Layered cobaltates: $\text{CoO}_2$ planes filled by a variable number of electrons

CoO$_2$ slabs  Na cobaltates  Misfit cobaltates

Edge-shared octahedra, 90-degree Co-O-Co bonds
Layered cobaltates

- *Extraordinary narrow (~200 meV)* qp-bands
- *Large thermopower, magn. field sensitive*
- *Magnetic and charge orderings*
- *Superconductivity* (*NaCoO*)

*Strongly correlated CoO$_2$ planes*
Two relevant valence states:

- **Small x:** many S=1/2 Co⁴⁺, few S=0 Co³⁺ ("doped Mott insulator")

  (strong corr.)

- **Large x:** few S=1/2 Co⁴⁺, many S=0 Co³⁺ ("doped band insulator")

  (weak corr.)

Two regimes accessible:

- **Small x:** paramagnetic metal, Pauli susceptibility, FL
- **Large x:** magn. order, enhanced thermopower, NFL, QCP...

...opposite trend to what expected!
Paramagnetic metal

Curie-Weiss metal

Charge ordered insulator

$\text{H}_2\text{O}$ intercalated superconductor

$\text{FL}$

$\text{NFL}$

Enhanced th.el. power

SDW metal

QCP?

$T(K)$

$T(K)$

$0$ $1/4$ $1/3$ $1/2$ $2/3$ $3/4$ $1$

$0$ $10$ $20$ $30$ $40$ $50$ $60$

$\text{Na content } x$

water intercalation

SC

$\text{C}_{\text{O}}^{4+}$ $S=1/2$

Cobalt valency

$\text{S}=0$ $\text{C}_{\text{O}}^{3+}$
Co-valence in superconducting $Na_xCoO_2 + H_2O$

Milne et al. PRL (2004): Water intercalation adds electrons into CoO$_2$ → SC-dome located far away from the Mott limit


Different result: NMR by Alloul et al.
Strong correlations develop at large $x$, near the band insulator (!) limit.
ARPES in misfits near the band insulator regime ($x \sim 0.7$)

Brouet et al., 2007

(a) peak-dip-hump structure
(b) strongly renorm. qp-band

c) strong scattering at $\sim 150$ meV

Spin-diluted system but correlations as strong as in doped Mott insulators
Experiment:

• Correlations are enhanced at large $x$, near the spinless band-insulator limit

• SC dome is located at valence compositions far away from the Mott limit

….things are very different from cuprates!

Different origin & functionality of correlations

„no double occupancy“ principle as in cuprates is insufficient
Oxide families

- **Ti, V** – weak JT $t_{2g}$ orbital $\rightarrow$ (orbital fluctuation)
- **Cr,Mn** – large spin, DE $\rightarrow$ (half metallicity)
- **Mn** – JT $e_g$ orb., polarons $\rightarrow$ (CMR effect)
- **Fe,Ni** – proxim. to M/I trans. $\rightarrow$ (spin-helix order)
- **Co** – spin-state degen. $\rightarrow$ (high th.el.power)
- **Cu** – quant.spin, no orbital $\rightarrow$ (high-Tc SC)

Correlations: *universal*
Functionality: *different*

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valence orbital spin lattice str.
```

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local Hilbert space communication rules
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The origin of strong correlations in layered cobaltates

A. Spin-state quasidegeneracy of Co ions
B. Edge-sharing octahedra, 90° d-p-d path

G. Khaliullin & J. Chaloupka

A. Spin-state quasidegeneracy in cobaltates

Co(2+): high-spin 3/2 \textit{(Hund coupling dominates)}

Co(4+): low-spin 1/2 \textit{(favored by 10Dq crystal field)}

⇒ Co(3+): S = 0, 1, 2 states are energetically close!

\[ \Delta E_S \sim 10Dq - 2J_H \text{ is small, fraction of eV only} \]

⇒ SPIN-STATE TRANSITIONS \textit{driven by temperature, doping (LaCoO}_3\ldots) \textit{...}
180° Co-O-Co bond (t\textsubscript{2g} and e\textsubscript{g} sectors separated)

B.

90° Co-O-Co bond \rightarrow strong mixing between t\textsubscript{2g} and e\textsubscript{g}

\textit{Spin-state fluctuations} \rightarrow \textit{spin-polaron physics}
Electron transfer matrix depends on Me–O–Me bond angle

<table>
<thead>
<tr>
<th>180-degree</th>
<th>90-degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_g$</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td>$t_{2g}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Units: $t_g^2 / \Delta_{pd}$

$t_{2g} - e_g$ overlap: *the largest element*
$e_{\gamma} = \tilde{\tau}$

$\mathcal{E} \sim \frac{t_o}{t_{\eta}} \sim 2$

$\mathcal{C}_0^{3+}$, $\mathcal{C}_0^{4+}$

- process generates $\mathcal{C}_0^{3+} (t_{2g}^e, S=0)$

$\tilde{\tau}$ - process generates $\mathcal{C}_0^{3+} (t_{2g}^5 e_\gamma, S=1)$

Relevant Hilbert space $\{\psi_1, \psi_2, \psi_3\}$:

- $S = \frac{1}{2}$
  - $\psi_1$  
  - $\psi_2$  
  - $\psi_3$  

- $S = 1$

$\mathcal{C}_0^{4+}$, $\mathcal{C}_0^{3+}$

$H \{\psi_1, \psi_2, \psi_3\}$
Model

\[ H = H_t + H_t' \]

- \( t_{2g} \rightarrow t_{2g} \)
- \( t_{2g} \rightarrow e_g \)

accompanied by \( S=1 \) exciton (present in \( \text{NaCoO}_2 \) but not in \( \text{LaCoO}_3 \))

\[
H_{t} = \frac{\tilde{t}}{\sqrt{3}} \sum_{ij} \left[ \mathcal{T}_{+1,\gamma}^{\dagger} (i) f_{j\downarrow}^{\dagger} f_{i\uparrow} - \mathcal{T}_{-1,\gamma}^{\dagger} (i) f_{j\uparrow}^{\dagger} f_{i\downarrow} \right]
+ \mathcal{T}_{0,\gamma}^{\dagger} (i) \frac{1}{\sqrt{2}} \left( f_{j\uparrow}^{\dagger} f_{i\uparrow} - f_{j\downarrow}^{\dagger} f_{i\downarrow} \right) + \text{h.c.}
\]

- \( S=1 \) exciton
- \( e_g \)-orbital label

Fermions dressed by spin-state fluctuations
1. Self-consistent Born approximation

2. Exact diagonalization (one s=1/2 hole on a hexagon)
$Im \ G(E,k)$ at $x = 0.7$ (fermionic density = 0.3)
With $t \sim 100$ meV, theory reproduces both qp- and hump dispersion consistent with LDA value
Brouet et al.  ARPES in misfits near the band insulator regime (x~0.7)

Quasiparticle damping

**experiment:** strong scattering at ~150 meV

**theory suggests:** S=1 virtual state energy
Scattering on spin-state fluctuations $\rightarrow$ qp destroyed below $E_T \sim 150$ meV
Interaction between $t_{2g}$ holes mediated by $S=1$ excitations
Spin-correlated hopping via the S=1 intermediate states

Step 1: S=1 exciton formed
Step 2: Exciton relaxed

Process sensitive to the spin orientation of holes

Effective interaction between fermions
Exchange by S=1 exciton \[\rightarrow\] fermionic pair-hopping
Interaction between $t_{2g}$-fermions in terms of:

- **singlet $S_{ij}$ and triplet $T_{ij}$ dimer-hopping**  
  \[ (SC \text{ pairing}) \]
- **nonlocal charge and spin interactions**  
  \[ (spin/ch. \text{ order}) \]

\[
H_{\text{eff}} = \frac{1}{2} V \sum_{\langle ijk \rangle} \cos(\phi_{ij} - \phi_{jk}) \left[ \hat{S}_{ij}^{\dagger} \hat{S}_{kj} + \frac{1}{3} \hat{T}_{ij}^{\dagger} \hat{T}_{kj} \right]
\]

\[
= V \sum_{\langle ijk \rangle} \cos(\phi_{ij} - \phi_{jk}) \left[ n_j n_{ik} - \frac{1}{3} s_j s_{ik} \right]
\]

(i) 1/3 factor: *Singlets move faster and gain more kinetic energy*

(ii) cos-factor: *Frustration*
$t_{2g} - e_g$ hopping is orbital selective.

(a) $t$, $t_\pi^-, t_\pi^+, \frac{1}{2} t_\sigma^-, \frac{1}{2} t_\sigma^+$

(b) $t$, $t_\pi^-, t_\pi^+, +\frac{\sqrt{3}}{2} t_\sigma^-, -\frac{\sqrt{3}}{2} t_\sigma^+$

(c) a-bond: $\tilde{t}$ ($yz \leftrightarrow 3x^2-r^2$)
   b-bond: $\tilde{t}$ ($zx \leftrightarrow 3y^2-r^2$)
   c-bond: $\tilde{t}$ ($xy \leftrightarrow 3z^2-r^2$)
\[ \langle 3z^2 - r^2 | 3z^2 - r^2 \rangle = 1 \]

Origin of \( \tilde{t}^2 \cos (\phi_{12} - \phi_{23}) \) factor due to \( e_g \) orbital overlap
Spin susceptibility

\[ H_{\text{spin}} = -\frac{1}{3} \frac{\tilde{t}^2}{E_T} \sum_{R, \delta \neq \delta'} \cos(\phi_\delta - \phi_{\delta'}) \hat{S}_R \cdot \hat{S}_{R+\delta, R+\delta'} \]

\[ = -\lambda \sum_q \hat{S}_{-q} \cdot \hat{D}_q = \quad \lambda = \frac{\tilde{t}^2}{3E_T} \]

\( \chi_{ss} = \quad + \quad + \quad \)

\( \chi_{ds} = \quad + \quad + \quad + \quad \)

RPA:

\[ S_q: \text{ on-site spin} \]

\[ D_q: \text{ bond-spin} \]

2\(k_F\)-fluctuations enhanced

Exp: Bragg peak at \( M \)

\( x=0.5 \)
Interaction between t\textsubscript{2g}-fermions in terms of pair hopping

\[
H_\text{eff} = \frac{1}{2} V \sum_{ij} \cos(\phi_{ij} - \phi_{jk}) \left[ \hat{S}_{ij} \hat{S}_{kj} + \frac{1}{3} \hat{T}_{ij} \hat{T}_{kj} \right]
\]

(i) 1/3 factor: Singlets move faster and gain more kinetic energy

(ii) cos-factor: Frustration

V = \bar{t}^2 / E_T
Coulomb repulsion $V_C$ between $t_{2g}$ holes suppresses $T_c$

$V_C/t = 0; 3; 20$

spin polarons, charge and magnetic order
• Spin-state quasidegeneracy of $\text{Co}^{3+}$:
  $\rightarrow$ proximity to the Mott physics

• 90° d-p-d bonding in $\text{NaCoO}_2$:
  $\rightarrow$ $S=1$ states accessible by $t_{2g}$-$e_g$ hopping, spin-polarons, incoherent ARPES, …

• Superconductivity:
  $\rightarrow$ pairing mediated by spin-state fluctuations
Coulomb repulsion between holes:

- reduces the pair-hopping process: \( V = p(n_d)V \)
- spatially separated spin-polarons (trapped by a random Na-potential)
- supports magnetic and charge order, suppresses SC

\[
p(n_d) = \frac{P(\circ_i \bullet_j \bullet_k) | V_C \neq 0}{P(\circ_i \bullet_j \bullet_k) | V_C = 0}
\]

...enjoying pair-hopping process
How good are the conditions for pair-hopping interaction?

$1/\beta \sim$ kinetic energy
LDA suggests:  band-flattening when water is present

Model predicts:  singlet s-wave $T_c$ enhanced
$T_c$ equation (both the pair-hopping $V$ and dispersion are renormalized by the Gutzwiller factor):

\[
1 = \sum_{|\tilde{\xi}_k| \leq E_T} \frac{\bar{V}_\alpha |\gamma_\alpha (k)|^2}{2\xi_k} \tanh \frac{\bar{\xi}_k}{2T_c}
\]
Pair-hopping term in cuprates is small

\[ \frac{t^2}{u} \cdot s_{ij} s_{jk} \]

order of \( J \), minor effect

- \( Na_xCoO_2 \): \( \frac{\tilde{\varepsilon}^2}{E_t} \) is large

\[ \tilde{\varepsilon} \approx 2t \]

\[ E_t \ll U \]

Pairing field \( \propto \frac{\tilde{\varepsilon}^2}{E_t} \gg J \)
$t_{2g}$ systems

NOT simple band insulators!!

$LaCoO_3$
$NaCoO_2$
$SrRh_2O_4$

SPINLESS MOTT INSULATORS

spin gap $\ll$ charge gap

$\ll 10-100$ meV
$
\sim 1-2$ eV

\[ \langle \vec{s}_i^2 \rangle \neq 0 \]

$\Delta_{\text{spin}}$

\[ \langle \vec{s}_i^2 \rangle \equiv 0 \]
fermions

$t-J$ model

magnetism

Mott ins.

$\Delta_{ch}$

$\Delta_{sf}$

Band ins.

$\LaCoO_2$ spinless Mott insulator

$3\uparrow, d^6$

$\tilde{S} = 1$

$g = 3.4$

$\Delta \approx 20 \text{ meV}$

$S, L = 0$

ESR, INS on $\tilde{S}$-triplet
Cobaltates

• Undoped

LaCoO$_3$, 3D cubic : nonmagnetic insulator

NaCoO$_2$, 2D triangular : nonmagnetic insulator

• Doped by holes

$La_{1-x}Sr_xCoO_3$ : spin-glass $\rightarrow$ ferromagnetic metal

$Na_{1-x}CoO_2$ : spin-glass $\rightarrow$ ferro-planes metal ($x < 0.25$)

$\rightarrow$ nonmagn. metal, supercond. ($x > 0.25$)

Similar ionic structure but different hopping geometry
1. **Spin-waves:** $J_c \sim -J_{ab}$

   (Keimer et al., Boothroyd et al.)

2. $\sum J(\mathbf{r}) > 0 \Rightarrow \Theta > 0$ positive (SW-data)

   however, $\Theta_{exp} \sim -200\,\text{K}$, negative

   Different from $\text{Na}_{1-x}\text{NiO}_2$: $\left| \frac{J_{ab}}{J_c} \right|\sim 15$, $\sim 2\,\text{D}$

$A \leftrightarrow \text{AF}$
Spin waves in $Na_{0.3}CoO_2$ (Keimer et al. /cond-mat)

$J_{ab} = -4.5 \text{ meV}$ (Ferro) $\int A$-type AF

$J_c = 3.3 \text{ meV}$ (AF)

3D-magnetism / 2D-transport

$\rightarrow$ not simple SDW
ORBITAL POLARON

Kilian & G. Kh.

PRB (1999)

doped hole

Oxygen

orbital stabilized

\[ \Delta_{\text{orb-char}} \]

\[ E_{\text{binding}} \sim z \cdot \Delta_{\text{orb-ch.}} \]

\[ E_b \geq W \]

polaron self-trapped
Doping of spinless Mott insulator NaCoO$_2$

Spin/orbital structure:
- Different from that in LaCoO$_2$

90° Co–O–Co bonds

- Co$^{3+}$–Co$^{3+}$ bonds are strongly AF!

Co$^{4+}$–Co$^{3+}$ bonds: Competing F & AF

Ground state: NET spin $\frac{1}{2}$

Resonance between two configurations
Exact diagonalization:

M.Daghofer, P.Horsch, and G.Kh. (PRL 2006)

Two contributions:
central-spin $\frac{1}{2}$ and ring-spins 1

Experimental data: $Na_{0.82}CoO_2$
Key control factors in oxides

A. „Internal“ structure of TM ions (Ti,…Co,…Cu)
   -- valence state, spin & orbital degeneracy
   -- local Hilbert space \{\psi_1, \psi_2, \psi_3,\ldots\}

B. Lattice symmetry
   -- dictates hopping geometry
   -- communication rules / structure of Bloch states