

Sodium Cobaltates: Superconductivity in the Triangular lattice t-J Model

Sriram Shastry

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.

APS March Meeting 24 March 2005 FRUSTRATED QUANTUM MAGNETISM



Work supported by **DMR 0408247**

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 NaCo₂O₄ single crystals

I. Terasaki* Superconductivity Research Laboratory, International Superconductivity Technology Center, 1-10-13 Shinonome, Koto-ku, Tokyo 135, Japan

Y. Sasago and K. Uchinokura

Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan (Received 18 July 1997)

We measured and analyzed the transport properties of single-crystal NaCo₂O₄, 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 NaCo₂O₄ is about 100 μ V/K at 300 K, which is nearly ten times larger than that of typical metals. The large thermoelectric power and the low resistivity suggest that NaCo₂O₄ is a potential thermoelectric material. [S0163-1829(97)52144-8]





FIG. 1. A schematic picture of the crystal structure of NaCo₂O₄.
(a) The layered structure; (b) the CoO₂ layer.

TABLE I. Various physical parameters for NaCo₂O₄ and Bi₂Te₃ (Ref. 6) at 300 K. ρ , S, and μ are resistivity, thermoelectric power, and mobility, respectively. Note that ρ and S of NaCo₂O₄ are the in-plane data.

Parameters	Unit	$NaCo_2O_4$	Bi ₂ Te ₃	
ρ	$m\Omega \ cm$	0.2	1	
S	$\mu V/K$	100	200	
S^2/ρ	$\mu W/K^2$ cm	50	40	
μ	cm ² /V s	13	150	

S=Seebeck Coefficient (also called Q),

 $Z = S^2/(\kappa \rho)$: Desirable for large Z is *low* electrical resistivity and *high* thermal resistivity and *high* S.

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

The dimensionless variable Z T exceeds unity at 800K !

Table I. Various parameters for Na_xCoO_{2- δ} single crystal, Na_xCoO_{2- δ} polycrystal and Si_{0.95}Ge_{0.05}²²⁾ are compared at 300 K and 800 K, ρ , S, $S^2 \cdot \rho^{-1}$, κ and Z are the resistivity, thermoelectric power, power factor, thermal conductivity and figure-of-merit, respectively.

		$Na_x CoO_{2-\delta}$ single crystal		Na _x CoO _{2-δ} polycrystal		Si _{0.95} Ge _{0.05} typical p-type	
		300 K	800 K	300 K	800 K	300 K	800 K
ρ	mΩ·cm	0.29	0.52	2	3.6	0.77	1.7
S	$\mu V K^{-1}$	83	200	100	170	200	338
$S^2 \cdot \rho^{-1}$	$mW m^{-1} K^2$	2.38	7.69	0.50	0.81	5.2	6.7
κ	$W m^{-1} K^{-1}$	19.0	5.1	2.0	2.1	10.0	9.5
Ζ	mK^{-1}	0.12	1.5	0.25	0.39	0.52	0.71
ZT		0.03	1.2	0.08	0.31	0.16	0.57

NCO compares well with best semiconductors like $Si_{.95}$ Ge_{.05} Although κ is a bit high

Superconductivity in twodimensional CoO₂ layers

Kazunori Takada*‡, Hiroya Sakurai†, Eiji Takayama-Muromachi†, Fujio Izumi*, Ruben A. Dilanian* & Takayoshi Sasaki*‡



Nature 2003 NATURE || VOL 422 || 6 MARCH 2003 ||



igure 4 Resistivity () of Na _CoO_) H_2O under zero magnetic field. The inset figure



•Since 2003, widely reproduced

• Type II superconductivity short coherence length ξ = 75 A^{0,} •T_C \sim 4.5 ^0K

•Uemura, using μ SR @ x=.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 H₂0 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}

 $\begin{array}{r} Na_{0.337}(H_{3}O)_{0.070}CoO_{2} \cdot nH_{2}O + 0.246 \cdot H_{2}O \rightarrow \\ Na_{0.337}(H_{3}O)_{0.234}CoO_{2} \cdot nH_{2}O + 0.041 O_{2} \end{array}$

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=.571 rather than .337 in this case

Phase diagram.



Sodium Ion Ordering in Na_xCoO₂

Superlattices from e diffraction studies

H.W. Zandbergen^{1,2}, M.L. Foo¹, Q. Xu², V. Kumar² and R. J. Cava¹

The most strongly developed superlattice is found for the composition $Na_{0.5}CoO_2$, which displays Co3+/Co4+ 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~1/3 or 2/3 are commensurate!).
- Surprisingly linear chains of Na seem to form.
- μ SR Reports of magnetism for T below 53^o (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?

Spin entropy as the likely source of enhanced thermopower in Na_xCo₂O₄

Yayu Wang*, Nyrissa S. Rogado†, R. J. Cava†‡ & N. P. Ong*‡



magnitude

1.4

1.2

Figure 1 The temperature (7) dependence of magnetic and transport properties of ingle-crystal Na_xCo₂O₄ and electronic states in the Colons. The in-plane thermopower Q NATURE | VOL 423 | 22 MAY 2003 |

H || - 77



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->0:

Success is quite surprising, and hints at localized character of electron spins despite being a good conductor.

ARPES/FS two preprints at x~.6,.7

ARPES on Na_{0.6}CoO₂: Fermi surface, extended flat dispersion, and unusual band splitting

H.-B. Yang,¹ S.-C. Wang,¹ A.K.P. Sekharan,¹ H. Matsui,² S. Souma,² T. Sato,² T. Takahashi,² T. Takeuchi,³ J.C. Campuzano,⁴ R. Jin,⁵ B.C. Sales,⁵ D. Mandrus,⁵ Z. Wang,¹ H. Ding¹

Fermi surface and quasiparticle dynamics of $Na_{0.7}CoO_2$ investigated by Angle-Resolved Photoemission Spectroscopy

M.Z. Hasan,^{1,2,3} Y.-D. Chuang,^{1,3} A.P. Kuprin,^{1,3} Y. Kong,¹ D. Qian,¹ Y.W. Li,¹ B.L. Mesler,³ Z. Hussain,³ A.V. Fedorov,³ R. Kimmerling,³ E. Rotenberg,³ K. Rossnagel,³ H. Koh,³ M. Rogado,^{2,4} M.L. Foo,^{2,4} and R.J. Cava^{2,4}



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 Γ -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 Γ -M (red dots) and a tight binding fit with t = -44 meV (solid line) (c) Extracted band positions along Γ -K (red dots) and two tight binding fits with t = -12 meV (solid line) and t = -26meV (dashed line).

Nature of Correlated Motion of Electrons in the Parent Cobaltate Superconductors M.Z. Hasan,^{1,*} D. Qian,¹ Y. Li,¹ A.V. Fedorov,² Y.-D. Chuang,² A.P. Kuprin,² M.L. Foo,³ and R.J. Cava³



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:



Class	$T_c(K)$	Bandwidth	Fermi velocity	Mass	Hubbard	Ref.
		$W_{APRES}(eV)$	$v_{f[ARPES]}(eV \cdot Å)$	${ m m}/{ m m}_{e}$	U(eV)	
Cobaltates(NaCoO)	5	$0.18{\pm}0.04$	$0.15{\pm}0.10$	$60{\pm}20$	>4.0	Present work
p-Cuprates(LSCO)	38	~ 0.4	1.8	$2 \pmod{2}$	3 - 5	[16]
n-Cuprates(NCCO)	22	~ 0.5	2.0	$2.4 \pmod{100}$	~ 3	[17]
Ruthanates(SrRuO)	1	0.5	0.4 (avg)	$\sim 9 ~(\mathrm{avg})$	1	[16]
$\operatorname{BCS-type}\operatorname{SCs}(\operatorname{Pb})$	7.2	9.5	12	2		[21]

TABLE I: ARPES Quasiparticle parameters for major classes of superconductors

Anomalous high-temperature Hall effect on the triangular lattice in $Na_x CoO_2$

Yayu Wang¹, Nyrissa S. Rogado², R. J. Cava^{2,3}, and N. P. Ong^{1,3}

The Hall coefficient R_H of Na_xCoO₂ (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.



How to model NCO- Start with band structure

Several LDA computations since this first one-

Electronic structure of NaCo₂O₄

D. J. Singh

Code 6391, Naval Research Laboratory, Washington, DC 20375

(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(ε) (hence large S)







•Notable features from Singh's calculation:

(assuming rigid bands with varying x)

•At x~.5 there is evidence of another band becoming relevant, lower band (electron like) tangents the fermi level hence large DOS. Suggests that at x=.5 there is a "chemical transition", possibly linked to Charge order!

•At x=~.7 there is only one hole like band that contains the fermi level: band maximum at Γ point hence hole like FS

•Below x=.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<.5!!!

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

$$\mathbf{H} = -t \sum_{\langle i,j \rangle,\sigma} \mathcal{P}c_{i\sigma}^{\dagger}c_{j\sigma}\mathcal{P} + \mathbf{J} \sum_{\langle i,j \rangle} (\vec{S}_{i} \cdot \vec{S}_{j} - \frac{n_{i}n_{j}}{4})$$

- 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.



A simple view of carriers in doped Cobalt oxide

 $Na_X Co O_2$ gives x as fraction of Co $^{3+}$



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! Simple minded Mean Field Theories can be done using the basic idea of RVB namely

"Exchange is Attraction"

 $J S.S = - J (c^* c^* - c^* c^*) (c c - c c)$

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

•Forced to choose t ~ 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")



δ

Both signs of t support superconductivity max T_c appxly 10^oK.

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 in this conference (Jan Haerter and SS) find singlet gs for this case, most probably three sublattice LRO but very soft order (without magnon scale) driven by purely kinetic terms.

Weak SDW state seen in muon experiments Tc ~22^0K (1-2 mev). Also neutrons see FM order in planes but AFM along c axis (type A order)

Hall Effect in Strongly Correlated Matter

Standard expression says that Hall constant is a measure of carrier concentration:

 $R_H = 1 / nec$

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

Real space versus k space!!

-1/|e|n





First serious effort to understand Hall constant in correlated matter: S S, Boris Shraiman and Rajiv Singh, Phys Rev Letts (1993)

Introduced object

 $R_{H}^{*} = \lim_{B \to 0} \lim_{\omega \to \infty} \frac{\rho_{xy}(\omega)}{B}$

•Easier to calculate than transport Hall constant

•Captures Mott Hubbard physics to large extent

Motivation: Drude theory has

$$\sigma_{xy}(\omega) = \sigma_{xy}(0)/(1+i\omega\tau)^2$$

$$\sigma_{xx}(\omega) = \sigma_{xx}(0)/(1+i\omega\tau)$$

Hence relaxation time cancels out in the Hall $\rho_{xy}(\omega) = \frac{\sigma_{xy}}{(\sigma_{xx})^2}$ resistivity Why not compute at high frequencies from Kubo's formulas directly:

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

$$\sim \frac{i < \tau_{xx} >}{N v \omega} + o(1 / \omega^3)$$

٠

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

$$\sigma_{xy}(\omega) = \frac{-i}{N v \omega Z} \sum \frac{e^{-\beta \varepsilon_n} - e^{-\beta \varepsilon_m}}{\varepsilon_m - \varepsilon_n - \omega} < n \mid J^x \mid m > < m \mid J^y \mid n >$$

$$\sim \frac{i}{Nv\omega^2} < [J^x, J^y] > + o(1/\omega^3)$$

$$R_{H}^{*} = \frac{-i2\pi}{hB} Nv < [J^{x}, J^{y}] > / < \tau_{xx} >^{2}$$

•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 ω to be larger than J





Behaviour for square lattice Mott Hubbard system. Also expected for triangular lattice at low T (work in progress). Notice there are THREE zero crossings



t>0 Triangular lattice at T> |t| is always electron like

t<0 Triangular lattice at T> |t| is always hole like. No zero crossings in either case.



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.



square lattice

29 MARCH 1993

Faraday Rotation and the Hall Constant in Strongly Correlated Fermi Systems

B. Sriram Shastry and Boris I. Shraiman AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Rajiv R. P. Singh



Comparison with Hidei Takagi and Bertram Batlogg data for LSCO showing change of sign of Hall constant at delta=.33 for squar e lattice [10] The lattice structure and the statistics of the particles plays a crucial role in the behavior of R_H^* , and through it on $R_H(\omega)$. This is brought out in a calculation of the leading high-temperature behavior of R_H^* in the triangular lattice t-J model. We find $R_H^* \sim (\beta t)^{-1} \frac{1+\delta}{\delta(1-\delta)}$, which in contrast to the square lattice result, Eq. (11), does not change sign with δ , but rather with t. Furthermore $R_H^* \sim T$ so that, in a sense, the semiclassical limit 1/nedoes not exist at all. This highly nontrivial behavior is a consequence of a "fermionic frustration" on the triangular lattice, the same calculation for hard core bosons gives $R_H^* \sim -(\beta t)^{-1} \frac{1-3\delta}{\delta(1-\delta)}$, which indeed changes sign at $\delta = \frac{1}{3}$.

IFA (IAAA)

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

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 $\omega >> \{J,t\}_{min}$ is (with v = volume of unit cell and x = δ)

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

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

•Conjecture: Transport Hall~ 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~.7 and $|t| \sim 30^{0}$ K hence bandwidth ~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 S. (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 Vg. 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.

$$C_{\Sigma} = 2C + C_g$$

 μ_A and μ_B are the electrochemical pots of quantum dot and leads, and C's are capacitances.

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

In the CW phase, we expect to see huge field effects, if the transport contribution is indeed small.

Prediction of time reversal violating superconducting state- observation? (despite μ 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? Li<sub>x</sub> Co O<sub>2</sub>
```

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.