Sodium Cobaltates: Correlated Matter with extreme frustration

The newly found sodium cobaltates provide a new and exciting challenge in the study of correlated matter in condensed matter physics. There appears to be a greater hope of ultimate resolution than in the case of high Temperature superconductors due to a drastically smaller Fermi temperature scale here. Electronic frustration (i.e. a dependence on the sign of electron tunneling amplitude) occurs along with spin frustration on the triangular lattice that underlies these compounds. I review some key experiments, and discuss the ongoing and evolving modeling of these systems. I discuss some theoretical results for the transport properties, particularly the Hall constant.

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Key Experiments: 1999-2005
(with apologies for omissions)

- Phase diagram
- Thermopower (Terasaki et al)
- Superconductivity (Takada et al)
- Magnetic Field dependence of Thermopower (Cava, Ong et al) Curie-Weiss metallic phase
- Fermi Surface mapping ARPES
- Frustrated Magnetism

Thanks to Phuan Ong, Bob Cava, Yayu Wang, Zahid Hassan for sharing data and wisdom.
Large thermoelectric power in NaCo$_2$O$_4$ single crystals

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(Received 18 July 1997)

We measured and analyzed the transport properties of single-crystal NaCo$_2$O$_4$, which is a metallic transition-metal oxide consisting of a two-dimensional triangle lattice of Co. Reflecting the crystal structure, the resistivity is highly anisotropic between in- and out-of-plane directions, and the in-plane resistivity is as low as 200 $\mu\Omega$ cm at 300 K. Most strikingly, the in-plane thermoelectric power of NaCo$_2$O$_4$ is about 100 $\mu$V K$^{-1}$ at 300 K, which is nearly ten times larger than that of typical metals. The large thermoelectric power and the low resistivity suggest that NaCo$_2$O$_4$ is a potential thermoelectric material. [S0163-1829(97)02144-8]

![Diagram of NaCo$_2$O$_4$ crystal structure]

**FIG. 1.** A schematic picture of the crystal structure of NaCo$_2$O$_4$. (a) The layered structure; (b) the CoO$_2$ layer.

**TABLE I.** Various physical parameters for NaCo$_2$O$_4$ and Bi$_2$Te$_3$ (Ref. 6) at 300 K. $\rho$, $S$, and $\mu$ are resistivity, thermoelectric power, and mobility, respectively. Note that $\rho$ and $S$ of NaCo$_2$O$_4$ are the in-plane data.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>NaCo$_2$O$_4$</th>
<th>Bi$_2$Te$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>$\mu\Omega$ cm</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>$S$</td>
<td>$\mu$V K</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>$S^2/\rho$</td>
<td>$\mu$W K$^{-2}$ cm</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>$\mu$</td>
<td>cm$^2$/V s</td>
<td>13</td>
<td>150</td>
</tr>
</tbody>
</table>
\( S = \text{Seebeck Coefficient} \) (also called \( Q \)),

\[ Z = \frac{S^2}{(\kappa \rho)} \] : Desirable for large \( Z \) is \textbf{low} electrical resistivity and \textbf{high} thermal resistivity and \textbf{high} \( S \).

Fuita, Mochida, Nakamura (2001): More recent studies:

The dimensionless variable \( Z \) exceeds unity at 800K!

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<table>
<thead>
<tr>
<th></th>
<th>( Na_x CoO_2-\delta ) single crystal</th>
<th>( Na_x CoO_2-\delta ) polycrystal</th>
<th>( Si_{0.95}Ge_{0.05} ) typical p-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (mΩ·cm)</td>
<td>0.29, 0.52</td>
<td>2, 3.6</td>
<td>0.77, 1.7</td>
</tr>
<tr>
<td>( S ) (μV K(^{-1}))</td>
<td>83, 200</td>
<td>100, 170</td>
<td>200, 338</td>
</tr>
<tr>
<td>( S^2 \cdot \rho^{-1} ) (mW m(^{-1}) K(^{-2}))</td>
<td>2.38, 7.69</td>
<td>0.50, 0.81</td>
<td>5.2, 6.7</td>
</tr>
<tr>
<td>( \kappa ) (W m(^{-1}) K(^{-1}))</td>
<td>19.0, 5.1</td>
<td>2.0, 2.1</td>
<td>10.0, 9.5</td>
</tr>
<tr>
<td>( Z ) (mK(^{-1}))</td>
<td>0.12, 1.5</td>
<td>0.25, 0.39</td>
<td>0.52, 0.71</td>
</tr>
<tr>
<td>( ZT )</td>
<td>—</td>
<td>0.03, 1.2</td>
<td>0.08, 0.31</td>
</tr>
</tbody>
</table>

NCO compares well with best semiconductors like \( Si_{0.95}Ge_{0.05} \)

Although \( \kappa \) is a bit high
Superconductivity in two-dimensional CoO$_2$ layers

Kazunori Takada$^{\ast,\dag}$, Hiroya Sakurai$^\dag$, Eiji Takayama-Muromachi$^\dag$, Fujio Izumi$^\dag$, Ruben A. Dilanian$^\ast$ & Takayoshi Sasaki$^{\ast,\dag}$

letters to nature

Figure 1: Structural views of Na$_{x}$CoO$_2$ (left) and Na$_{x}$CoO$_2$.yH$_2$O (right), where Na and

Figure 4: Resistivity ($\rho$) of Na$_{x}$CoO$_2$.yH$_2$O under zero magnetic field. The inset figure

$H = 20$ Oe

$H = 20$ Oe, $H = 100$ Oe

$H = 30$ kOe, $H = 1$ kOe

$H = 50$ Oe, $H = 10$ kOe

$H = 70$ kOe
Since 2003, widely reproduced

- Type II superconductivity short coherence length $\xi = 75 \text{ A}^0$.
- $T_C \sim 4.5 \text{ K}$

Uemura, using $\mu$SR at $x = 0.33$ they find no evidence of broken time reversal invariance of a particular type. Not clear that this excludes all time reversal violating states. OP symmetry is a big issue - more later.

Role of H$_2$O somewhat confusing:

- Screening of one electron potential between Na dopants and electrons
- Oxonium ion (H$_3$O$^+$) is formed so electron count is tricky. Takada et al.04
- This ion sits in same sites and donates an electron just like Na. Detected by Raman signature of oxonium

Chemical composition and crystal structure of superconducting sodium cobalt oxide bilayer-hydrate

Kazunori Takada, $^{*a,e}$

This implies that the sc sample has a very different electron count than originally guessed. Phase diagrams of hydrated systems need to be treated with extreme caution. $x = 0.571$ rather than $0.337$ in this case
Phase diagram.

Electron count here needs to be treated with caution, it may well be closer to 0.5 than it appears.

Ong Cava, Nature 04
The most strongly developed superlattice is found for the composition $\text{Na}_{0.5}\text{CoO}_2$, which displays $\text{Co}^{3+}/\text{Co}^{4+}$ charge ordering at low temperatures. The structural principle for some of the observed ordering schemes, particularly near $x=0.5$, is, surprisingly, the presence of lines of Na ions and vacancies rather than simply maximized Na-Na separations.

At $x=.5$ the charge ordered state is an insulator, and is is not very well understood theoretically ($x=.5$ is not a commensurate filling for triangular lattice for which $x\sim 1/3$ or $2/3$ are commensurate!).

- Surprisingly linear chains of Na seem to form.
- $\mu$SR Reports of magnetism for $T$ below $53^0$ (AFM LRO?).
- Perhaps understanding this insulating state will be a key issue in the physics of NCO. Its competitor is the $x=0$ state, argued later to be a Mott Hubbard insulating state. Which one is more important? Possibly both?
Static χ inverse looks linear already at 500, this is remarkable for a good metal (ρ ~ 1 mΩ cm)!!

Strongly magnetic field dependent thermopower, already anomalous due to large magnitude

Spin entropy as the likely source of enhanced thermopower in NaCoO$_2$. Yapu Wang, Nivissa S. Rogado, R. J. Cava, N. P. Ong.
All data for different $T$ collapses to single curve

Entropy of free spin $\frac{1}{2}$ particles!!

$$\sigma(H, T)/\sigma(0, T) = \{\ln[2 \cosh(u)] - u \tanh(u)\}/\ln(2)$$

$$u = g\mu_B H/2 k_B T.$$  

Remarkably successful fit possible to Heikes Zener Mott formula for thermopower, interpreted as spin contribution of entropy per particle (i.e. neglecting transport issues, a great simplification of Kubo’s exact formula)

G Beni (1974), P Chaikin and Beni for Hubbard model in limit of $t \rightarrow 0$:

Success is quite surprising, and hints at localized character of electron spins despite being a good conductor.
Fermi surface and quasiparticle dynamics of Na$_{0.7}$CoO$_2$ investigated by Angle-Resolved Photoemission Spectroscopy

M.Z. Hasan,1,2,3 V.-D. Chau,1,3 A.P. Kuprin,1,3 Y. Kong,1 D. Qian,1 Y.W. Li,1 B.L. Mesler,2 Z. Hussain,3 A.V. Fedorov,3 R. Kimerling,3 E. Rotenberg,3 K. Rossmeisel,3 H. Koh,3 M. Rogado,2,4 M.L. Foo,2,4 and R.J. Cava2,4

FIG. 2: Fermi Surface : (a) $\Gamma \rightarrow$ M Fermi crossing. Color red reflects the highest intensity - yellow to green to blue is in the order of decreasing intensity. (b) EDCs corresponding to the image plot in (a). (c) n(k) plot generated by integrating within 75 meV of Fermi level. A large hole-pocket is centered around the $\Gamma$-point. The Fermi surface, exhibiting some hexagonal anisotropy, is the inner edge of pocket as shown over the complete Brillouin zone.

FIG. 4: (a) Measured FS crossings (symbols) comparing to the calculated FS in $k_z = 0$ (black solid lines) and $k_z = 0.5$ (red dashed lines) planes. The blue hexagon is the 2D Brillouin zone. (b) Extracted band positions along $\Gamma$-$M$ (red dots) and a tight binding fit with $t = -44$ meV (solid line) (c) Extracted band positions along $\Gamma$-$K$ (red dots) and two tight binding fits with $t = -12$ meV (solid line) and $t = -26$ meV (dashed line).
x=0.3 FS on left, and with x=0.7 on right. Γ point is unoccupied, so this is a hole FS with hexagonal anisotropy a la triangular lattice.

Evidence of strong correlations:

<table>
<thead>
<tr>
<th>Class</th>
<th>$T_c$(K)</th>
<th>Bandwidth</th>
<th>Fermi velocity $v_f$(eV Å)</th>
<th>Mass $m/m_e$</th>
<th>Hubbard U(eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobaltates(NaCoO)</td>
<td>5</td>
<td>0.18±0.04</td>
<td>0.15±0.10</td>
<td>60±20</td>
<td>&gt;4.0</td>
<td>Present work</td>
</tr>
<tr>
<td>p-Cuprates(LSCO)</td>
<td>38</td>
<td>~0.4</td>
<td>1.8</td>
<td>2 (nodal)</td>
<td>3 - 5</td>
<td>[16]</td>
</tr>
<tr>
<td>n-Cuprates(NCCO)</td>
<td>22</td>
<td>~0.5</td>
<td>2.0</td>
<td>2.4 (nodal)</td>
<td>~3</td>
<td>[17]</td>
</tr>
<tr>
<td>Ruthenates(SrRuO)</td>
<td>1</td>
<td>0.5</td>
<td>0.4 (avg)</td>
<td>~9 (avg)</td>
<td>1</td>
<td>[16]</td>
</tr>
<tr>
<td>BCS-type SCs(Pb)</td>
<td>7.2</td>
<td>9.5</td>
<td>12</td>
<td>2</td>
<td></td>
<td>[21]</td>
</tr>
</tbody>
</table>
Anomalous high-temperature Hall effect on the triangular lattice in Na$_x$CoO$_2$

Yayu Wang$^1$, Nyrissa S. Rogado$^2$, R. J. Cava$^{2,3}$, and N. P. Ong$^{1,3}$

The Hall coefficient $R_H$ of Na$_x$CoO$_2$ ($x = 0.68$) behaves anomalously at high temperatures ($T$). From 200 to 500 K, $R_H$ increases linearly with $T$ to 8 times the expected Drude value, with no sign of saturation. Together with the thermopower $Q$, the behavior of $R_H$ provides firm evidence for strong correlation. We discuss the effect of hopping on a triangular lattice and compare $R_H$ with a recent prediction by Kumar and Shastry.

Hall constant as a function of $T$ for $x=.68$ (CW metal). $T$ linear over large range 200$^0$ to 436$^0$ (predicted by theory of triangular lattice transport KS)

STRONG CORRELATIONS & Narrow Bands

T Linear resistivity
How to model NCO- Start with band structure

Several LDA computations since this first one-

Electronic structure of NaCo$_2$O$_4$

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(Received 10 January 2000)

Fermi level for $x = .5$ in a hole like band tangents an electron like band which might get emptied for $x < .3$

DOS for relevant band showing large slope of $N(\varepsilon)$ (hence large $S$)

Note largish bandwidth $\sim 1.8$ ev !!
• Notable features from Singh’s calculation:
  (assuming rigid bands with varying x)

• At $x \sim 0.5$ there is evidence of another band becoming relevant, lower band (electron like) tangents the fermi level hence large DOS. Suggests that at $x = 0.5$ there is a “chemical transition”, possibly linked to Charge order!

• At $x \sim 0.7$ there is only one hole like band that contains the fermi level: band maximum at $\Gamma$ point hence hole like FS

• Below $x = 0.5$, Fermi surface is many sheeted, additional electron like band is operative.

• Indeed second sheet is visible in recent electronic structure calculations, e.g. W Pickett et al. (2004).

• Hence 1 band models are probably in trouble for $x < 0.5$!!!
Interpret $x$ as number of electrons in a Gutzwiller projected model. NMR is consistent with this, experiments show $x$ as the relative fraction of 3+ and 4+ states of Cobalt. This is called a low spin CF splitting and familiar in Co chemistry.

$X= 0$ gives 1 electron per “site” and should be a Mott Insulator. Prediction of this view point, material exists but not yet probed!
Baskaran, 2003, Kumar and Shastry 2003
Q H Wang, Dung Hai Lee, Patrick Lee 2003
Anderson’s RVB ideas ideally testable in this context!

• **t-J Model**

\[
H = -t \sum_{<i,j>,\sigma} \mathcal{P} c_{i\sigma}^\dagger c_{j\sigma} \mathcal{P} + J \sum_{<i,j>} (\vec{S}_i \cdot \vec{S}_j - \frac{n_i n_j}{4})
\]

Idea is to see if the RVB ideas give superconductivity in triangular lattice. Existence of J inferred from magnetic susceptibility results of Ong/Cava, J ~60^0 K (antiferromagnetic). Scale of “t” unknown, but electronic structure suggests large scale (say .1 ev)- we will argue strongly against that scale and favor a much LOWER energy scale, t~100^0K.

• **Non s-wave pairing** guaranteed by “bond attraction” type theories e.g. RVB, in contrast to “site attraction” type theories, e.g. phononic.
Simple minded Mean Field Theories can be done using the basic idea of RVB namely

“Exchange is Attraction”

\[ J \text{S.S} = -J (c^* c^* -c^* c^*) (c \ c - c \ c) \]

(symbolically, where \(c^* c^* -c^* c^*\) is a Cooper pair operator)

• Forced to choose \(t \sim 2\) or \(3\) J, otherwise do not get superconductivity in large part of phase diagram.

• Must keep in mind that single band t-J model may be incapable of describing cases where multi-sheeted FS’s become operative! (Pinch of salt needed in “phase diagrams”)
Here $t<0$

“Counter Nagaoka-Thouless” regime. Not good for FM correlations.
Both signs of $t$ support superconductivity max $T_c \approx 10^0K$.

$T$ reversal violating SC state, ratios $D(0) : D(60) : D(120)$ are cube roots of unity, necessarily complex order parameter, perhaps measurable prediction though hard.

Other calculations predict real order parameters, f wave or d-wave (Dagotto early work), a good problem to test theories.

**MAGNETISM**

Ferromagnetism for $t>0$ but for $t<0$ Nagaoka-Thouless theorem does not tell us nature of GS for $J=0$. Recent work (Jan Haerter and SS) find singlet gs for this case, most probably three sublattice LRO but soft order driven by purely kinetic terms. An example of KINETIC antiferromagnetism!!

Weak SDW state seen in muon experiments $T_c \approx 22^0K$ (1-2 mev). Also neutrons see FM order in planes but AFM along c axis (type A order)
Standard expression says that Hall constant is a measure of carrier concentration:

\[ R_H = \frac{1}{neC} \]

Question: What is “n” for a Mott Hubbard system? Electron number of hole number (measured from half filling)?

Real space versus \( k \) space!!
First serious effort to understand Hall constant in correlated matter:

Introduced object

\[ R_{H}^{*} = \lim_{B \to 0} \lim_{\omega \to \infty} \rho_{xy}(\omega)/B \]

\[ \omega \to \infty \]

\[ \omega \to \infty \]

\[ \Rightarrow \]

\[ \rho_{xy}(\omega) = \frac{\sigma_{xy}(0)}{(1 + i\omega\tau)^2} \]

\[ \sigma_{xx}(\omega) = \frac{\sigma_{xx}(0)}{(1 + i\omega\tau)} \]

Motivation: Drude theory has

Easier to calculate than transport Hall constant

Captures Mott Hubbard physics to large extent

Hence relaxation time cancels out in the Hall resistivity

\[ \rho_{xy}(\omega) = \frac{\sigma_{xy}}{(\sigma_{xx})^2} \]
Why not compute at high frequencies from Kubo’s formulas directly:

\[
\sigma_{xx}(\omega) = \frac{i}{Nv\omega} \left[ \langle \tau_{xx} \rangle - \frac{1}{Z} \sum \frac{e^{-\beta \varepsilon_n} - e^{-\beta \varepsilon_m}}{\varepsilon_m - \varepsilon_n - \omega} \langle n | J^x | m \rangle \langle m | J^x | n \rangle \right]^2
\]

\[
\sim \frac{i \langle \tau_{xx} \rangle}{Nv\omega} + o\left(1/\omega^3\right)
\]

Here \( \tau \) is the stress tensor (k.e.) and \( v \) the cell volume

\[
\sigma_{xy}(\omega) = \frac{-i}{Nv\omega Z} \sum \frac{e^{-\beta \varepsilon_n} - e^{-\beta \varepsilon_m}}{\varepsilon_m - \varepsilon_n - \omega} \langle n | J^x | m \rangle \langle m | J^y | n \rangle
\]

\[
\sim \frac{i}{Nv\omega^2} \langle [J^x, J^y] \rangle + o\left(1/\omega^3\right)
\]
\[ R_H^* = \frac{-i2\pi}{\hbar B} NV < [J^x, J^y] > / < \tau_{xx} >^2 \]

• Very useful formula since

  • Captures Lower Hubbard Band physics. This is achieved by using the Gutzwiller projected fermi operators in defining J’s

  • Exact in the limit of simple dynamics ( e.g. few frequencies involved), as in the Boltzmann eqn approach.

  • Can compute in various ways for all temperatures ( exact diagonalization, high T expansion etc.....)

  • We have successfully removed the dissipational aspect of Hall constant from this object, and retained the correlations aspect.

  • Very good description of t-J model, not too useful for Hubbard model.

  • This asymptotic formula usually requires \( \omega \) to be larger than J
Naïve expectation from Band theory for Hall constant with one zero crossing (at half filling).

INSTEAD the strong correlation theory gives surprising and yet understandable results

Behaviour for square lattice Mott Hubbard system. Notice there are THREE zero crossings

To leading order in T/J we find
0 < n < 1

\[ R = -\frac{v}{|e|c} \left[ \frac{kT}{4t} \frac{(2-n)}{n(1-n)} + \frac{(1-n/2)(1-3n/2)}{n(1-n)} \right] \]

1 < n < 2

\[ R = -\frac{v}{|e|c} \left[ \frac{kT}{4t} \frac{(n)}{(2-n)(n-1)} + \frac{n(4-3n)}{4(2-n)(n-1)} \right] \]

\[ t > 0 \text{ Triangular lattice at } T > |t| \text{ is always electron like} \]

\[ t < 0 \text{ Triangular lattice at } T > |t| \text{ is always hole like. No zero crossings in either case.} \]
As a function of $T$, Hall constant is LINEAR for triangular lattice!!

We suggest that transport Hall = high frequency Hall constant!!

- Origin of $T$ linear behaviour in triangular lattice has to do with frustration. Loop representation of Hall constant gives a unique contribution for triangular lattice with sign of hopping playing a non trivial role.

![Diagram of triangular lattice with $O(\beta t^3)$ and square lattice with $O(\beta t^4)$]
Here $\delta = \rho^{-1}$.

Since Fermi temperature seems low, the large $T$ limit may work, so we predict: $R_H$ will not saturate with $T$.

Predict    linear $T$ dependence and known slope.
Prediction for $\omega >> \{J, t\}_{\text{min}}$ is (with $v = \text{volume of unit cell}$ and $x = \delta$)

$$R_H^* = -\frac{v}{4|e|} \frac{k_B T}{t} \frac{1 + \delta}{\delta(1 - \delta)}$$

From Cava Ong (transport) Hall measurement we find on comparing with our prediction (for large frequencies):

- **Conjecture:** Transport Hall $\sim$ High frequency Hall
- Indeed Hall constant is linear in $T$ over large range (200 to 400 K)
- Slope can be used to deduce hopping: $t < 0$ for $x \sim 0.7$ and $|t| \sim 30^0K$ hence bandwidth $\sim 300^0K$. VERY low but similar to ARPES results.
- Suggest that Hall measurements give bandwidth and also carrier concentration through such formulas. Similar story with Infrared conductivity sum rules.
Suggested experiment for checking Heikes Zener Mott formulas for validity. (with Onuttom Narayan in preparation)

We can check experimentally through a SET setup, the magnetic field dependence of the electrochemical potential from conductance peaks as one changes magnetic field and the gate voltage $V_g$. This (Magneto coulomb oscillations) experiment has been already done for some ferromagnetic nano systems (Ni/Co/Ni SET). It is said to be hard for oxides - but not impossible. Very worthwhile since we can check the Kubo versus Heikes formulas here.

$C_\Sigma = 2C + C_g$

$\mu_A(H, V_g) - \mu_B = \mu_A(0, 0) + \frac{C_g}{C_\Sigma} eV_g + [\mu_A(H, 0) - \mu_A(0, 0)]$

In the CW phase, we expect to see huge field effects, if the transport contribution is indeed small.
Open Questions:  Several directions:

Prediction of time reversal violating superconducting state-observation? ( despite $\mu$SR negative result )

Possibly a fermi surface switching transition as a function of $x$? $t<0$ to $t>0$ due to competing bands, a chemical transition. Carrier concentration of superconductors is pretty uncertain due to oxonium issue.

Multi band description for $x<.5$ ?

Battery connections? $\text{Li}_x \text{CoO}_2$

Why is there a low energy scale in this problem? $T_f$ should be 3-4,000 degrees but seems to be in 100’s. We don’t quite understand this at the moment: **BUT we can exploit this feature.** This is a system where non degenerate interacting regions ( the easy cases) are close to the degenerate regions, so we should be able to interpolate.