Sodium Cobaltates: Correlated Matter with extreme frustration

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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 drastically smaller a 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.

Significant Experiments:

1999-2003

- **Thermopower (Terasaki et al)**
- **Superconductivity (Takada et al)**
- **Magnetic Field dependence of Thermopower (Cava, Ong et al)**
- **Fermi Surface mapping ARPES**
- **Phase diagram (The “official version”)**

Large thermoelectric power in $NaCo_2O_4$ single crystals

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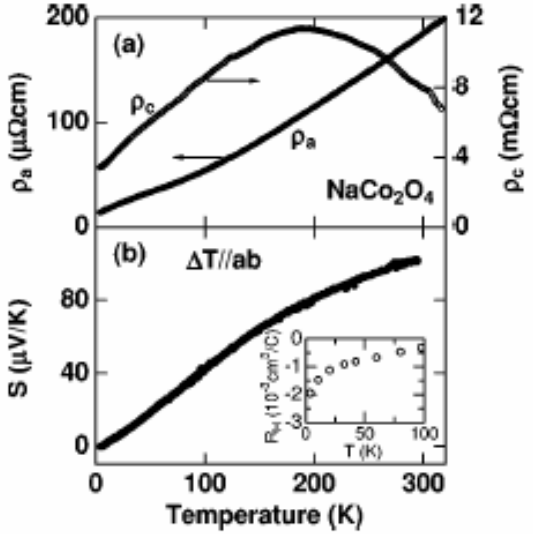
(Received 18 July 1997)

We measured and analyzed the transport properties of single-crystal $NaCo_2O_4$, 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 $NaCo_2O_4$ is about 100 μV/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 $NaCo_2O_4$ is a potential thermoelectric material. [S0163-1829(97)52144-8]



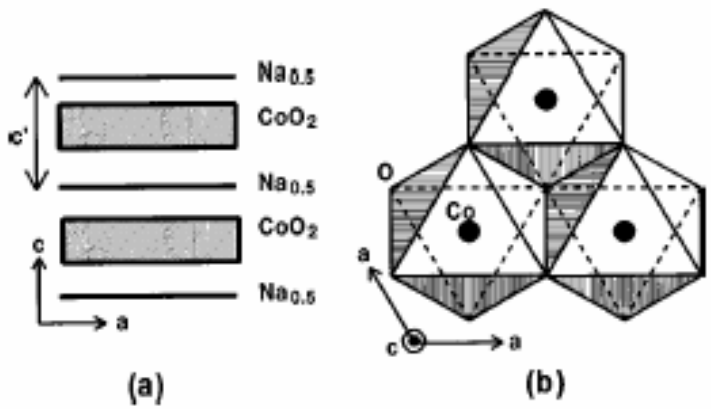


FIG. 1. A schematic picture of the crystal structure of $NaCo_2O_4$. (a) The layered structure; (b) the CoO_2 layer.

TABLE I. Various physical parameters for $NaCo_2O_4$ and Bi_2Te_3 (Ref. 6) at 300 K. ρ, S, and μ are resistivity, thermoelectric power, and mobility, respectively. Note that ρ and S of $NaCo_2O_4$ are the in-plane data.

Parameters	Unit	$NaCo_2O_4$	Bi_2Te_3
ρ	mΩ cm	0.2	1
$\lvert S\rvert$	μV/K	100	200
S^2/ρ	μW/K^2 cm	50	40
μ	cm^2/V s	13	150

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

The dimensionless variable Z T exceeds unity at 800K !

Table I. Various parameters for $Na_xCoO_{2-\delta}$ single crystal, $Na_xCoO_{2-\delta}$ 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.

		$Na_xCoO_{2-\delta}$ single crystal		$Na_xCoO_{2-\delta}$ polycrystal		$Si_{0.95}Ge_{0.05}$ typical p-type	
		300 K	800 K	300 K	800 K	300 K	800 K
ρ	$m\Omega\cdot cm$	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
Z	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

Superconductivity in two-dimensional CoO_2 layers

NATURE | VOL 422 | 6 MARCH 2003

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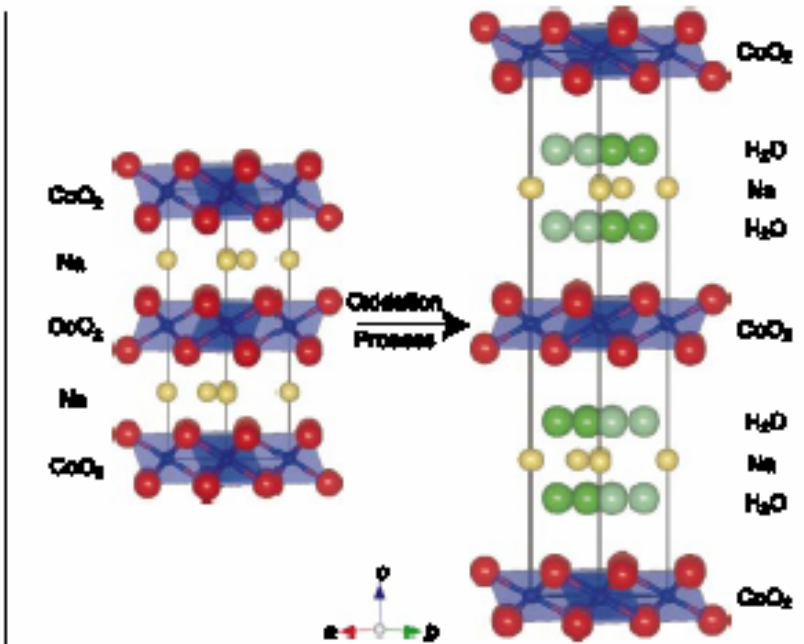


Figure 1 Structural views of $Na_{0.7}CoO_2$ (left) and $Na_xCoO_2 \cdot yH_2O$ (right), where Na and

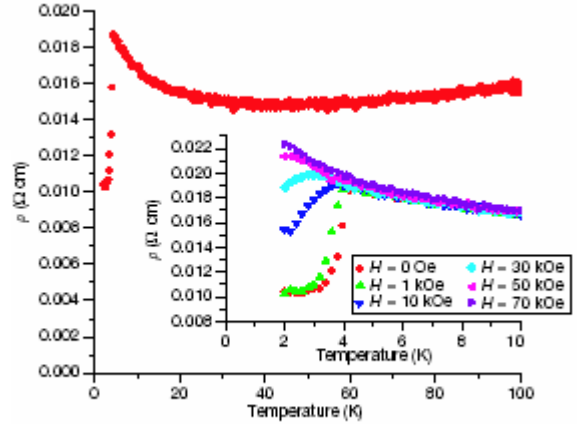
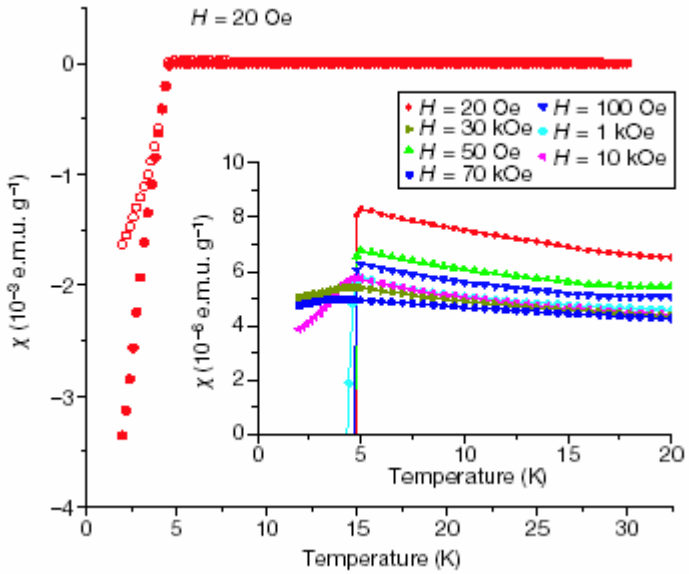


Figure 4 Resistivity (ρ) of $Na_xCoO_2 \cdot yH_2O$ under zero magnetic field. The inset figure



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Spin entropy as the likely source of enhanced thermopower in $Na_xCo_2O_4$

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

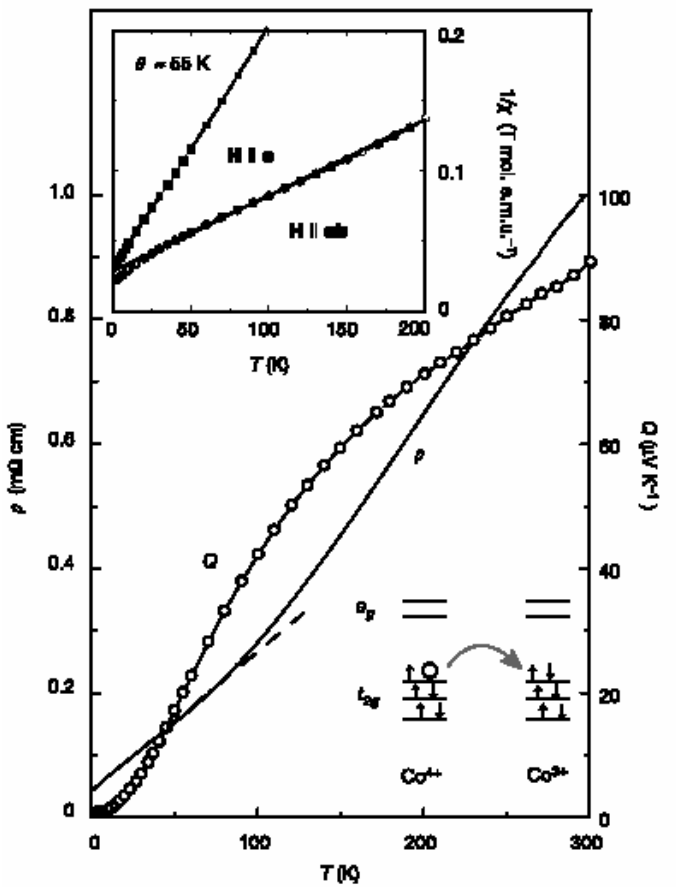


Figure 1 The temperature (T) dependence of magnetic and transport properties of single-crystal $Na_xCo_2O_4$ and electronic states in the Co ions. The in-plane thermopower Q

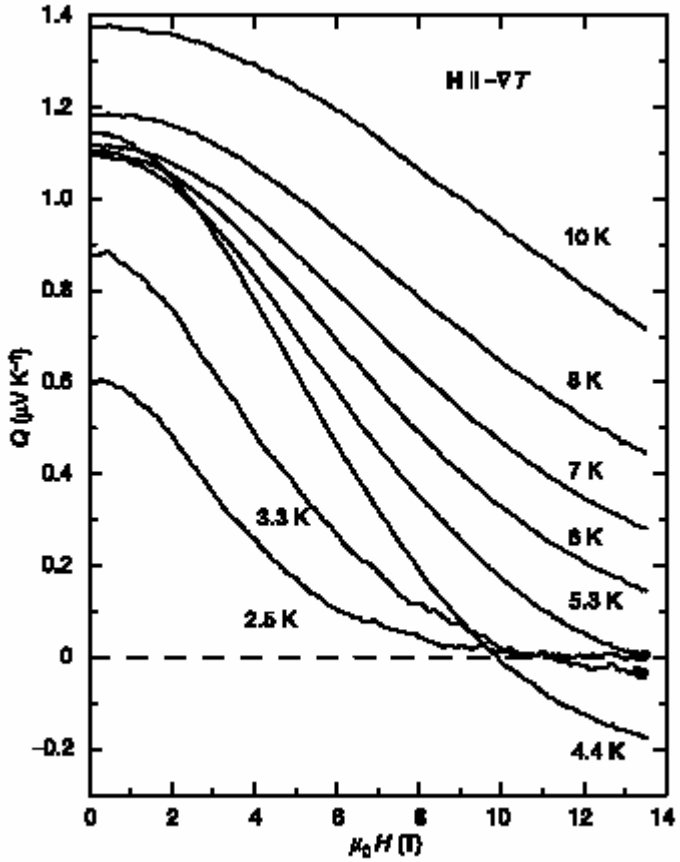


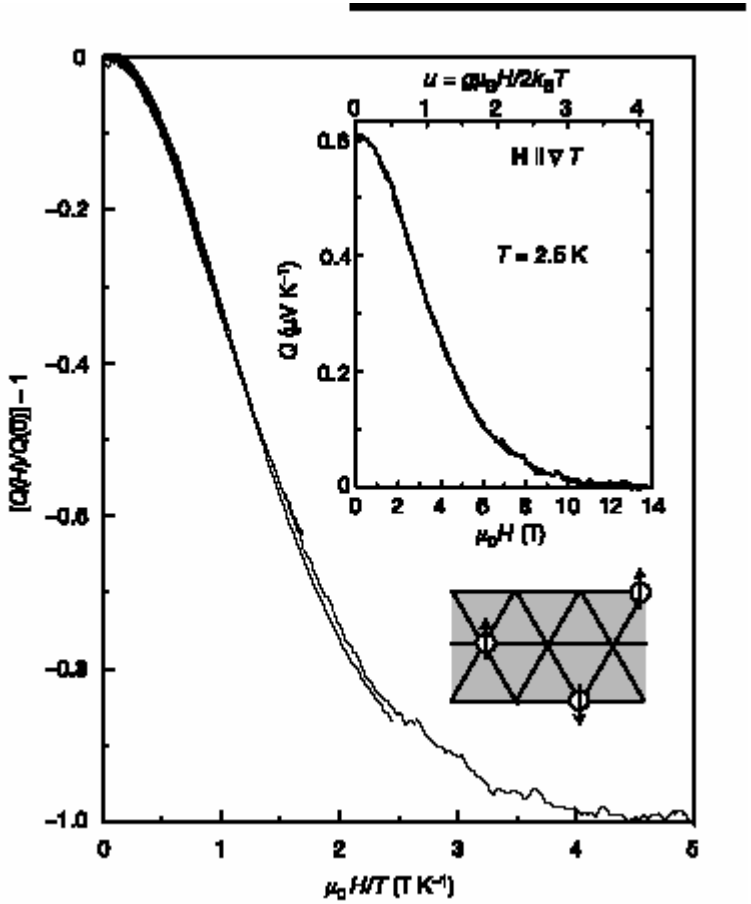
Figure 2 The in-plane thermopower Q versus an in-plane $\mathbf{H}\|(-\nabla T)$ at selected T. At

Hubbard model in small hopping limit (Heikes Formula): G Beni (1974):Q=-1/T($S_2/S_1+\mu/e$) Q~- entropy/e, entropy~k_B Log(g_{spin} g_{config}):

All data for different T collapses to single curve →

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

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



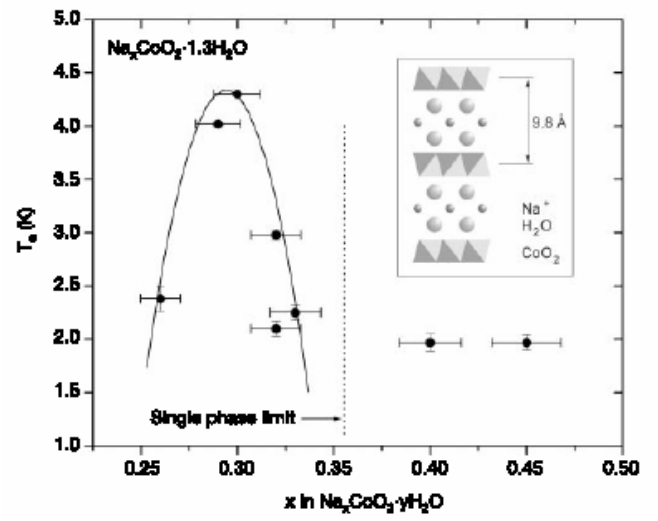


Figure 4 The superconducting phase diagram for $Na_xCoO_2 \cdot 1.3H_2O$. Main panel, T_c as a

← Cava, Nature May 03 Tc versus x

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

ARPES on $Na_{0.6}CoO_2$: Fermi surface, extended flat dispersion, and unusual band splitting

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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]

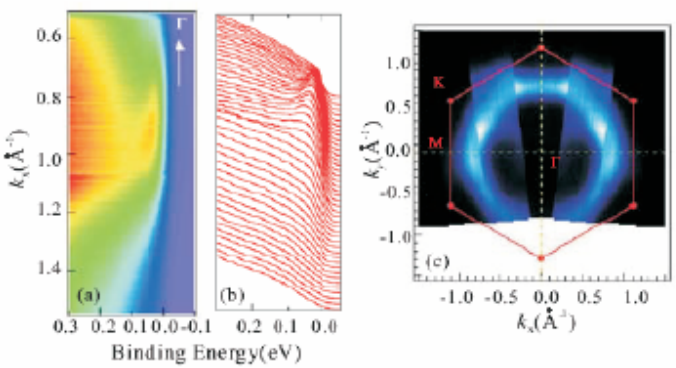


FIG. 2: Fermi Surface : (a)Γ →M Fermi crossing. Color red reflects the highest intensity - yellow to green to blue is in the order of decreasing intensity. (b) EDCs corresponding to the image plot in (a). (c) n(k) plot generated by integrating within 75 meV of Fermi level. A large hole-pocket is centered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

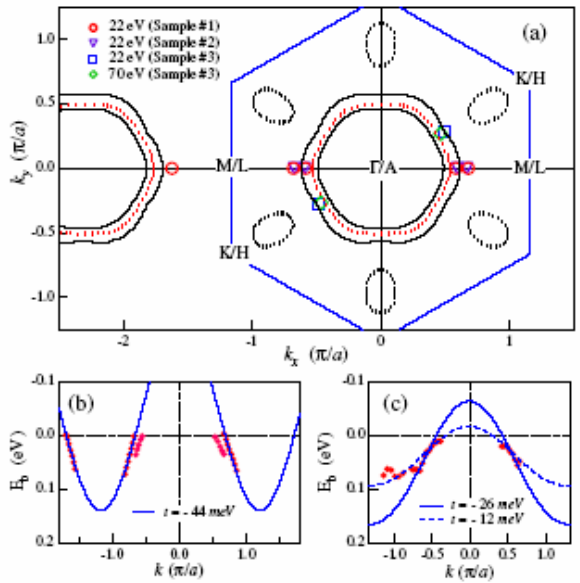
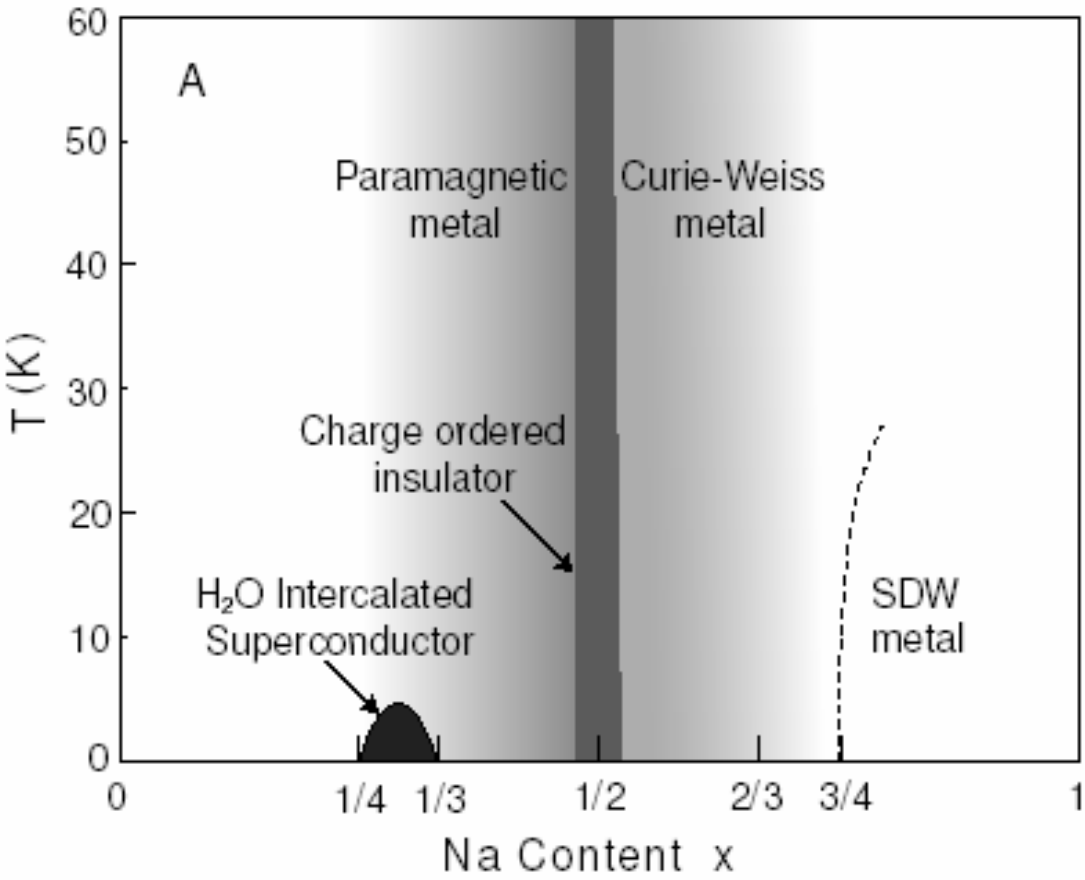


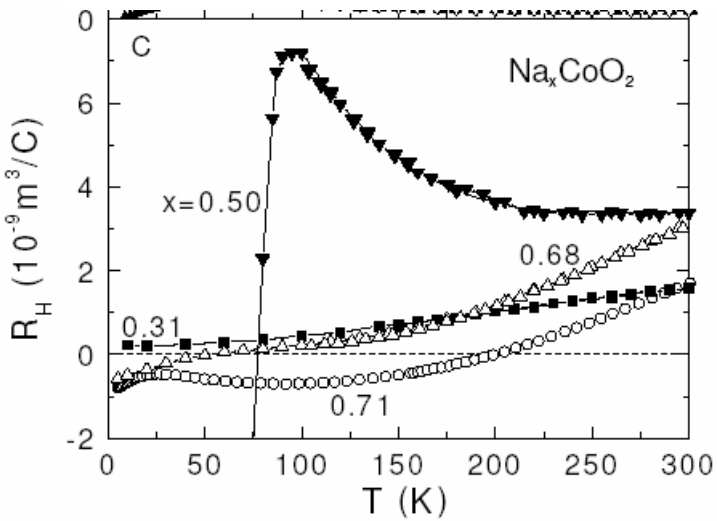
FIG. 4: (a) Measured FS crossings (symbols) comparing to the calculated FS in $k_z = 0$ (black solid lines) and $k_z = 0.5$ (red dashed lines) planes. The blue hexagon is the 2D Brillouin zone. (b) Extracted band positions along Γ-M (red dots) and a tight binding fit with $t = -44\ meV$ (solid line) (c) Extracted band positions along Γ-K (red dots) and two tight binding fits with $t = -12\ meV$ (solid line) and $t = -26\ meV$ (dashed line).



Most recent experiments by Cava/Ong show a phase diagram that has new components: charge ordering at x=.5

(condmat Dec 18, 2003)

Is this due to degenerate bands and a "chemical transition"?



How to model NCO- start with band structure

Electronic structure of $NaCo_2O_4$

D. J. Singh
Code 6391, Naval Research Laboratory, Washington, DC 20375
(Received 10 January 2000)

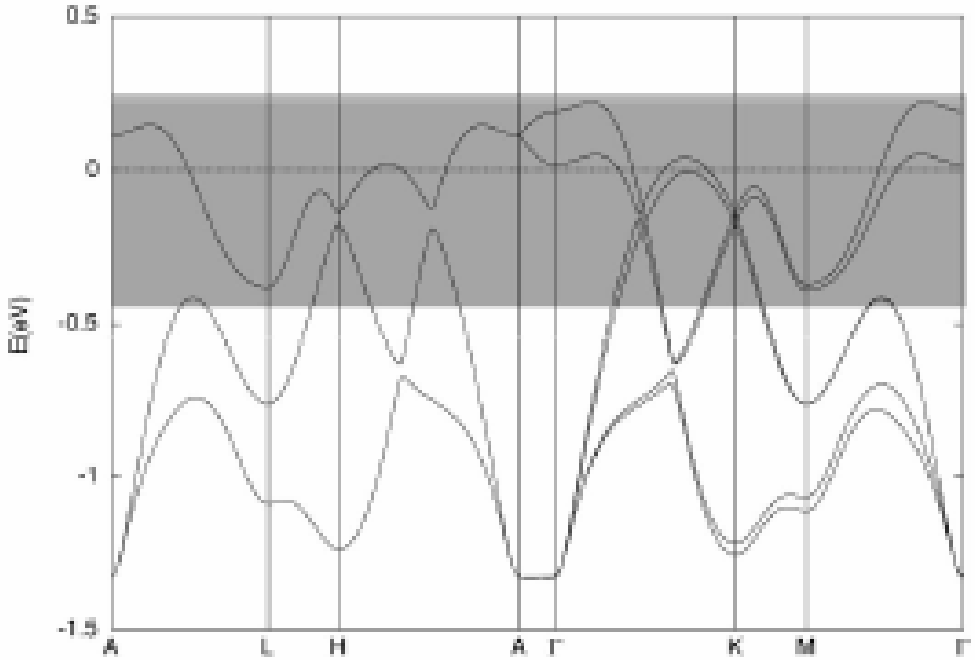


FIG. 1. LDA paramagnetic band structure of $NaCo_2O_4$. The

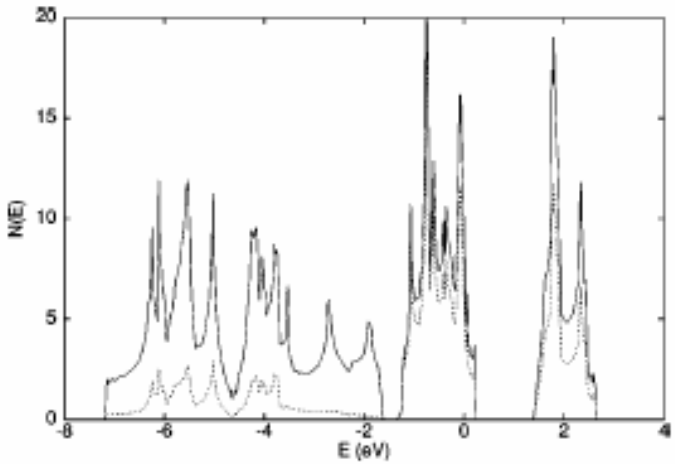


FIG. 2. LDA paramagnetic DOS, $N(E)$, of $NaCo_2O_4$. The DOS

- **Notable features from Singh's calculation:**

  (assuming rigid bands with varying x)

- **At x=.75 there is only one hole like band that contains the fermi level: band maximum at Gamma point hence hole like FS**

- **At x~.5 there is evidence of another band becoming relevant, lower band (electron like) tangents the fermi level hence large DOS. Suggest that at x=.5 there is a "chemical transition"**

- **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!!!**

Kumar and SS

Baskaran, 2003

Q H Wang, Dung Hai Lee, Patrick Lee 2003

- t-J Model

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

The fermi surface for triangular lattice tight binding band structure, $\epsilon(\mathrm{k}) = -2t(\cos(k_x) + 2\cos(k_x/2)\cos(\sqrt{3}k_y/2)$, gives a density of states

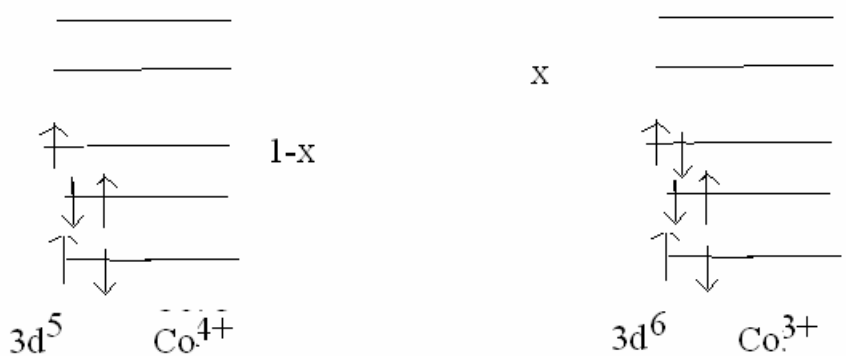
Idea is to see if the RVB ideas give superconductivity in triangular lattice. Existence of J inferred from magnetic susceptibility results of Ong/Cava, J ~60^0 K (antiferromagnetic). Scale of "t" unknown, but electronic structure suggests large scale (say .1 ev)- we will argue strongly against that scale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

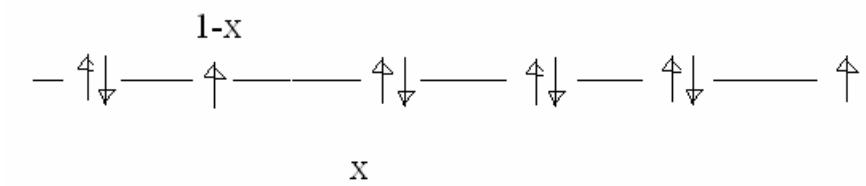
- **Non s-wave pairing guaranteed by "bond attraction" type theories e.g. RVB, in contrast to "site attraction" type theories, e.g. phononic.**

Co: $3d^7\ 4s^2$
Co^{4+} ---> $3d^5$
Co^{3+} ----> $3d^6$

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

Hence number of "singlons" i.e. projected electrons is "x"





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

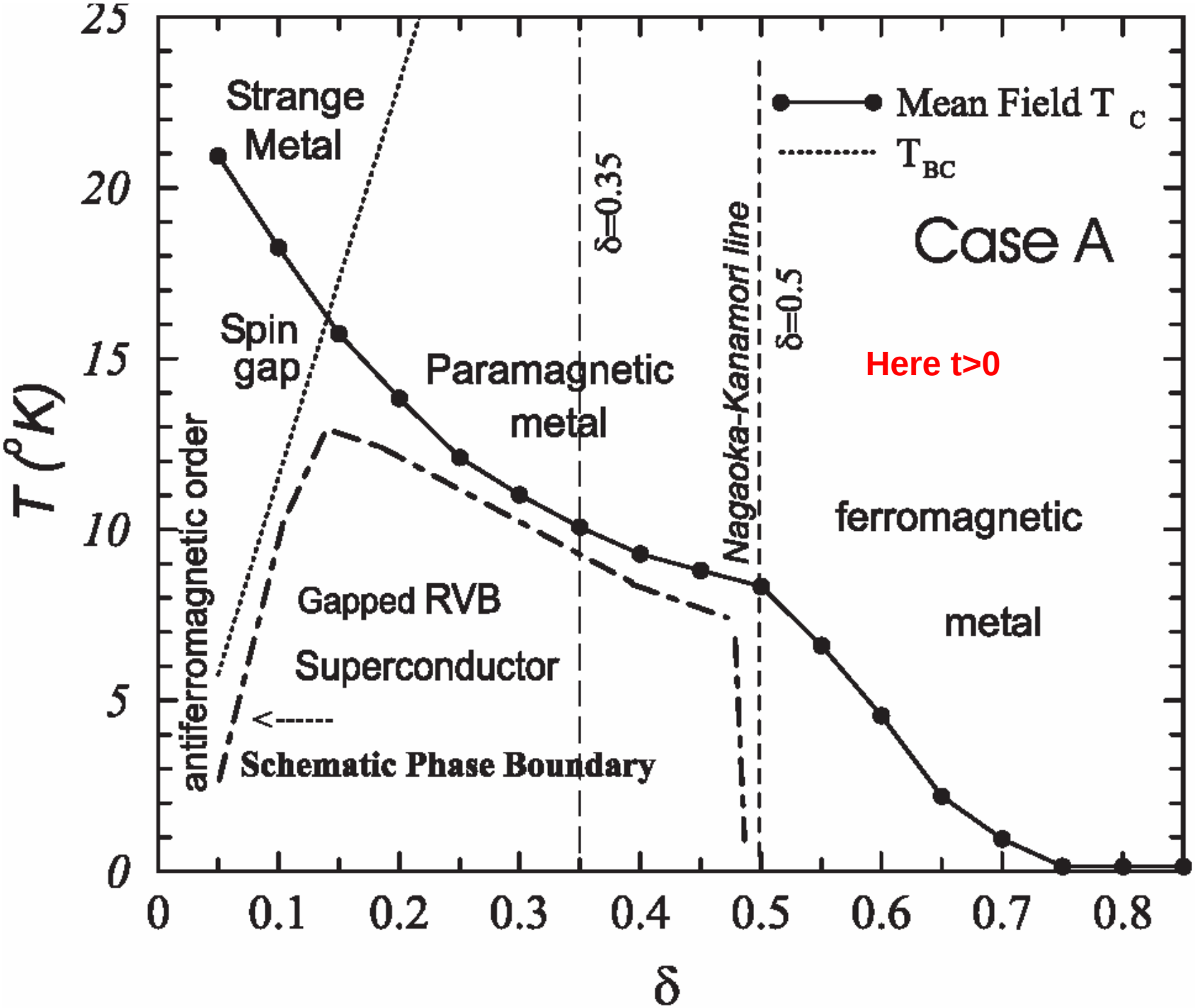
“exchange is also attraction”

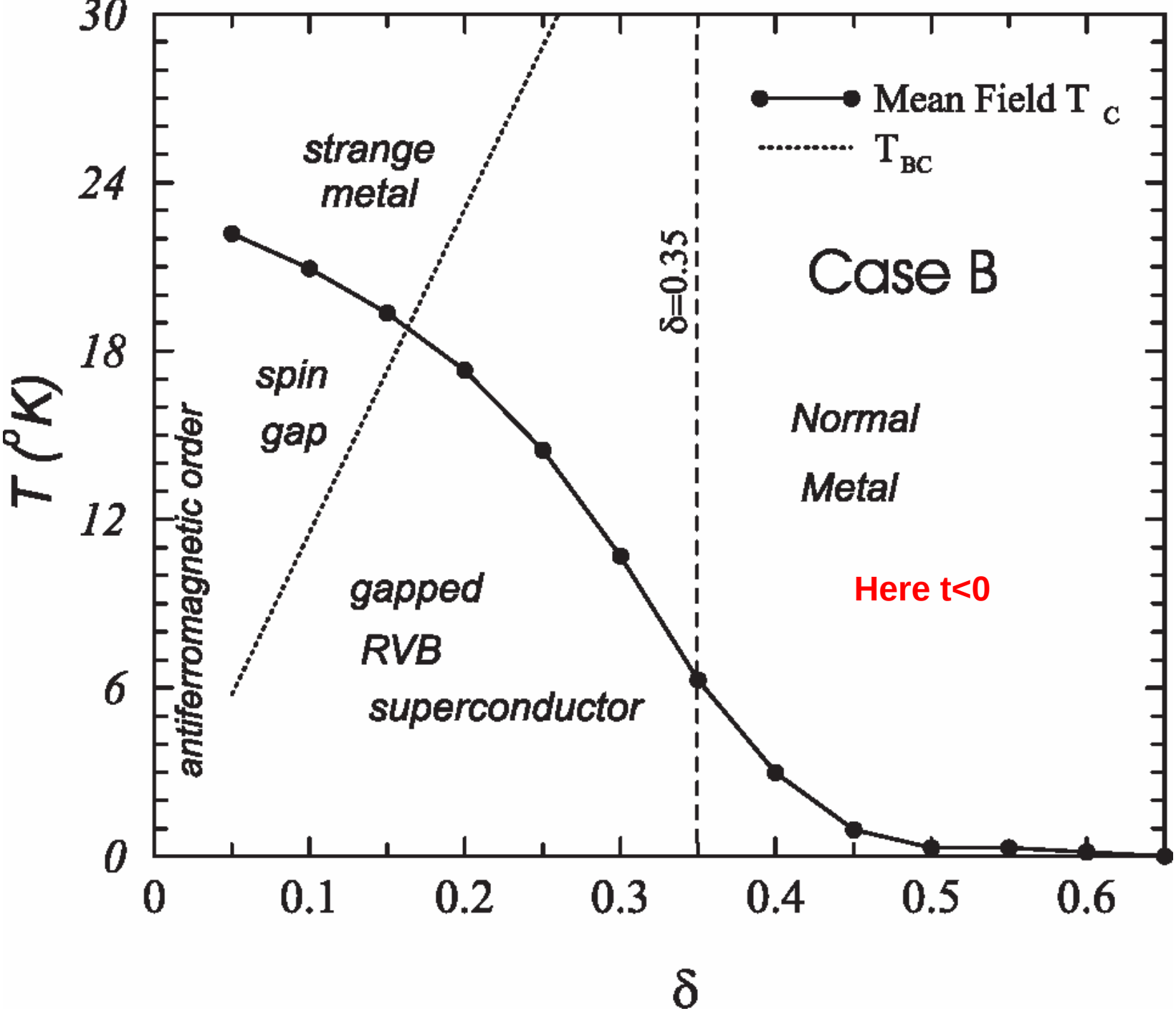
J S.S = - J (c* c* -c* c*) (c c – c c)

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

Calculations for t>0 and t<0 are both done and we need to finally interpret these in the light of earlier comments on applicability of 1 band models.

Forced to choose t ~ 2 or 3 J, otherwise do not get superconductivity in large part of phase diagram .


Strange Metal
Spin gap
Paramagnetic metal
antiferromagnetic order
Gapped RVB Superconductor
<------
Schematic Phase Boundary
δ=0.35
δ=0.5
Nagaoka-Kanamori line
ferromagnetic metal
Mean Field T c
T BC
Case A
Here t>0
T (°K)
δ
0
5
10
15
20
25
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8


30
24
18
12
6
0
T (°K)
0
0.1
0.2
0.3
0.4
0.5
0.6
δ
Mean Field T c
T BC
strange metal
spin gap
antiferromagnetic order
gapped RVB superconductor
δ=0.35
Case B
Normal Metal
Here t<0

Both signs of t support superconductivity max Tx appxly 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.

MAGNETISM

Notice ferromagnetism for t>0 in phase diagram,

This is a consequence of Nagaoka type physics of Hubbard model.

Although we have argued that t<0 for x=.7, there are reports of magnetic fluctuations out to 10 mev in neutron scattering (Boothroyd, condmat 04), could these be signs that multiband physics is important here too?

Weak SDW state seen in muon experiments Tc 22^0K (1-2 mev).

Triangular lattice magnetism for t<0 is also fascinating theoretical topic, suggestions of three sublattice order being CONSISTENT with kinetic energy…

Hall Constant in Strongly Correlated Electron systems

[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 $1/ne$ does 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 $\delta = \frac{1}{3}$.

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

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):

- **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| ~ 60^0K hence bandwidth ~550^0K.
- Fermi surface for this sign has unoccupied region around Γ point, ie hole like as seen in two recent experiments.
- Particularly interesting would be x~0 where Mott Hubbard physics is dominant.
- **Business with frequency**: **wanted $\rho_{xy}(w)$ for correlated systems from transport to large w.**

ρ preferable to σ

Anomalous high-temperature Hall effect on the triangular lattice in Na_xCoO_2

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[1]*Department of Physics,* [2]*Department of Chemistry,* [3]*Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544.*

(Dated: May 8, 2003)

The Hall coefficient R_H of Na_xCoO_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.

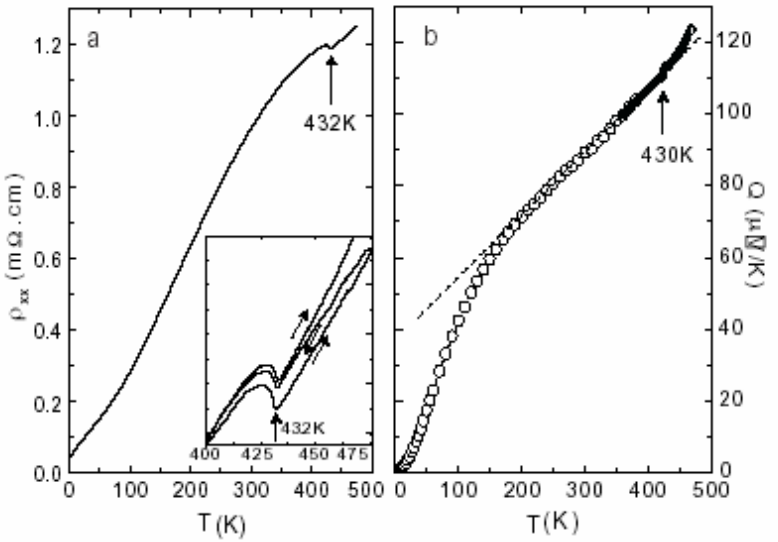


FIG. 1: (a) The in-plane resistivity ρ of Na_xCoO_2 ($x = 0.68$). ρ is linear in T from 2 to 80 K, but has a steeper slope above 100 K. The inset shows slight hysteresis in ρ in the vicinity of the transition at $T_D = 430$ K. (b) The in-plane thermopower Q of Na_xCoO2. The anomaly at T_D is just resolved in Q.

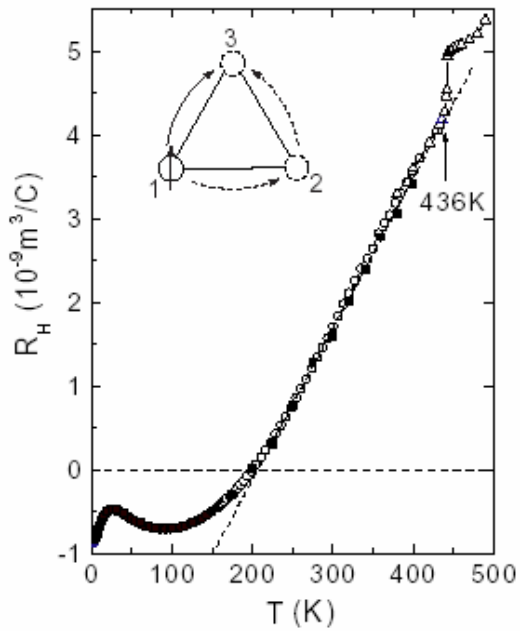
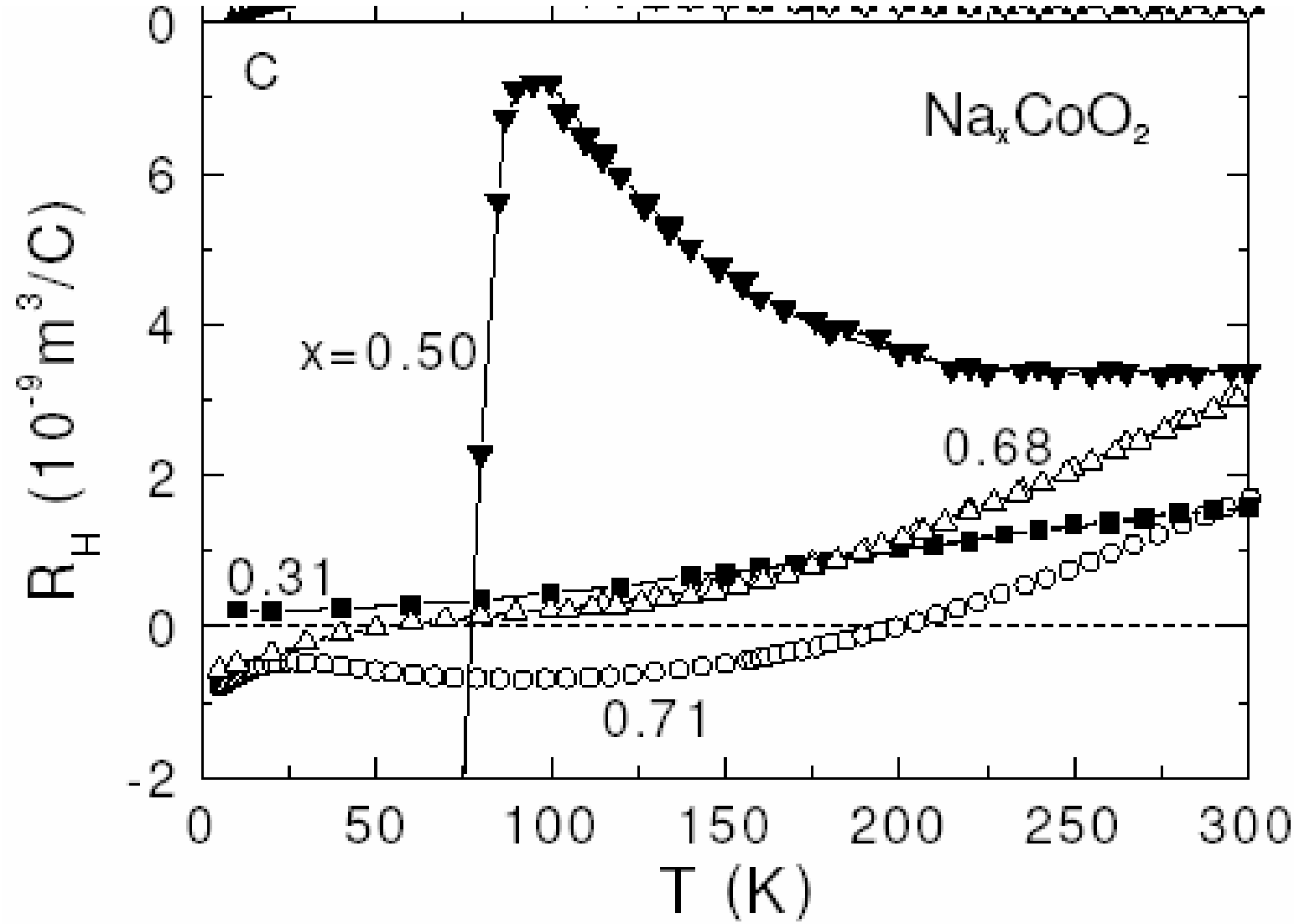


FIG. 2: The T dependence of the Hall coefficient R_H in Na_xCoO_2 showing anomalous T-linear increase between 200 and 500 K. The open circles are measurements using Method


C
Na_xCoO_2
x=0.50
0.68
0.31
0.71
R_H ($10^{-9}m^3/C$)
T (K)
0
6
4
2
0
-2
0
50
100
150
200
250
300

Open Questions:

Fermi surface, renormalization effects, sign of t?

Optimium Tc?

Prediction of time reversal violating superconducting state?

Magnetism? Ferro : Nagaoka/Kanamori for t>0 and other orderings for t<0.

Possibly a fermi surface switching transition as a function of x? t<0 to t>0 due to competing bands, a chemical transition.

Battery connections? Li_x Co O_2

Question:

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. Chemistry point of view (Goodenough Kanamori Anderson rules) seem to explain this more easily than LDA