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ICTP 40th Anniversary

SMR.1572 - 7

Workshop on
Novel States and Phase Transitions in Highly Correlated Matter

12 - 23 July 2004

Electrons on a triangular lattice in Na-doped cobalt oxide

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Electrons on a triangular lattice in Na-doped Cobalt Oxide

**Yayu Wang, Maw Lin Foo, Lu Li, Nyrissa Rogado,
S. Watauchi, R. J. Cava, N.P.O.
Princeton University**

1. Frustration on triangular lattice
2. Large thermopower in Na_xCoO_2
3. Superconductivity
4. ARPES
5. Hall effect
6. Phase diagram

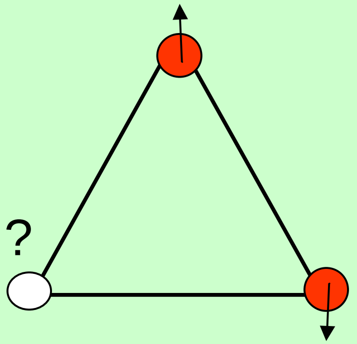
Supported by NSF, ONR

ICTP 2004

Geometrical Frustration on triangular lattice

$$H = -J \sum_{(i,j)} S_i S_j$$

Antiferromagnetic Ising model



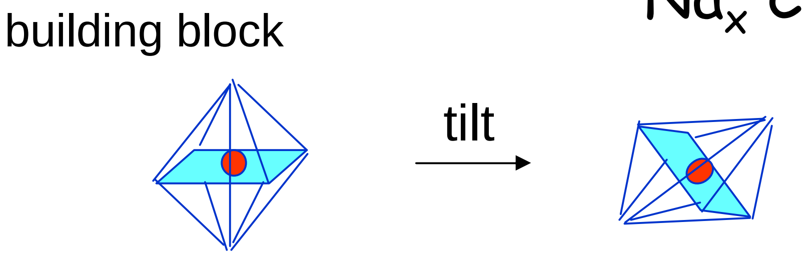
Impossible to have
AF alignment
on all 3 bonds

Ground state is disordered and highly degenerate

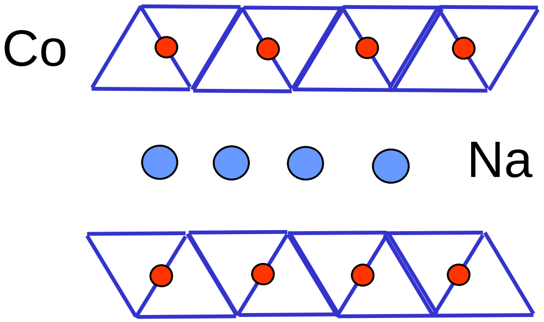
Resonating valence bond model(s) 1971, 1987
Spin Ice in pyrochlores 1998
Frustrated magnetic states in spinels 1999

$Na_x CoO_2$

Terasaki, Uchinokura 1997

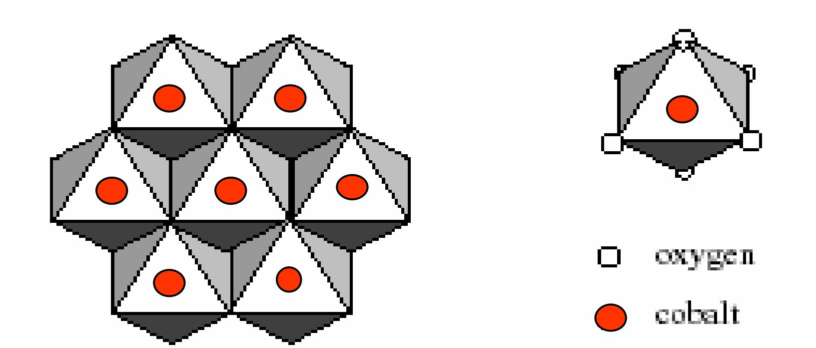


Octahedra tilted to
form a layer



Na ions (dopants) sandwiched btw
layers of tilted CoO_2 octahedra

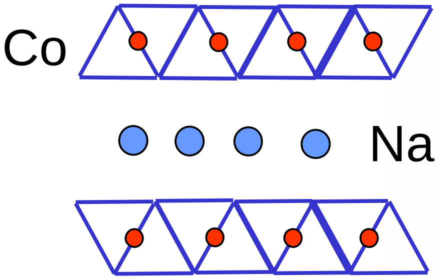
Co ions define a triangular lattice

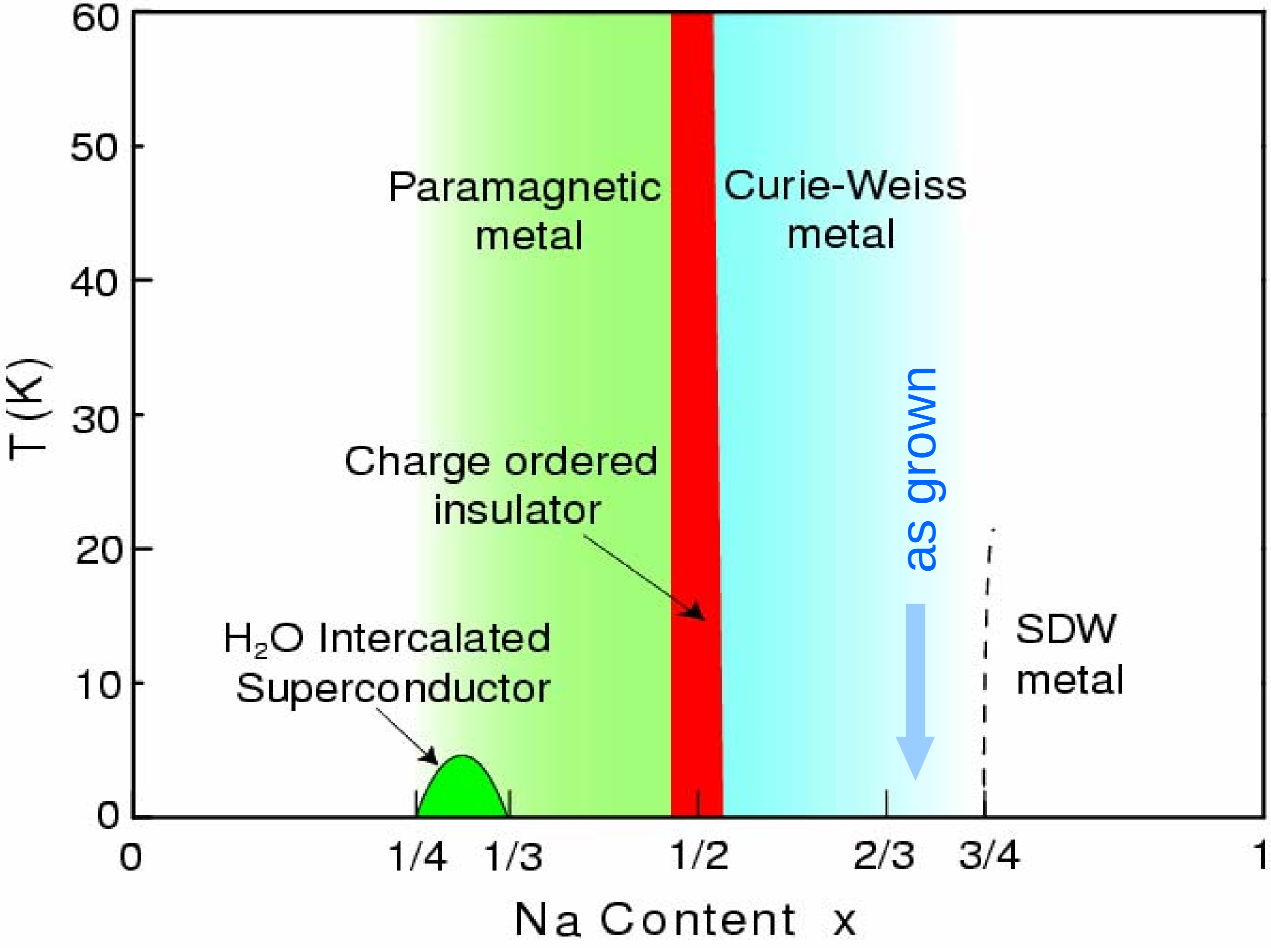


Na_xCoO_2

Multiple electronic phases vs. Na content

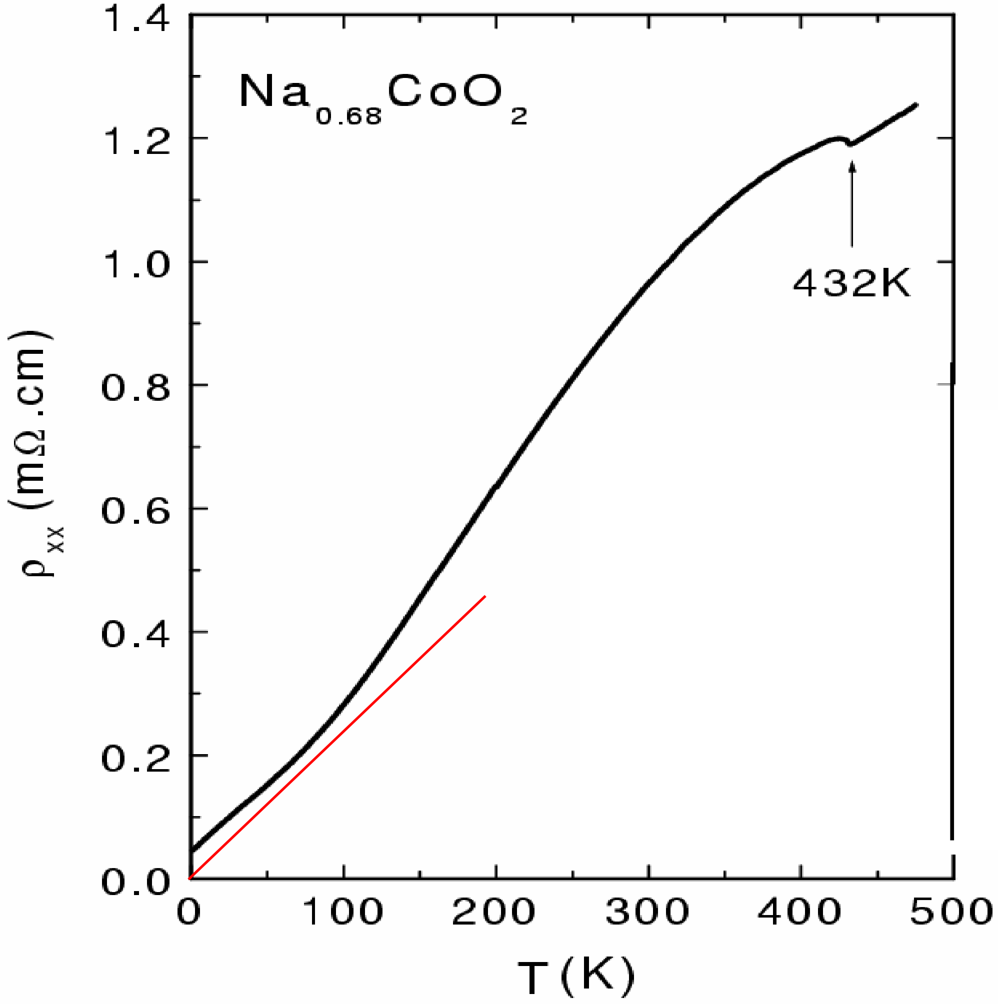
Foo et al.
PRL ‘04



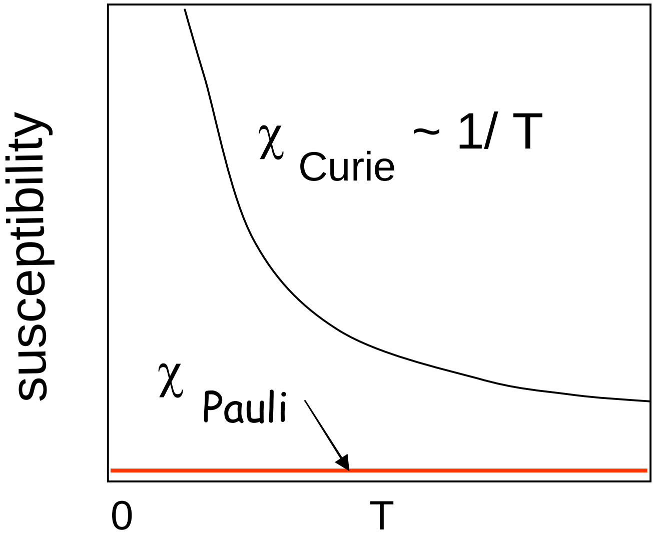


Resistivity of Na_xCoO_2 (x ~ 0.71)

Terasaki *et al.*, PRB 1997
Wang *et al*. Nature ‘03

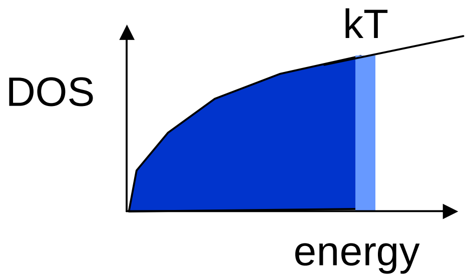


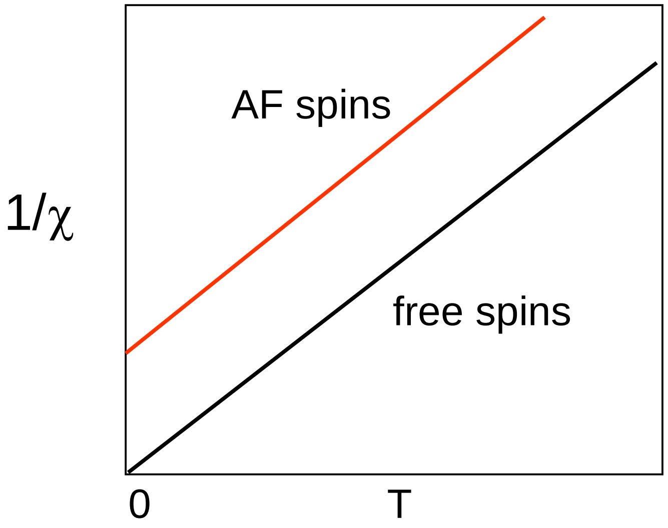
Susceptibility of insulators vs metals



Susceptibility
$\chi = dM/dH$

In metals, χ small and indept of T



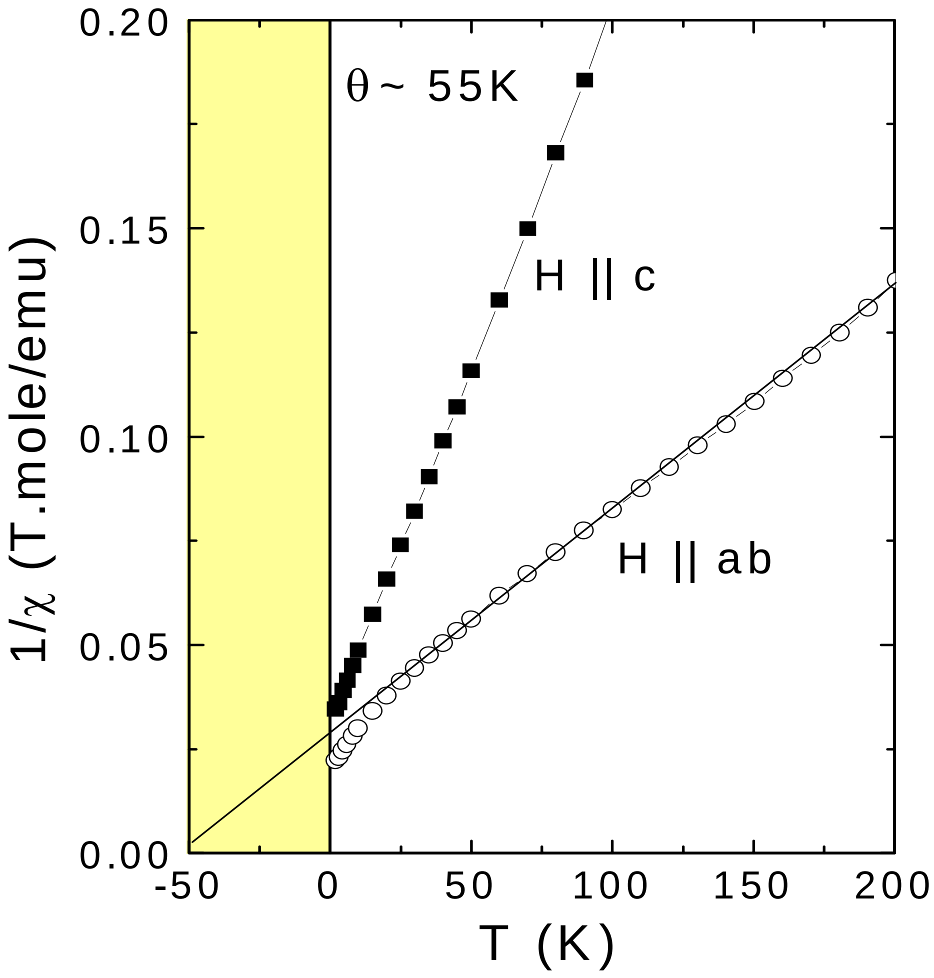


In Antiferromagnets

$\chi = C/(T + \theta)$

$\theta = T_N$(Neel temp)

Susceptibility χ has Curie-Weiss form

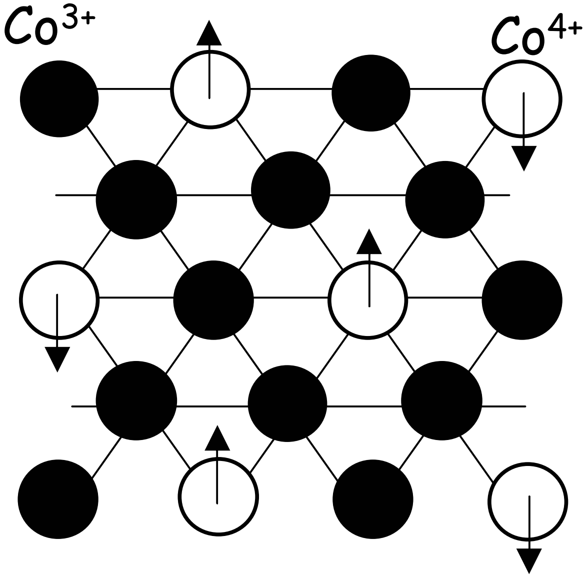


- AF Neel temperature

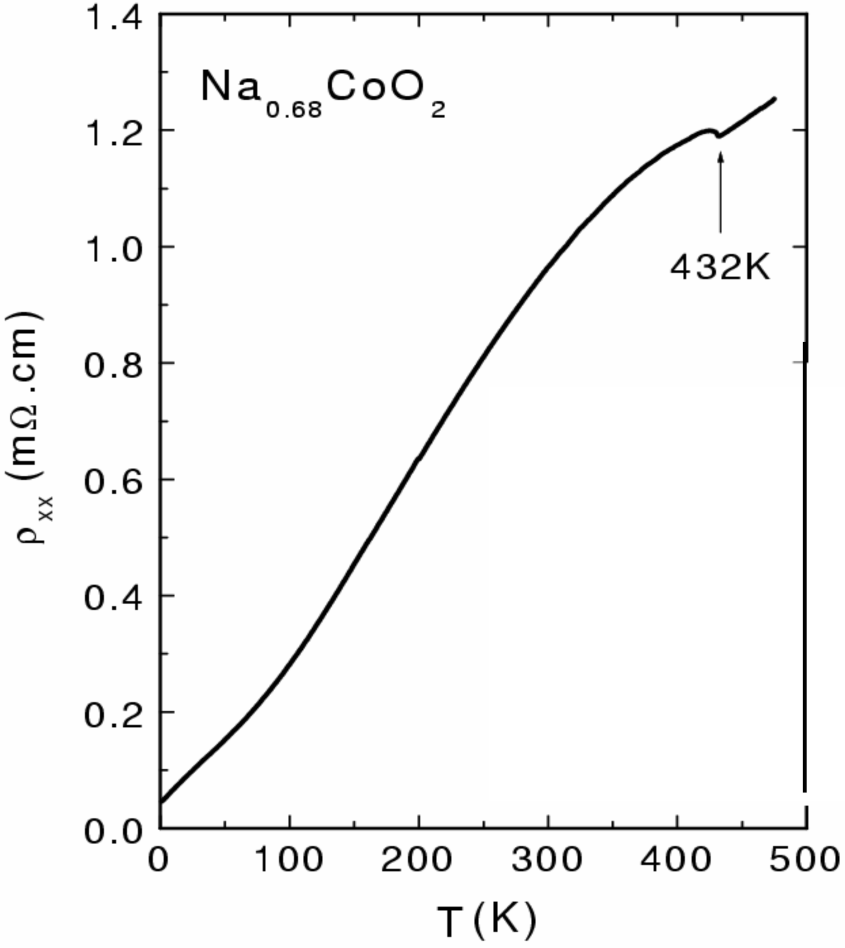
  $T_N \sim$ 60-100 K
- Magnitude of χ implies

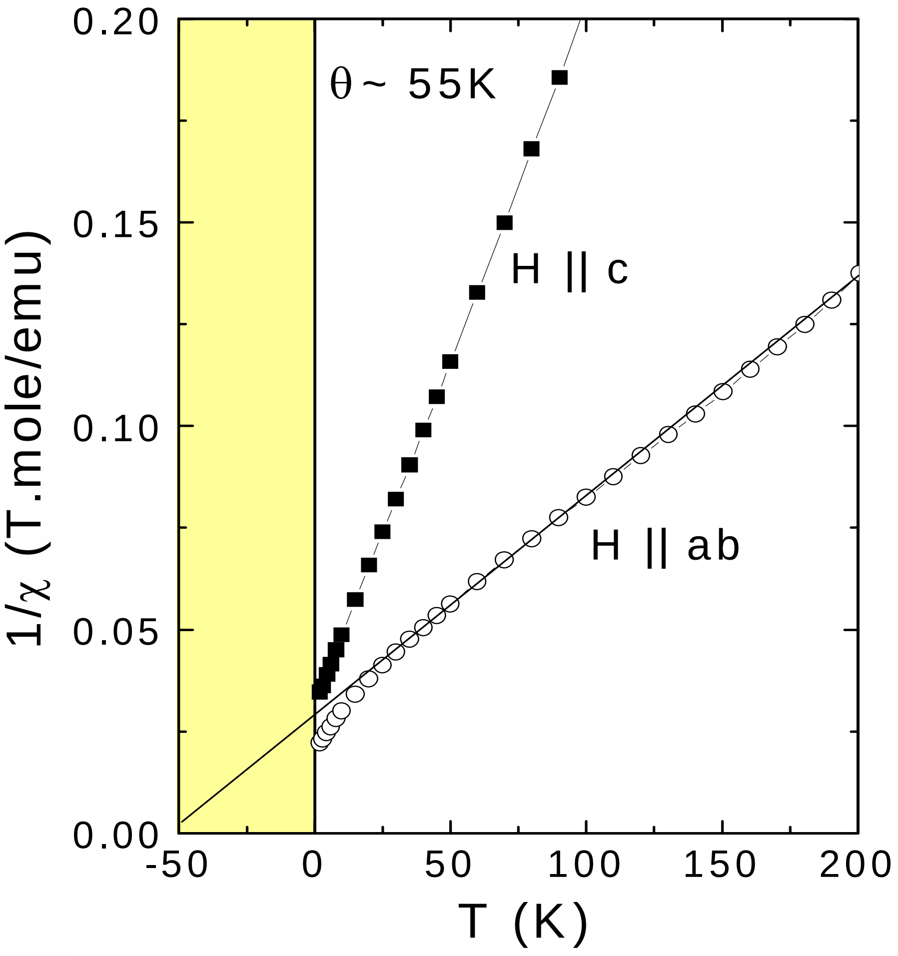
  Co^{4+} ions spin S = ½

  Co^{3+} is diamagnetic (S = 0),

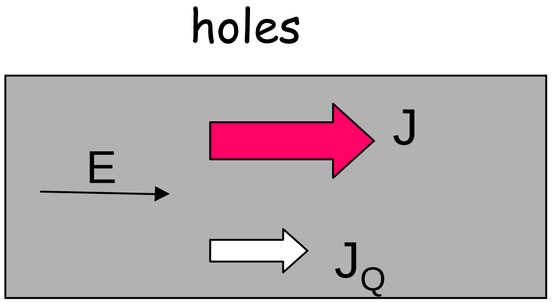


Metallic resistivity but antiferromagnetic in spin response
(Curie-Weiss Metal)





Thermopower and Peltier coef.



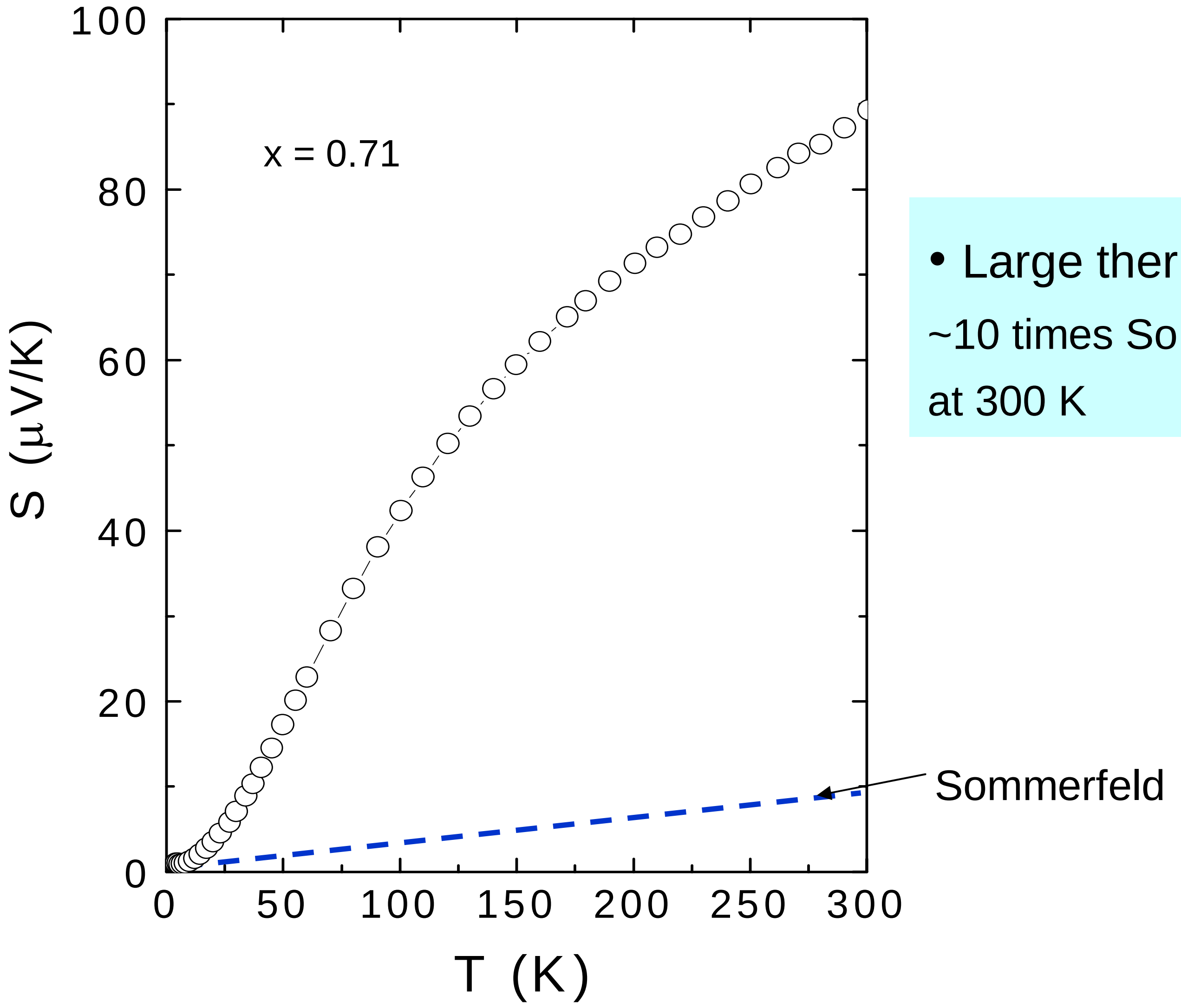
Heat current density J_Q
accompanies charge current density J

Ratio of currents $J_Q/J = \Pi$ (Peltier coeff)

$$S = \Pi / T = J_Q / JT$$

Large thermopower S of Na_xCoO_2

Terasaki *et al* Phys. Rev. B (1997)



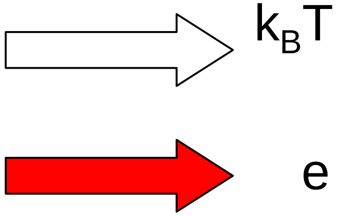
- Large thermopower

~10 times Sommerfeld value

at 300 K

Thermopower

Classical gas



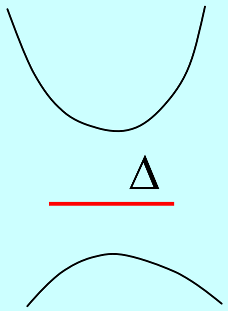
$J = nev$
$J_Q = n\,k_BT\,v$

Peltier coef.
$\Pi = J_Q/J = k_BT/e$

Seebeck coef.
$S = \Pi / T = k_B/e$

Natural unit of S
$k_B/e = 86\ \mu V/K$

Semiconductor

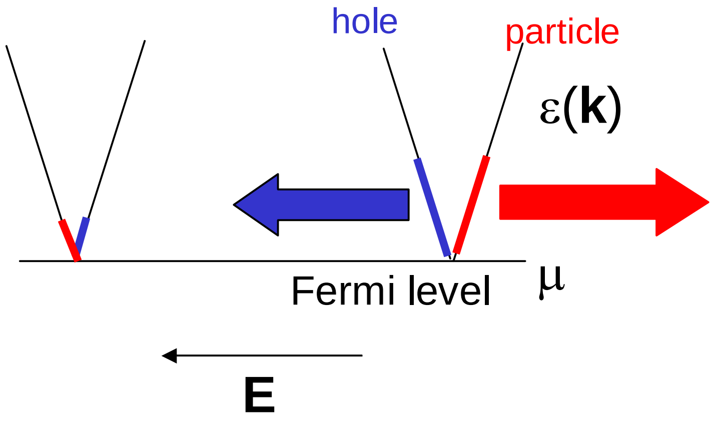


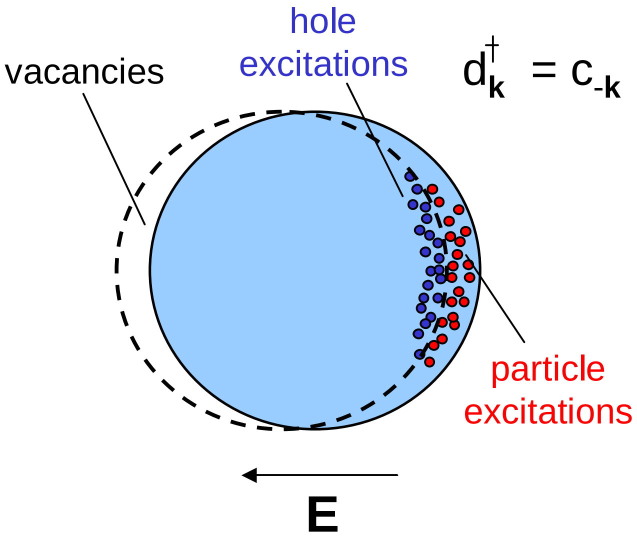
$J_Q = n\,v\,\Delta$

$S = (k_B/e)(\Delta/k_BT)$

Thermopower of conventional metals

“Excitation picture”





Fermi Gas in **E** field

Charge currents add
mass currents cancel

Heat currents cancel

$S = J_Q/JT$ strongly suppressed

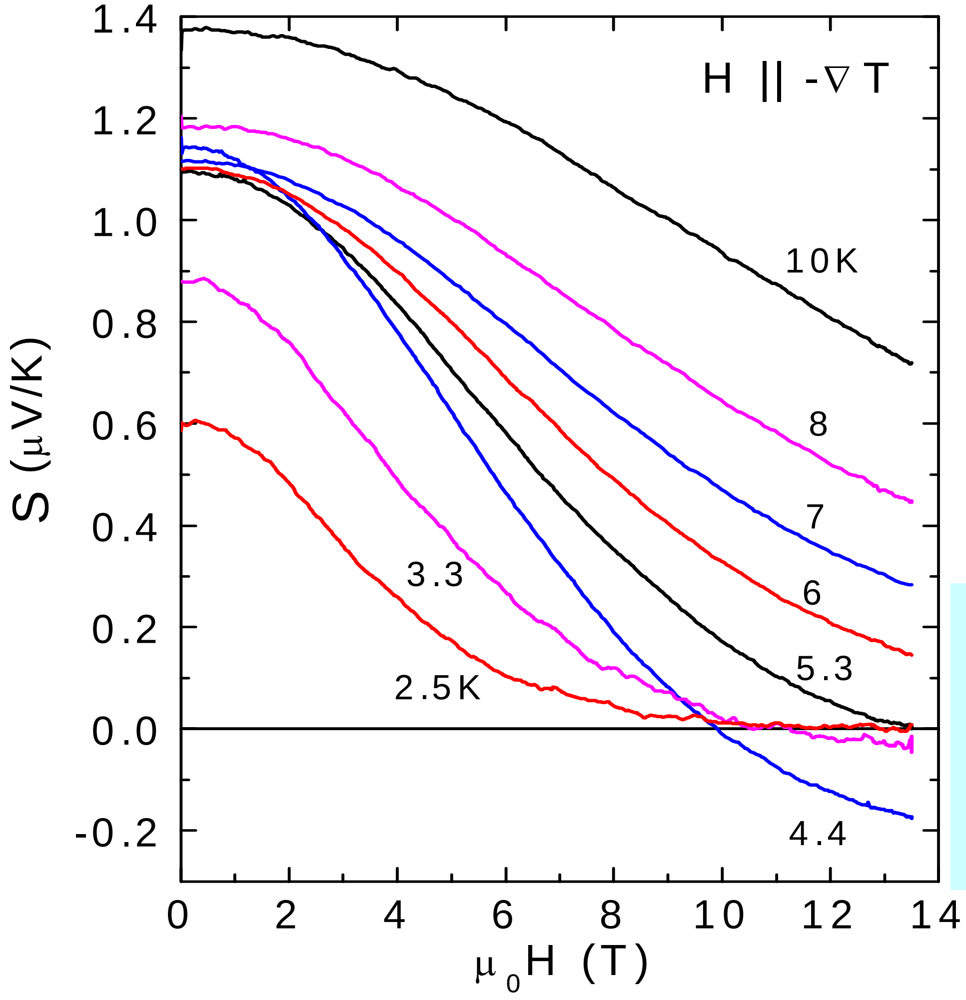
$S \sim (k_B/e)\,(T/T_F)$ $T_F \sim 50{,}000$ K

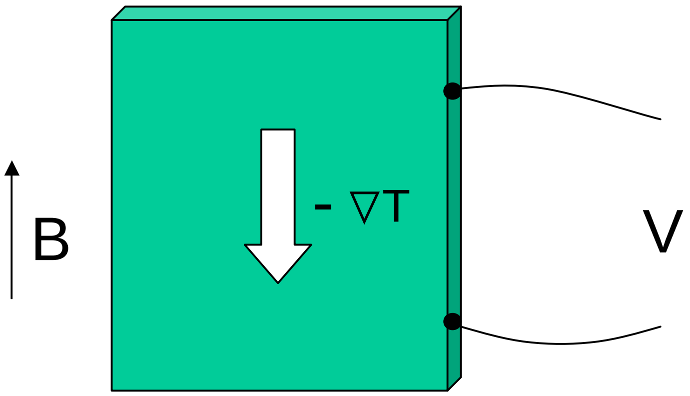
$\sim 86 \times 10^{-2}\ \mu V/K$

S virtually indepndnt of H

Field dependence of S in Na_xCoO_2

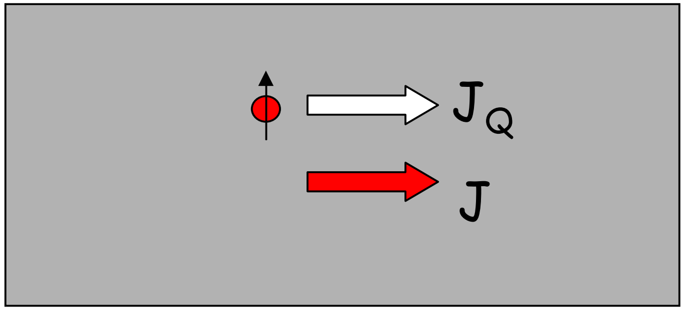
Wang et al. Nature '03





- In-plane field **H** || - ∇T
- Strong field suppression of Thermopower

Spin contribution to thermopower (Chaikin Beni, 1976)



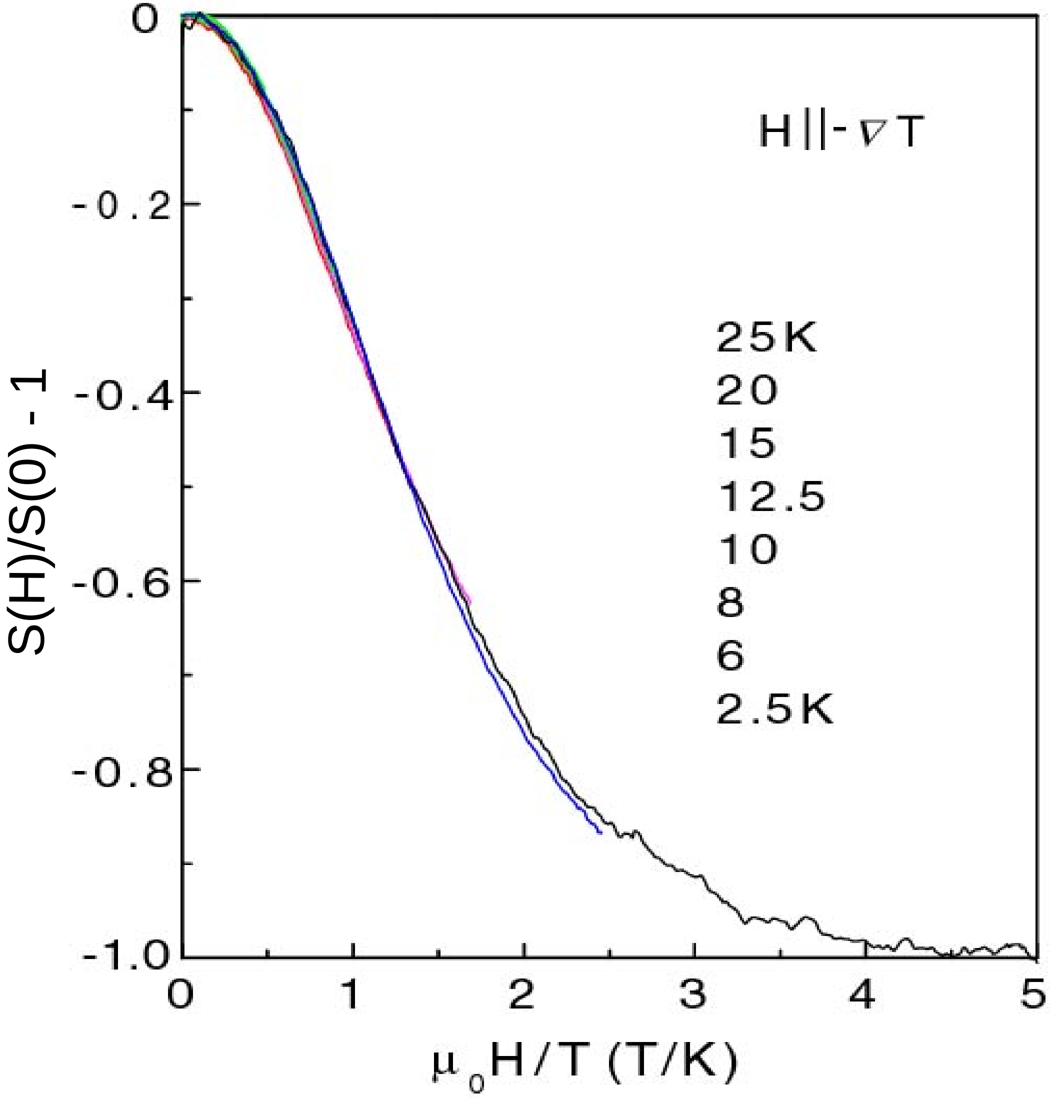
J = nev

Spin entropy per carrier = $k_B \log 2$

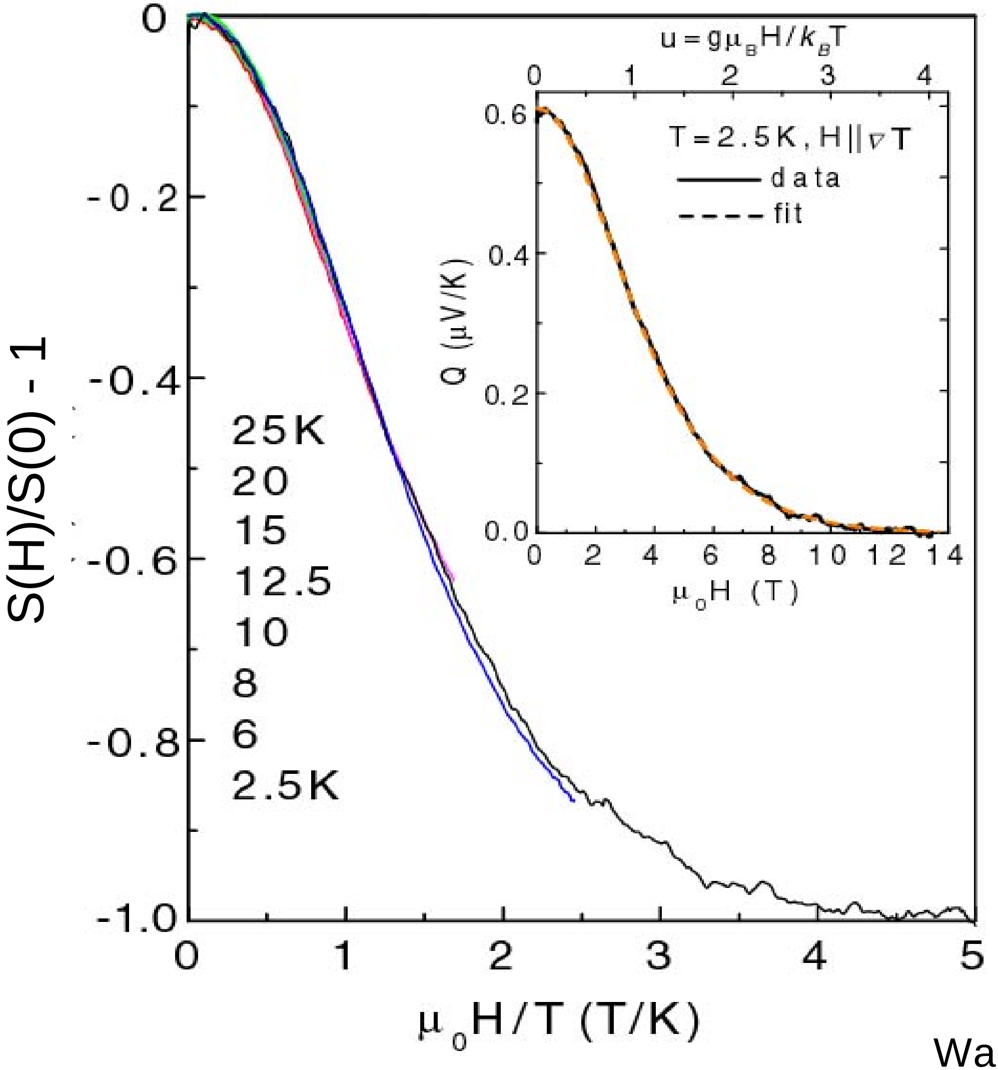
$J_Q = nv\, k_B T \log 2$

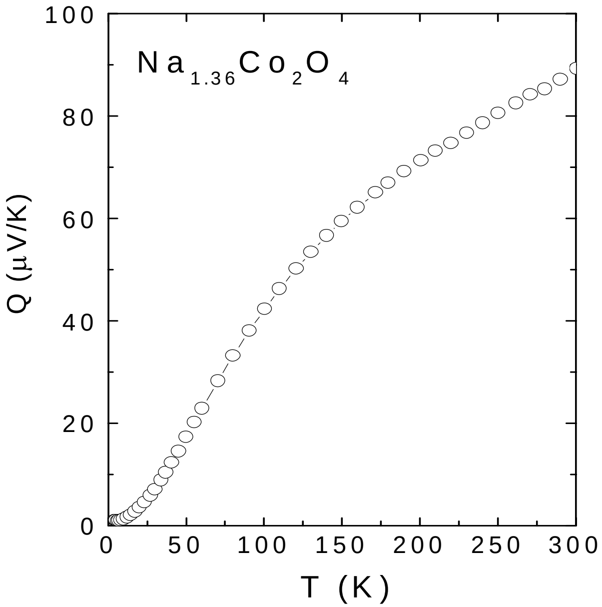
$S = J_Q/JT = (k_B/e) \log 2 \sim 60\ \mu V/K$

Not signif. in conv. metals



S(H,T) curve is a function of H/T only



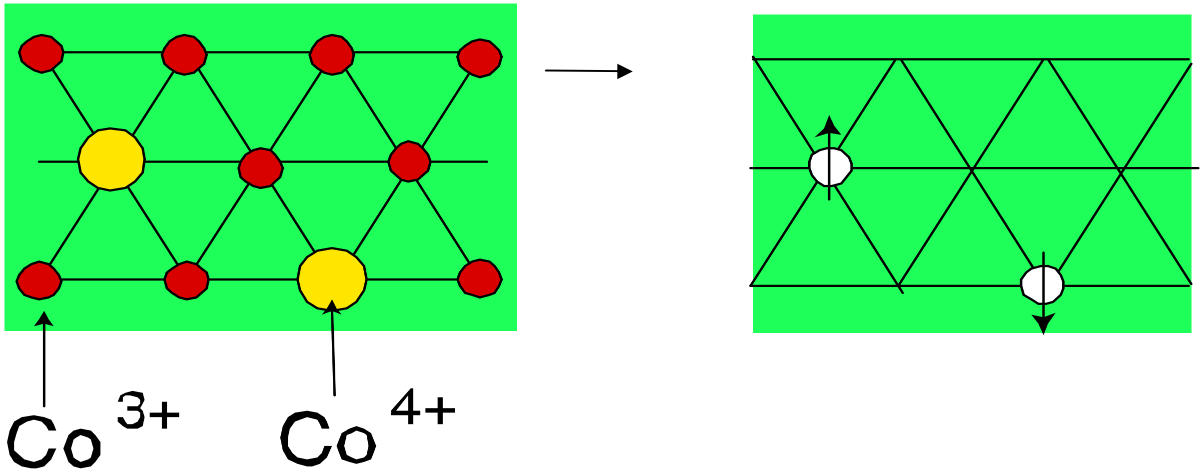


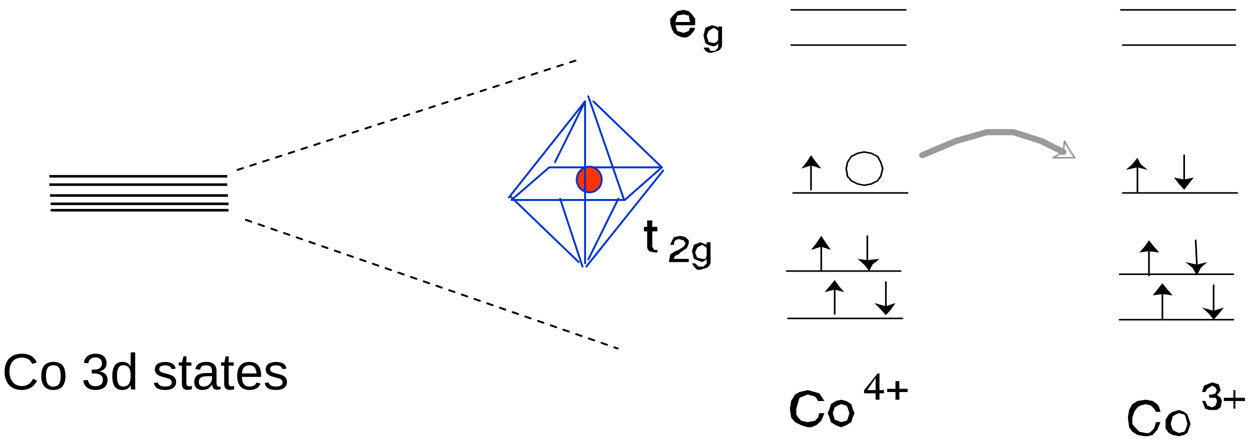
Conclusion:

1. Spin entropy is the source for enhanced thermopower
2. Key for new thermo-electric materials -- Spin

Wang et al. Nature ‘03

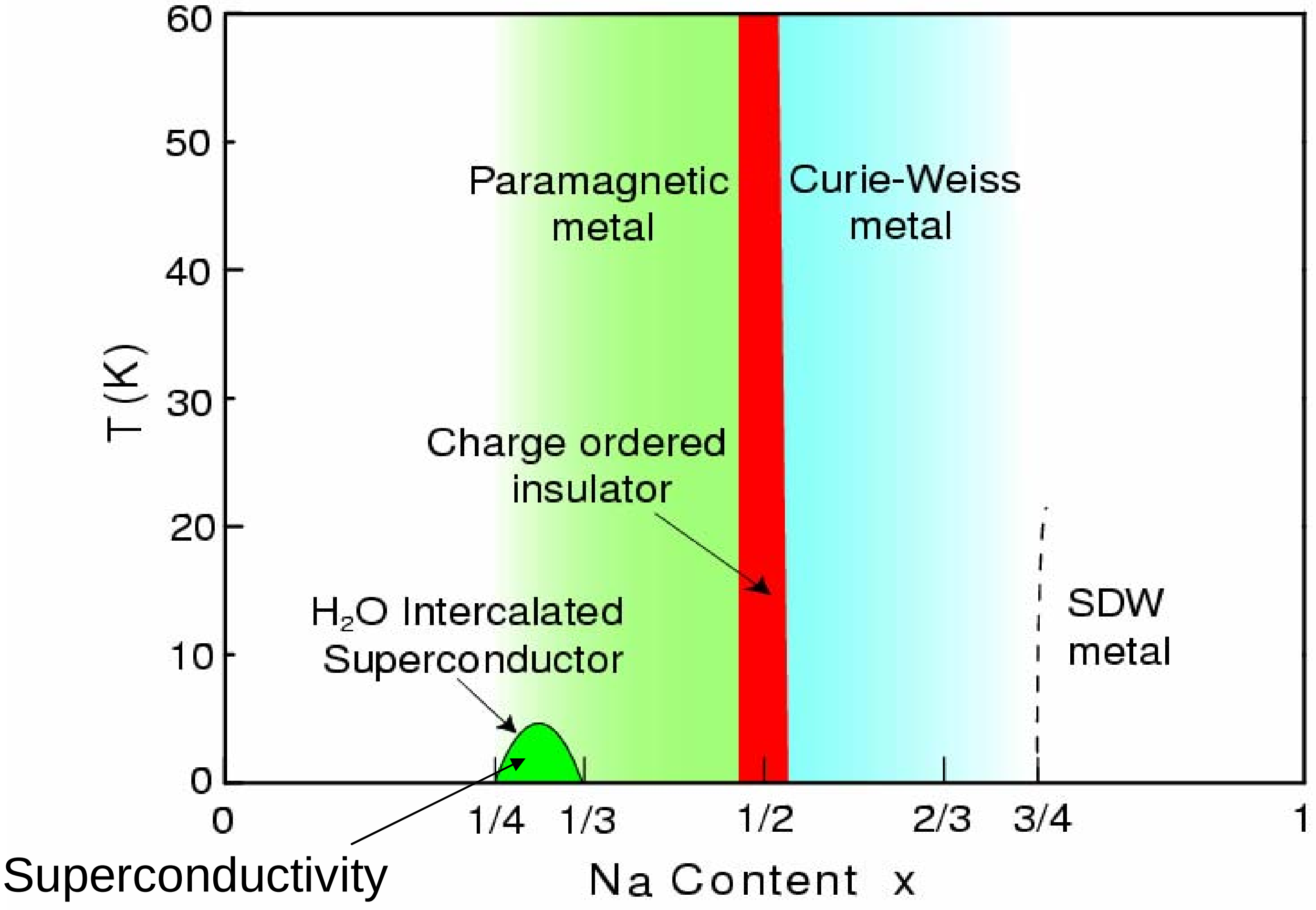
In Na_xCoO_2, hole density $n_h = 1-x$





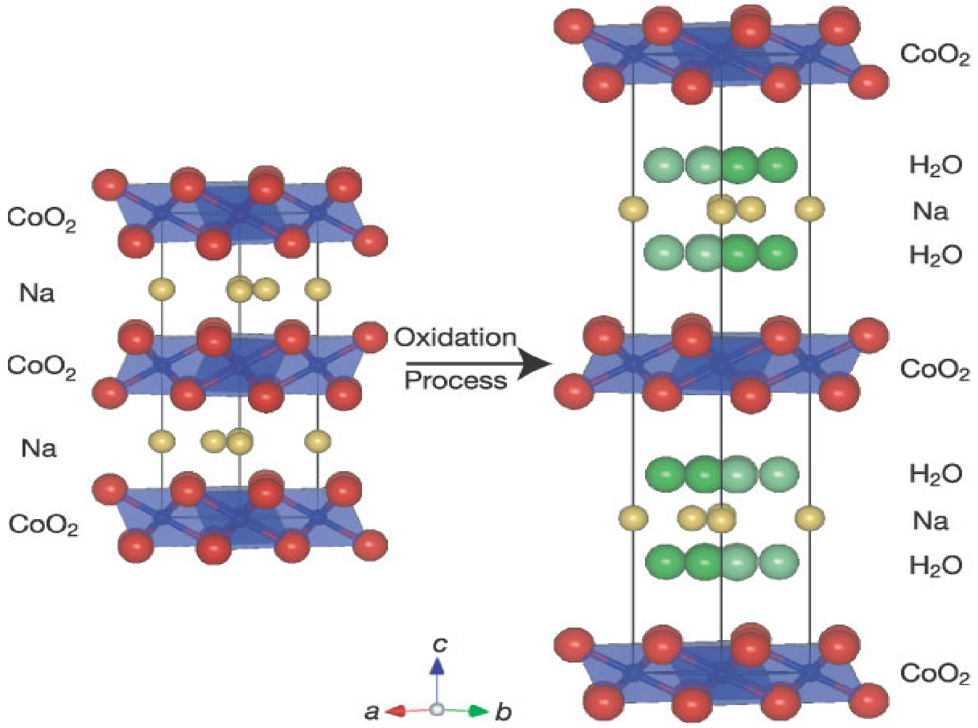
Na_xCoO_2
Multiple electronic phases vs. Na content

Foo et al.
PRL ‘04



Water intercalated superconductor

Takada et al., Nature (2003).



- pairing symmetry:
  s, p or d-wave?
- Why is water essential?
- What is pairing mechanism:
  e-ph or e-e or magnetic?

$Na_xCoO_2 \cdot y\,H_2O$, $x \sim 0.35$, $y \sim 1.30$

Superconductor with $T_c \sim 4.5K$

VOLUME 92, NUMBER 15 PHYSICAL REVIEW LETTERS week ending 16 APRIL 2004

Thermodynamic and Transport Measurements of Superconducting $Na_{0.3}CoO_2 \cdot 1.3H_2O$ Single Crystals Prepared by Electrochemical Deintercalation

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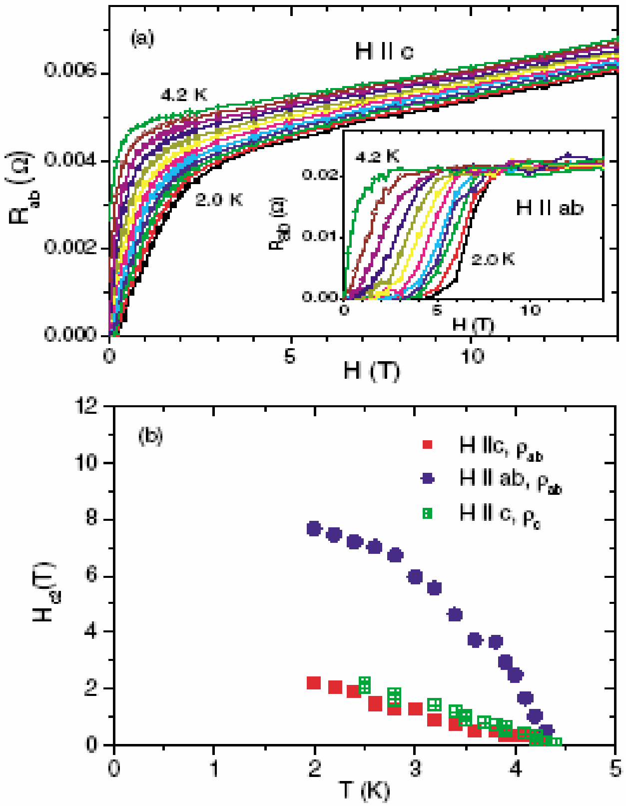
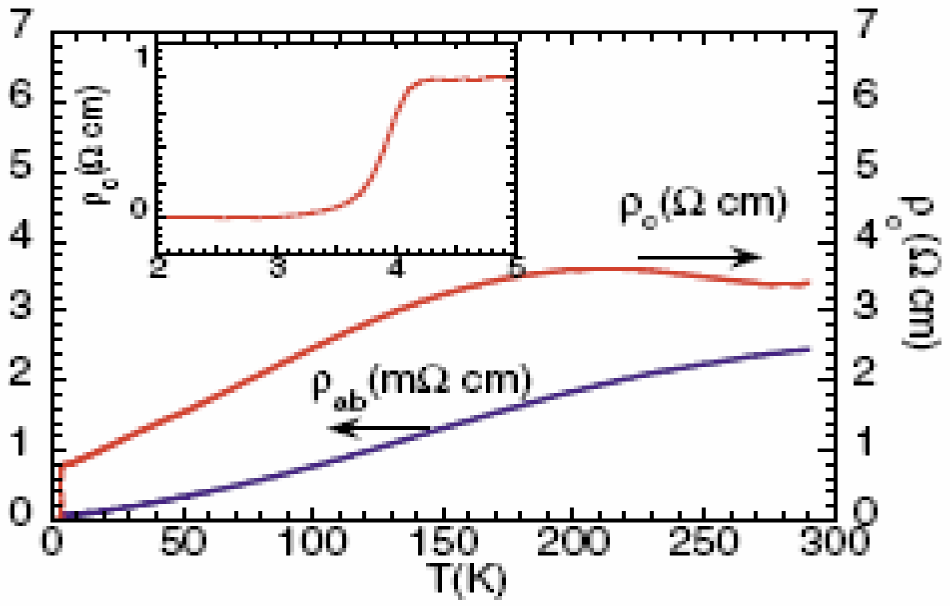
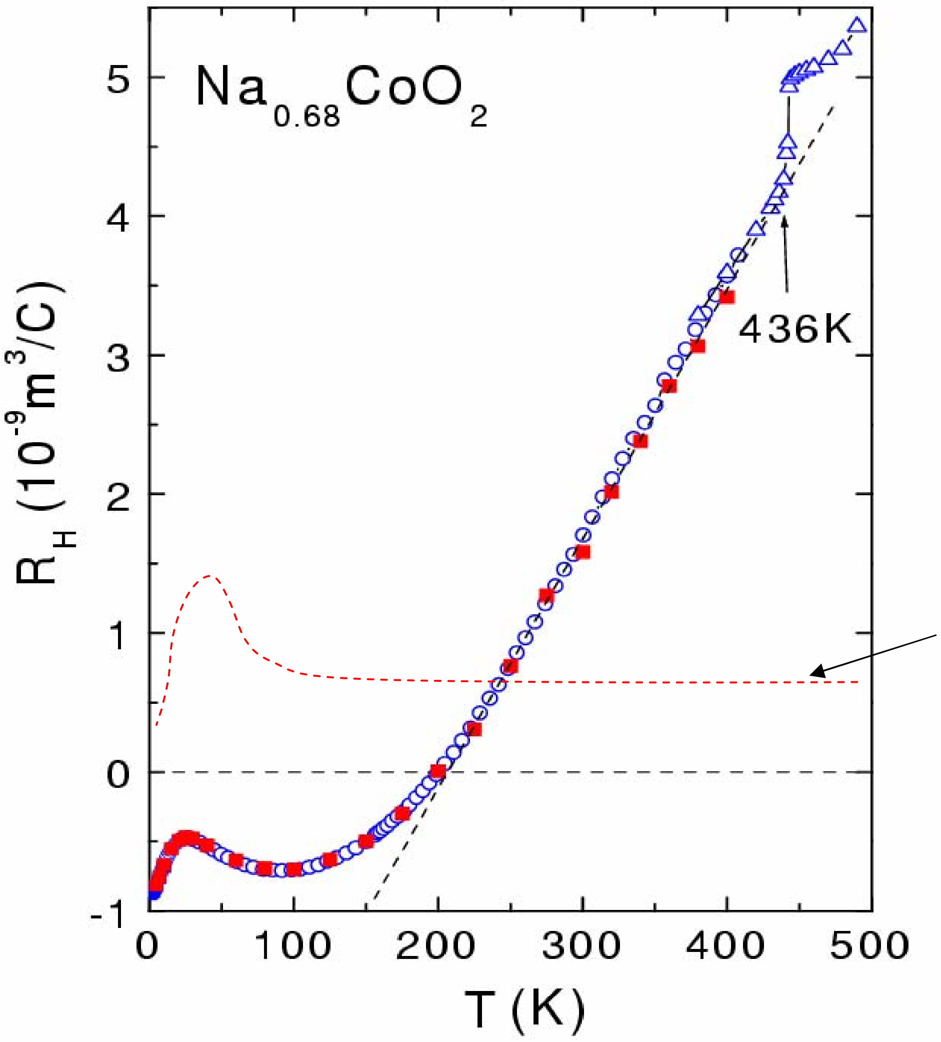




T-linear Hall coefficient

Yayu Wang, 03



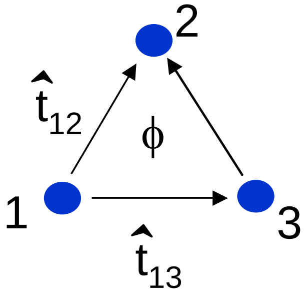
R_H conv. metal

Why is R_H *T*-linear?

Hopping Hall current in triangular lattice (Holstein, ‘61)

$$\sigma_H \sim \hat{t}_{12}\,\hat{t}_{23}\,\hat{t}_{31} \sim i\,t^3 \exp(i\alpha)$$

Peierls phase $\alpha = 2\pi\,\phi/\phi_0$



High-frequency R_H^* in *tJ* model (B.S. Shastry ‘93, ‘03)

$\sigma_H \sim i(\beta t)^3 \exp(i\alpha)$ $\qquad$ $\beta t \ll 1 \;\; (\beta = 1/T)$

$\sigma \sim (\beta t)^2$

$R^*_H \sim \sigma_H / H\sigma^2 \sim (\beta t)^{-1}$ $\qquad$ *T*-linear

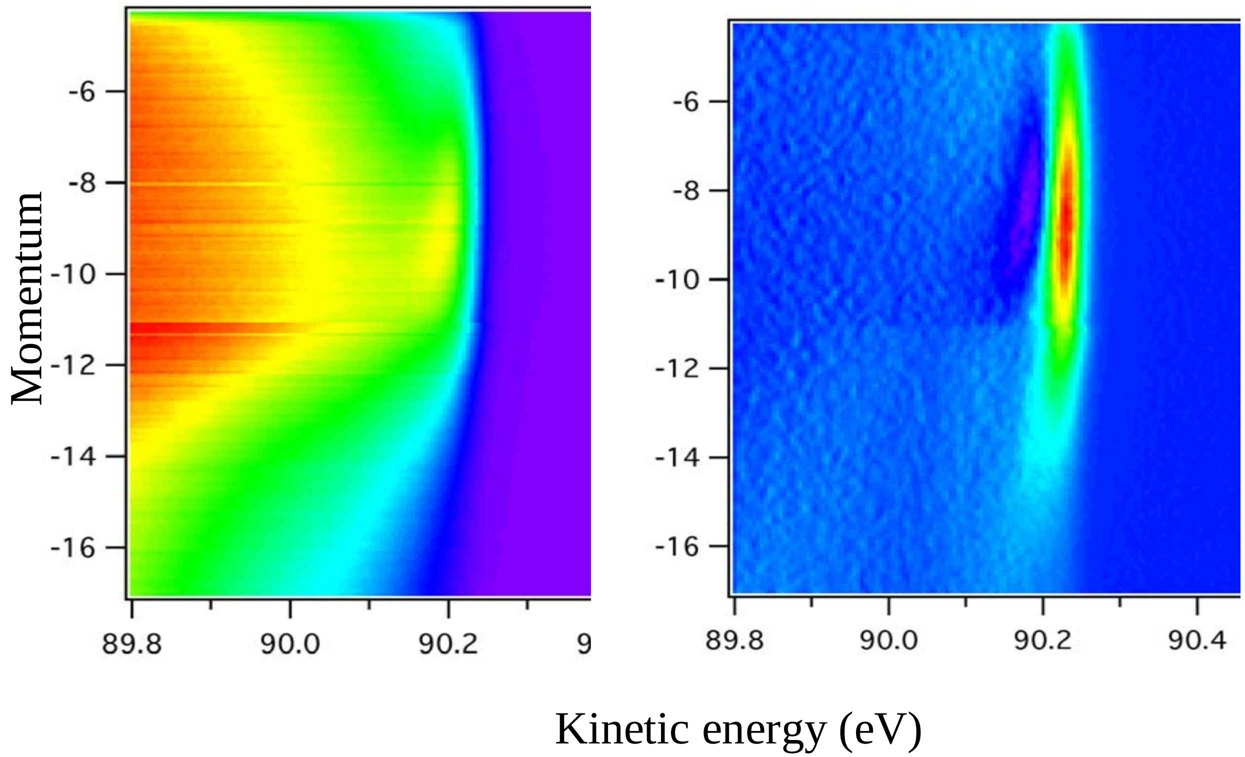
ARPES: Weak quasiparticle dispersion

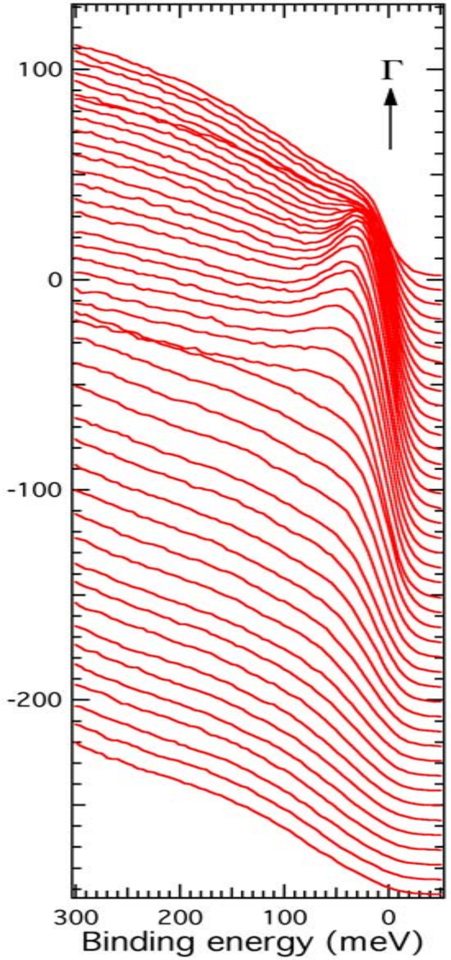
Z. Hasan et al. (PRL ‘04)

Single-particle hopping :

Small bandwidth → Low degeneracy T

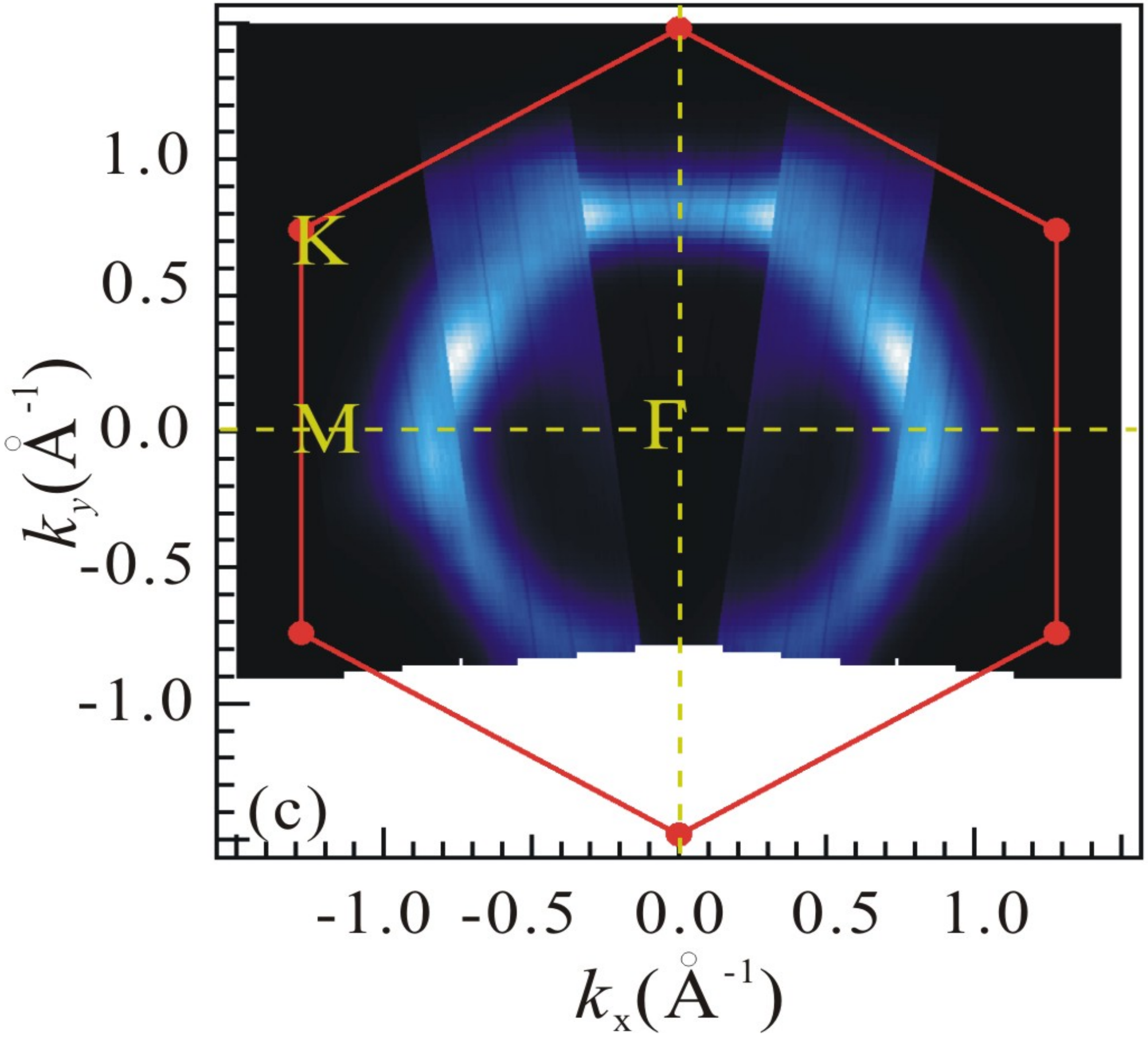
$t < 0$ and $|t| \sim 10$ meV (bandwidth < 100 meV)





Fermi Surface of $Na_{0.71}CoO_2$ measured by ARPES

Hasan et al.

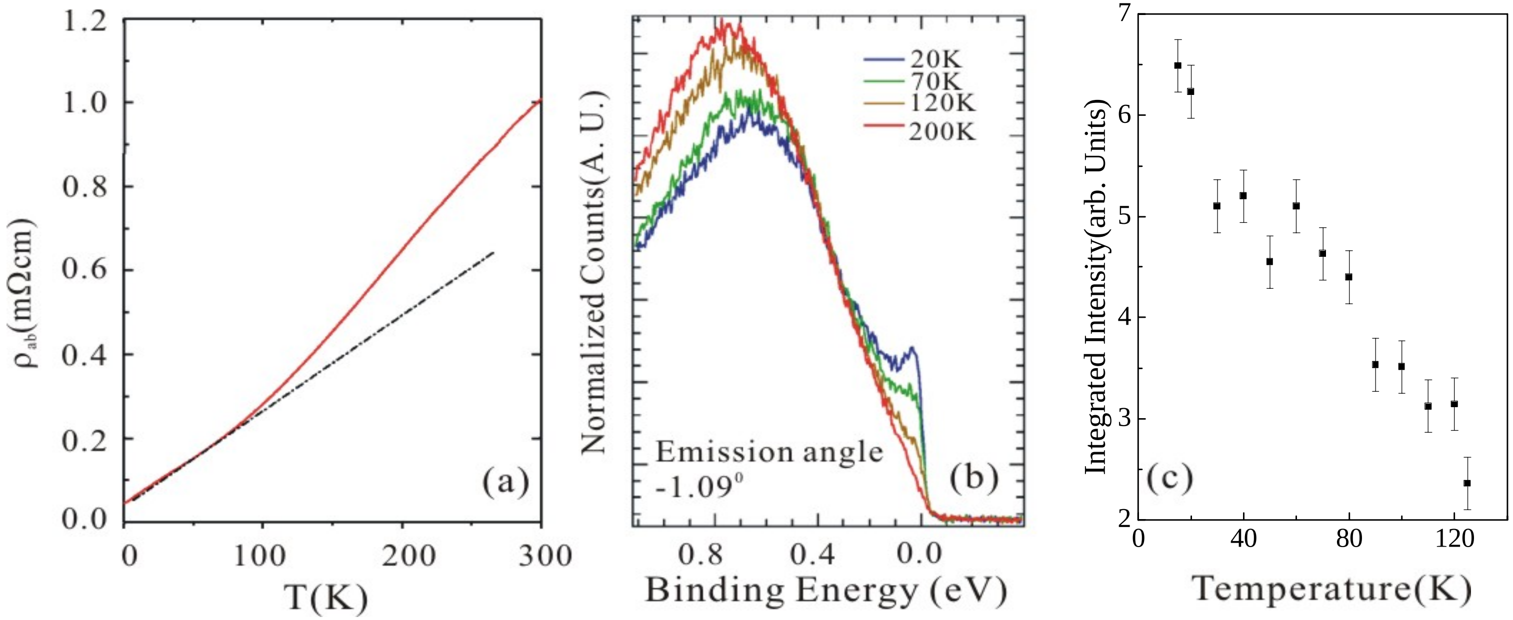


Large hole-like FS

Hopping integral
t ~ 10 meV

Fermi velocity < 0.4 eV.A

Behavior of quasi-particles versus temperature



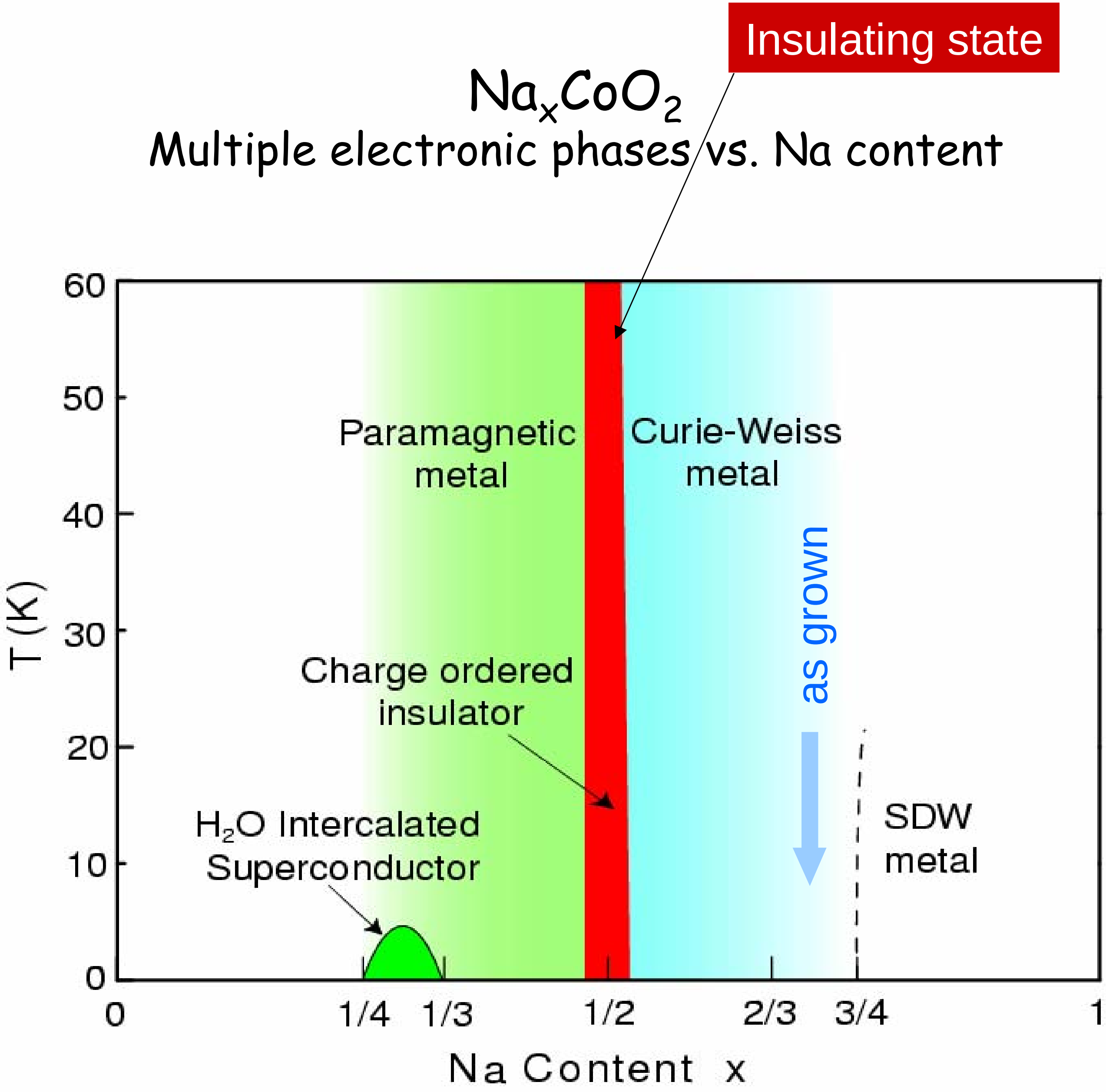
Resistivity is T-linear below 100K

ARPES Quasiparticles are coherent only below 150K

Na_xCoO_2

Multiple electronic phases vs. Na content

Foo et al.
PRL ‘04



Fine-tuning of Na content in Na_xCoO_2 single crystals

Foo et al., condmat/0312174 (2003), PRL ‘04

- Reduce the Na content by a series of chemical de-intercalation
- $x = 0.75$, as grown crystals of Floating zone or flux method

$x = 0.68$: $NaClO_3$ in water

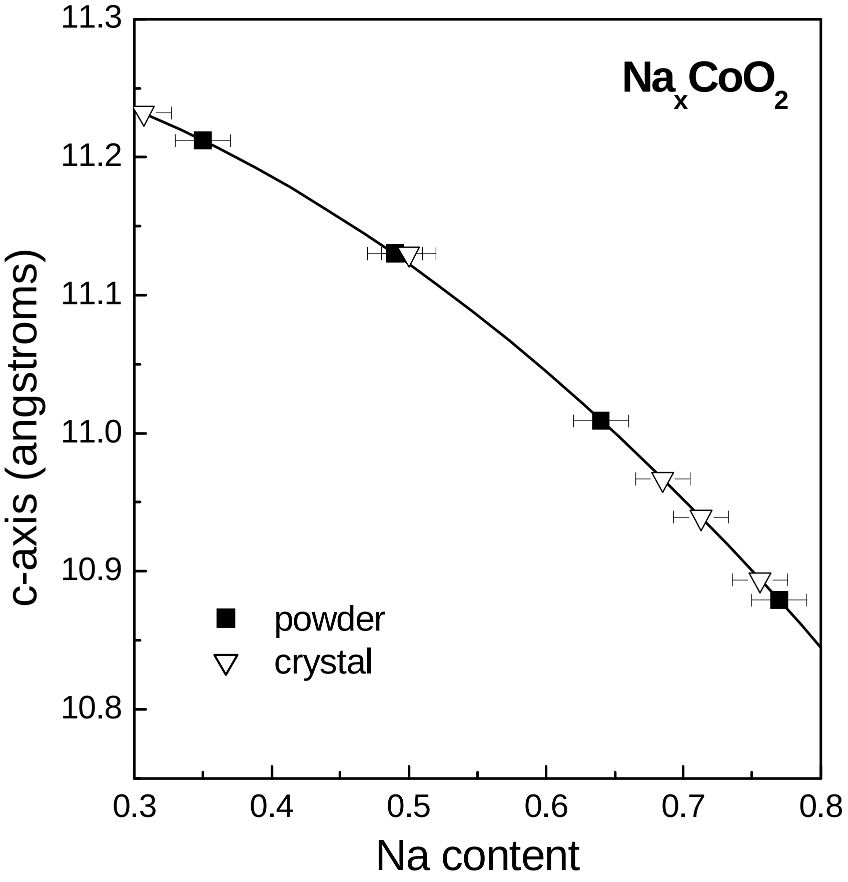
$x = 0.50$: I_2 in Acetonitrile

$x = 0.31$: Br_2 in Acetonitrile

Stronger oxidation agent

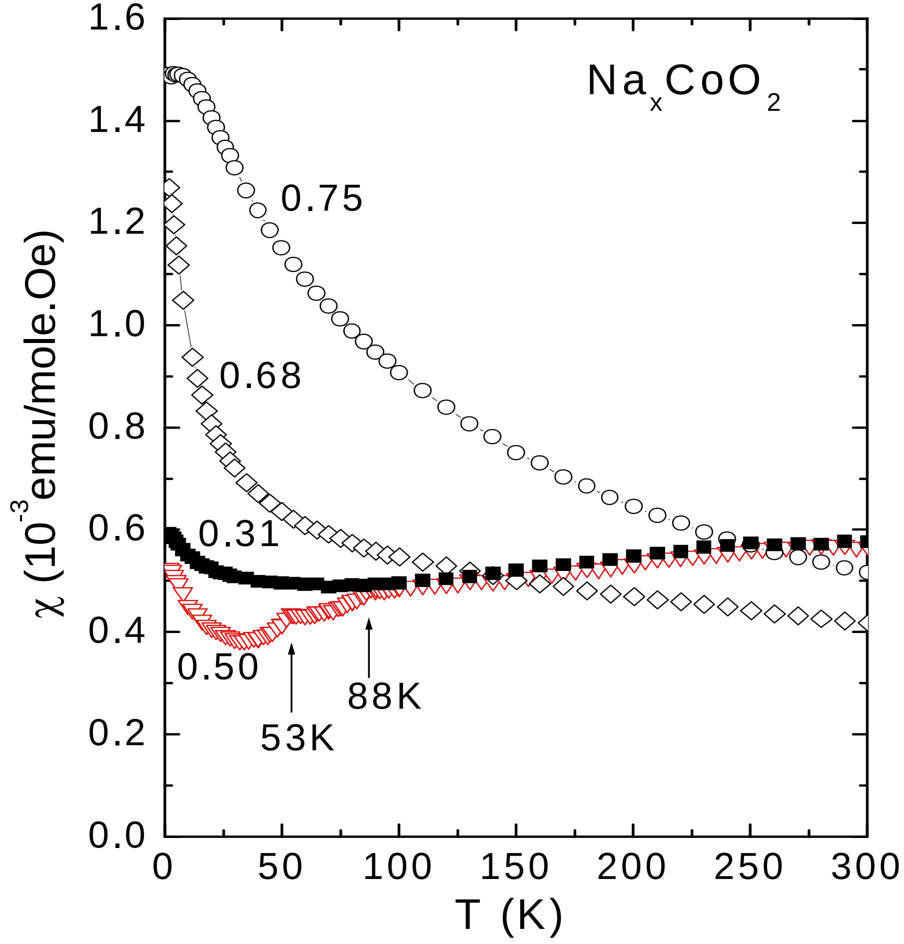
High-quality crystals with Na content $0.31 < x < 0.75$

Calibration of the Na content vs. c-axis lattice parameter



Calibration procedure

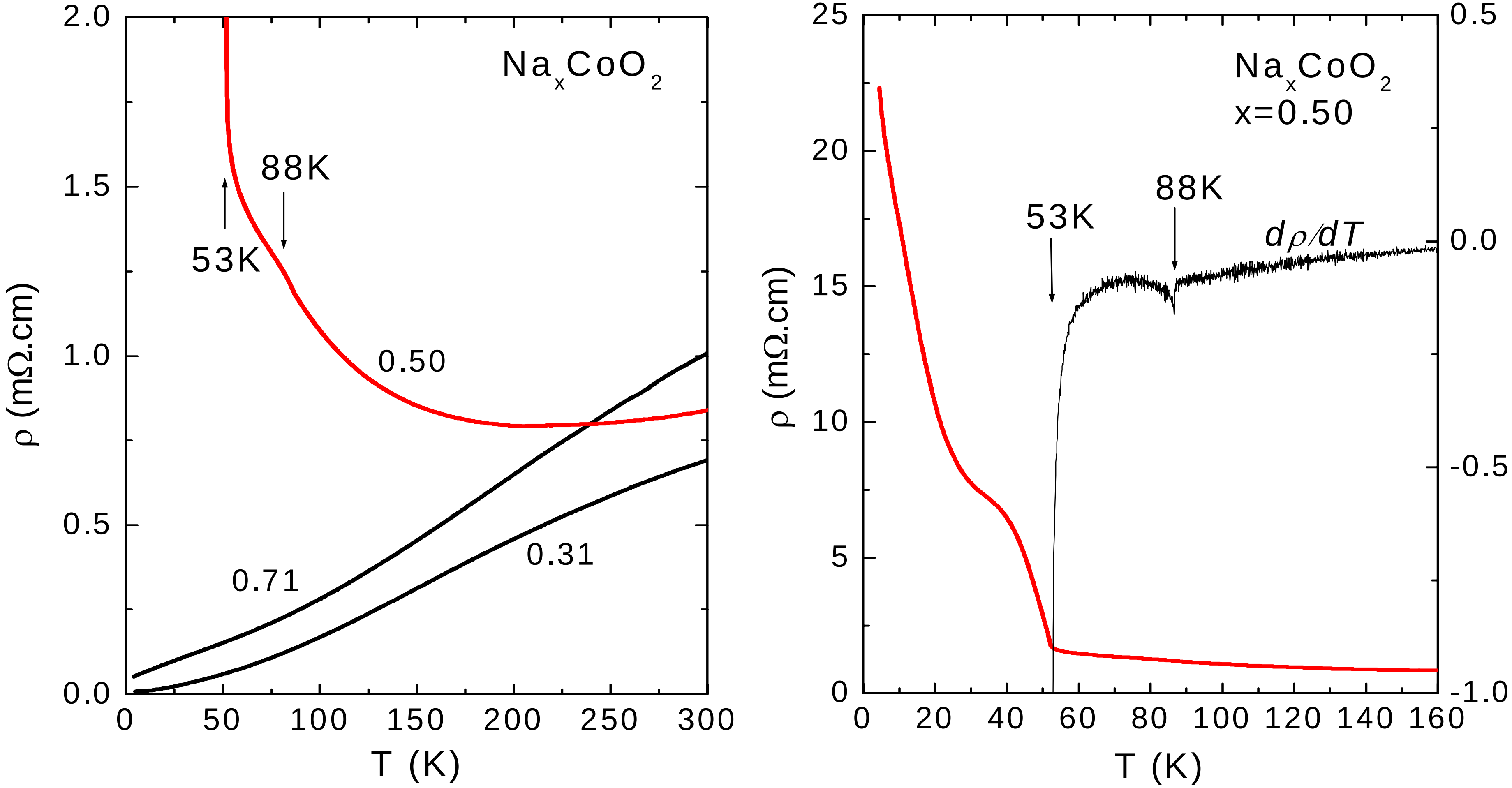
- treat powder and crystals under same conditions
- powder x-ray diffraction to get c-axis lattice constant
- ICP-AES to determine the Na contents of powders
- x vs. c-axis calibration curve
- from the c-axis of crystal, extract the Na content

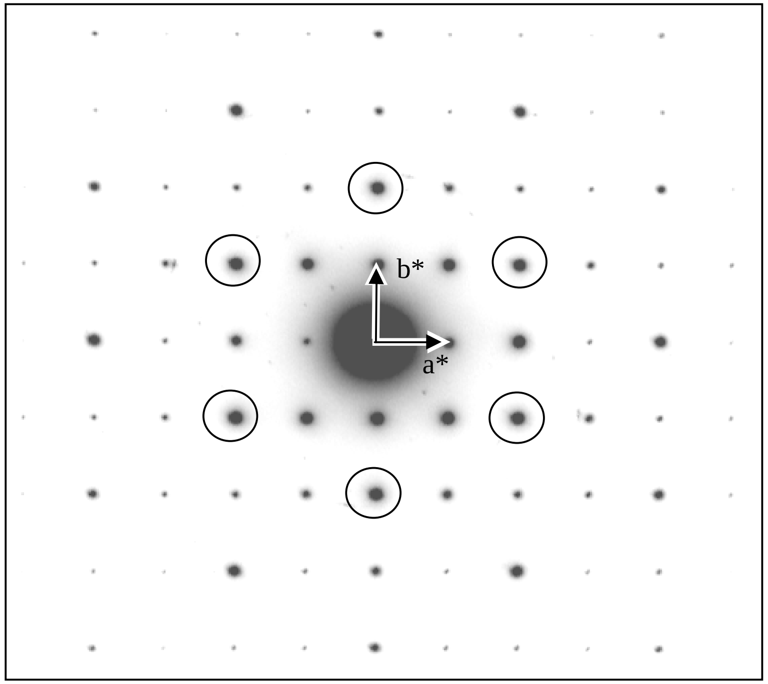


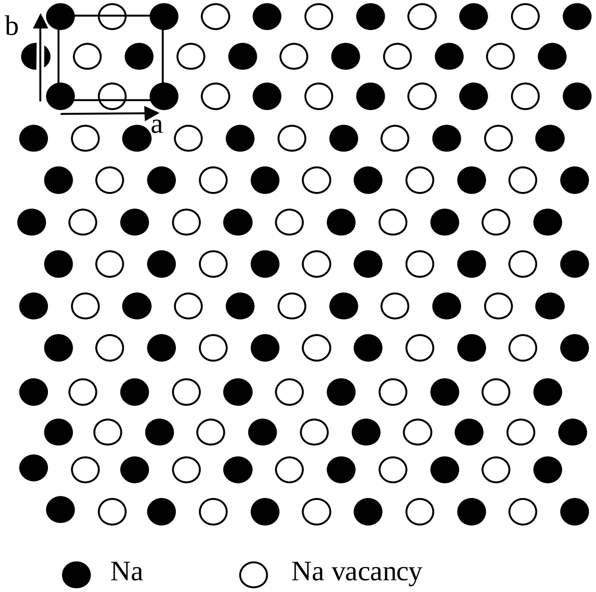
x = 0.50 (1/2):

- Two kinks at T_{c1}=88K and T_{c2}=53K in χ
- Resistivity shows insulating behavior below T=53K

An unexpected insulator at x = ½







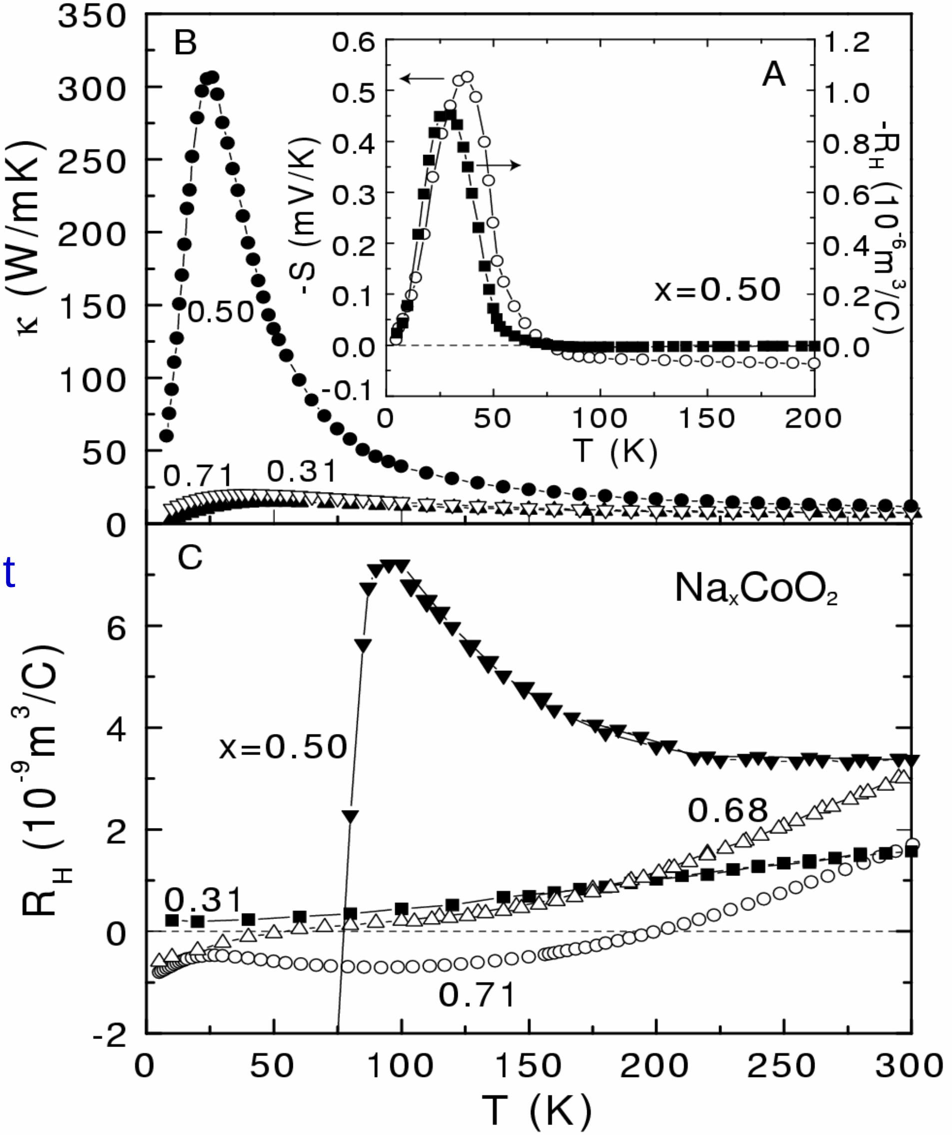
Electron diffraction at 300K shows the superlattice formed by the Na ions, consistent with a zig-zag order

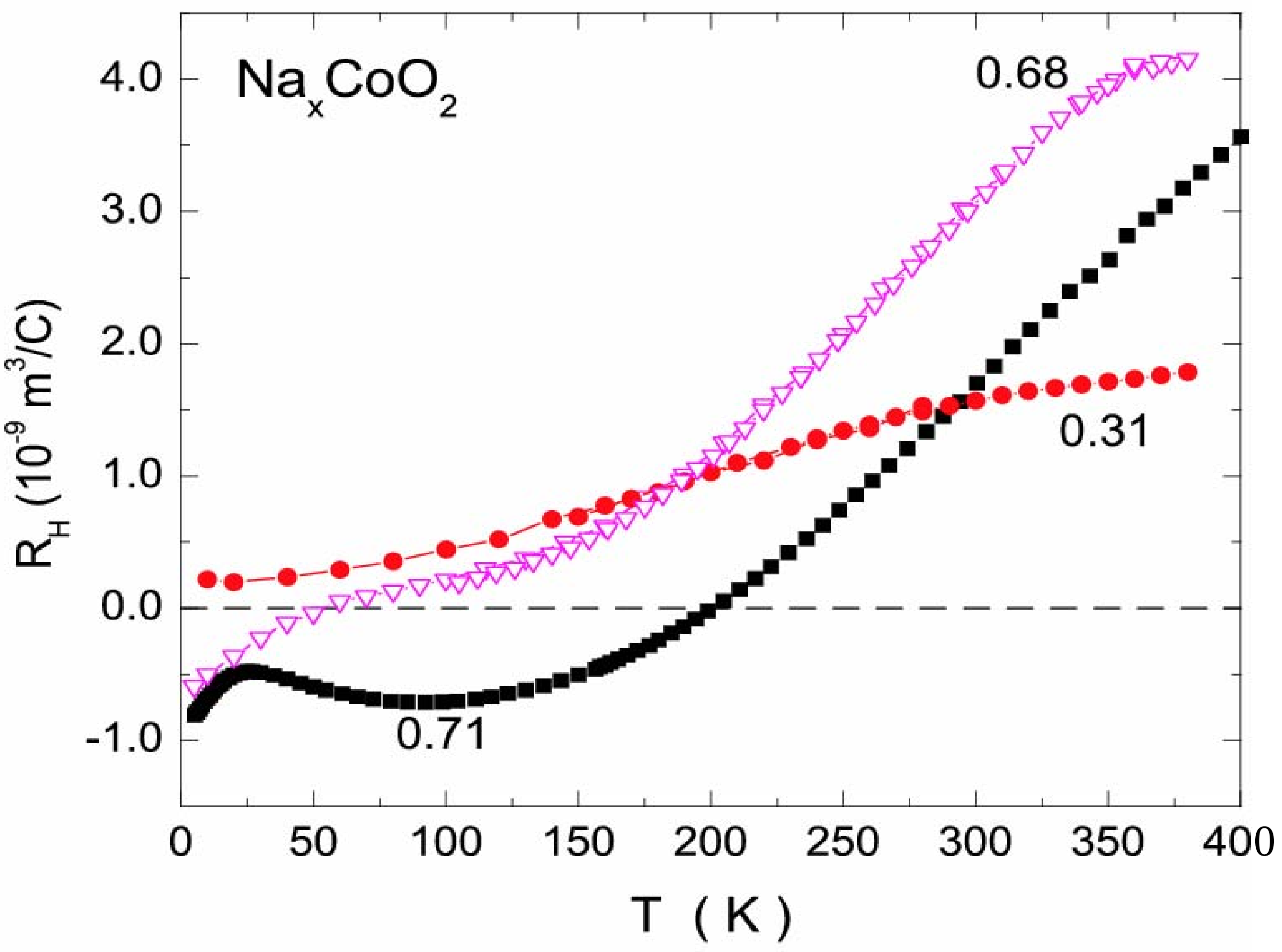
Zendbergen et al., condmat/0403206 (2004)

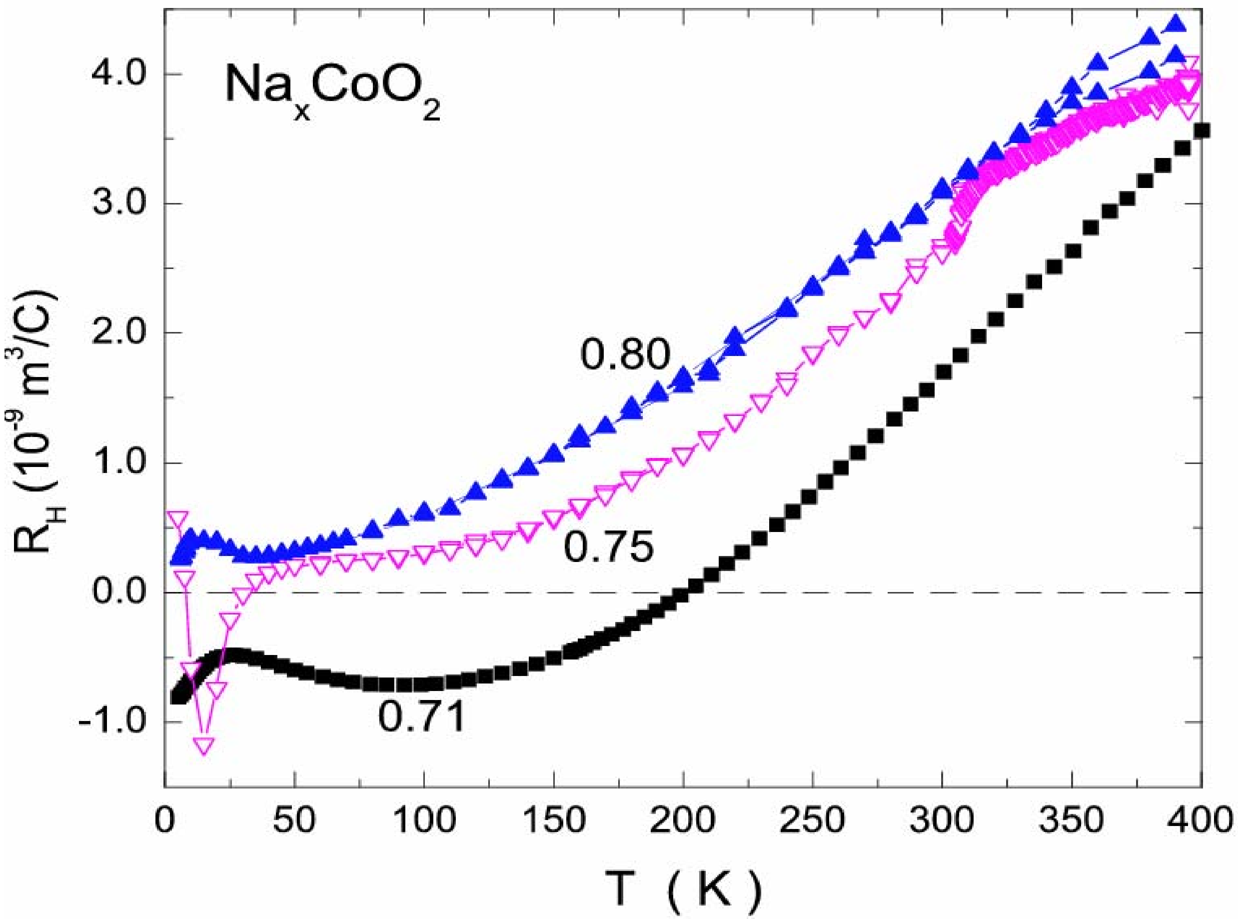
Foo et al., PRL ‘04

Thermal Conductivity

Hall coefficient



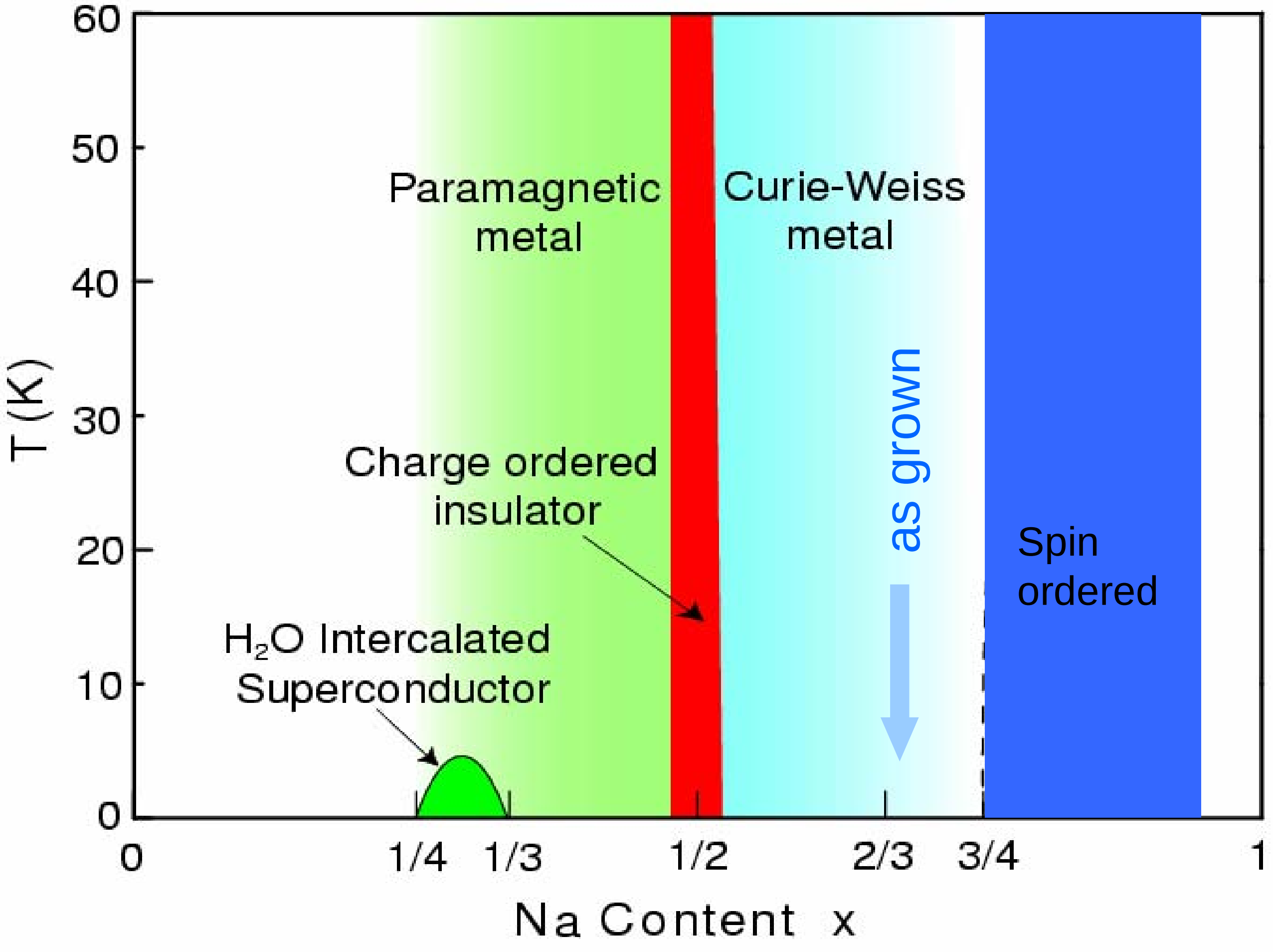

Na_xCoO_2
0.68
0.31
0.71
R_H (10^{-9} m^3/C)
T (K)
4.0
3.0
2.0
1.0
0.0
-1.0
0
50
100
150
200
250
300
350
400


Na_xCoO_2
0.80
0.75
0.71
R_H (10^{-9} m^3/C)
T (K)
4.0
3.0
2.0
1.0
0.0
-1.0
0
50
100
150
200
250
300
350
400

Na_xCoO_2

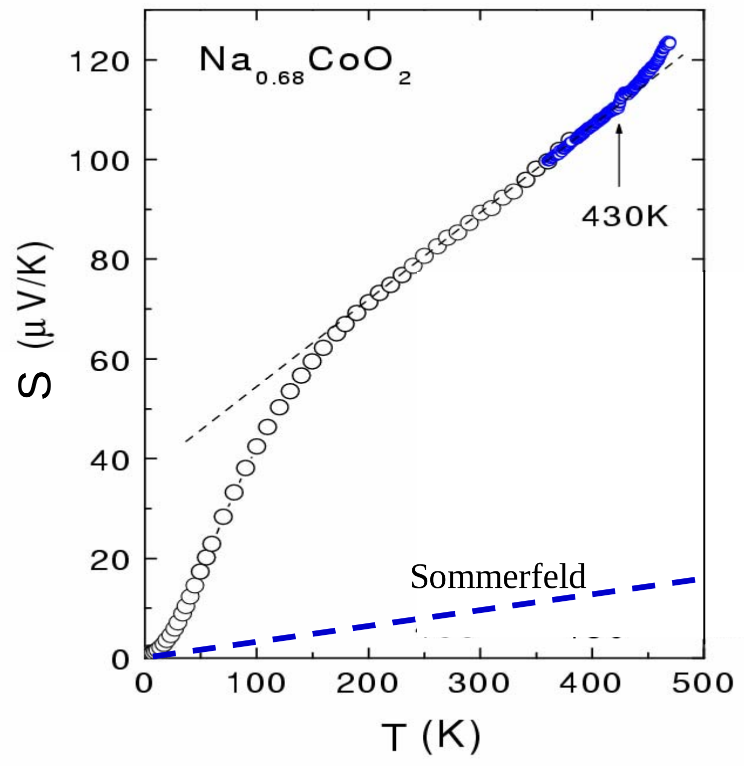
Multiple electronic phases vs. Na content

Foo et al.
PRL ‘04

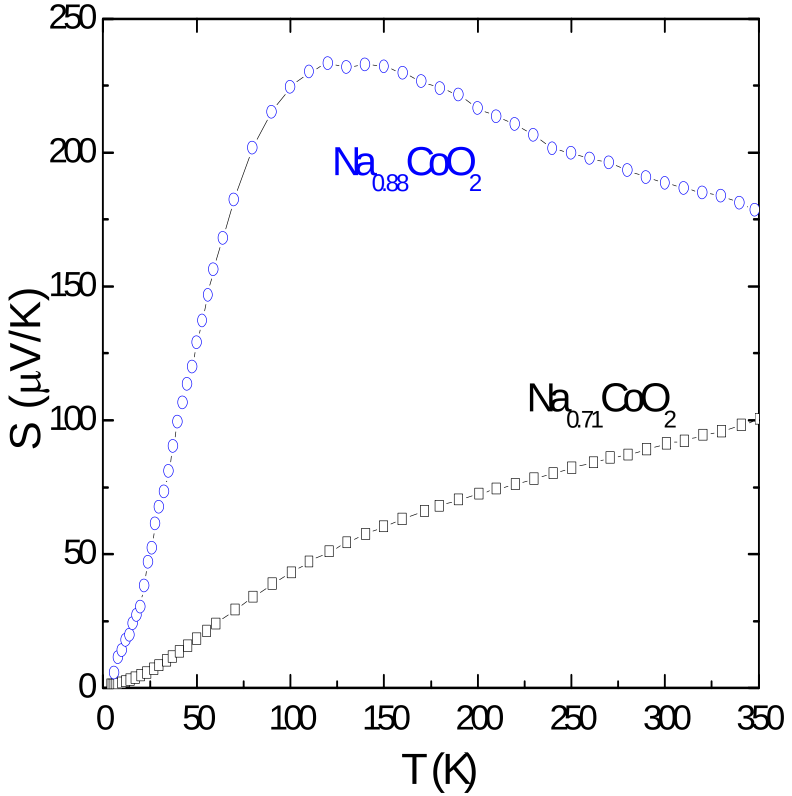


Further enhancement of thermopower

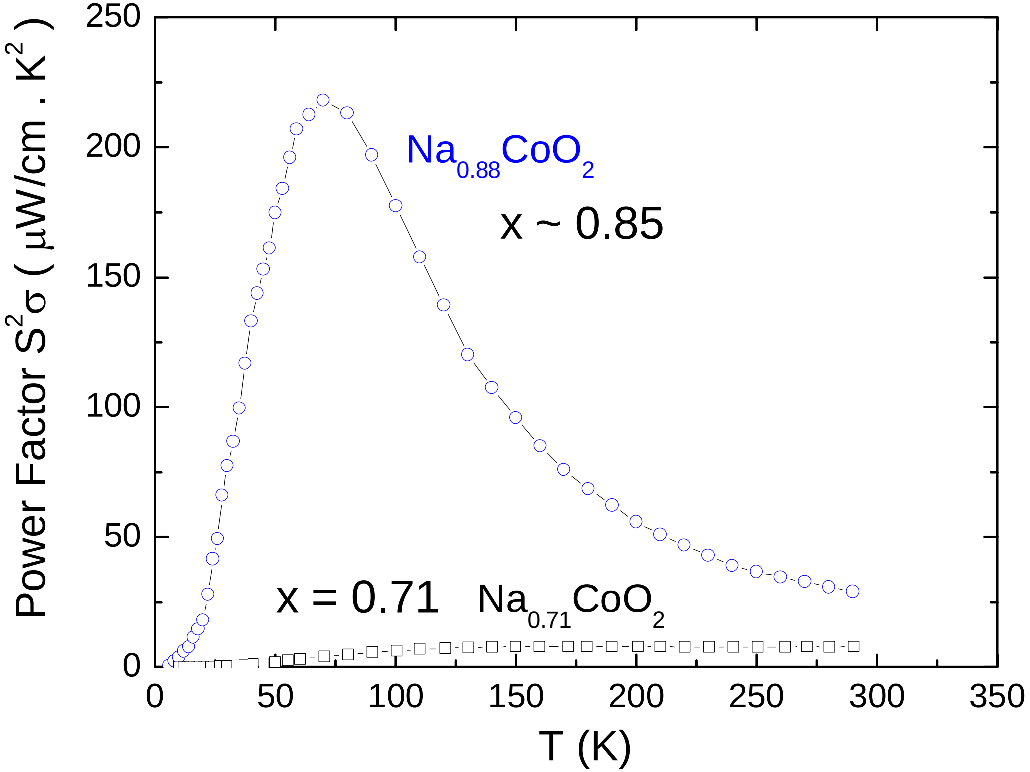
x = 0.71



x = 0.88



Power factor of Na_xCoO_2 $P = S^2\sigma$



Unusual electronic behavior in Na_xCoO_2

Strongly correlated s = ½ holes hopping on triangular lattice

- Paramagnetic Metal (x ~ 1/3)

High conductivity, superconducting with H_2O intercalatn.

- Charge-ordered Insulator (x = ½)

Na ion ordering, hole ordering (stripes?),
giant thermal conductivity

- Curie-Weiss metal (x ~ 2/3)

Curie-Weiss susceptibility, metallic cond., large thermopower from spin entropy, T-linear Hall coef.

- Spin Ordered Phase (x > ¾)

Even larger thermopower, field-induced metamagnetism