJ/mol\ K^2$	Exp: Insulator	$\gamma_{exp} \sim 27\ mJ/mol\ K^2$
$\lambda = 0.27$		$\lambda = 1.96$

itinerant | localized

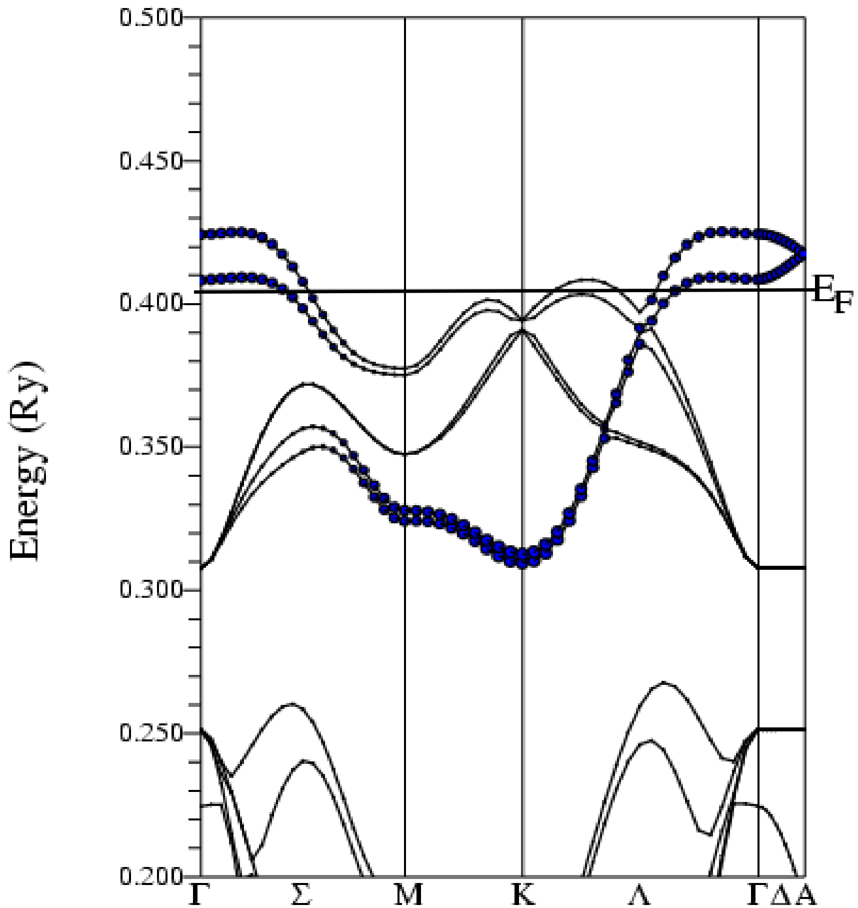
LDA typically finds *smaller* magnetic moments than experiment

Exception: the vicinity of a quantum critical point

Consistent overestimation of magnetism suggests spin fluctuations

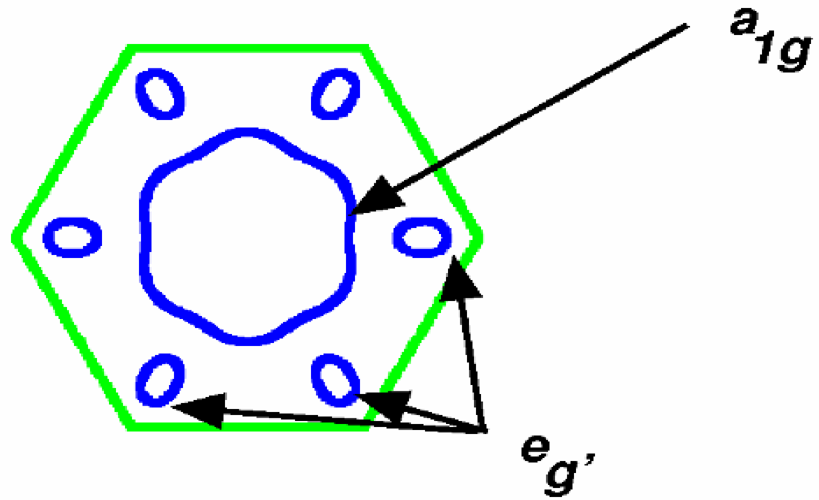
Multi-Orbital Nature of Fermi Surfaces

$Na_{0.7}CoO_2$



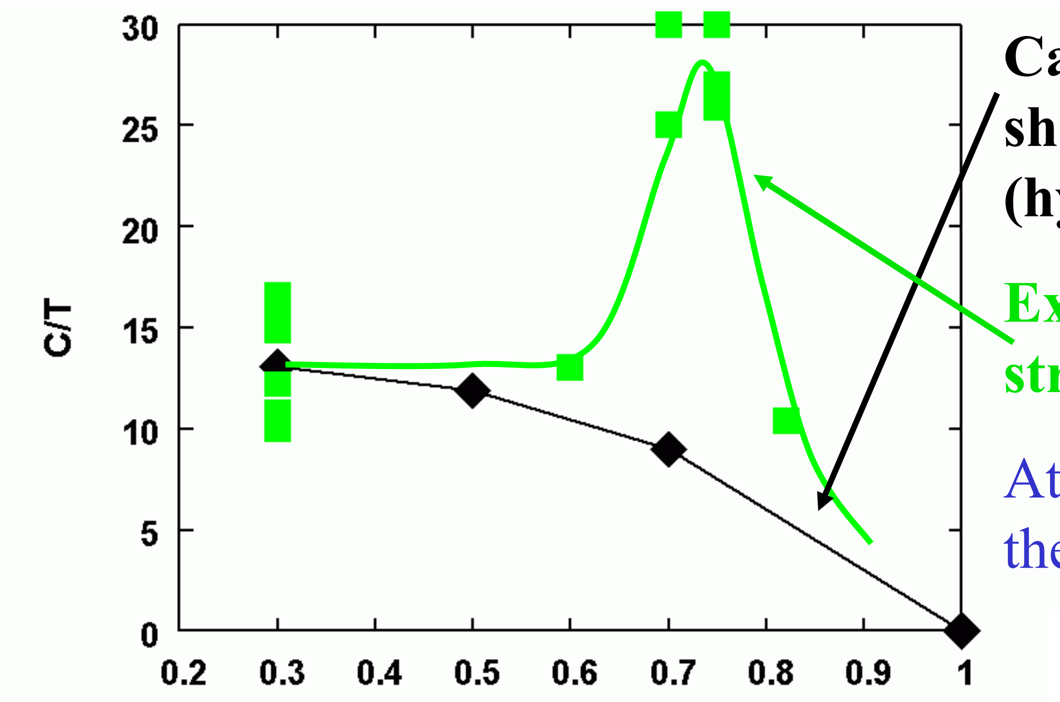
$$a_{1g} = (xy) + (yz) + (zx) = 3z^2 - r^2$$

$$e_g' = (xy) + e^{\pm 2\pi i/3}(yz) + e^{\pm 4\pi i/3}(zx)$$



Two distinct Fermi surface types are predicted by calculation.

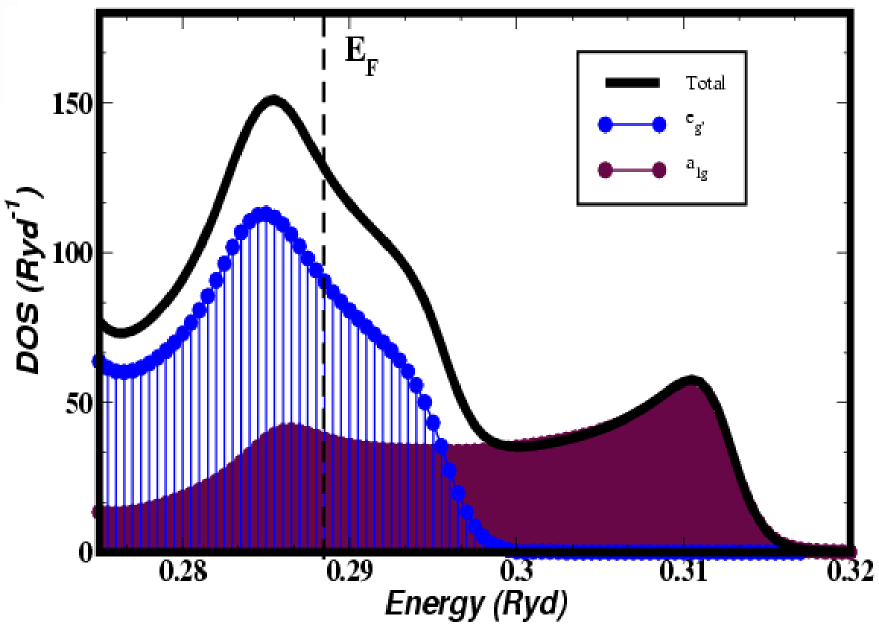
Specific heat



Calculations (not very accurate) show gradual decay towards (hypothetical) $NaCoO_2$

Exp. (not very reliable) show a strong enhancement near x=0.7

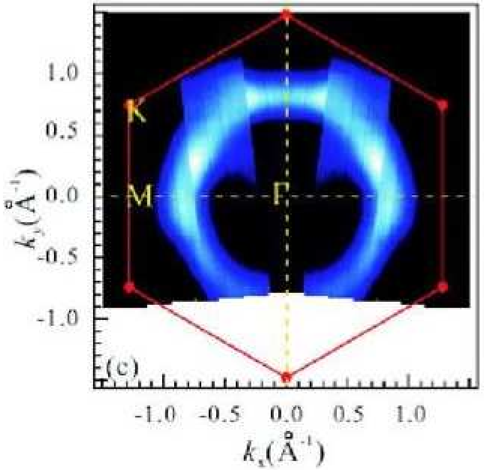
At x=0.3, 70% of DOS comes from the small e' pockets!



Practically all data at x<0.5 are consistent with weak or no correlations

Practically all data at x>0.5 are consistent with strong correlations

Comparison with Experiment



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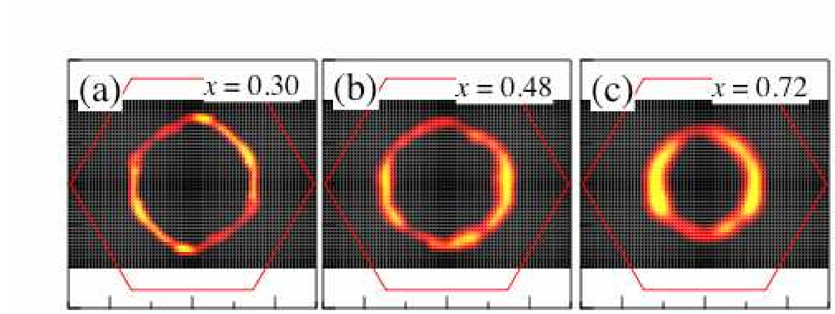

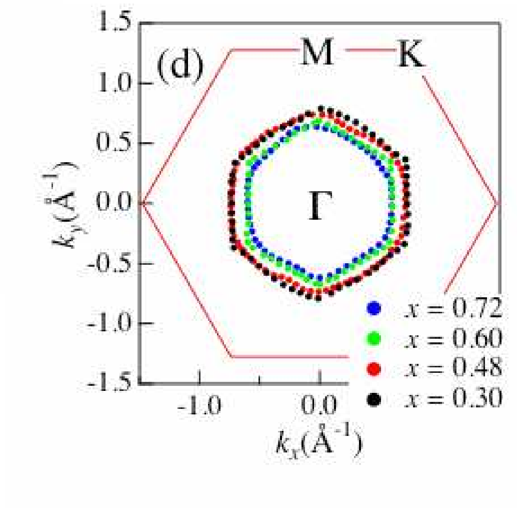

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The large (a_{1g})Fermi Surface is clearly seen by ARPES

The smaller (e_g’) surfaces are absent

WHY?

- Correlations beyond LDA
- Surface effects (relaxation, surface bands, Na content)
- Matrix elements

How does correlation affect the electronic structure?

Strongly correlated systems are characterized by large U/t

What is U in Na_xCoO_2?

LMTO: 3.7 eV (for all 5 d-bands)

Narrow t_{2g} bands screened by
Empty e_g orbitals … U < 3.7eV

(A.Liebsch)

LDA+U: Corrects on-site Coulomb repulsion

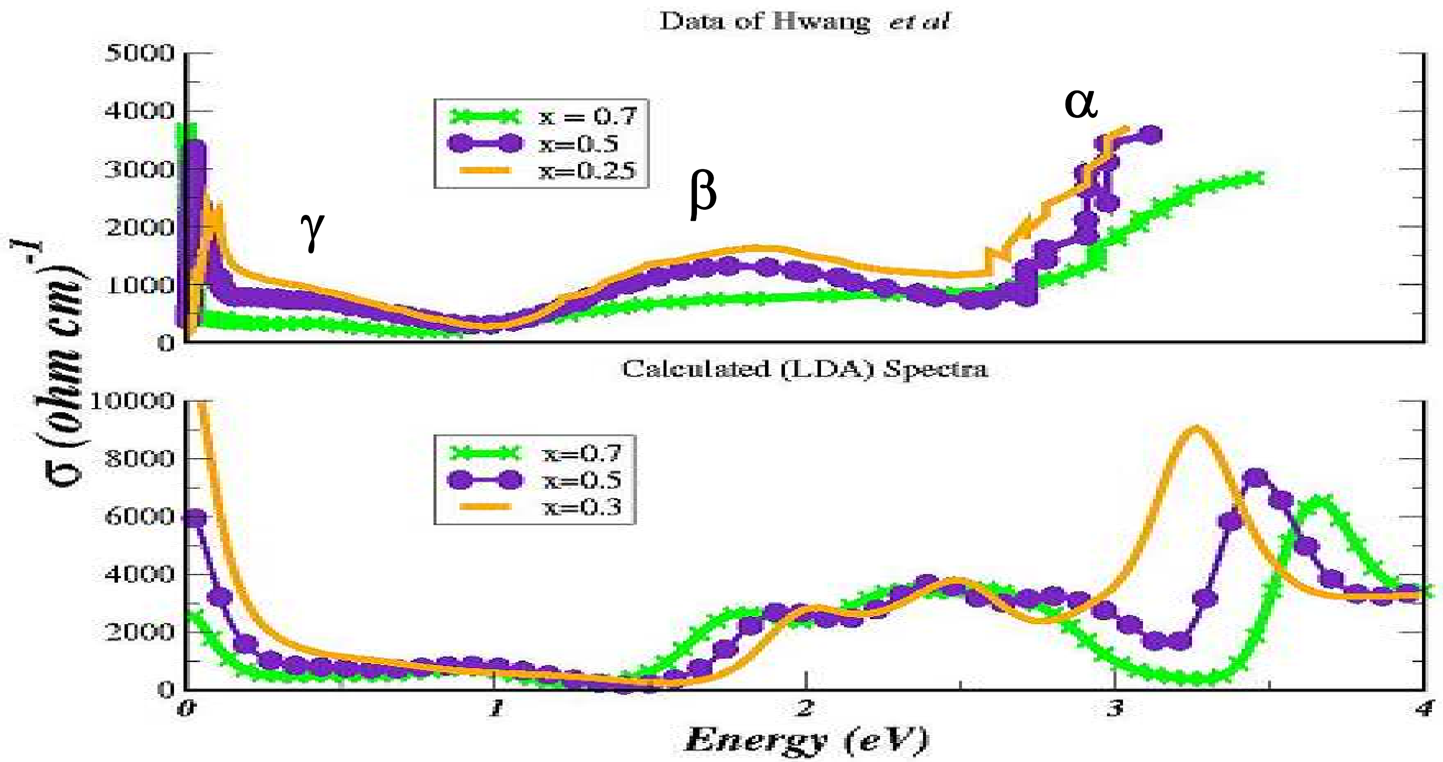
Gets good FS match for U= 4 eV (P. Zhang, PRL **93** 236402)

But U=4 eV > U_C = 3eV for unobserved charge disproportionation (K-W. Lee PRL **94** 026403)

For U<2.5 eV, small pockets remain

Spin fluctuations: Renormalize bands, similarly to phonons
Fermi surface is preserved, less weight

Optics: A Probe of Bulk Electronic Structure



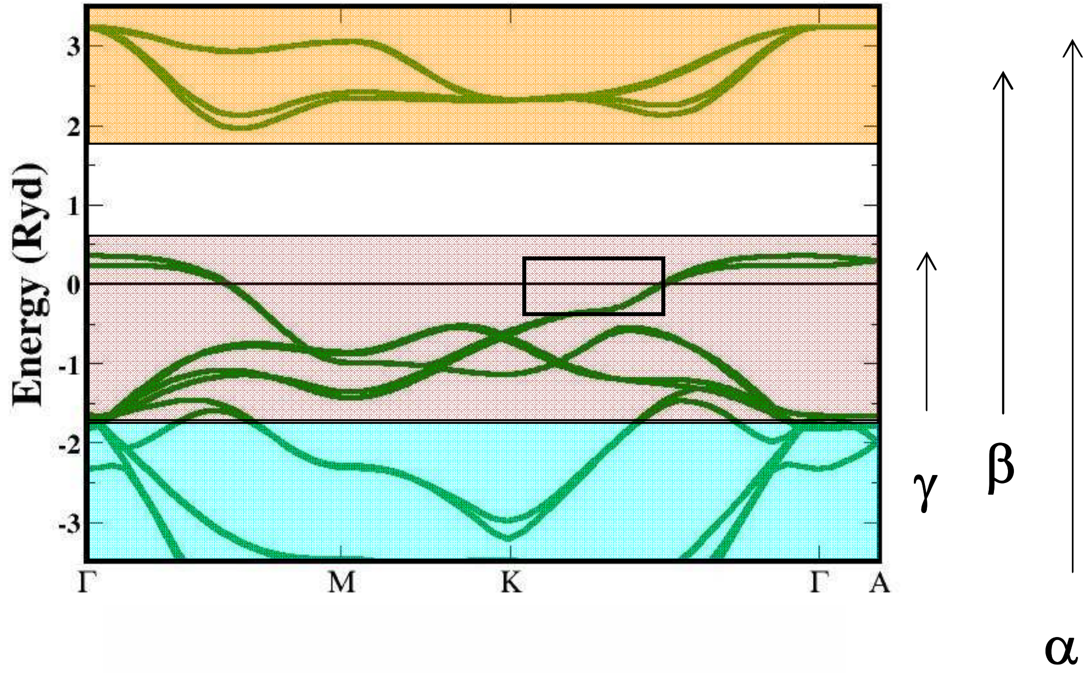
There are three basic peaks: α, β, γ.

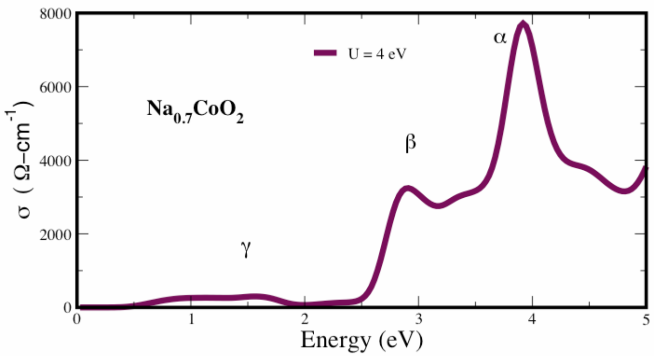
Peak shifts with changing Na content are reproduced.

Peak heights and energy positions are exaggerated.

Optics: Effect of LDA+U

How does electronic correlation manifest itself?



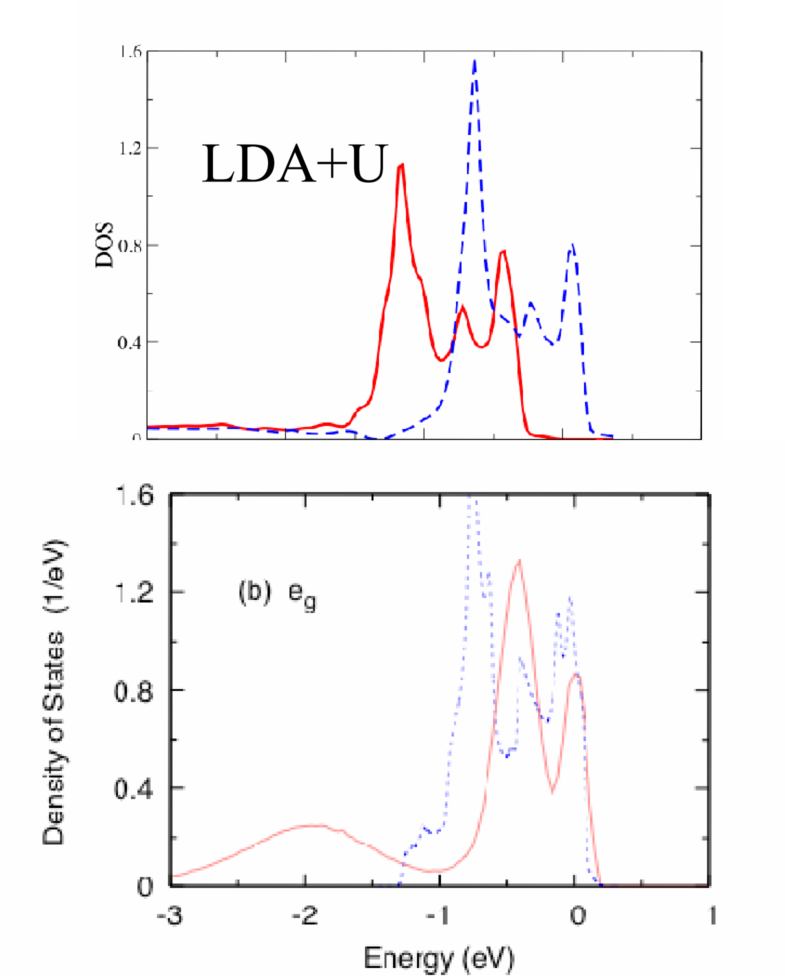


Application of LDA+U *worsens* agreement with experiment.

Mott-Hubbard type correlation is not exhibited for any x!

Dynamical Correlation: DMFT

Dynamical Mean Field Theory gives a very different picture of correlation effects:



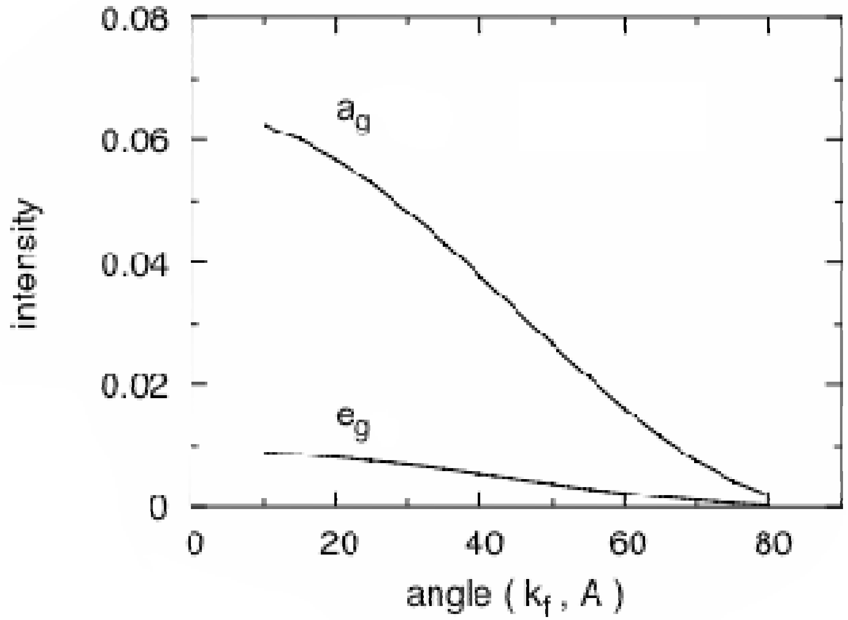
Small e_g' holes <u>grow</u>

A.Liebsch, '05

<u>Some</u> spectral weight shifts downward

Matrix elements and surface effects

ARPES measurements have either s or p polarized light



For p-polarized light, the dipole matrix element is substantially different for the two symmetries.

(A. Liebsch)

Bulk calculations suggest that surface relaxation of O ions could diminish or eliminate small FS pockets

Summary of Part I

- **Na_xCoO_2 has an unusual magnetic phase diagram**
- **The system does not behave as a Mott-Hubbard insulator, despite a rather narrow t_{2g} bandwidth**
- **The LDA+U method *worsens* agreement with optical measurements**
- **Dynamical correlations show weight transfer from $a_{1g} \rightarrow e_g'$ *i.e.* holes grow!**
- **Calculations, in conjunction with experiment, suggest the presence of spin fluctuations**

Part II: Superconductivity

What kind of superconductor is $Na_{0.35}CoO_2 \bullet yH_2O$?

Pairing state: Singlet? Triplet?

Order parameter: *s,p,d,f* …?

Experimental evidence for pairing state

...singlet order parameter with s-wave symmetry is realized in NaxCoO2 yH2O - *JPSJ 72, 2453 (2003)*

...an unconventional superconducting symmetry with line nodes - *cond-mat/0410517 (2004)*

Unconventional superconductivity in NaxCoO2 yH2O - *cond-mat/0408426 (2004)*

Possible unconventional super-conductivity in NaxCoO2.yH(2)O probed by muon spin rotation and relaxation - *PR B70, 13458 (2005)*

Possible singlet to triplet pairing transition in NaxCoO2 H2O - *PR B70, 144516 (2005)*

Evidence of nodal superconductivity in Na0.35CoO2 . 1.3 H2O - *PR B71, 20504 (2005)*

...magnetic fluctuations play an important role in the occurrence of supe *05)*

… superconducting electron pairs are in the singlet state

- *JPSJ 74 (2005)*

ducting NaxCoO2 a clear candidate pairing - *cond-mat/0503010 (2005)*

What pairing states can we exclude?

$\{1, k_x^2+k_y^2, k_z^2$

$k_x k_z$
$k_y k_z$
$k_z(k_x+ik_y)$

$k_x^2-k_y^2$
$k_x k_y$
$(k_x+ik_y)^2$

$\hat{x}k_x+\hat{y}k_y, \hat{z}k_z$
$\hat{x}k_x-\hat{y}k_x$
$\hat{z}k_x(k_x^2-3k_y^2), \; k_z[(k_x^2-k_y^2)\hat{x}-2k_xk_y\hat{y}$ …
$\hat{z}k_y(k_y^2-3k_x^2), \; k_z[(k_y^2-$ …

$\hat{x}k_z, \; \hat{z}k_x$
$\hat{y}k_z, \; \hat{z}k_y$
$\hat{z}(k_x+ik_y), \; k_z(\hat{x}+i\hat{y})$

$\hat{x}k_x-\hat{y}k_y$
$\hat{x}k_y+\hat{y}k_x$
$(\hat{x}+i\hat{y})(k_x+ik_y)$

MP **63** 240 (1991)

μSR
- No static magnetic moments

» **No states with L≠0**
» **No non-unitary triplet states**

Two dimensionality
- c/a ratio ~ 3.5
- $\rho_{ab}/\rho_c \sim 10^3$

» **k_z-dependent order parameter unrealistic**

DOS Probes
- Non-exponential decay of C/T vs. T
- No coherence peak in $1/T_1$
- Non-exponential decay of relaxation time

» **Superconducting state not fully gapped**

How can pairing state be further resolved?

All remaining states are triplet *f*

***f* states**

$$\hat{\mathbf{z}}k_x(k_x^2 - 3k_y^2)$$
$$\hat{\mathbf{z}}k_y(k_y^2 - 3k_x^2)$$

Both *f* states are axial

<u>Knight Shift can distinguish:</u>

- Spin direction is $\perp$ to vector order parameter
- KS constant across T_C for planar spins (axial order parameter)
- KS decreases across T_C for axial spins (planar order parameter)

Presently, results are contradictory

Evidence of Spin Fluctuations in $Na_{0.35}CoO_2$•$1.4H_2O$

There is growing evidence that SF have a role in the superconductivity:

•Curie-Weiss like behavior of $1/T_1$ (above T_C), with negative θ

•Correlation of T_C with magnetic fluctuations as measured by NQR

•Direct neutron observation of spin fluctuations in related compounds

•LDA calculations indicate proximity to quantum critical point

Details of pairing/pair-breaking in a particular system depend on:

i) Fermiology

ii) spin fluctuation spectrum - $\mathrm{Im}\chi(\mathbf{q},\omega)$