Triangular Lattice Transport, Magnetism andsuperconductivity in Na_x Co O_2

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The recently discovered Sodium Cobalt Oxide system provides a fascinating platform for the study of strong correlations coupled with frustration. We review some recent experiments, and suggest that these can be modeled by a triangular lattice t-J model.A study of this model suggests that It supports a Time reversal violating superconducting state, a ferromagnetic metallic state and possibly a spin gap phase in a narrow composition range. We predict an unsaturated T linear dependence of the Hall constant in this system which seems to be corroborated by recent data.

Plan of Talk

Experiments :

- Early papers:
  - Terasaki (1997) Discovered high thermopower in a reasonable metal
  - Thermopower calculation within Band Structure: D J Singh (2000).
- Recent surge of activity:
  - Takada et al (2003 March 6, Nature) Superconductivity in hydrated system
  - Ong and Cava (2003 May Nature) Magnetic Field dependence of S.
  - Lots more since
- Theory:
  - RVB Scenario, Kumar & SS (April 9) RVB type calculation+ Hall constant prediction, Baskaran (March 31) cond-mat Wang, Lee and Lee (April 16) cond-mat RVB
  - Some unresolved issues.

Large thermoelectric power in $NaCo_2O_4$ single crystals

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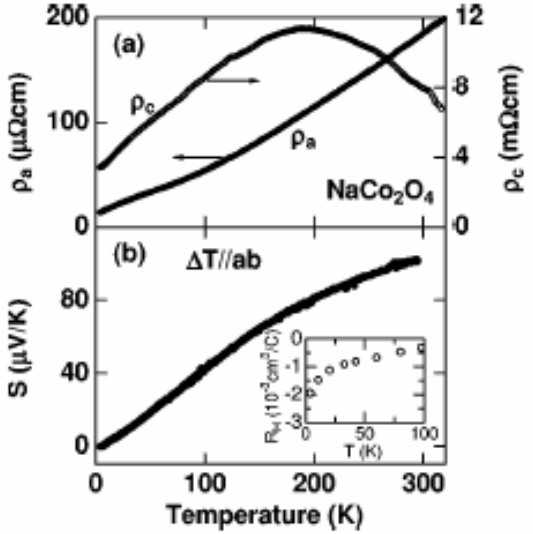
(Received 18 July 1997)

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]



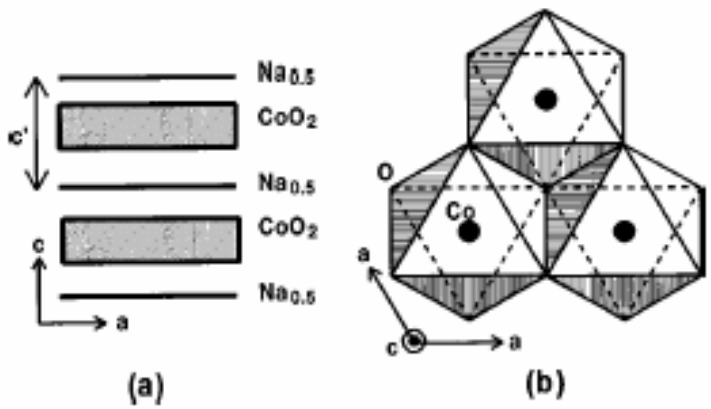


FIG. 1. A schematic picture of the crystal structure of $NaCo_2O_4$. (a) The layered structure; (b) the CoO_2 layer.

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

Electronic structure of $NaCo_2O_4$

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(Received 10 January 2000)

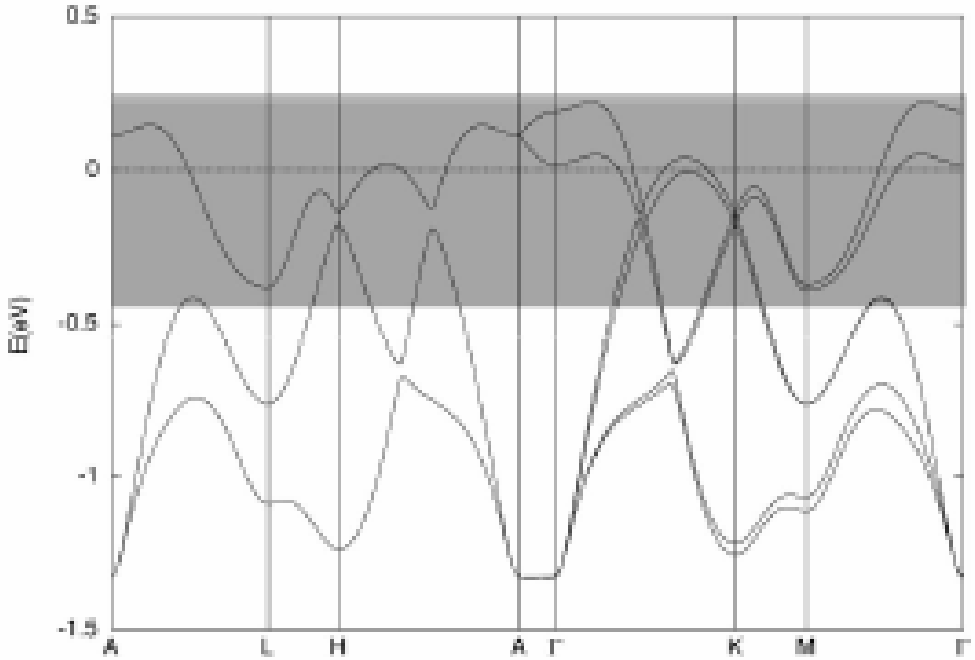


FIG. 1. LDA paramagnetic band structure of $NaCo_2O_4$. The

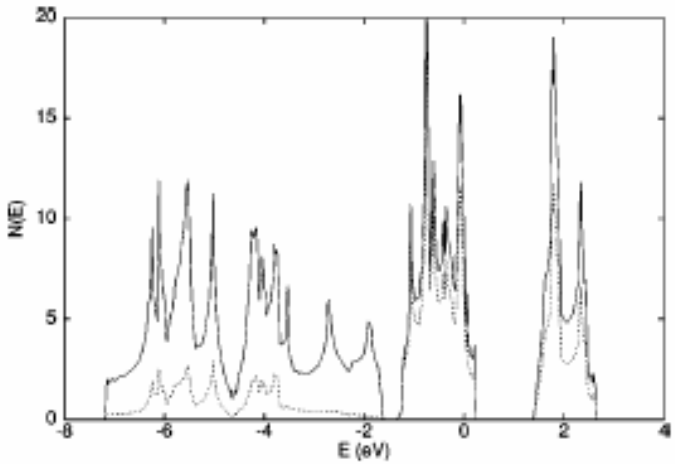


FIG. 2. LDA paramagnetic DOS, $N(E)$, of $NaCo_2O_4$. The DOS

Superconductivity in two-dimensional CoO_2 layers

NATURE | VOL 422 | 6 MARCH 2003

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

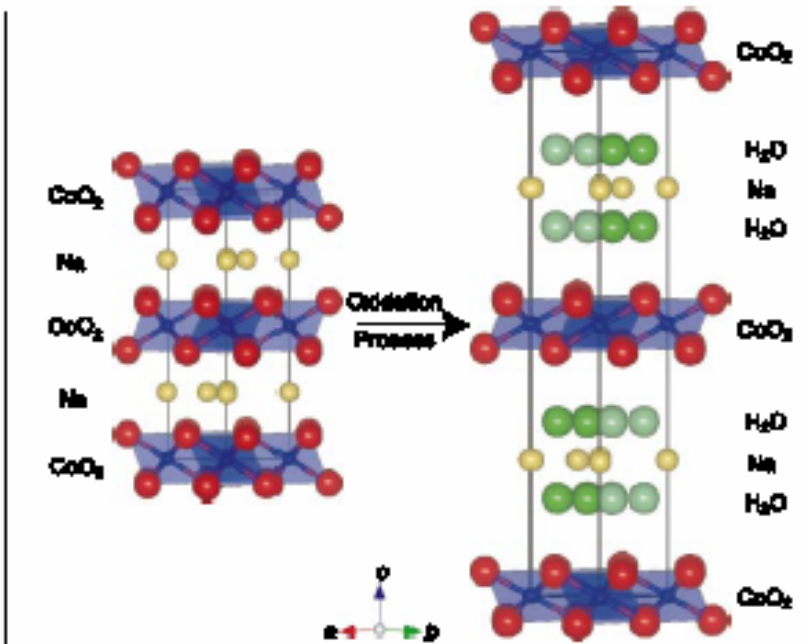


Figure 1 Structural views of $Na_{0.7}CoO_2$ (left) and $Na_xCoO_2 \cdot yH_2O$ (right), where Na and

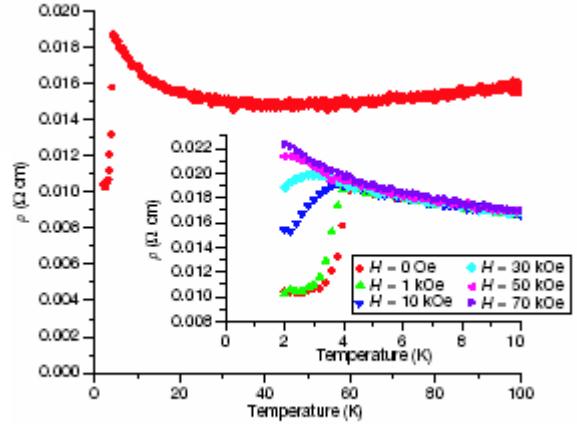
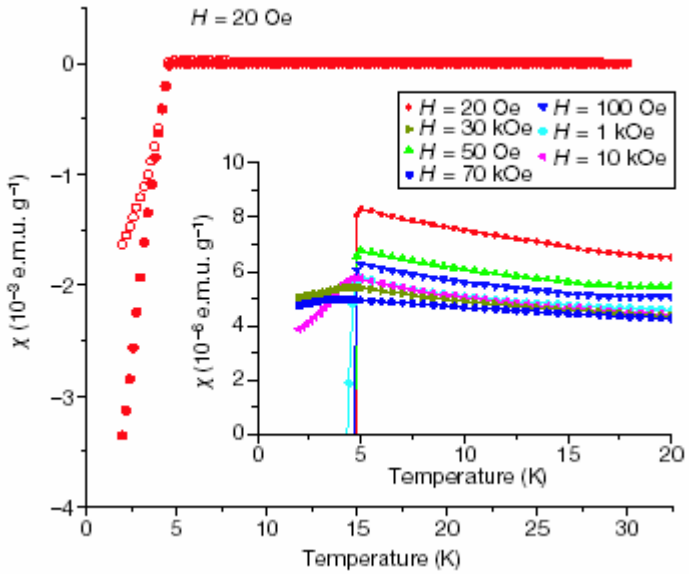


Figure 4 Resistivity (ρ) of $Na_xCoO_2 \cdot yH_2O$ under zero magnetic field. The inset figure



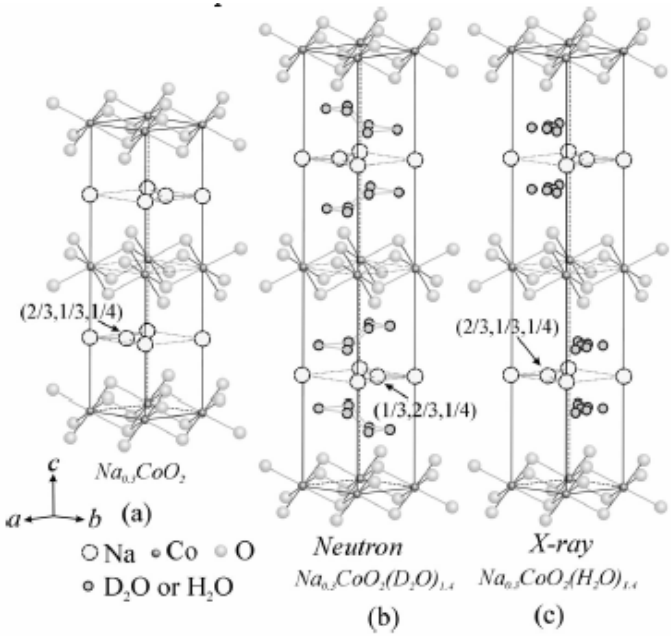


Fig 5. Structures of (a) $Na_{0.3}CoO_2$, (b) the superconducting phase model used in the present work and (c) the model reported in ref. [4]. Note that the positions for the Na and water centers are different in (b) and (c).

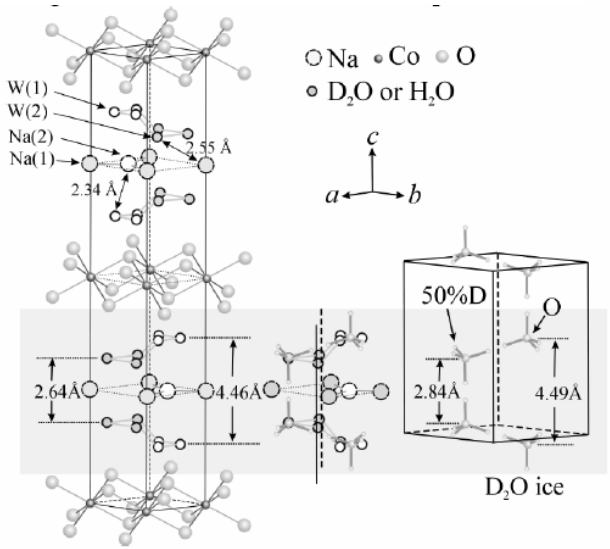


Fig. 4. Structure model for the Na_xCoO_2 1.4(D_2/H_2O) superconductor (left). The figure on the right shows the D_2O ice structure.[24] For comparison, the figure in the middle shows the ice molecule superposed on the water block in the structure of the superconducting phase, demonstrating that the dimensions of the water block are close to those found in free ice.

Neutron data:
Cava/Lynn

NATURE | VOL 423 | 22 MAY 2003 |

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*‡

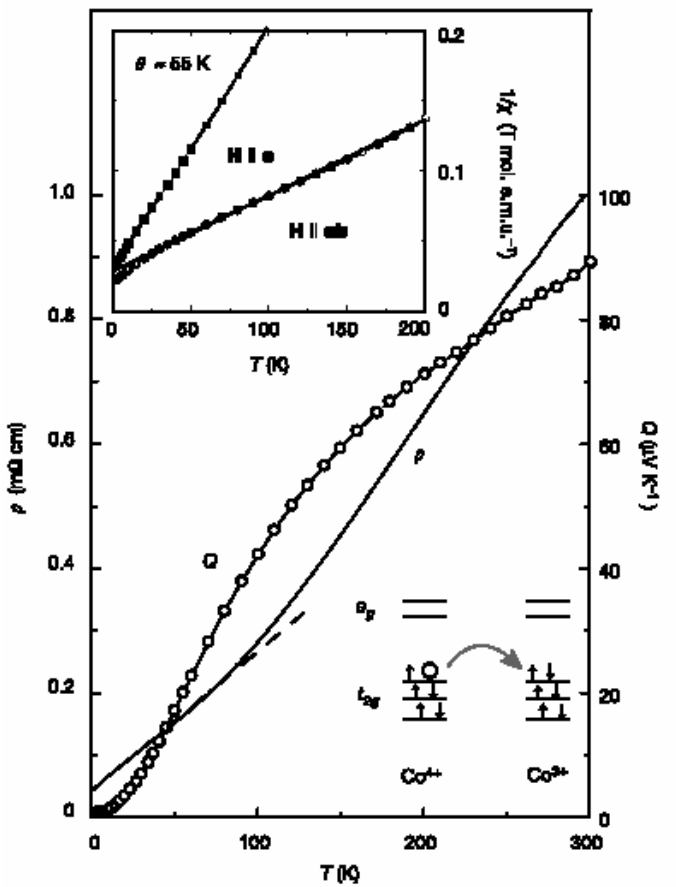


Figure 1 The temperature (T) dependence of magnetic and transport properties of single-crystal $Na_xCo_2O_4$ and electronic states in the Co ions. The in-plane thermopower Q

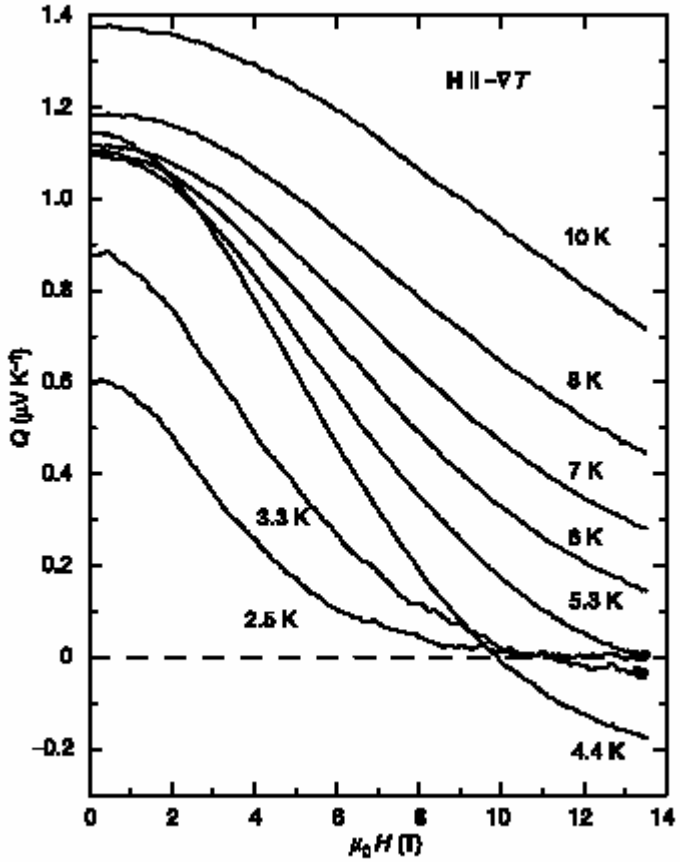


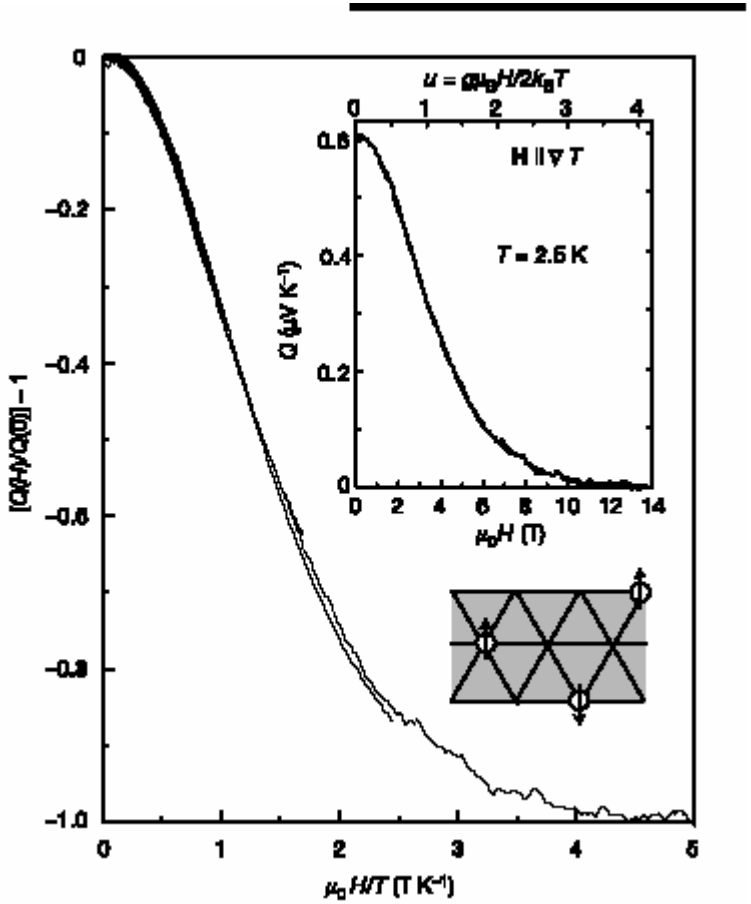
Figure 2 The in-plane thermopower Q versus an in-plane $\mathbf{H}\|(-\nabla T)$ at selected T. At

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 →

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

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



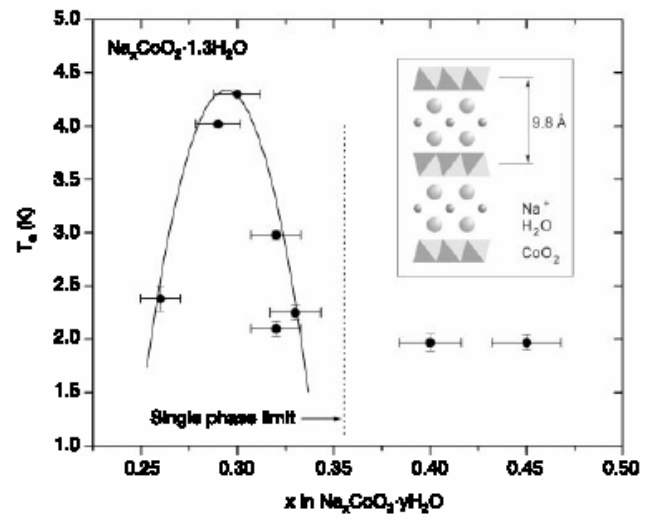


Figure 4 The superconducting phase diagram for $Na_xCoO_2 \cdot 1.3H_2O$. Main panel, T_c as a

← Cava, Nature May 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

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. Ding[1]

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]

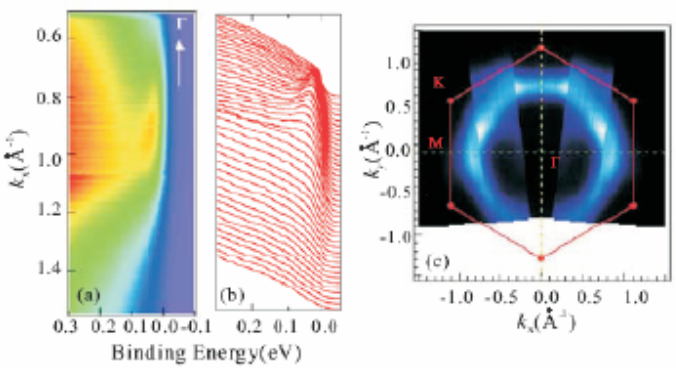


FIG. 2: Fermi Surface : (a)Γ →M Fermi crossing. Color red reflects the highest intensity - yellow to green to blue is in the order of decreasing intensity. (b) EDCs corresponding to the image plot in (a). (c) n(k) plot generated by integrating within 75 meV of Fermi level. A large hole-pocket is centered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

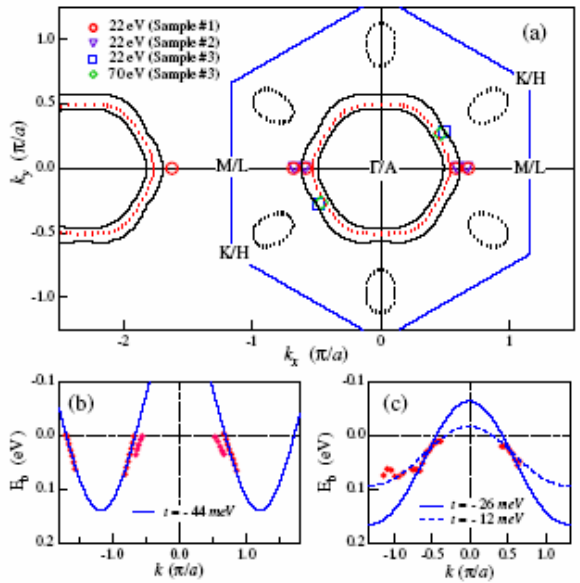


FIG. 4: (a) Measured FS crossings (symbols) comparing to the calculated FS in $k_z = 0$ (black solid lines) and $k_z = 0.5$ (red dashed lines) planes. The blue hexagon is the 2D Brillouin zone. (b) Extracted band positions along Γ-M (red dots) and a tight binding fit with $t = -44\ meV$ (solid line)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

- Theoretical ideas:
  - Triangular lattice, hence frustrated in electronic sense as well as usual spin language
  - Possibility of non phononic SC, perhaps RVB, “the original lattice”, since low Tc
  - Temperature dependent susceptibility suggest low energy scale, hence possibly strongly correlated
  - Ferromagnetism / Antiferromagnetism? SDW state?

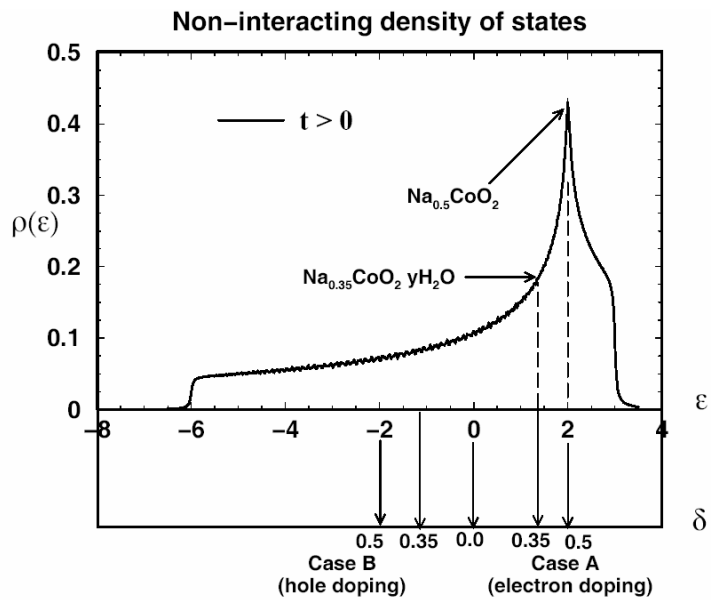
Kumar and SS

- 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

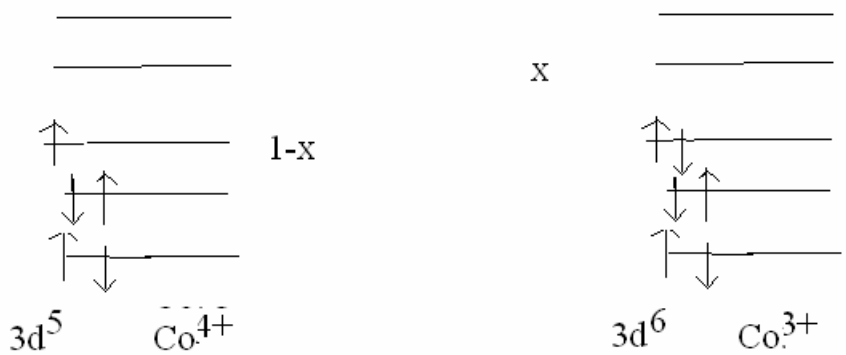
- Case A: Here we have either
  - (i) $t > 0$ and electron doping, or
  - (ii) $t < 0$ with hole doping, and
- Case B: where we have either
  - (i) $t > 0$ and hole doping, or
  - (ii) $t < 0$ and electron doping.



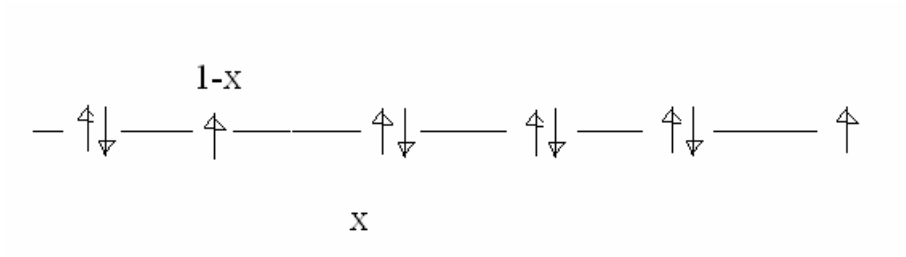
Co: $3d^7\ 4s^2$
Co^{4+} ---> $3d^5$
Co^{3+} ----> $3d^6$

$Na_x\ Co\ O_2$ 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

•Triangular lattice Ferromagnetism for the U=infinity Hubbard model

- •SS, Andersn Krishnamurthy (1993) studied instability of Nagaoka ferromagnetism on various lattices, and noted that for triangular lattice:
- •Case A (t>0) leads to ferromagnetism easily for most fillings whereas
- •Case B (t<0) ferromagnetism is not achieved.

•Turning back a U or J, we expect: where J=~ 4 t^2/U

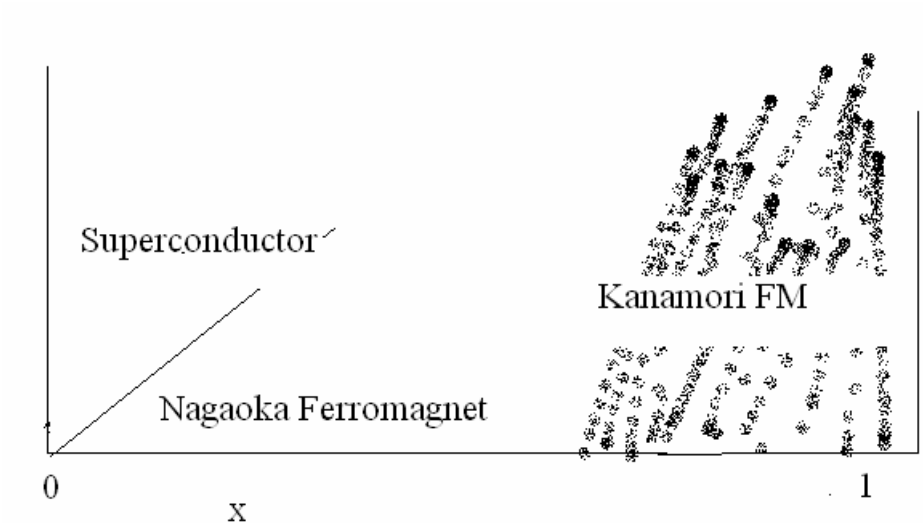
> Date: Tue, 13 May 2003 05:59:21 GMT (80kb)

Static magnetic order in Na$_{0.75}$CoO$_2$ detected by muon spin rotation and relaxation

Authors: Jun Sugiyama, Hiroshi Itahara, Jess H. Brewer, Eduardo J. Ansaldo, Teruki Motohashi, Maarit Karppinen, Hisao Yamauchi

condmat 0305272

Experiments support SDW state rather than ferromagnet.



Hall Constant in a strongly interacting fermi system:

•Highly mysterious. Boltzmann theory is not a good starting point, since z is either zero or very very small, so quasiparticle dominance fails.

•Big anomalies in High Tc: Boebinger etal (Nature 2003) show failure of Boltzmann theory

•R~1/(nec) ~ 1/(1+x)n' ec is far from seen, actually one sees R~1/x e c divergent as x->0.

•Theory is in poor shape, a new direction was charted by us 1993 using high frequency Hall constant. Started with the amusing observation that in the Drude model, while $\sigma(\omega)$ is frequency dependent, $\rho(\omega)$ is **independent** of ω due to complete cancellation. While cannot calculate anything at low ω, large ω is still managable:

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Faraday Rotation and the Hall Constant in Strongly Correlated Fermi Systems

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(Received 30 December 1992)

$$\sigma_{\alpha,\beta}(\omega) = \frac{ie^2}{\omega\Omega}\left[\langle\tau_{\alpha,\beta}\rangle - \frac{1}{\mathcal{Z}}\sum \frac{\exp-(\beta\epsilon_\nu) - \exp-(\beta\epsilon_\mu)}{\epsilon_\mu - \epsilon_\nu - \omega - i\eta}\langle\nu|J_\alpha|\mu\rangle\langle\mu|J_\beta|\nu\rangle\right].$$

The Hall resistivity, at a frequency ω, may be obtained from

$$R_H(\omega) = a_0^3\frac{\partial}{\partial B}\left(\frac{\sigma_{x,y}(\omega)}{\sigma_{x,x}(\omega)\sigma_{y,y}(\omega) - \sigma_{x,y}(\omega)\sigma_{y,x}(\omega)}\right)_{B=0}$$

in the weak field regime. The relevant part of $\sigma_{x,y}$ is antisymmetric in x, y, and h

$$\sigma_{[x,y]}(\omega) = -\frac{ie^2}{\mathcal{Z}\Omega}\sum \frac{\exp-(\beta\epsilon_\nu) - \exp-(\beta\epsilon_\mu)}{(\epsilon_\mu - \epsilon_\nu)^2 - \omega^2}\langle\nu|J_x|\mu\rangle\langle\mu|J_y|\nu\rangle.$$

For large ω ($>> \epsilon_\mu - \epsilon_\nu$), we have

$$\sigma_{[x,y]}(\omega) = \frac{ie^2}{\Omega\omega^2}\left[\langle[J_x, J_y]\rangle + \frac{1}{\omega^2}\langle[[[J_x, H], H], J_y]\rangle + O(1/\omega^4)\right],$$

while

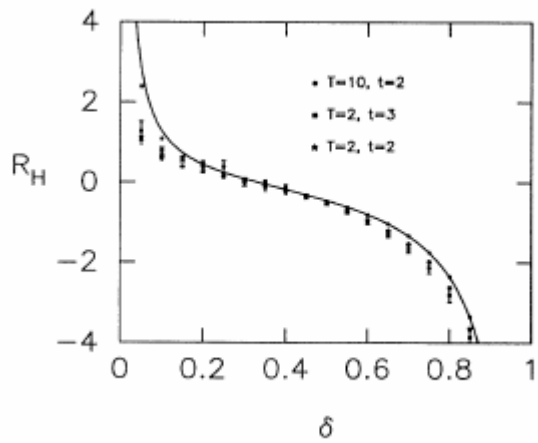
$$\sigma_{x,x}(\omega) = \frac{ie^2}{\Omega\omega}\left[\langle\tau_{x,x}\rangle + \frac{1}{\omega^2}\langle[[J_x, H], J_x]\rangle + O(1/\omega^4)\right].$$

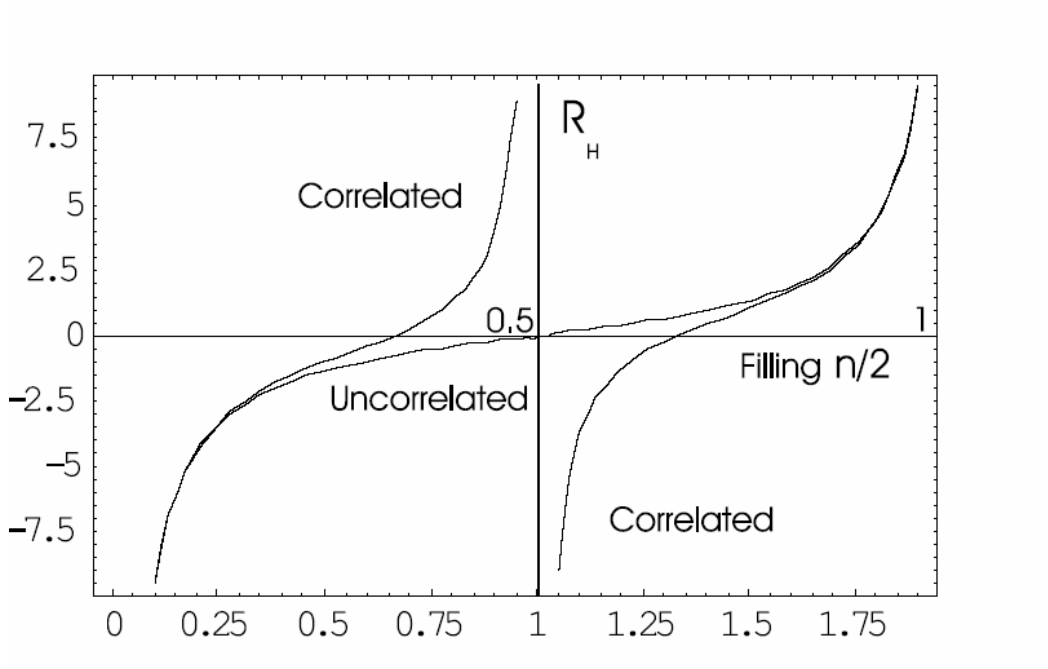
$$R_H^* = \frac{\tau_0}{4}\left[\frac{1 - \frac{3\beta J}{2}}{\delta} - \frac{4}{1-\delta} + 3 + \frac{3\beta J}{2}\right] + O(\beta^2).$$

$$R_H(\omega) = \frac{R_H^*}{1 - \Sigma_H(\omega)},$$

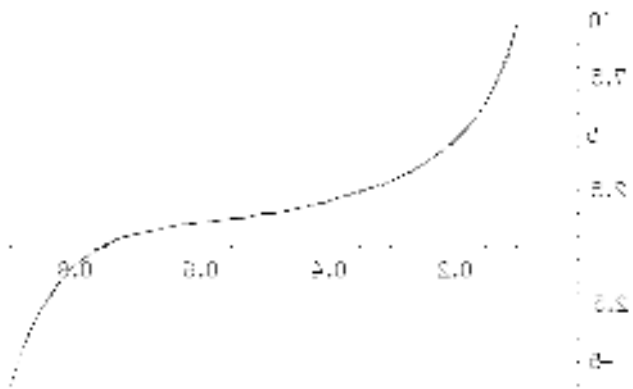
with

$$R_H^* = \lim_{B\to 0}\left(-\frac{ia_0^3 N}{Be^2}\frac{\langle[J_x, J_y]\rangle}{\langle\tau_{x,x}\rangle^2}\right).$$





Correlated e's n square lattice: Hall constant is shown to have **THREE** zero crossings, in contrast to single crossing for free e's



Free e' Hall constant versus filling for triangular lattice at fixed T versus filling.

[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 $\delta = \frac{1}{3}$.

$$R_H^* = -\frac{v}{8|e|}\frac{k_B T}{t}\frac{1+\delta}{\delta(1-\delta)}$$

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.

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

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(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.

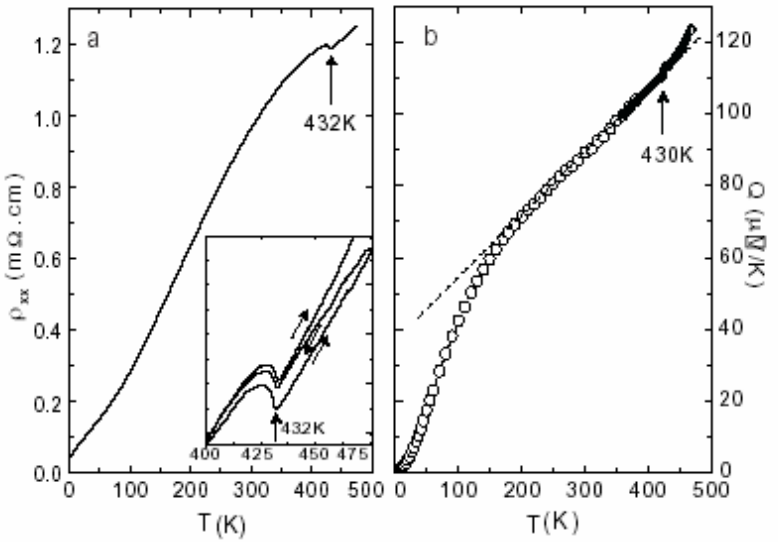


FIG. 1: (a) The in-plane resistivity ρ of Na_xCoO_2 ($x = 0.68$). ρ is linear in T from 2 to 80 K, but has a steeper slope above 100 K. The inset shows slight hysteresis in ρ in the vicinity of the transition at $T_D = 430$ K. (b) The in-plane thermopower Q of Na_xCoO2. The anomaly at T_D is just resolved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

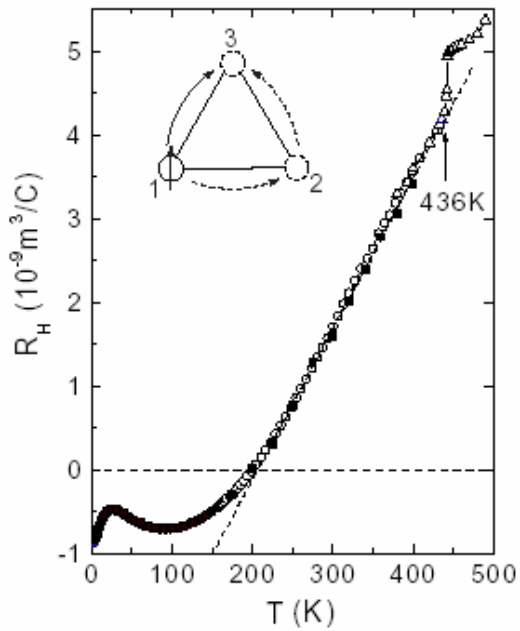


FIG. 2: The T dependence of the Hall coefficient R_H in Na_xCoO_2 showing anomalous T-linear increase between 200 and 500 K. The open circles are measurements using Method

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

$$R_H^* = -\frac{v}{8|e|}\frac{k_B T}{t}\frac{1+\delta}{\delta(1-\delta)}$$

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| ~ 30^0K hence bandwidth ~300^0K.

•Fermi surface for this sign has unoccupied region around Γ point, ie hole like as seen in two recent experiments.

•Further experiments at different values of filling should be useful to check the details of the prediction

•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.

Superconductivity: RVB calculation and phase diagaram:

$$-\mathrm{J}\,\Sigma_{i,j}\,\mathrm{b}^{\dagger}_{ij}\mathrm{b}_{ij}, \qquad \mathrm{b}^{\dagger}_{ij} = (c^{\dagger}_{i\uparrow}c^{\dagger}_{j\downarrow} - c^{\dagger}_{i\downarrow}c^{\dagger}_{j\uparrow})/\sqrt{2}, \qquad \Delta_{ij} = \langle b_{ij}\rangle$$

$$\mathrm{D}(\mathbf{k}) = \cos(k_x) + e^{i\theta}\cos(k_x/2 + \sqrt{3}k_y/2) + e^{i\phi}\cos(k_x/2 - \sqrt{3}k_y/2)$$

$$\langle c^{\dagger}c^{\dagger}\rangle \sim \langle bb\rangle\langle f^{\dagger}f^{\dagger}\rangle$$

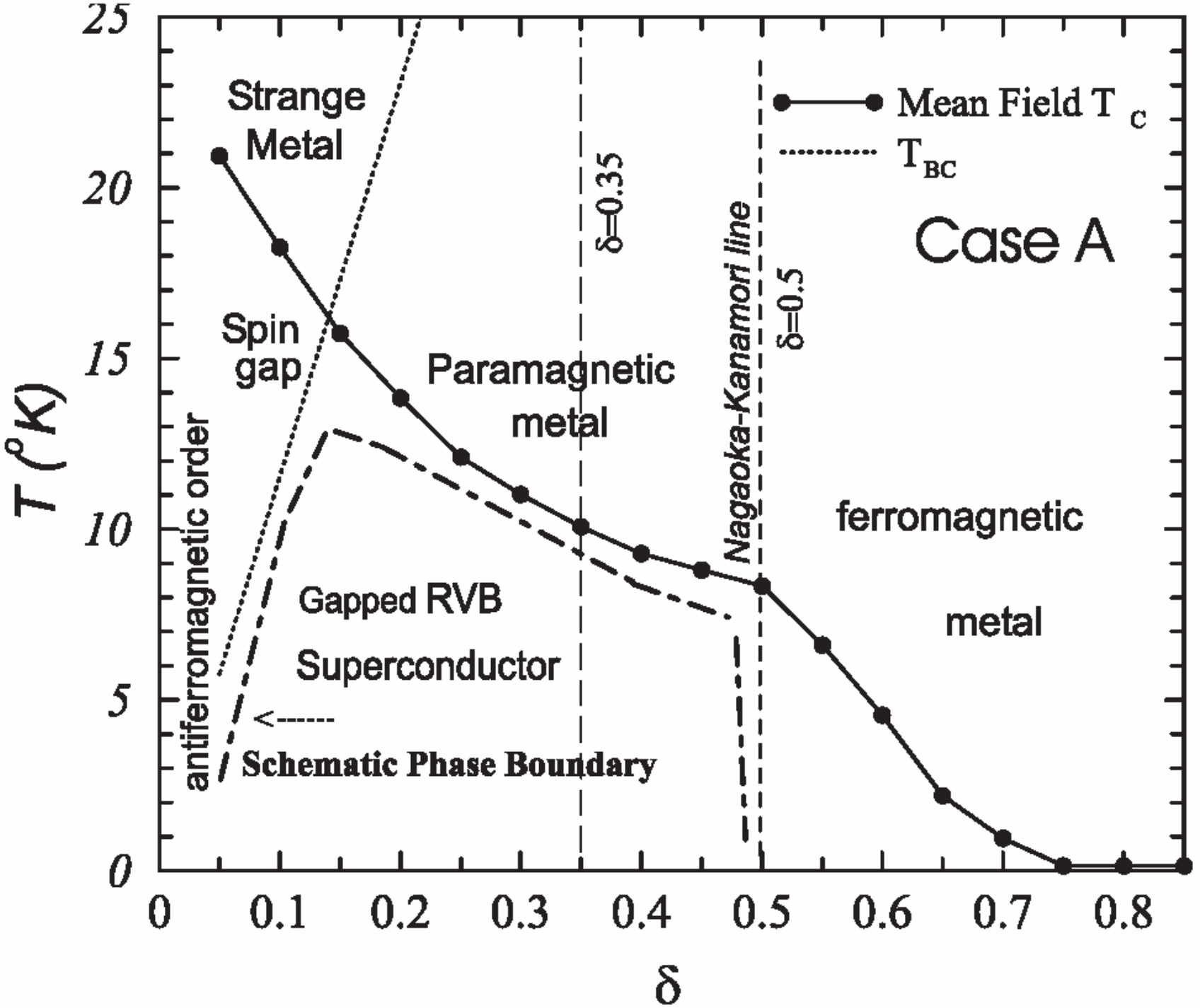
$$\Delta = \frac{1}{6\mathrm{J}L}\sum_{\mathbf{k}}\frac{\partial \mathrm{E}(\mathbf{k})}{\partial\Delta}\tanh(\frac{\beta \mathrm{E}(\mathbf{k})}{2})$$

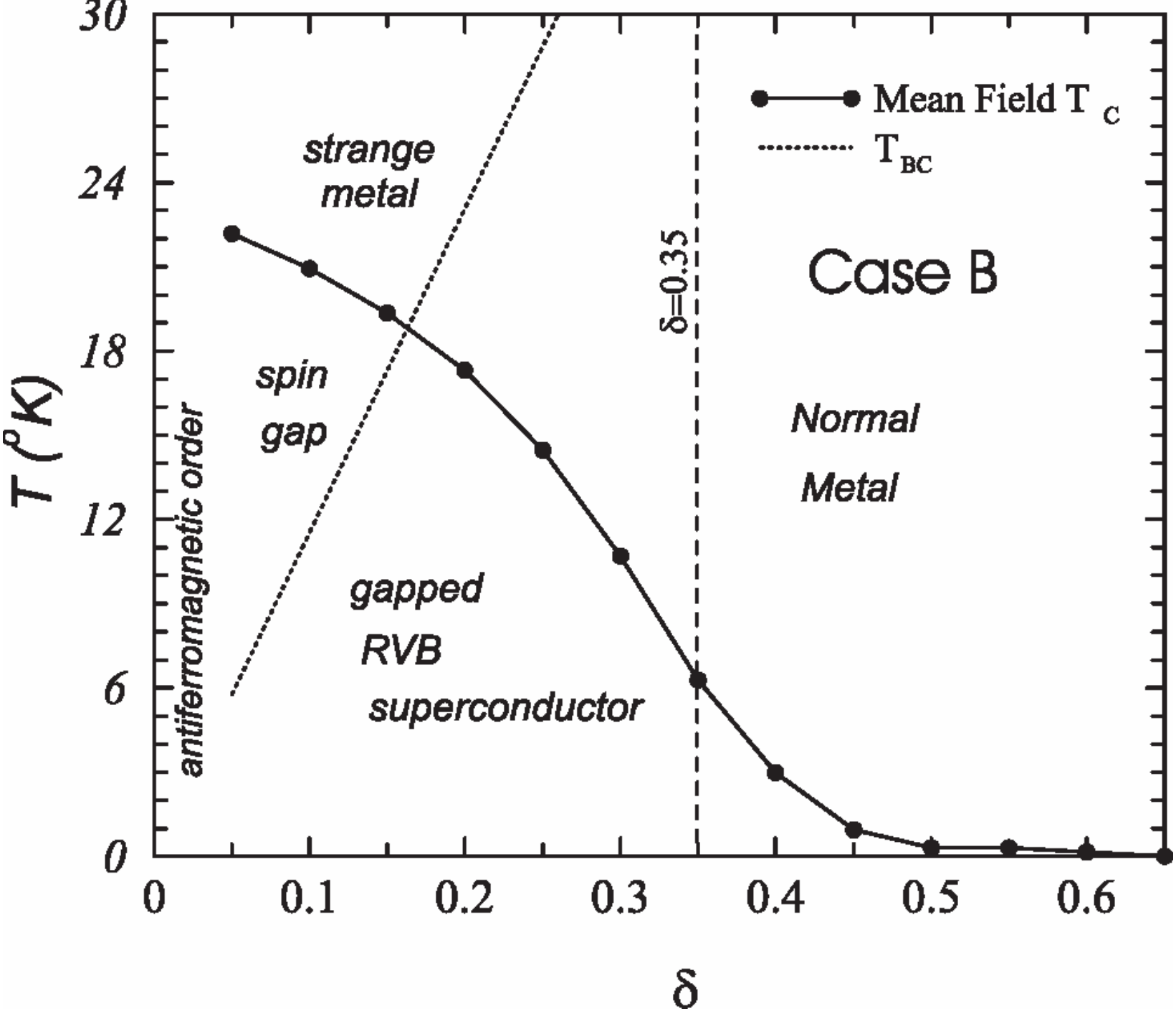
$$\delta = -\frac{1}{L}\sum_{\mathbf{k}}\frac{\partial \mathrm{E}(\mathbf{k})}{\partial\mu}\tanh(\frac{\beta \mathrm{E}(\mathbf{k})}{2})$$

$$\mathrm{E}(\mathbf{k}) = \sqrt{(\epsilon(\mathbf{k}) - \mu)^2 + 2\mathrm{J}^2\Delta^2|D(\mathbf{k})|^2}$$

$$\delta = \tfrac{1}{L}\Sigma_{\mathbf{k}}\,1/(e^{\beta_{BC}(\epsilon(\mathbf{k})-\epsilon_{min})} - 1).$$

$$T_{BC} \approx \frac{\delta}{\rho^*}\frac{1}{2 + \log(4\gamma/\pi)}$$


Strange
Metal
Spin
gap
Paramagnetic
metal
antiferromagnetic order
Gapped RVB
Superconductor
Schematic Phase Boundary
δ=0.35
Nagaoka-Kanamori line
δ=0.5
ferromagnetic
metal
Mean Field T c
T BC
Case A
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

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

Biggest 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.

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Spin Liquid State in an Organic Mott Insulator with a Triangular Lattice

Y. Shimizu,[1,2] K. Miyagawa,[2] K. Kanoda,[2,3] M. Maesato,[1] and G. Saito[1]

1H NMR and static susceptibility measurements have been performed in an organic Mott insulator with a nearly isotropic triangular lattice, -BEDT-TTF2Cu2CN3, which is a model system of frustrated quantum spins. The static susceptibility is described by the spin S 1=2 antiferromagnetic triangular-lattice Heisenberg model with the exchange constant J 250 K. Regardless of the large magnetic interactions, the 1H NMR spectra show no indication of long-range magnetic ordering down to 32 mK, which is 4 orders of magnitude smaller than J. These results suggest that a quantum spin liquid state is realized in the close proximity of the superconducting state appearing under pressure.