Memory and pressure effects in Na_xCoO_2 cobaltites

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ESRF, ID 27

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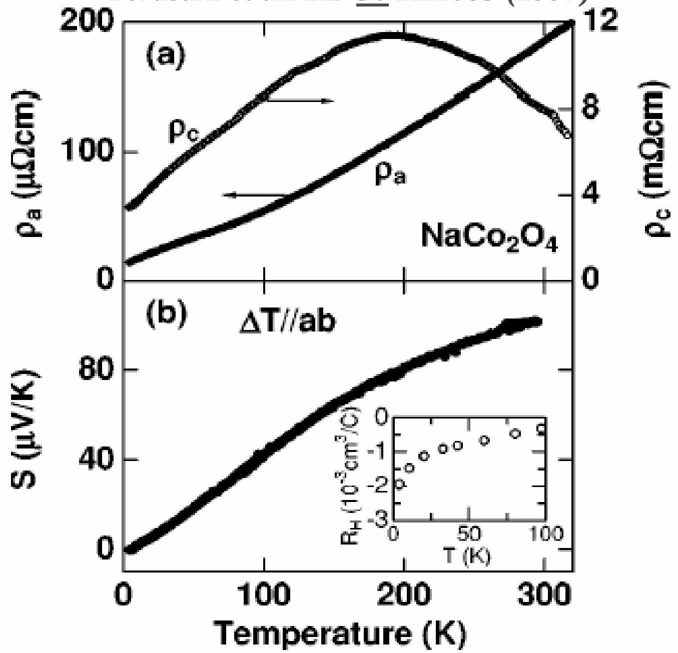
Outline:

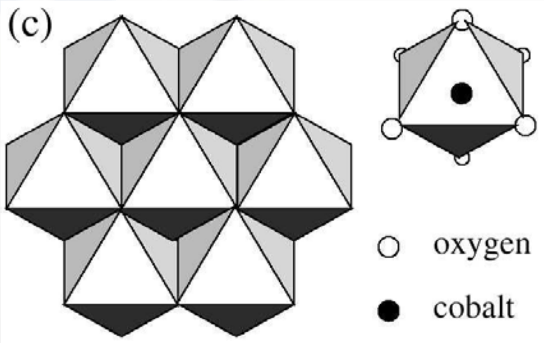
- Introduction
- Results in $Na_{0.5}CoO_2$
  - Crystallography: powder and crystal
- Results in $Na_{0.5}CoO_2$
  - Resistance Control
- Conclusions

Introduction: Na_xCoO_2 (0<x<1)

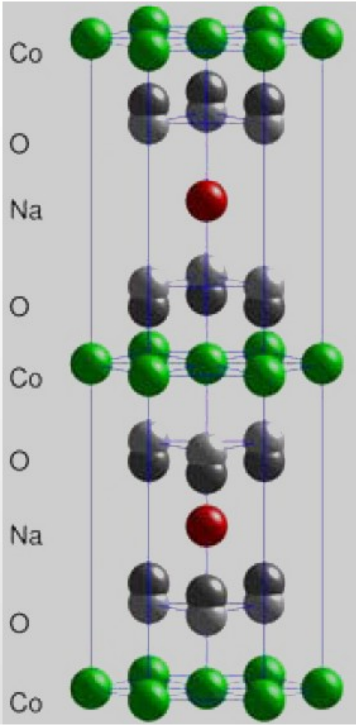
Terasaki et al PRB 56 R12685 (1997)



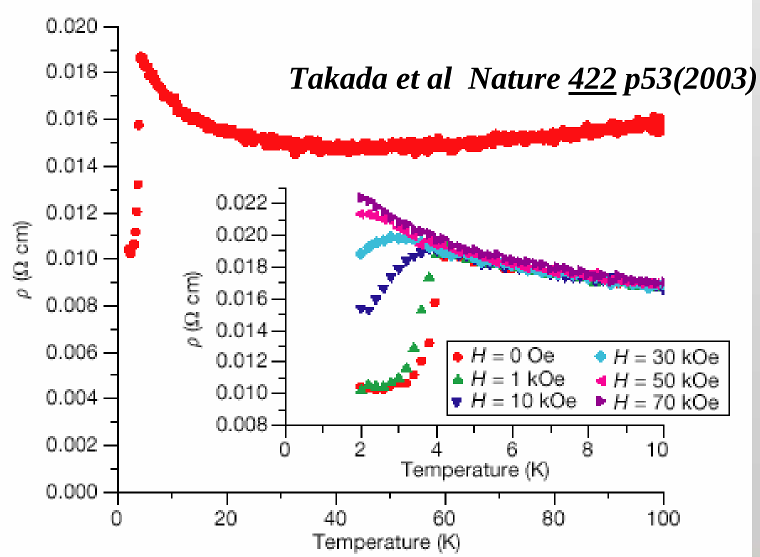
Structure

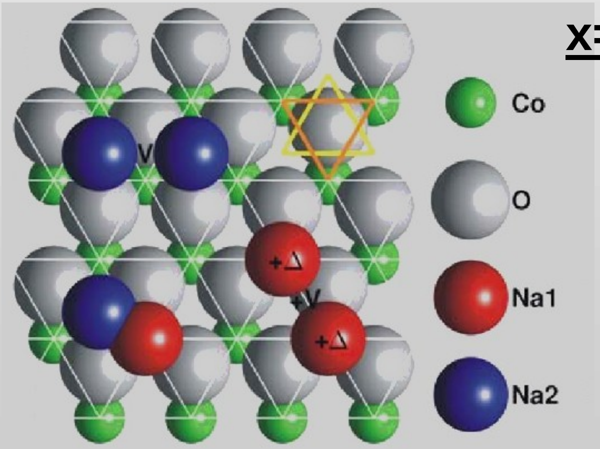


Triangular lattice of octahedra CoO_2

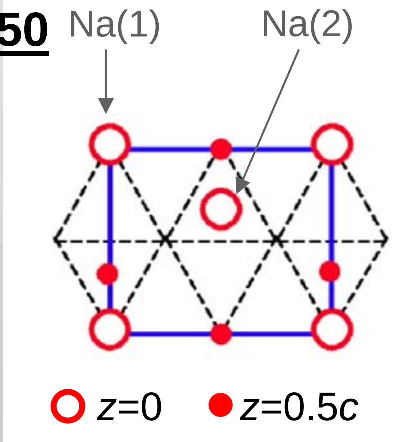


Takada et al Nature 422 p53(2003)



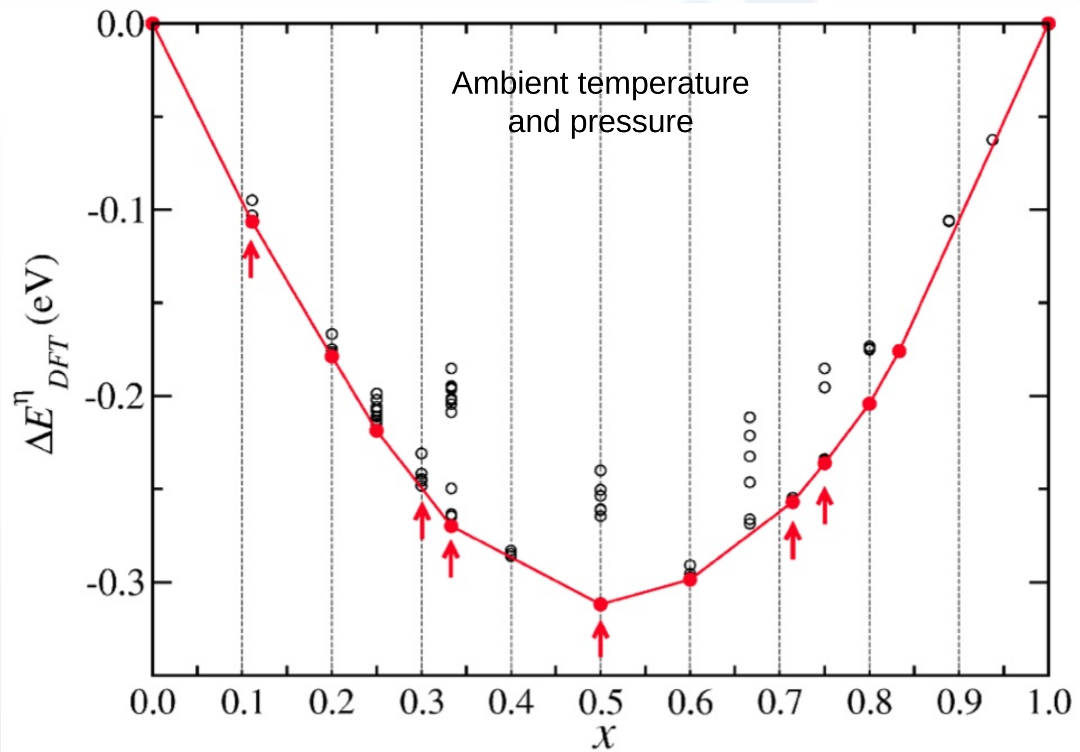


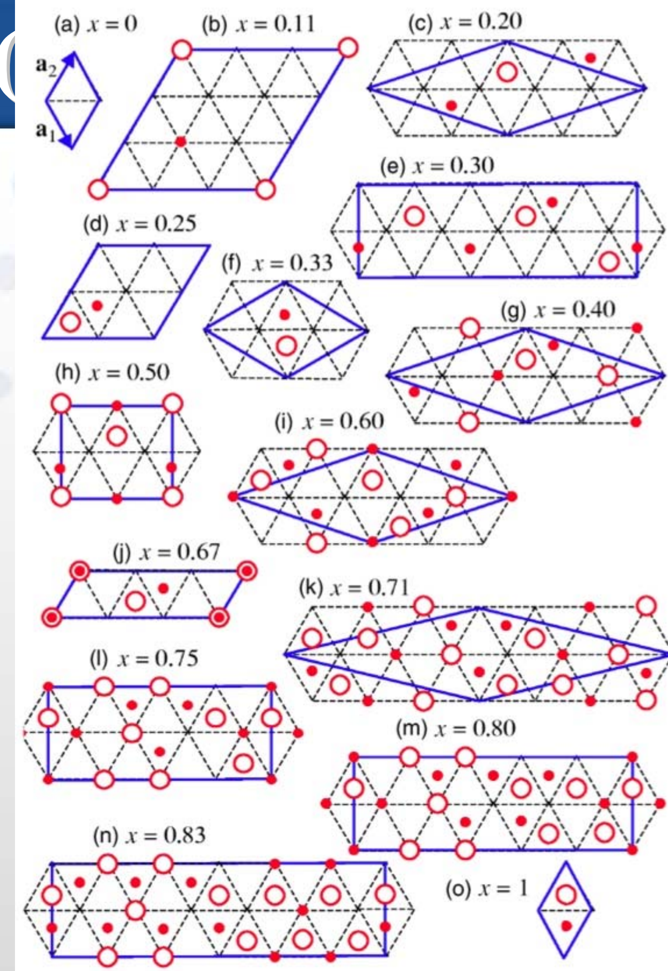
x=0.50



Two possible positions for Na ions

Introduction: Na_xCoO_2 (





- Screened electrostatic interactions → Na ordering

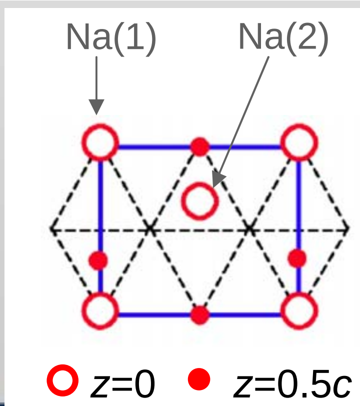
- Na-Na interaction stronger than Na-Co

- Charge and magnetic orderings on CoO_2 at low energy scale → Affected by Na ordering

- Na(2) is ~0.1eV/Na lower in energy than Na(1)

x=0.50

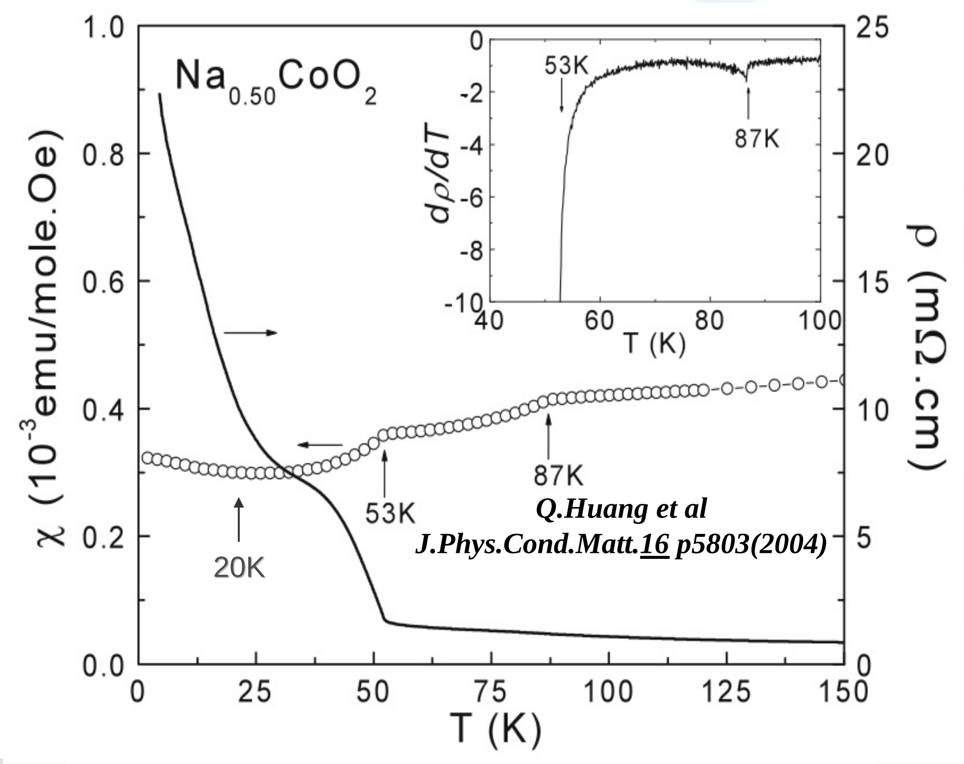
○ z=0
● z=0.5c



Zhang et al
PRB 71 p153102 (2003)

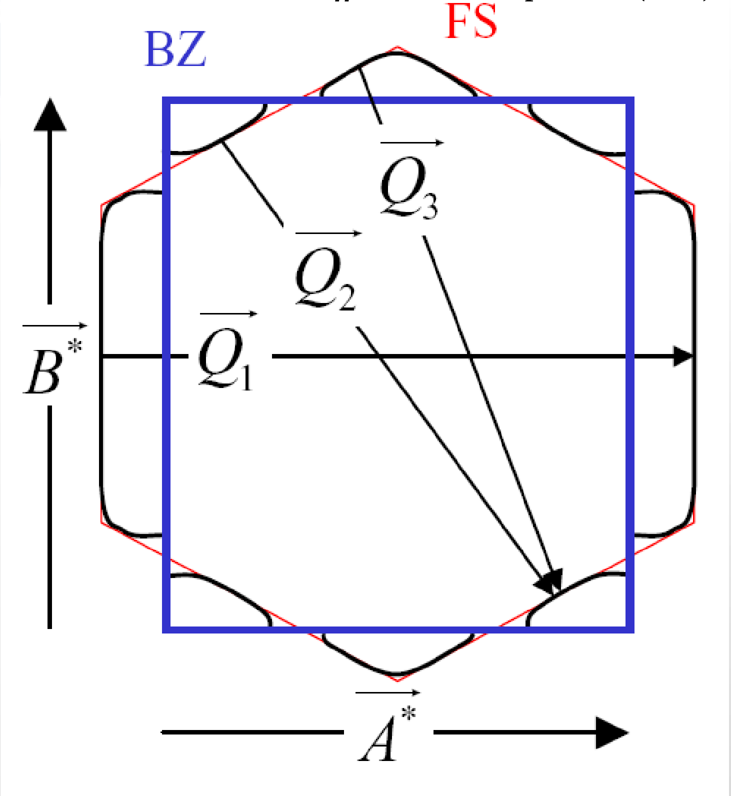
For x=0.50 occupied in equal ratios

Introduction: $Na_{0.50}CoO_2$



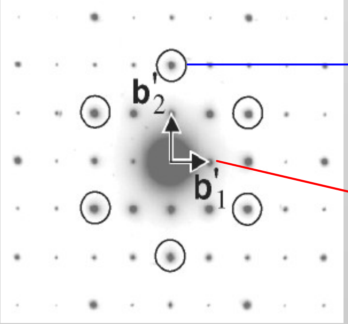
$T_{Co\ SPIN}$ ~ 20K, T_{CO} = 53K, T_{MAG} = 87K

J Bobroff et al PRL 96 p107201 (2006)



FS: Hexagonal due to CoO_2

BZ: Ortorrombic due to Na^+

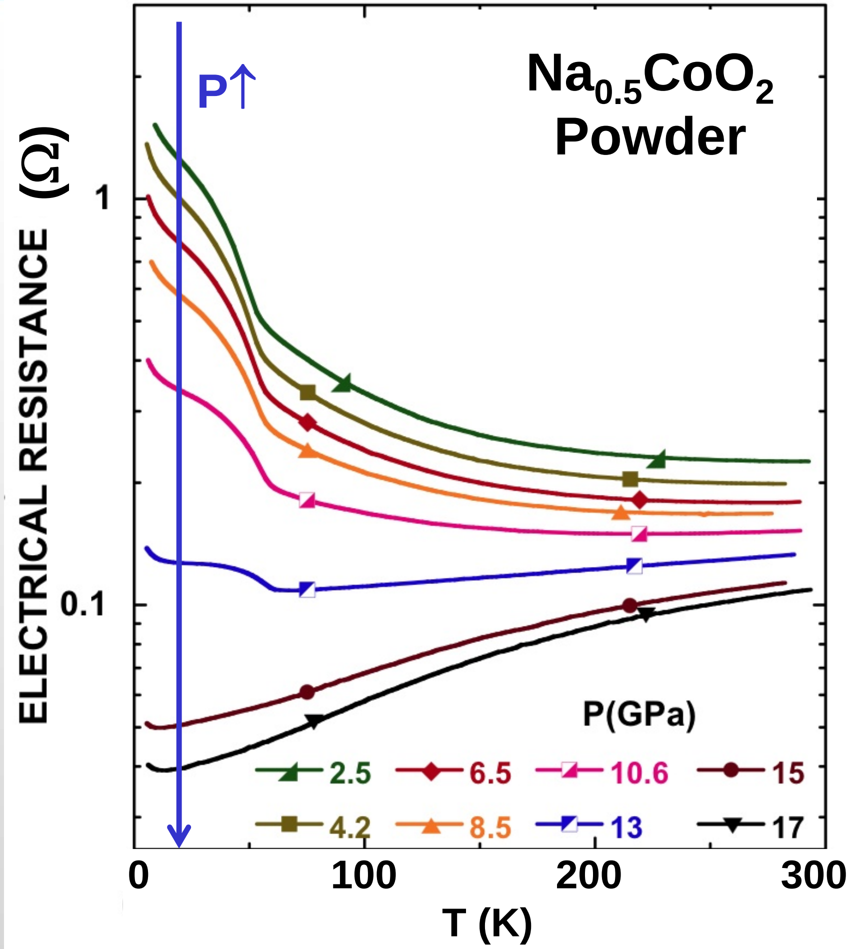


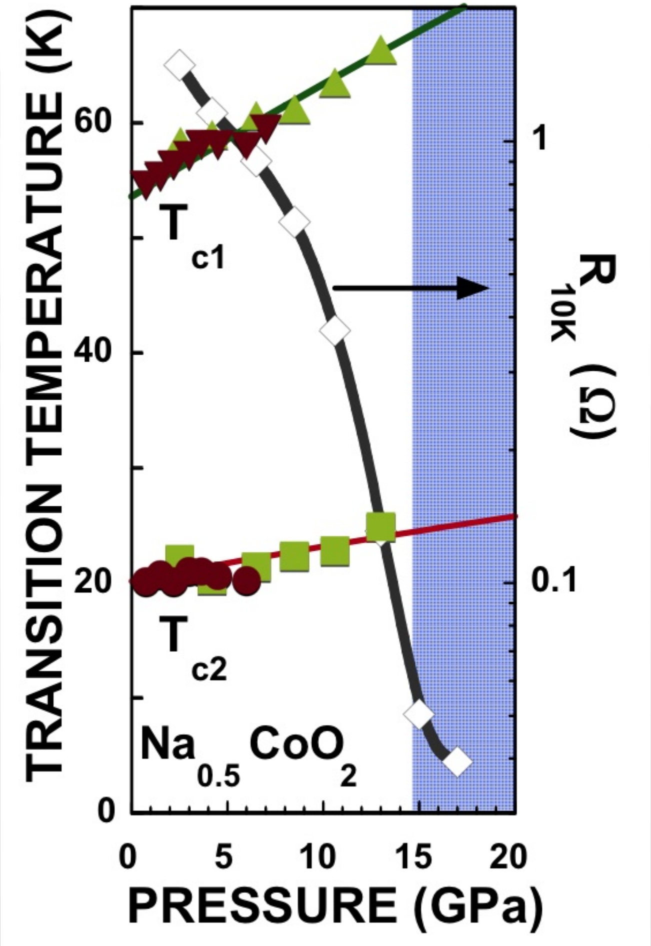
Bragg spot of hexagonal lattice

Spots of supercell $a_1{}'$ & $a_2{}'$ (Na order)

Three transitions due to three nesting vectors

Results: Transport



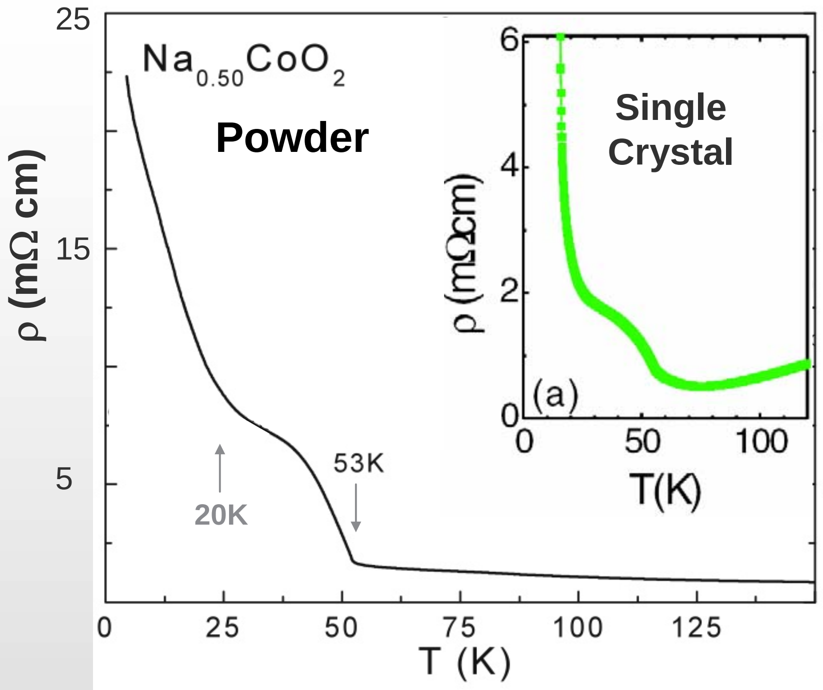


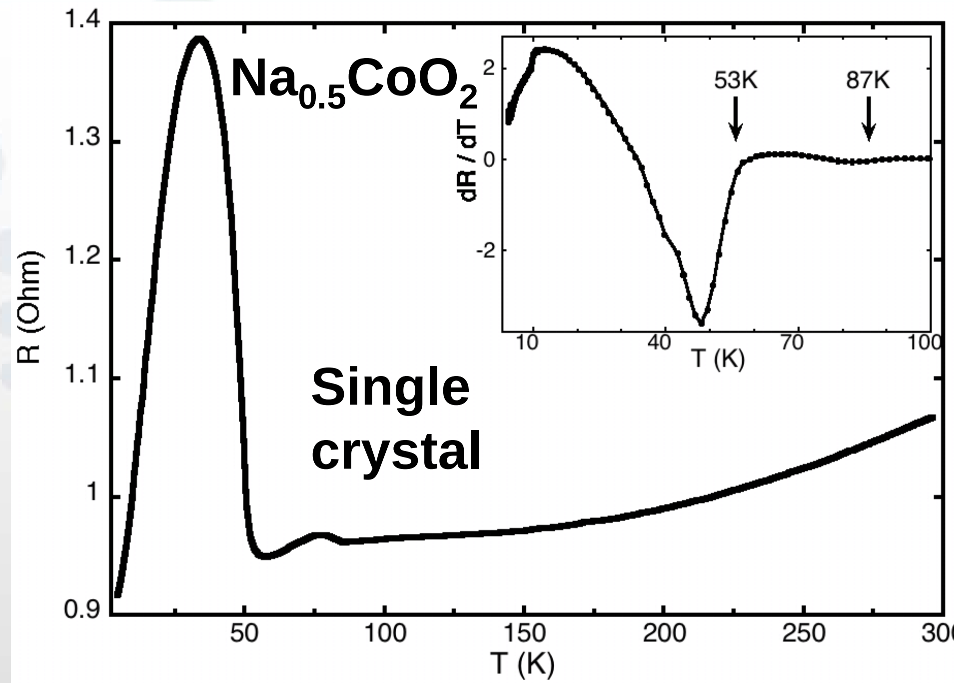
- Polycrystalline samples
- T_{CO} = 53K
- Anomaly for T ~ 20K
- Insulator at Low T

Ordering disappears?

<u>P~15GPa:</u> Change in shape of dR/dT and metallic behavior

Results: Transport





<u>"Violent" chemistry</u> (Br_2 or I_2)
- Disorder of Na ions
- Pinning of charge carrier

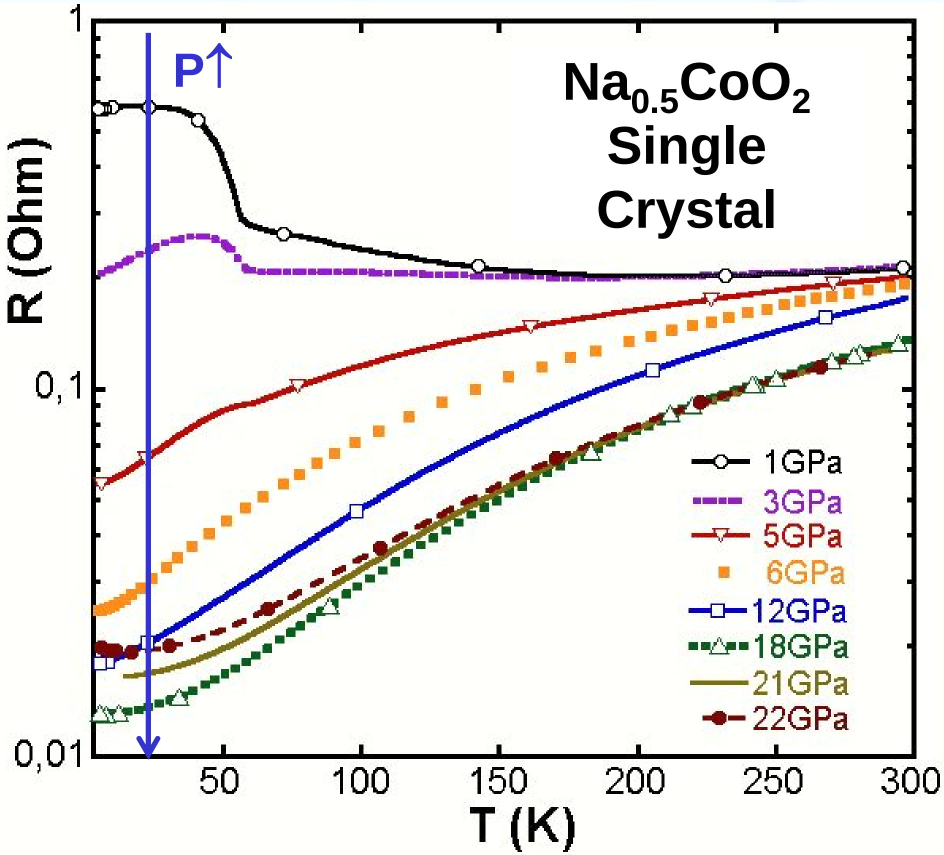
<u>"Soft" chemistry</u> (organic)
- Order in Na ions
- "Less" pinning of charge carrier
- No cycling effect

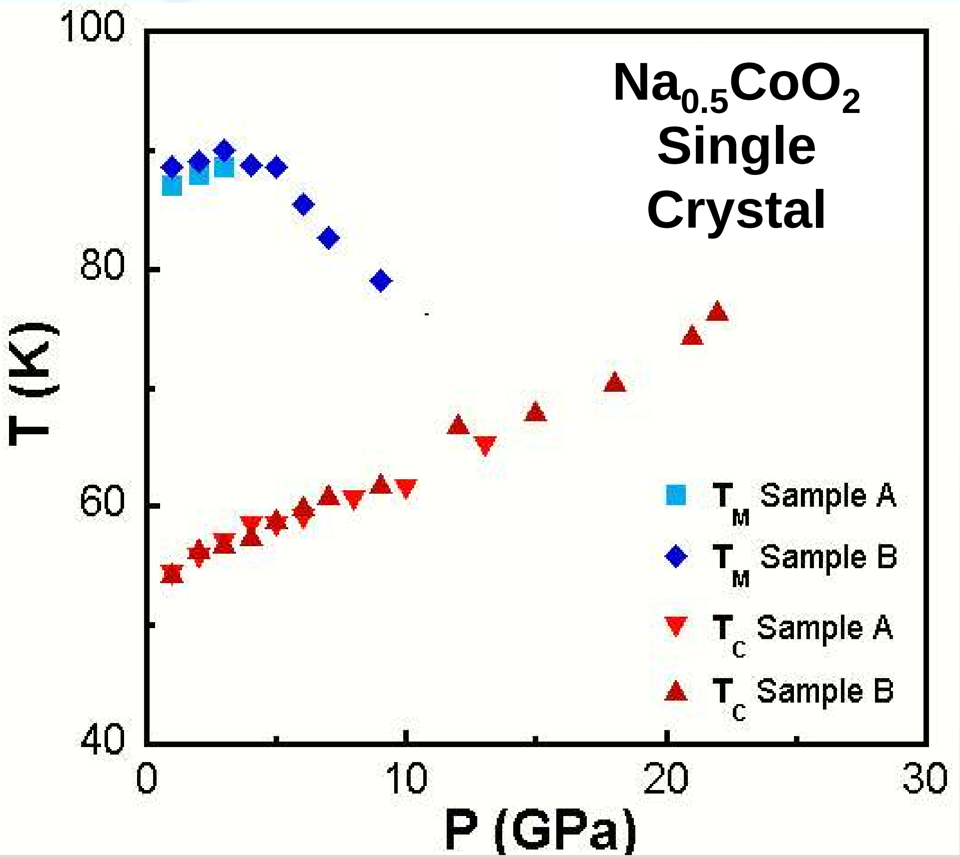
T=88K
Very good quality of single crystals

T=53K
Abrupt transition to insulator state

T~25K
First evidence of a transition to a metallic ground state in x=0.50!!

Results: Transport



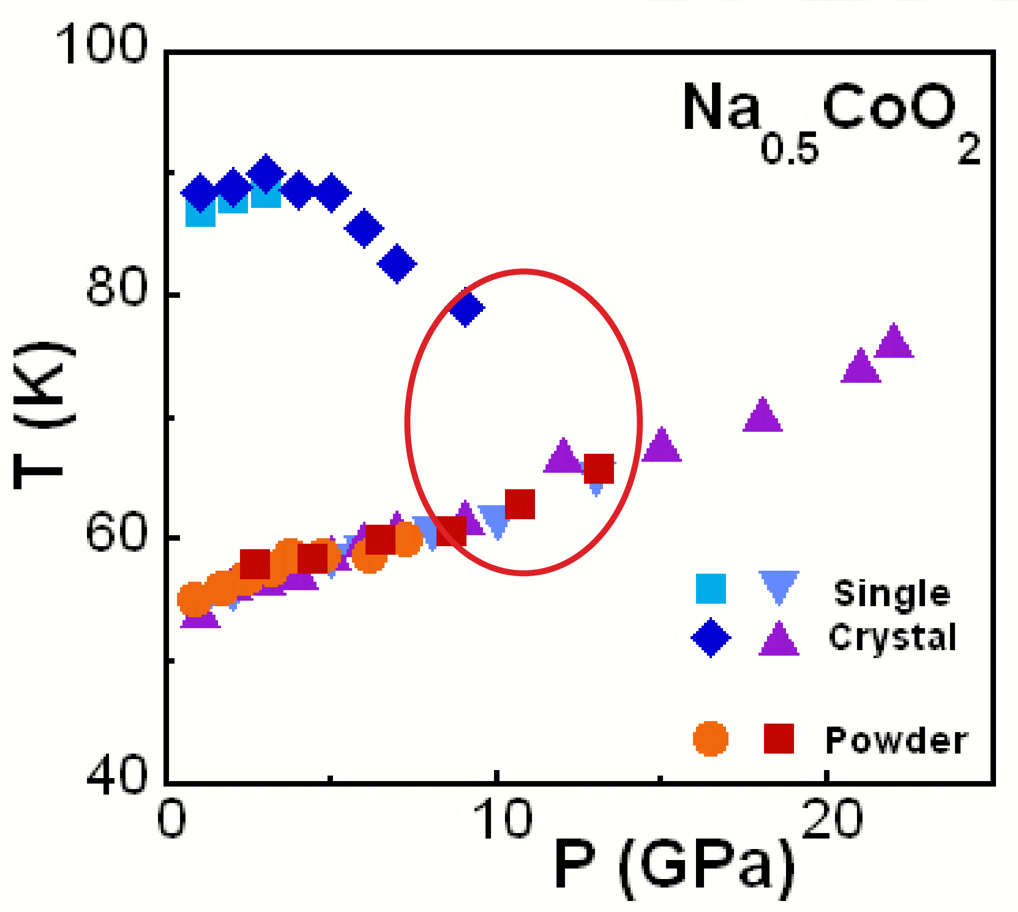


- Good quality single crystal samples
- T_M = 88K
- T_{CO} = 53K
- Metallic at Low T

T_{CO} vs P
same behavior as
in powder samples

G Garbarino et al., EPL <u>81</u> p 47005 (2008)

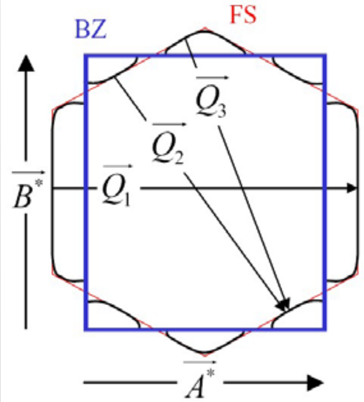
Results: Transport



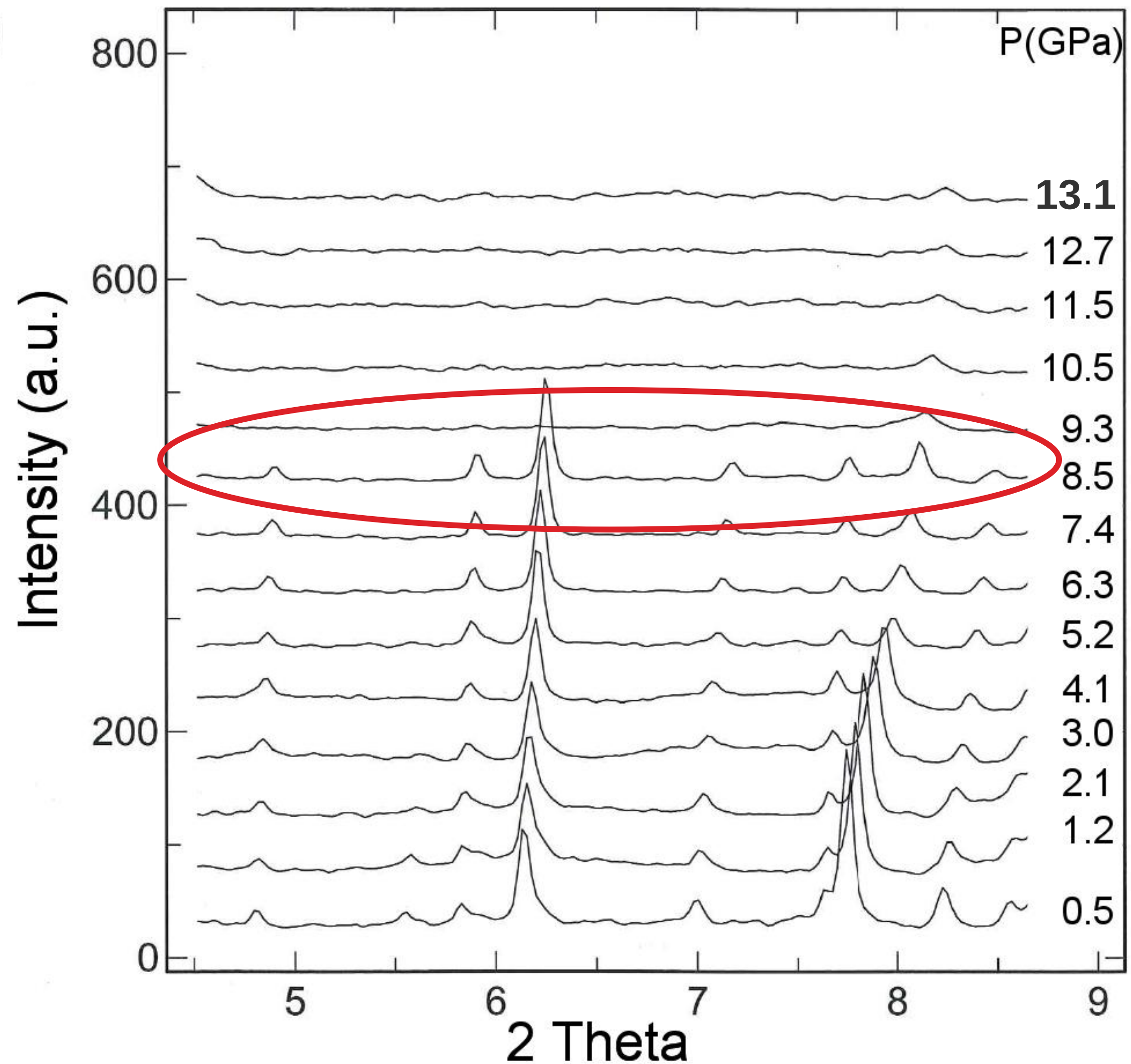
Ordering DOES NOT disappear!
Increase with pressure

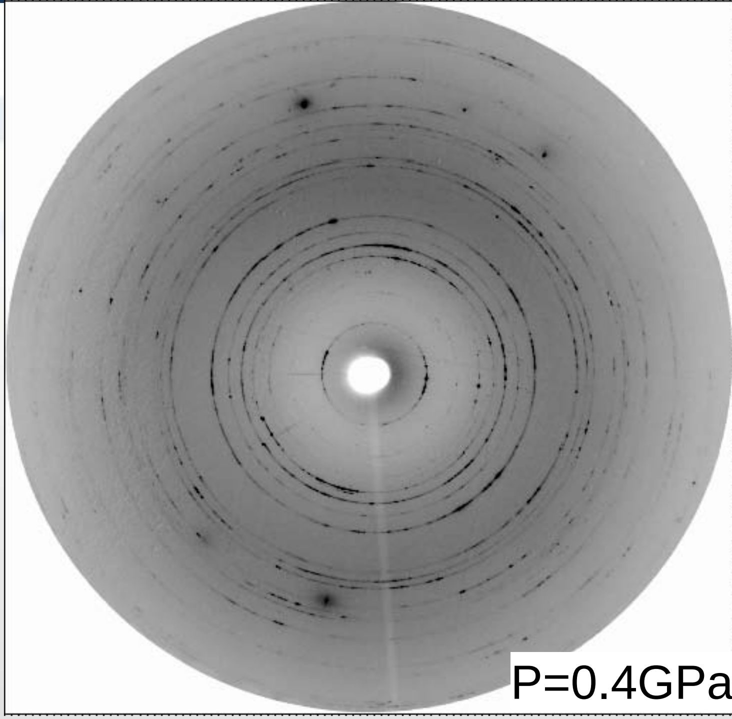
T_M ~ 88K disappears @ ~9GPa

Which is the origin?



Results: Crystallography





At ambient temperature

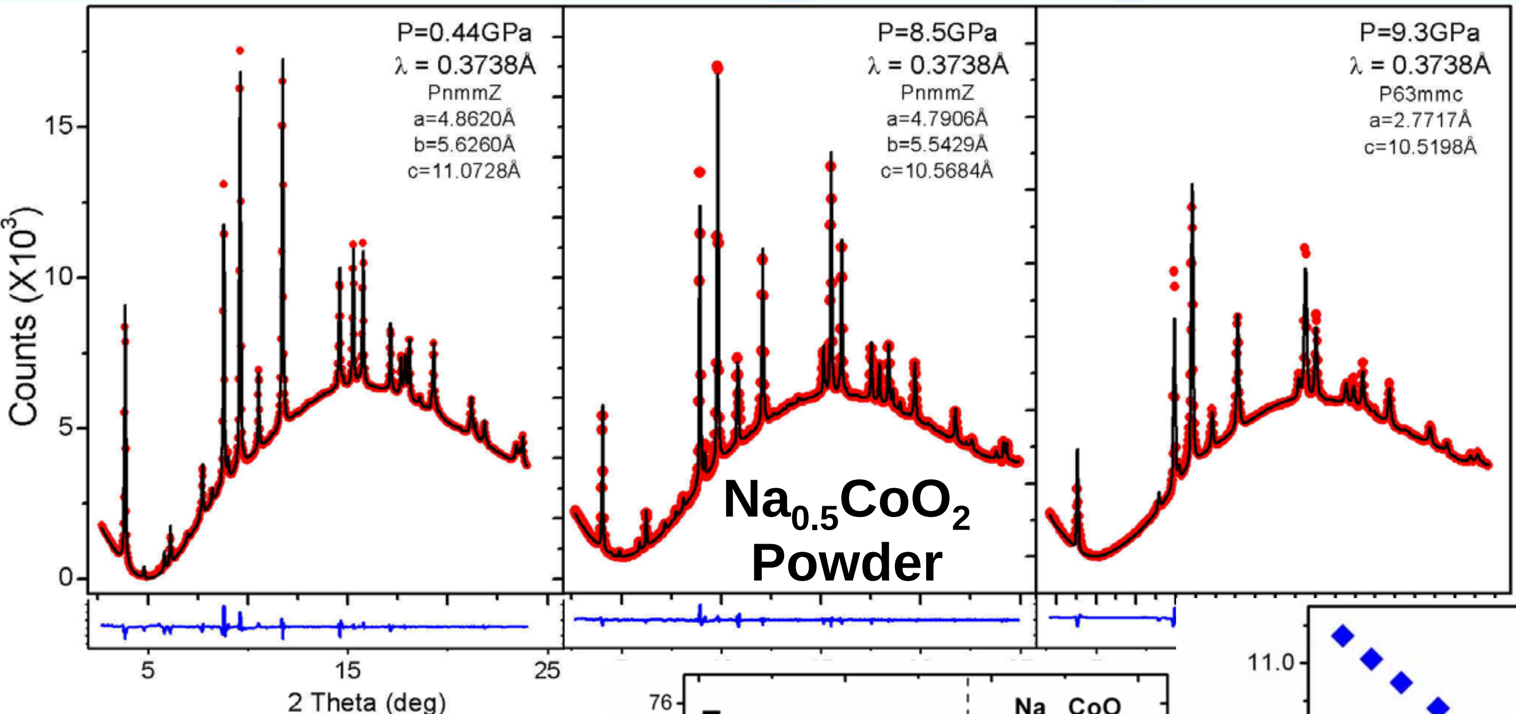
Phase transition @ 9GPa

P<9GPa to P>9GPa

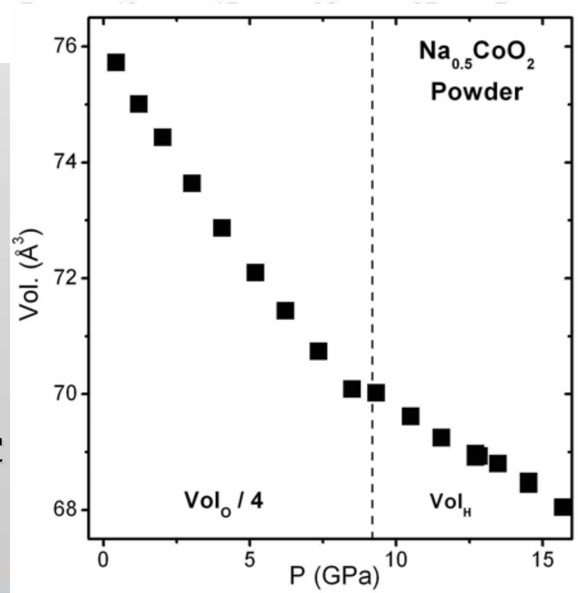
Ortho to Hexa

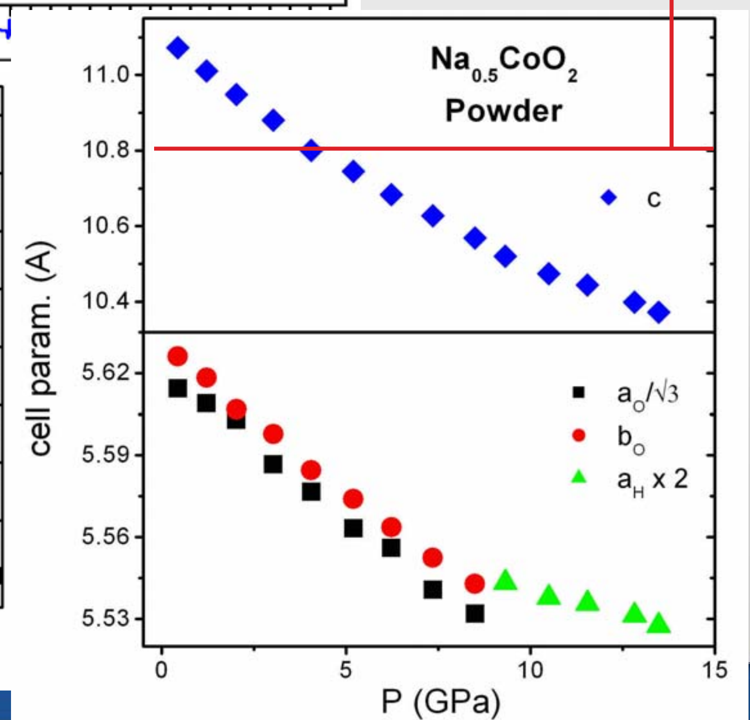
Pnmm to $P6_3$/mmc

Results: Crystallography



c value
of x=0.75





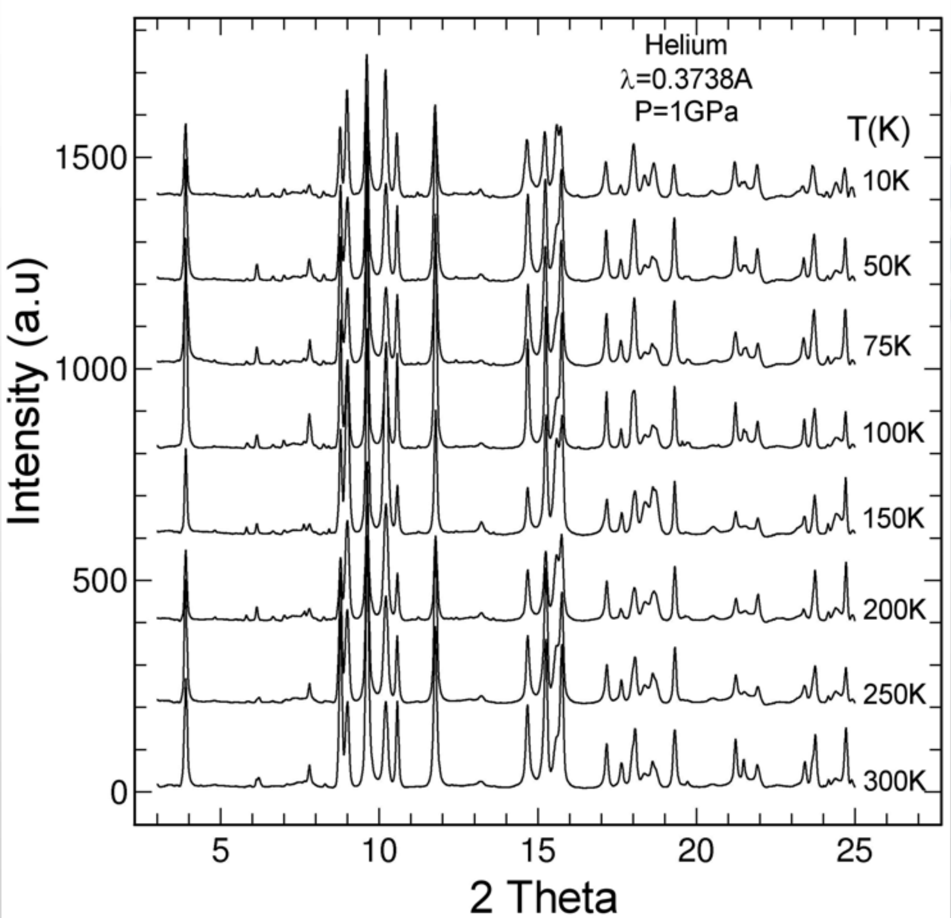
Rietveld refinement of low pressure phases:

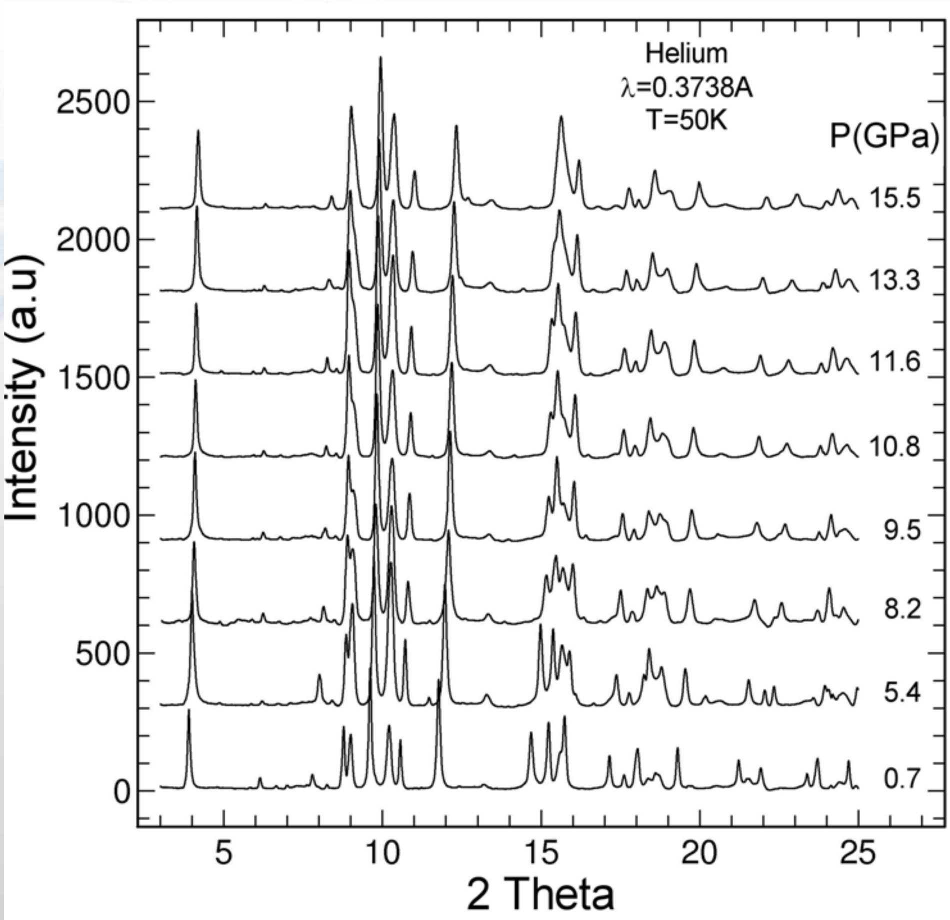
0GPa<P<9GPa **Pnmm**

9GPa<P **$P6_3$/mmc**

Results: Crystallography

At low temperature



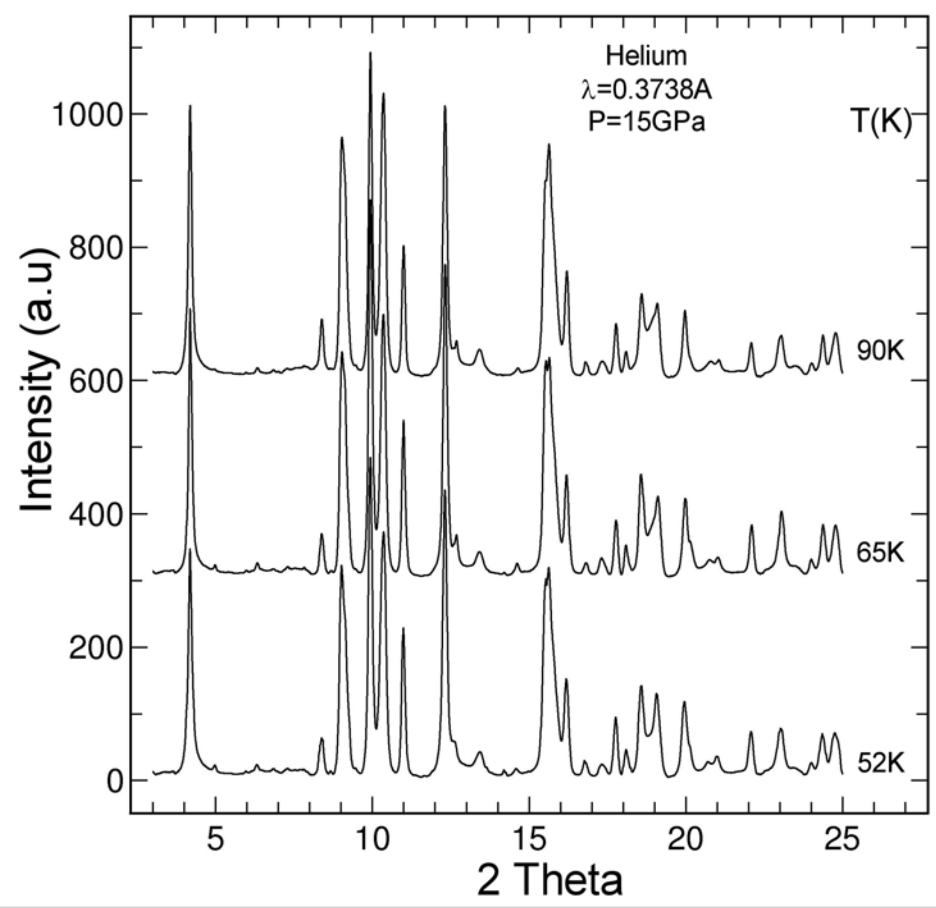


<u>P = 1GPa</u> Orthorhombic phase stable up to 10K

P_C>15GPa at 50K

Results: Crystallography

At low temperature

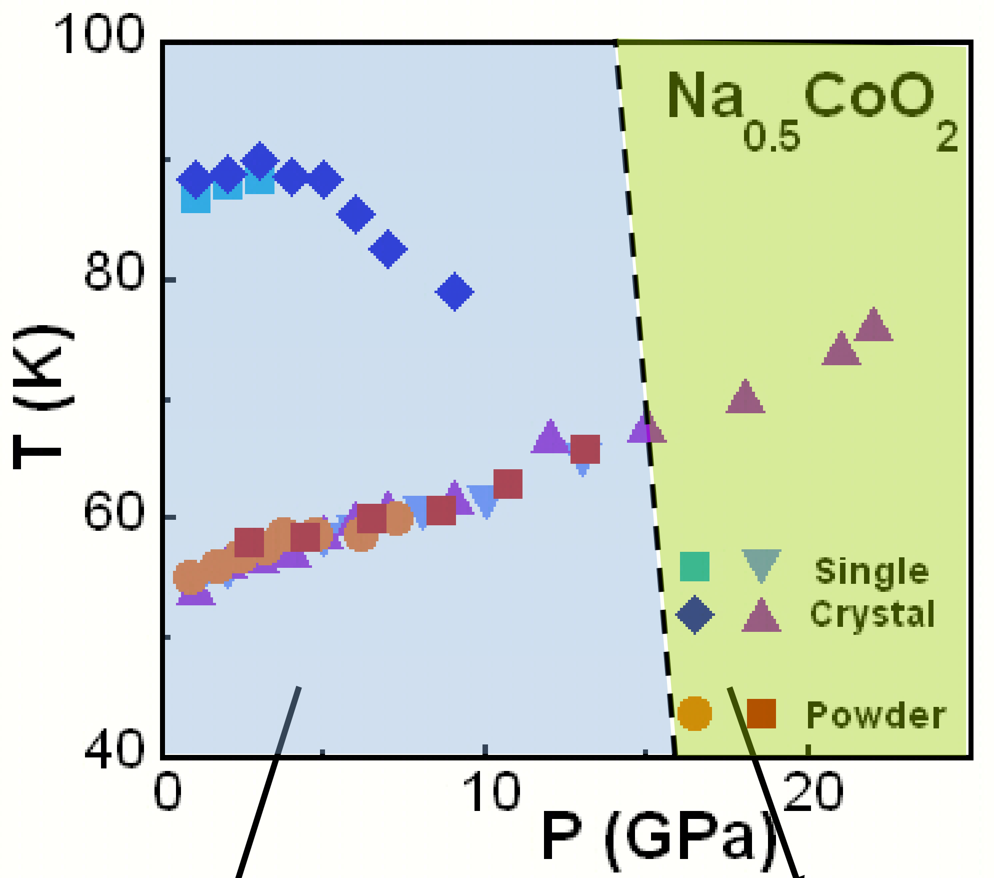


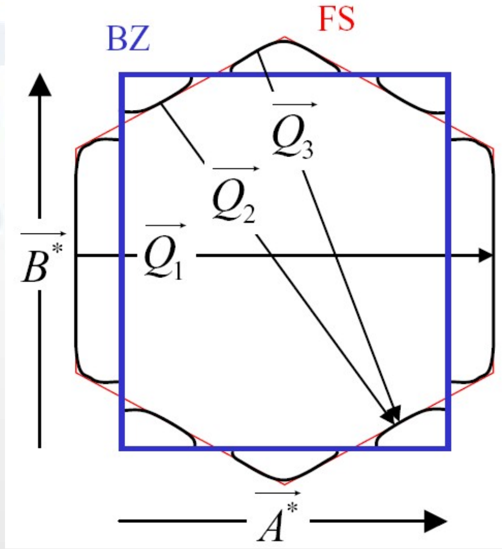
P = 15GPa Orthorhombic phase stable up to 90K

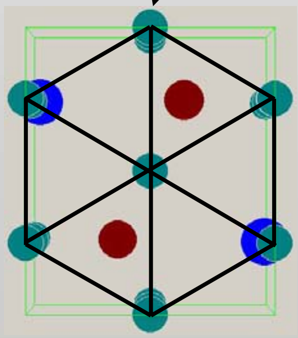
T=300K
- **P<9GPa** Orthorhombic phase
- **P>9GPa** Hexagonal phase

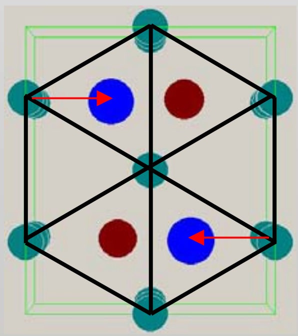
T=90K
- **P<15GPa** Orthorhombic phase
- **Pc = ???** Hexagonal phase

Results: Crystallography









T=300K

- **P=0GPa** Hexa FS, Ortho BZ $\Rightarrow$ Three nesting vector
  - Three transitions (87K,53K,20K)
- **P>9GPa** Hexagonal phase $\Rightarrow$ One nesting vector
  - One transition

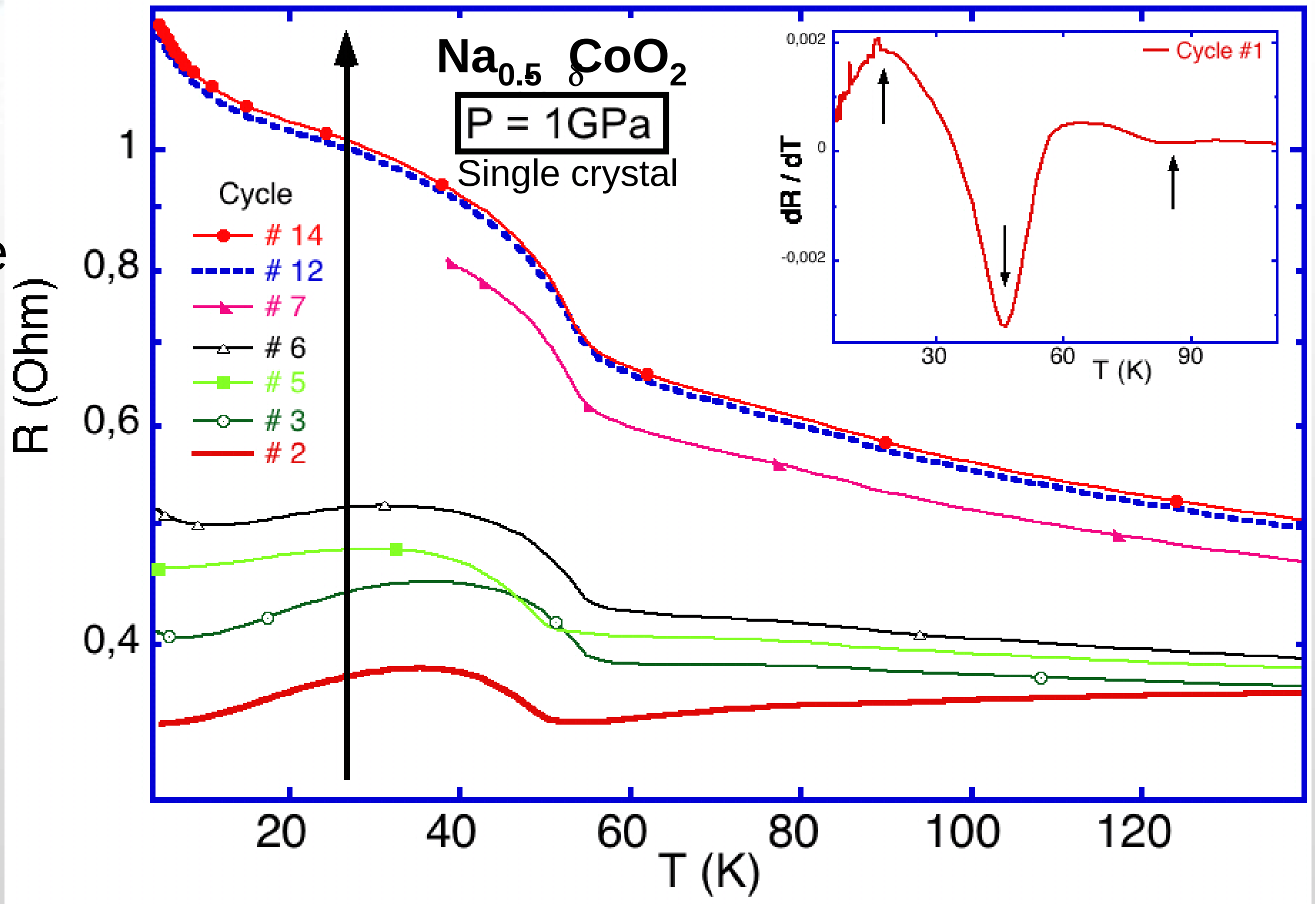
T=90K

- **P=0GPa** Orthorhombic FS
- **P_C** Hexagonal phase

Introduction

P=1GPa Fixed

- Cycling temperature
  → resistance increase
- **Metallic → Insulator**
  "Soft" → "Violent"
  chemistry
- In each cycle charge carrier are localized in "pinning" positions.

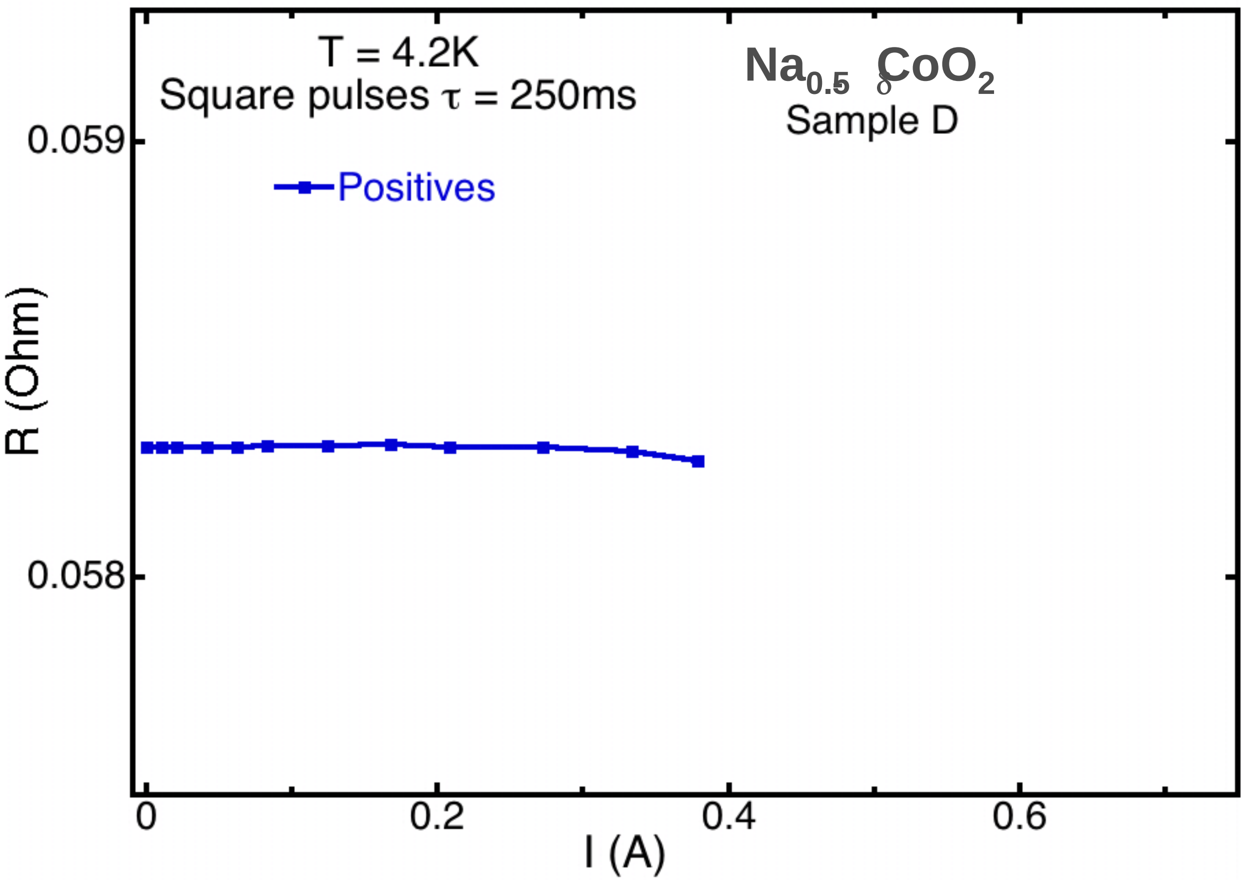


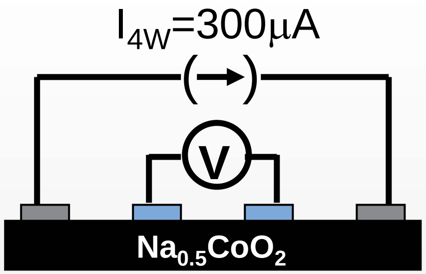
It will be interesting to study non linear effects in the low temperature region

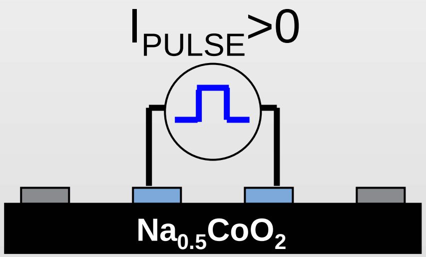
Garbarino et al, EPL 80 p47005 (2008)

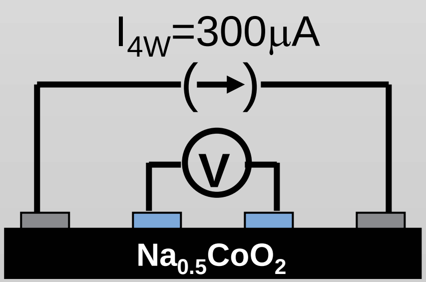
Resistance Control

- Sample at 4.2K, 4 wire resistivity measurement (I_{4W}=300μA)
- Positive current pulses of increasing amplitude and 250ms









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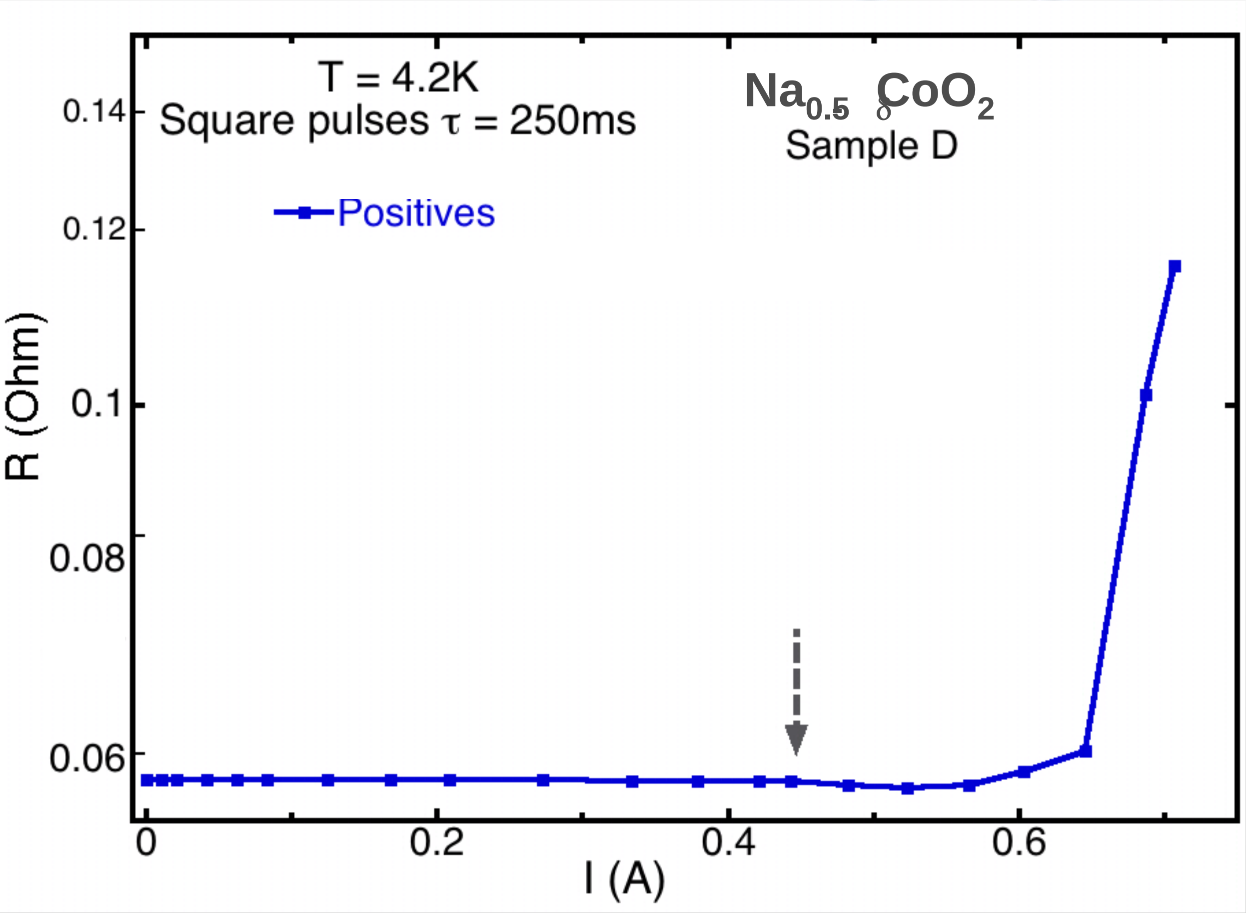
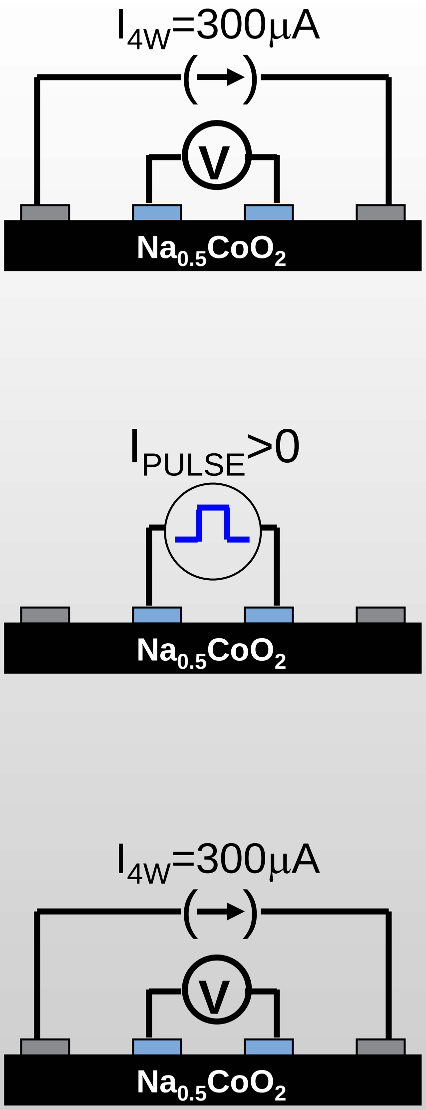
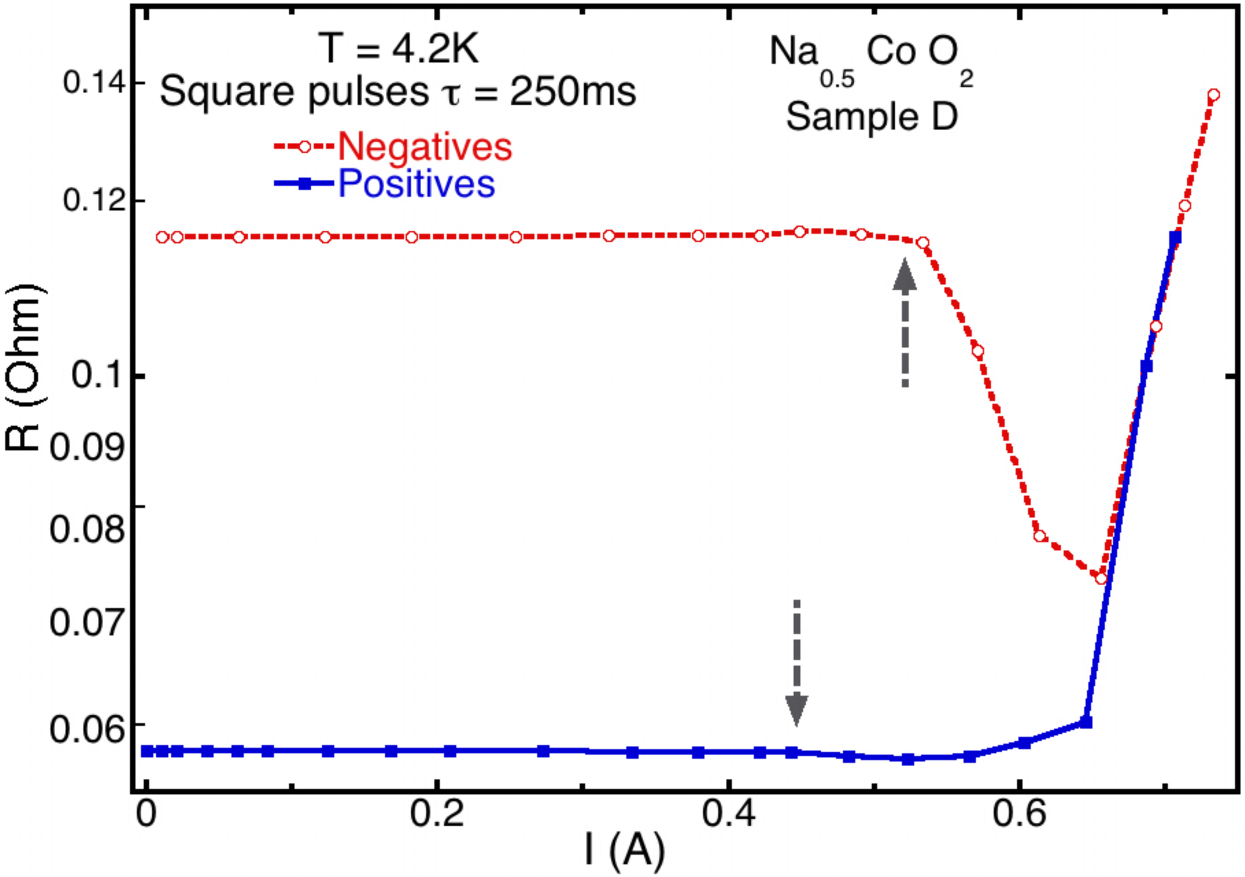
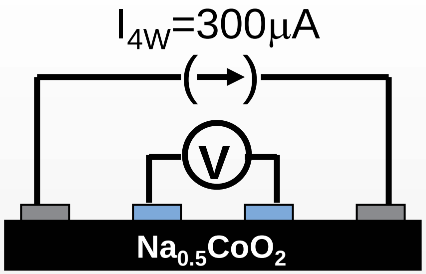


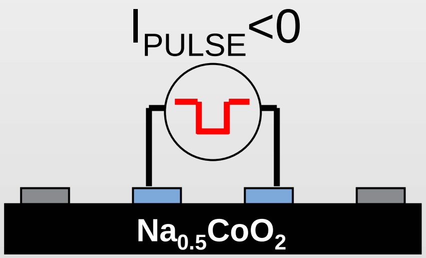


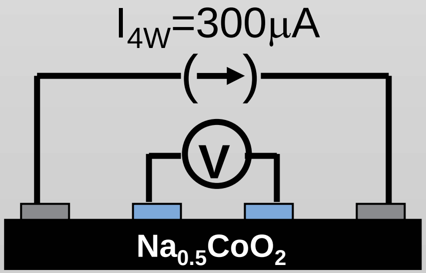
Resistance Control

- Sample at 4.2K, 4 wire resistivity measurement (I_{4W}=300μA)
- Positive current pulses of increasing amplitude and 250ms
- Negative current pulses of increasing amplitude and 250ms







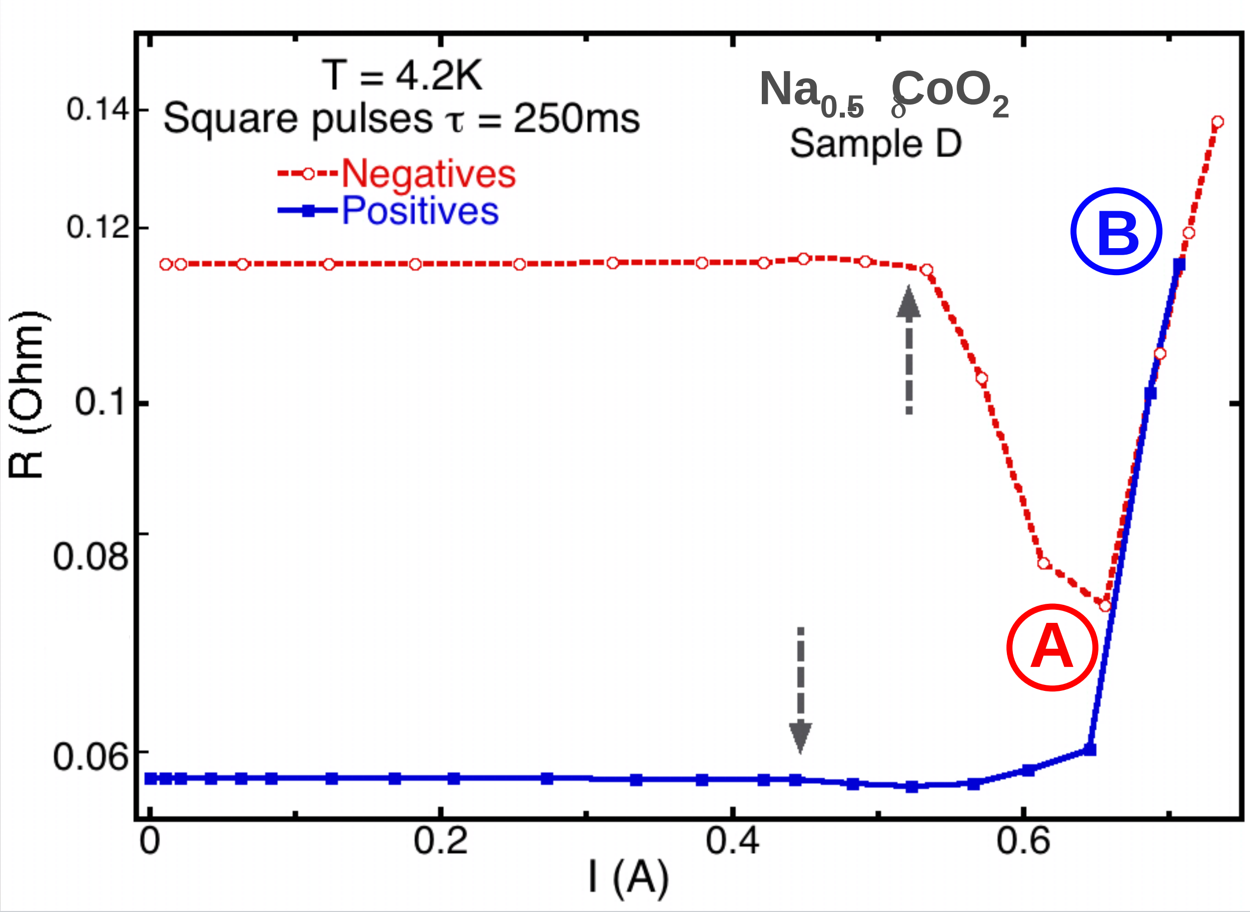


Results

Resistance Control

- Sample at 4.2K
- Negative pulse (**A**) and positive pulse (**B**)

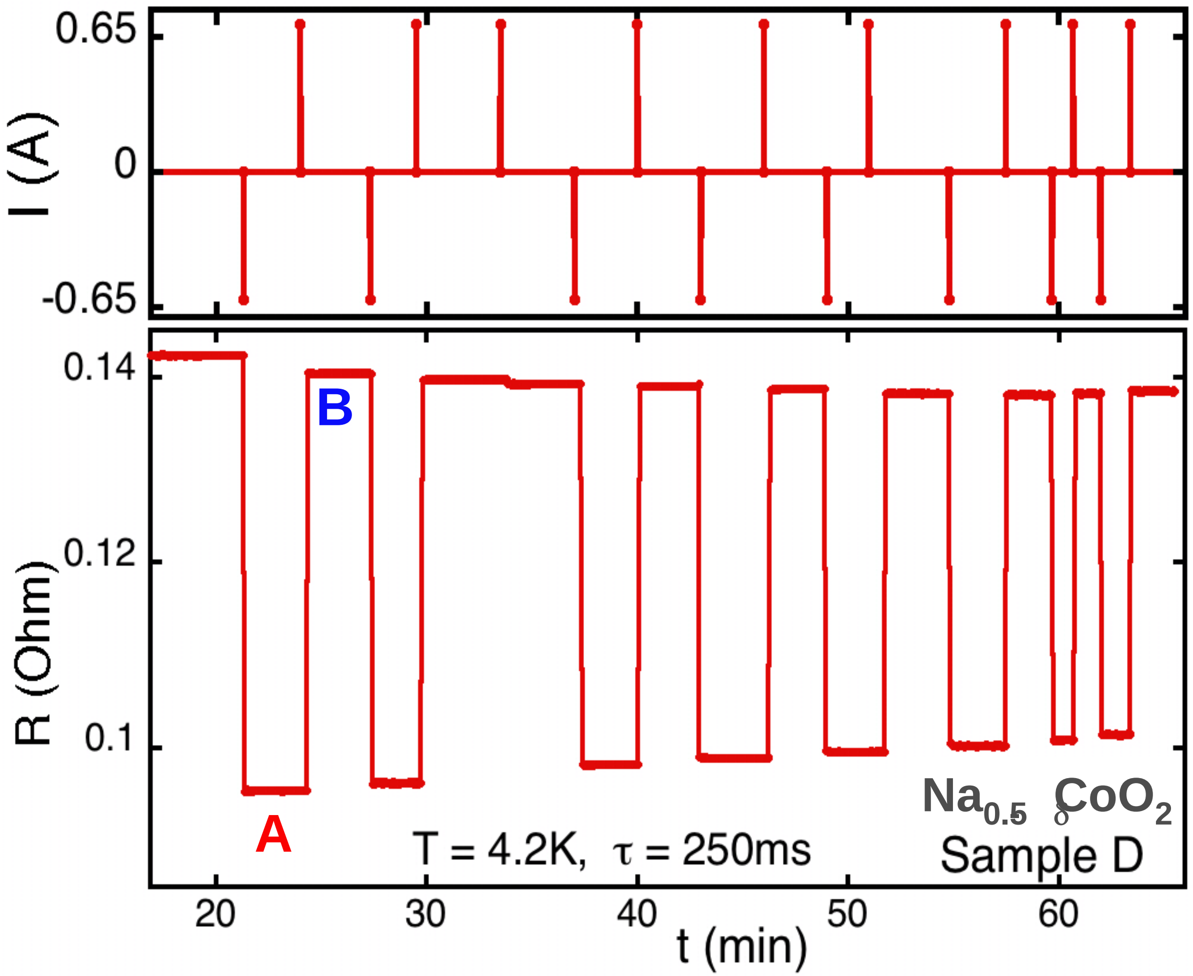
Possibility to control the resistance state

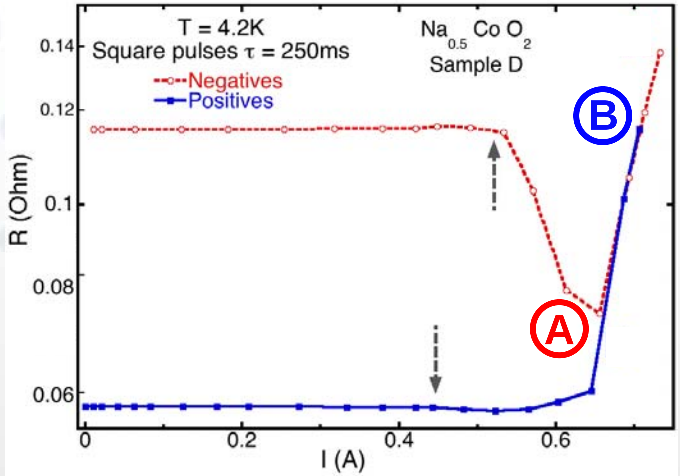


Garbarino et al, APL93p152110 (2008)

Results

Resistance Control





Bistable resistance state system

Write: High R
Positive Pulse

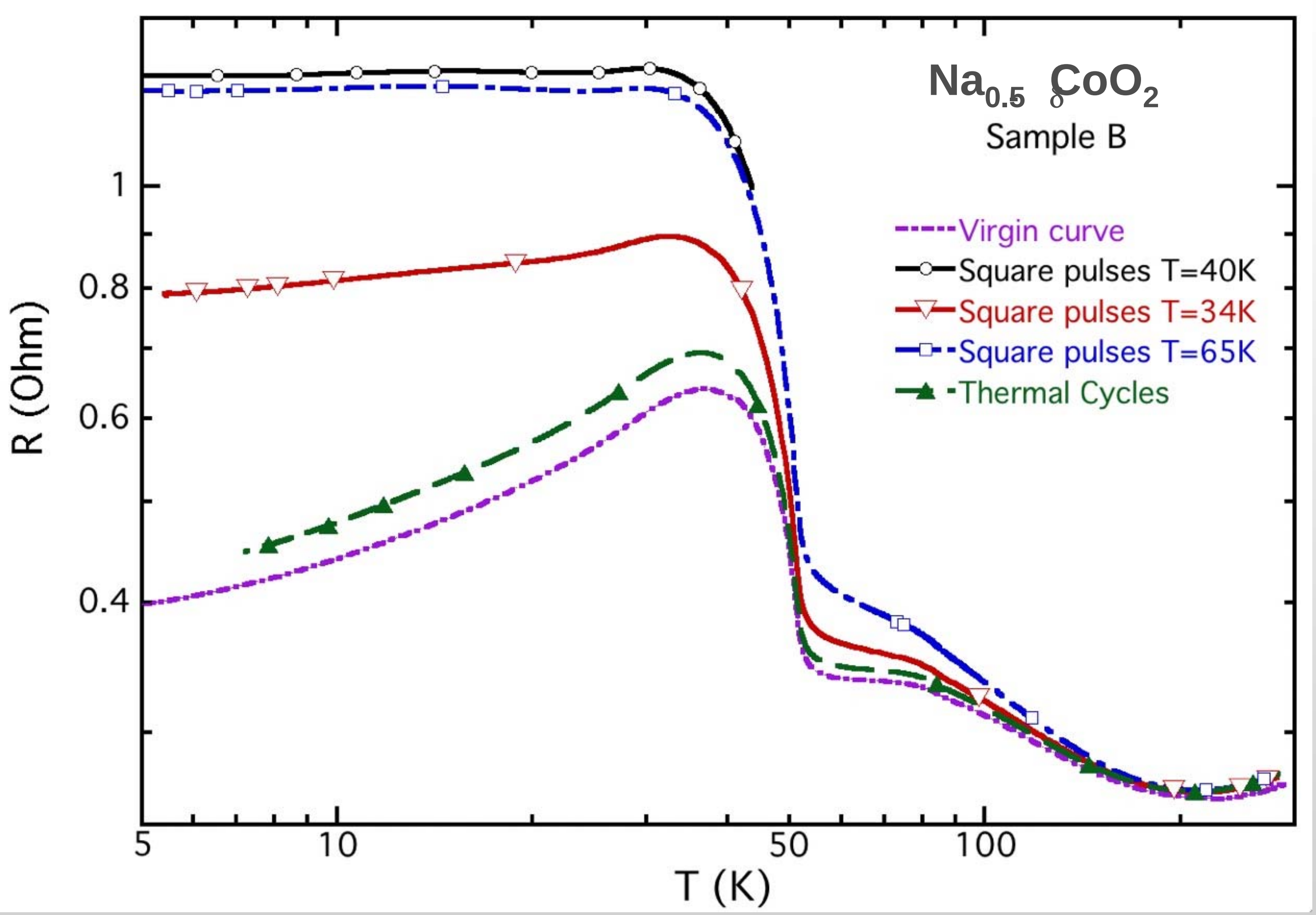
Erase: Low R
Negative Pulse

Read: Low courrent

Possibility to be used as **multistable resistance state system** by choosing diferent values of courrent

Garbarino et al, APL93p152110 (2008)

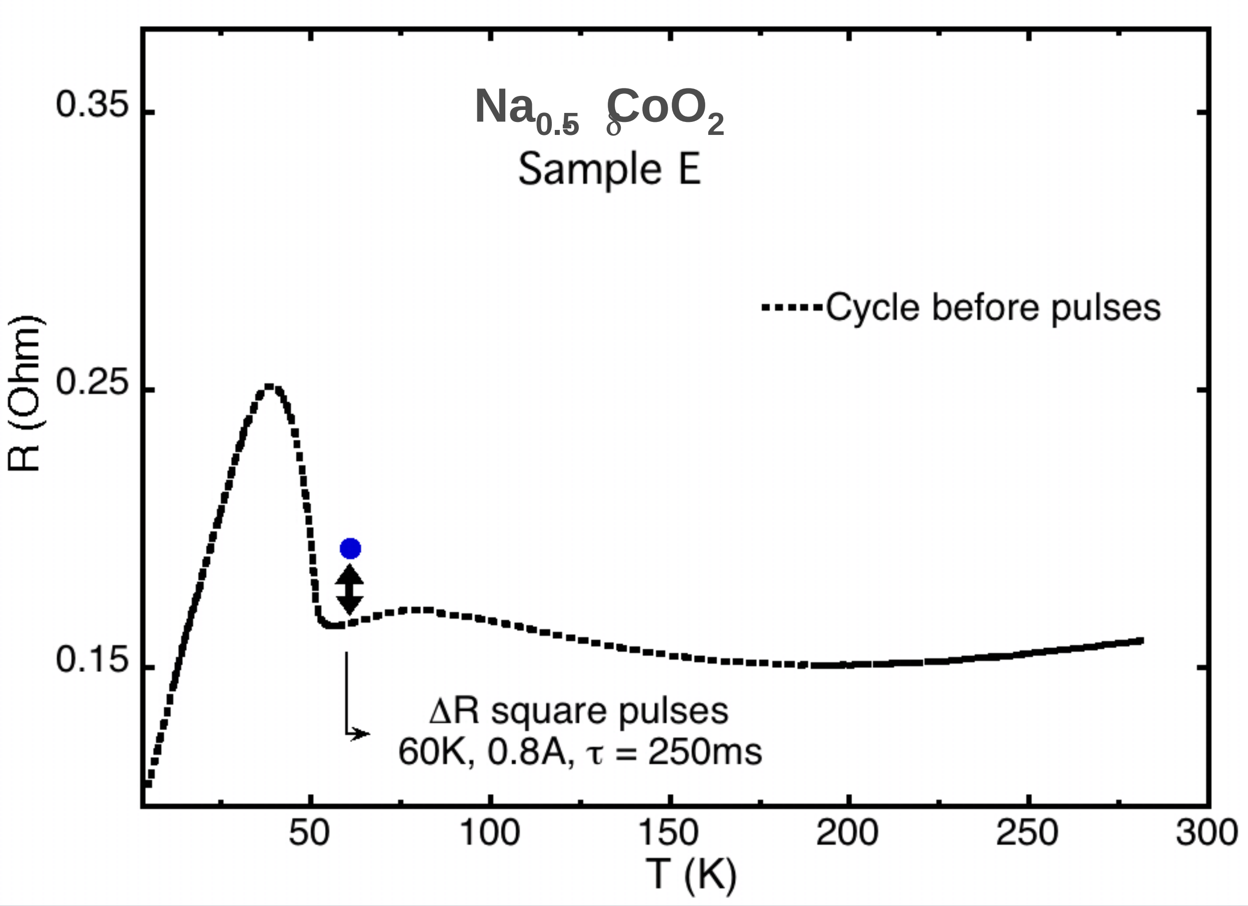
Resistance Control



By pulse application, we can induce an insulator state at low temperature

Temperature cycling

- Resistance changed by pulses
- Become to initial state by cycling up to ambient temperature



Temperature cycling

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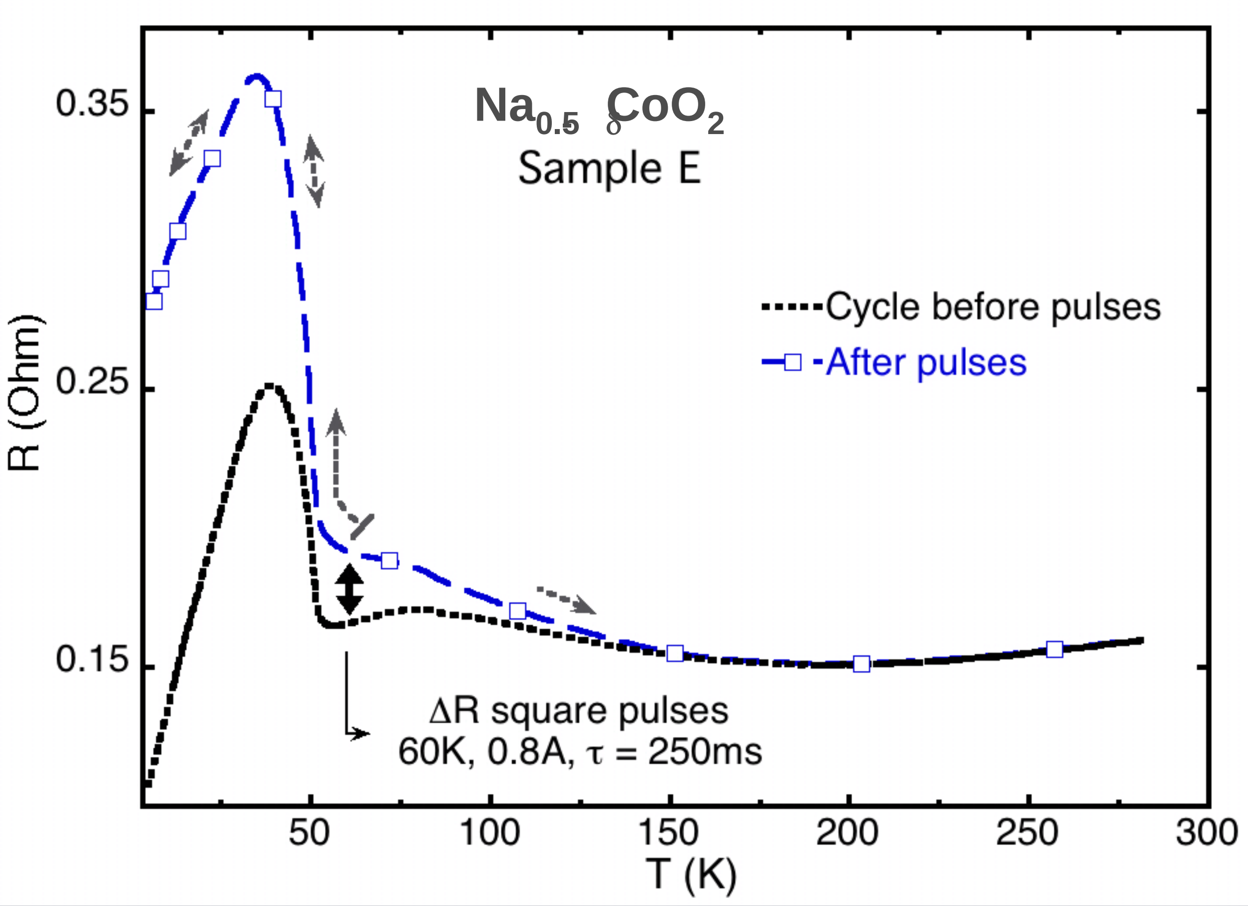


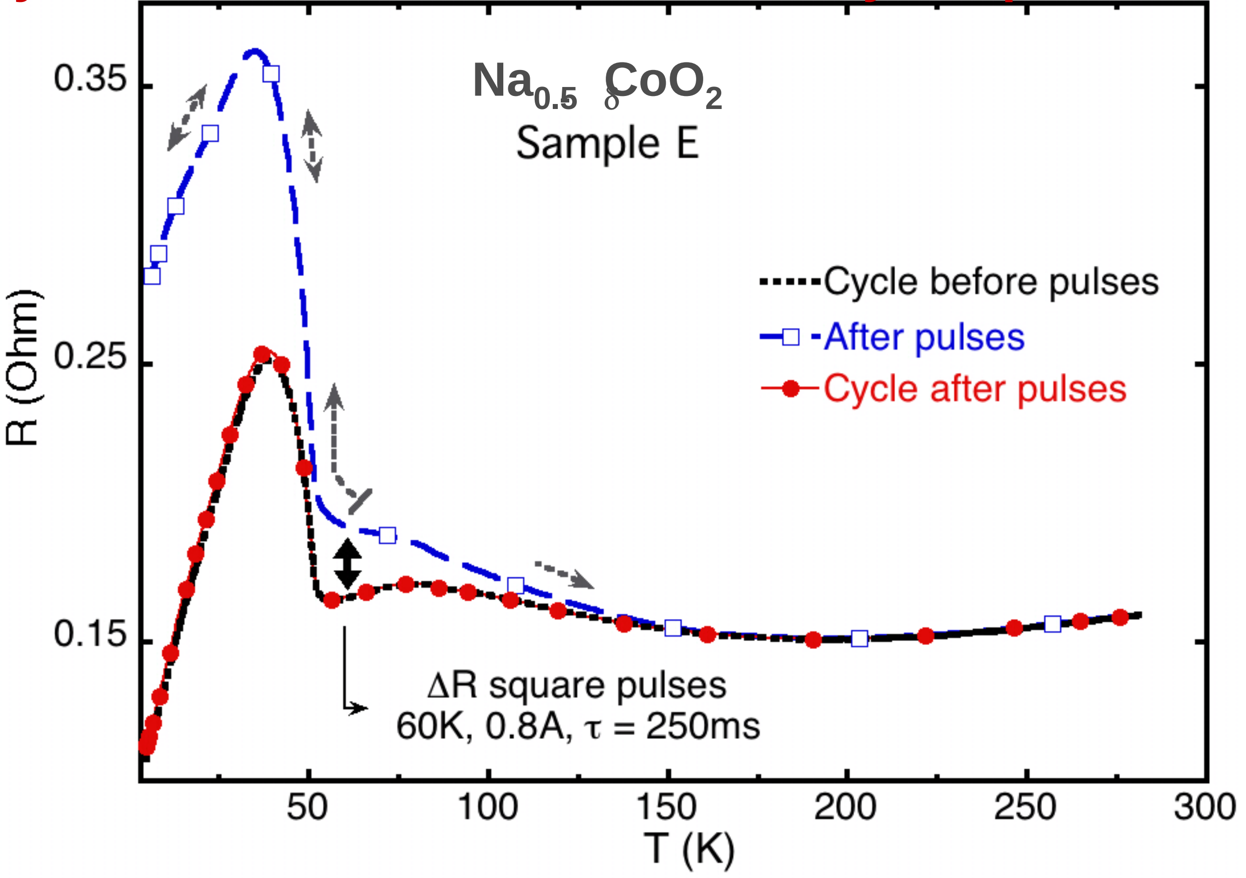
Results

Temperature cycling

- Resistance changed by pulses

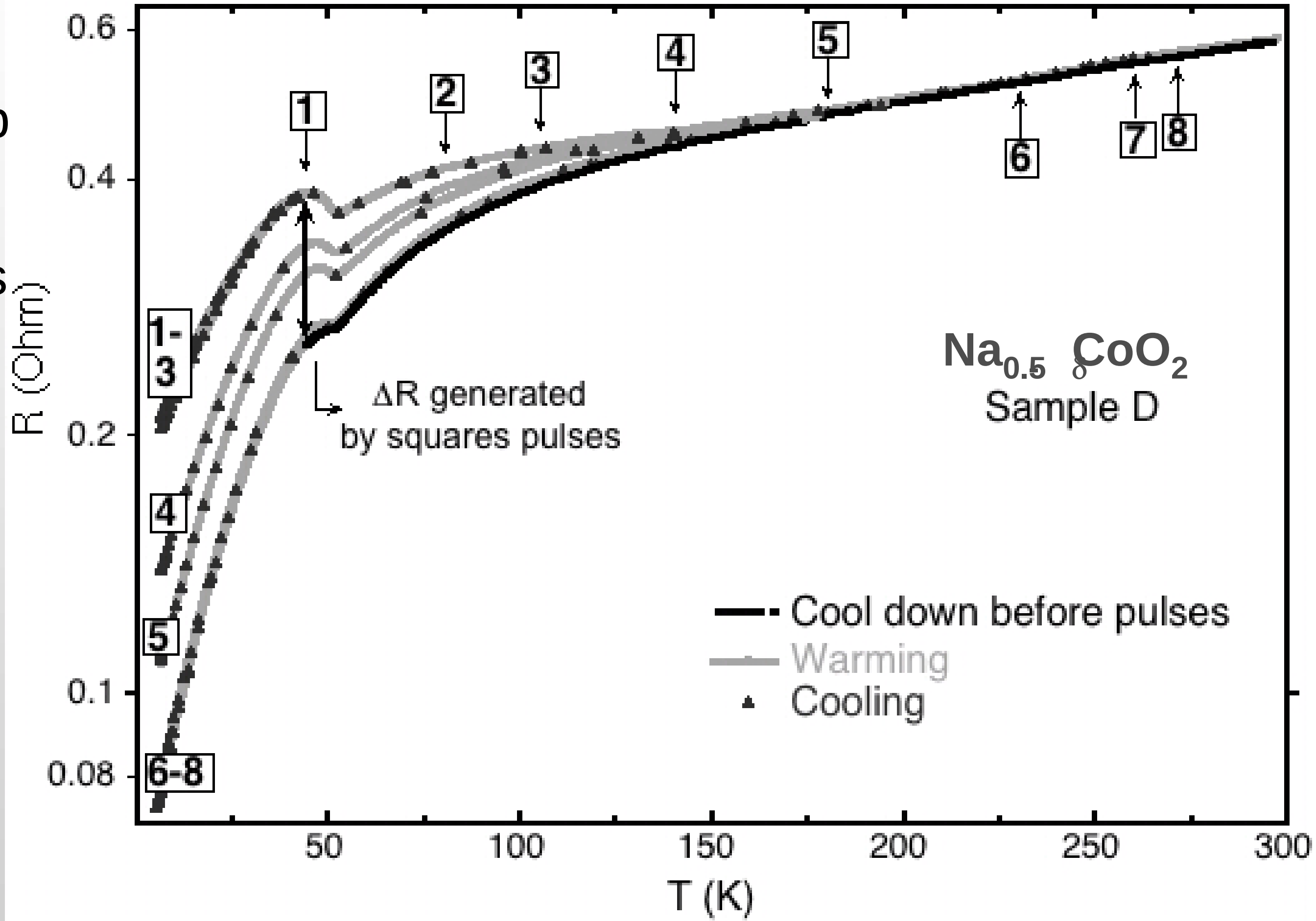
- Become to initial state by cycling up to ambient temperature

Possibility to control the resistance state by temperature cycling



Temperature cycling

- Sample cool down up to 50K
- ΔR induced by pulses
- Temperature cycles from 4.2K
- Low temperature resistance depends on the maximum temperature reached

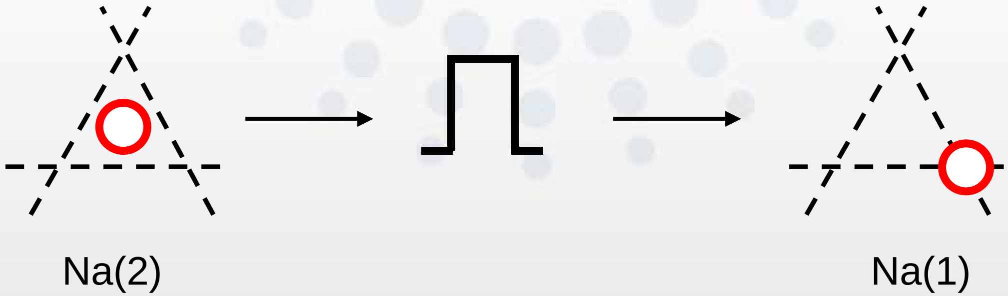


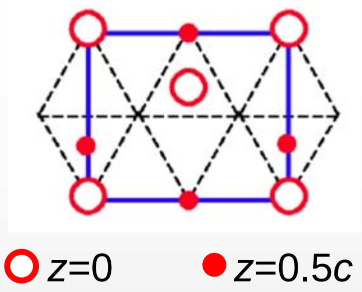
Garbarino et al, APL93p152110 (2008)

Possibility to be used as
monitoring of temperature sensitive system

Resistance Control

First order interpretation

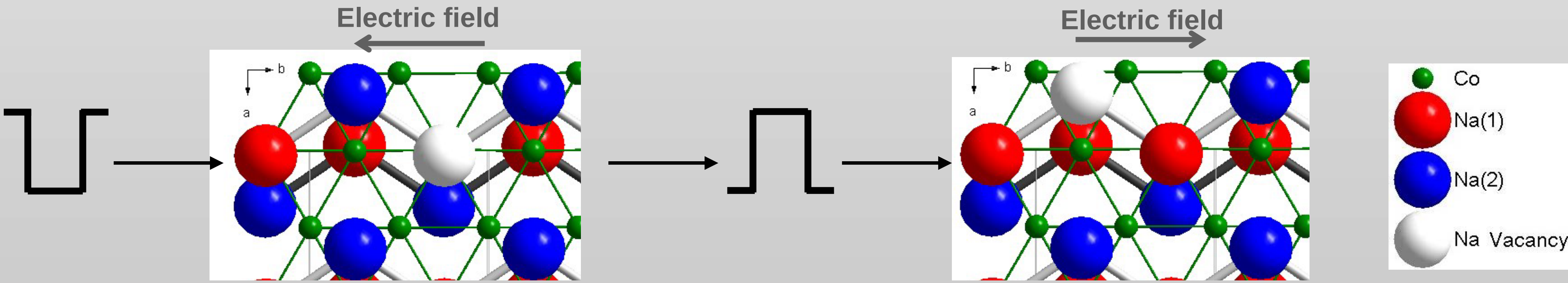




Current pulse induce the displacement of Na^+ from Na(1) to Na(2) position,

$$Co^{+3.5} \longrightarrow Co^{+3.5-\delta}$$

Transport properties are very sensitivity upon doping



Conclusions

- We have developed transport and crystallographic studies in powder and single crystal samples of $Na_{0.5}CoO_2$, under pressure up to 20GPa

- At 9GPa, a structural phase transition have been observed

- The disappearance of the transition at 88K under pressure, could be associated with the modification in the nesting of the Fermi surface, induced by the orthorhombic-hexagonal phase transition

- The transition at 53K increase with pressure

- Low temperature studies at higher pressure are necessary to better understand this results

- Simultaneous techniques are necessary to assure the analysis

Conclusions

• We are able to control the low temperature resistance of single crystals $Na_{0.5-\delta}CoO_2$ (T<130K) between a metalic and insulator state by applying current pulses.

• We show that it is a bistable or multistable system at low temperature, so it give the possibility to this compound to be used as a memory cell device (write, read and erase).

• The erase protocol can be replace by cycling in temperature, so it can also be monitoring of temperature sensitive system (cold chain indicator).

Perspectives

• X ray diffraction studies at low temperature to corroborate the concomitante transitions in transport and structure measurements

• Other techniques will allow to better understand Na_xCoO_2 system:

- Raman
- EXAFS-XANES very important change in Co neighbours

• Simultaneous measurements of X-ray diffraction and transport & magnetic properties in DAC.

Not only very interesting for this compounds but also in superconductors-delafossite-fluorite-charge density wave compounds.

Ex.: superconductivity in doped C60 under pressure

• Extend the Resistance Control studies to other systems: like layered compounds in order to obtain the same effect at room temperature

Acknowledgements

M. Núñez Regueiro Institut Néel, CNRS, France

W. Crichton, P. Bouvier, M. Mezouar,
J.P. Perrillat, G. Morard, S.Bauchau ESRF, Grenoble, France

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M. Armand LRCS, Univ. Jules-Verne, France

M. L. Foo, R. J. Cava Department of Chemistry, Princeton Univ., USA

Thank you for your attention!!!

Experimental

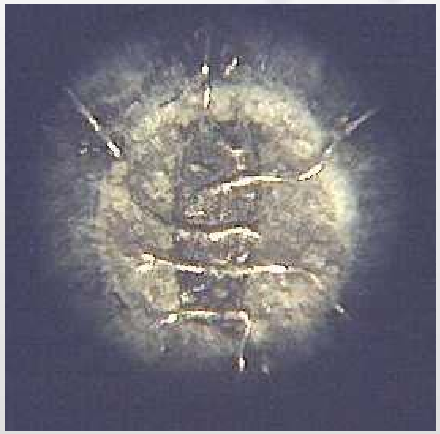
Transport and magnetic properties under pressure

- Quasi-hydrostatic cell (P<30 GPa)
- Hydrostatic cell (P<1.2 GPa)
- Uniaxial cell (P<100MPa)

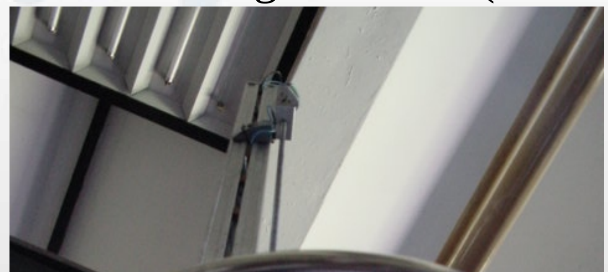
Temperature 2 K < T < 360 K

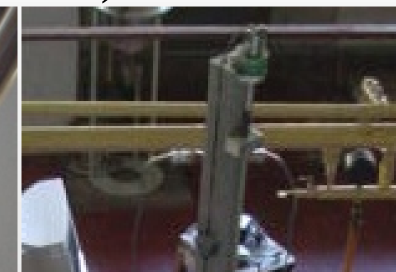
Completely automatized

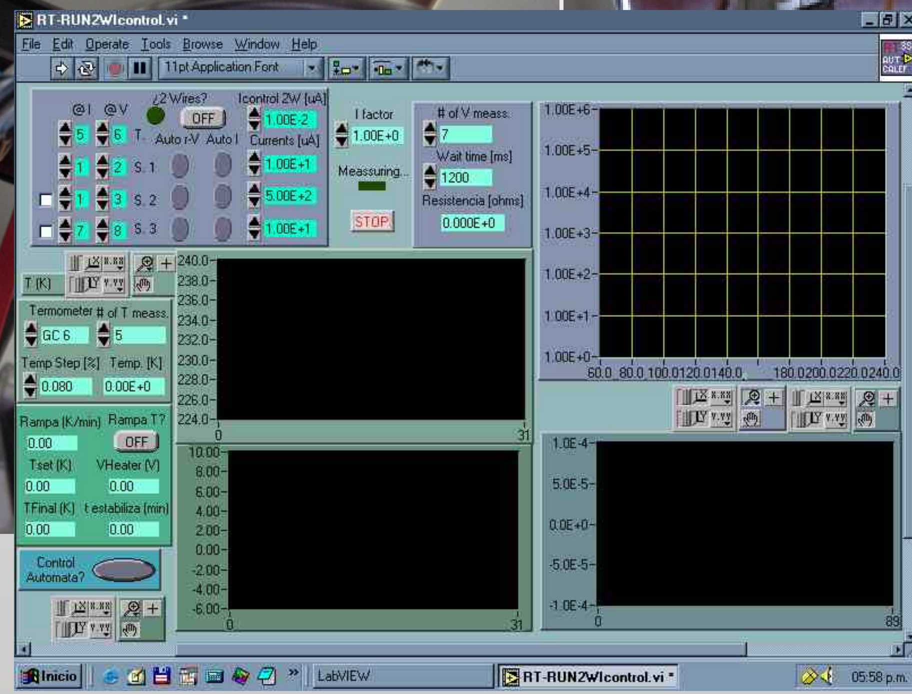
- Resistance (4W y 2W) (P<30GPa)
- ac Susceptibility (P<1.2GPa)
- Magnetization (P<50MPa)



200µm



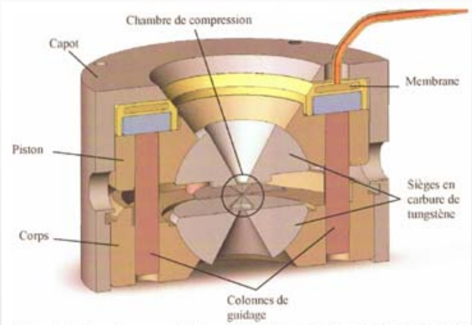




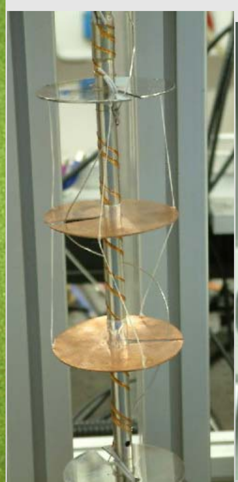
Experimental

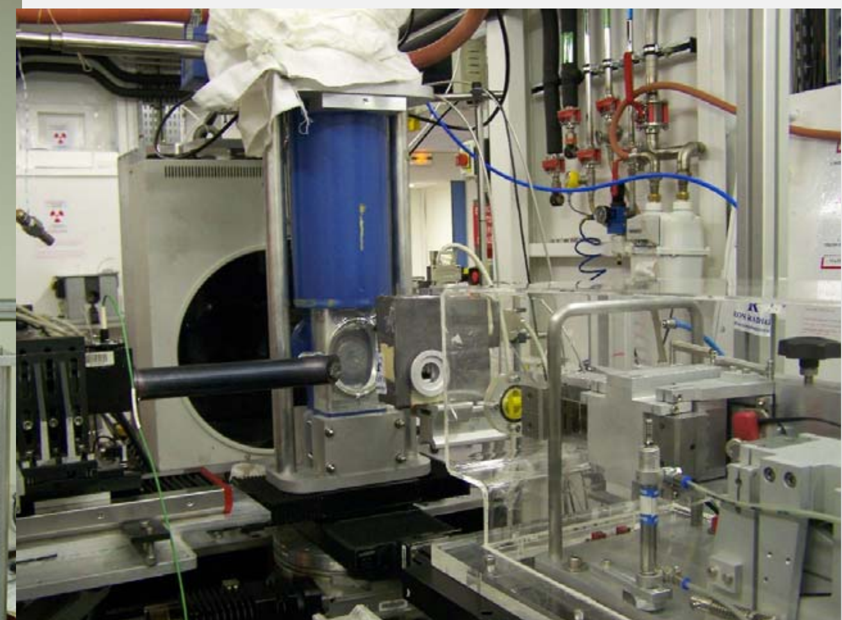
Structural properties under pressure

- Membrane Diamond Anvil Cell @ room temperature



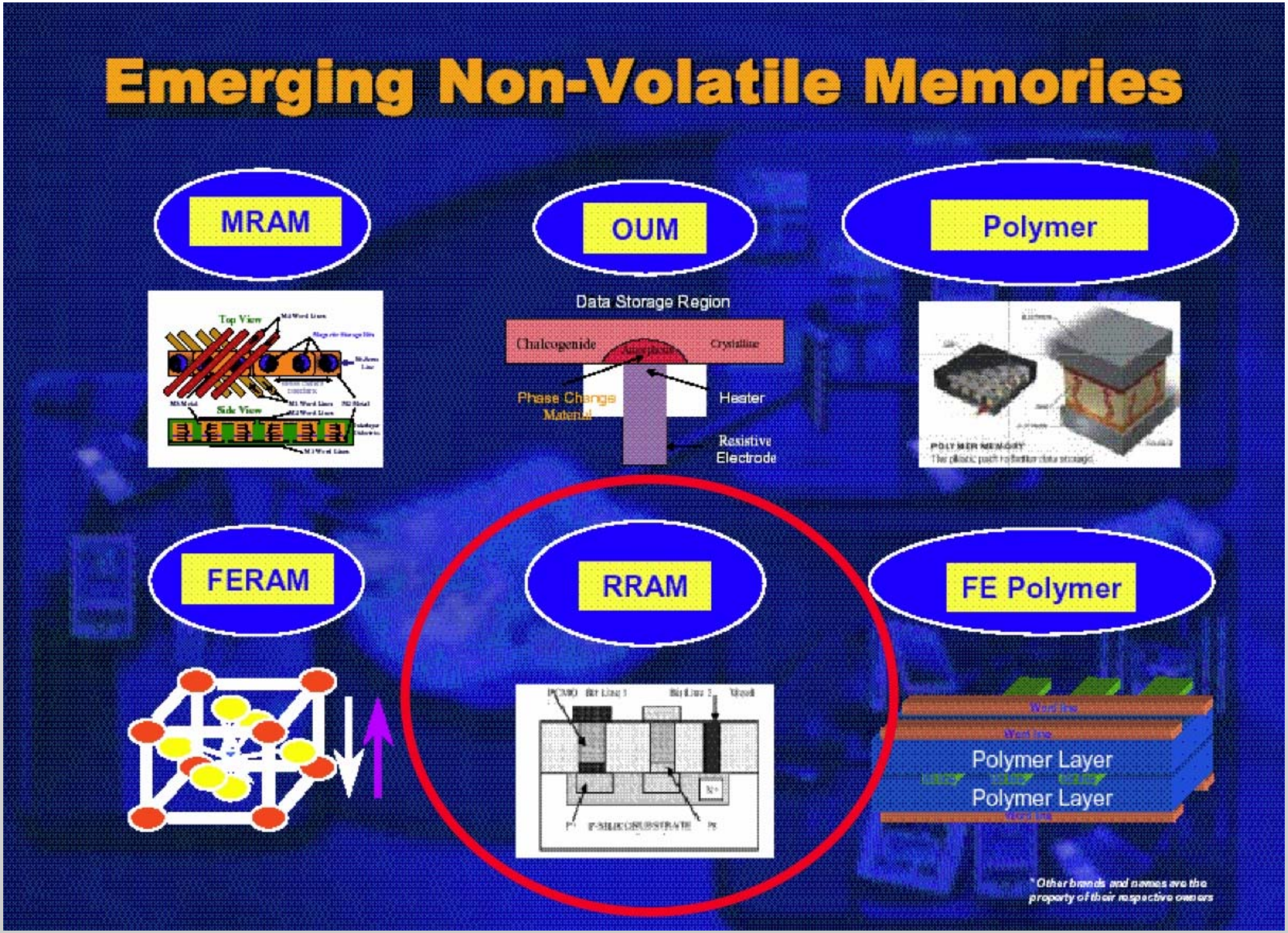
- Helium flow Cryostat, **T ≥ 4K, comsuption ~1l/h@30K**
- **Completely automatized**
- **Future Raman measurements & other techniques**
- Permanent facility at ID27

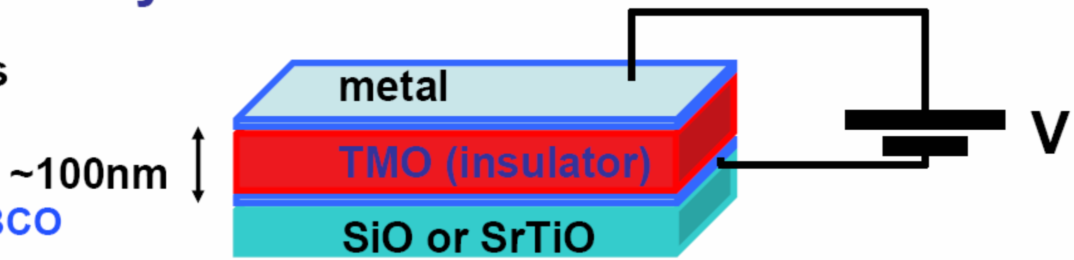
Proposed new technologies

From Intel website



Typical RRAM systems

PLD made films

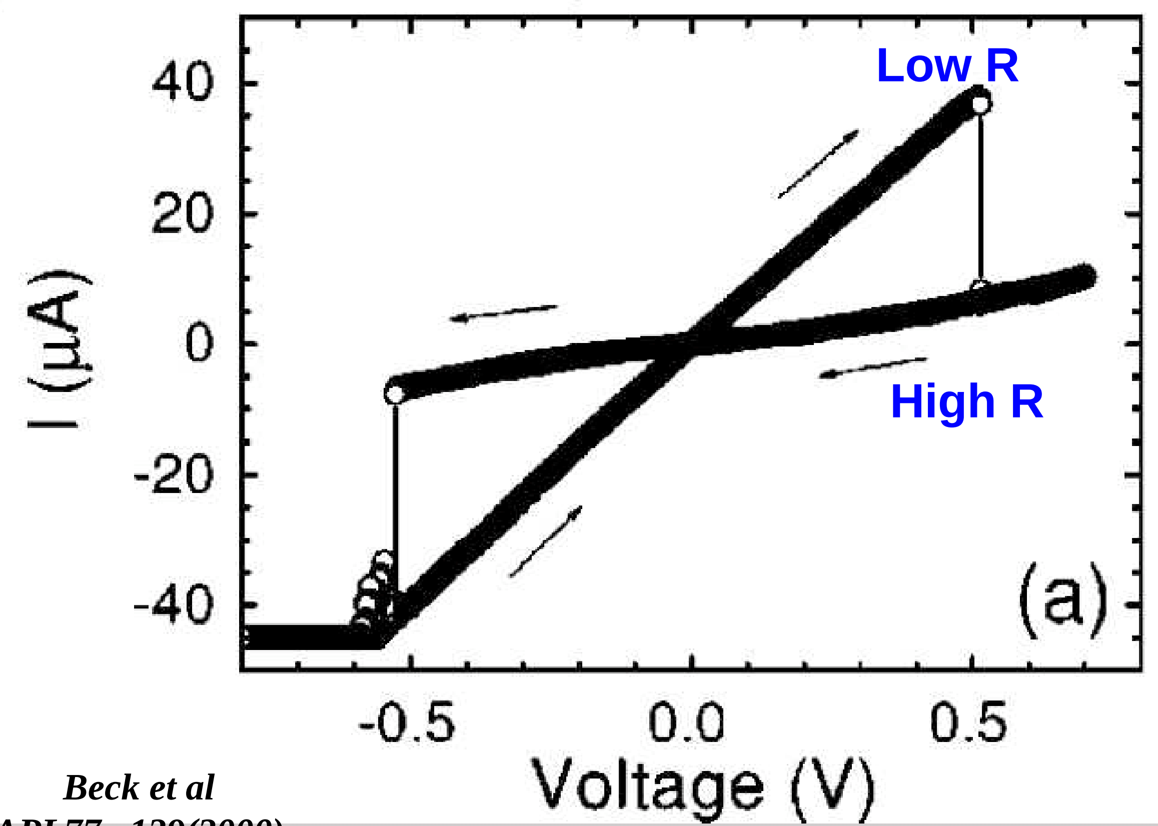


Au, Pt, SrRuO, YBCO

PrCaMnO, (Ba,Sr)TiO, SrZrO, Cr or V doped, CeO, NiO, etc…

Memory device

Metal-Insulator-Metal
FET like-structure
Pt-$SrZrO_3$-Au
- 20nm<e<300nm
- $80\mu m^2 < A < 4*10^4 \mu m^2$



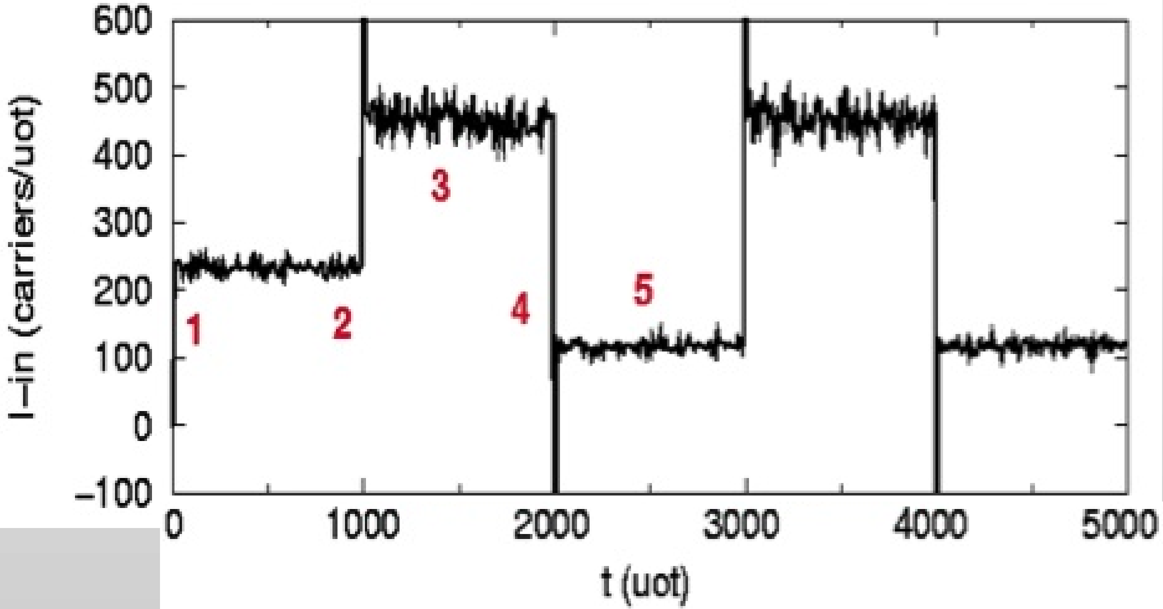
Beck et al
APL 77 p139(2000)

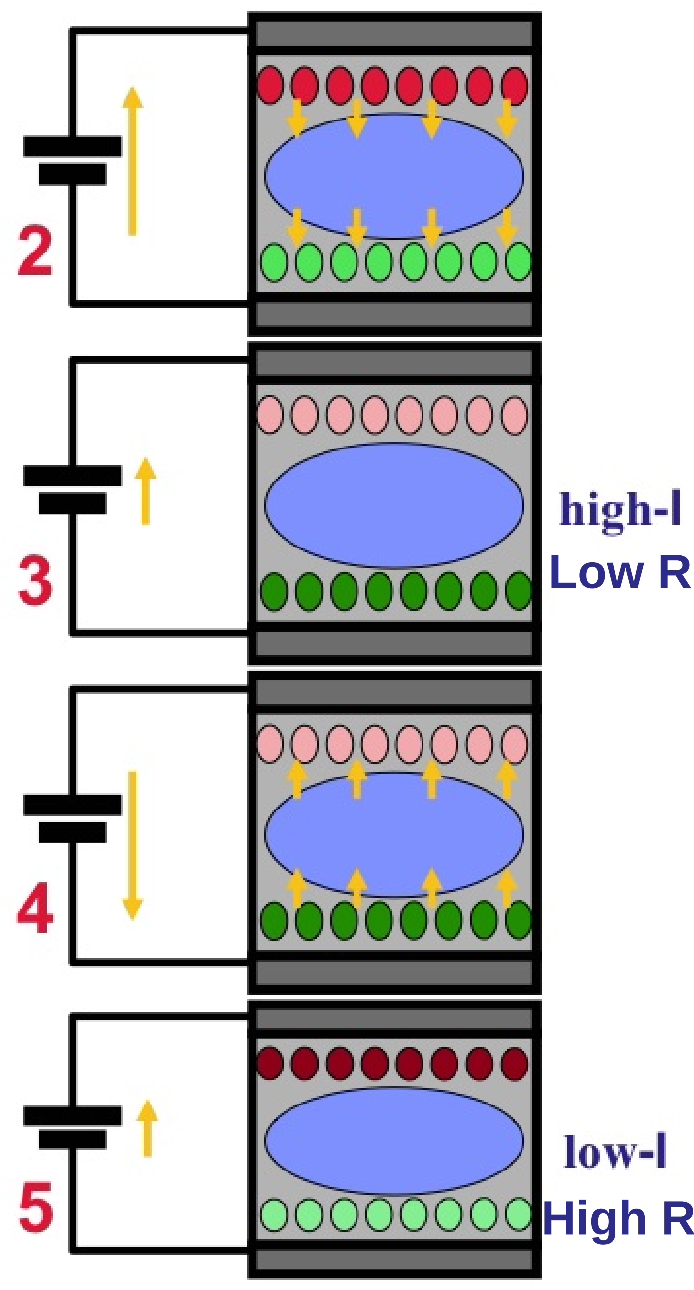
Introduction

Phenomenological model

M.J.Rozenberg et al PRL92 p178302 (2004)

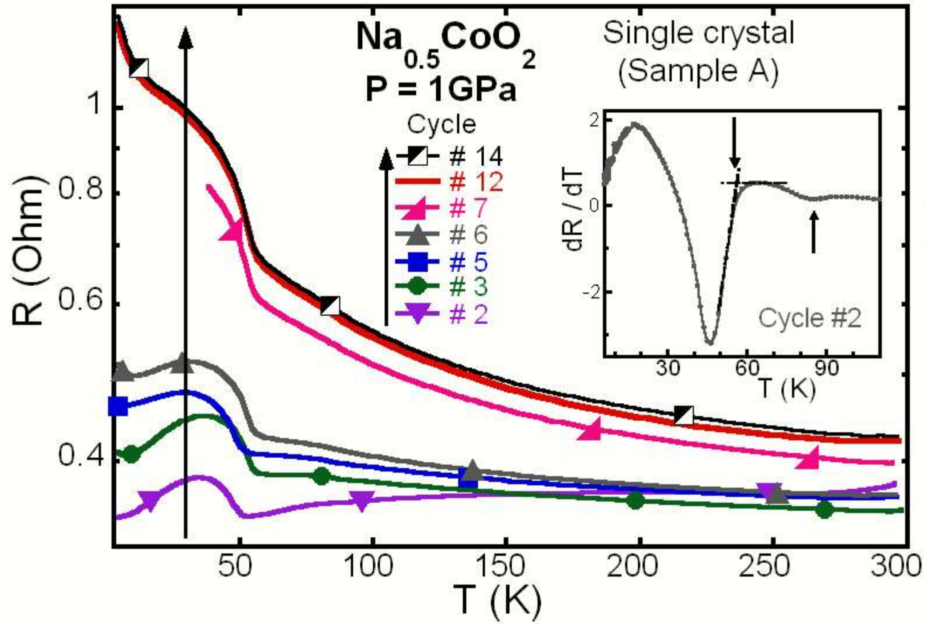
- **Inhomogeneities** are ubiquitous in TMOs
  - Dagotto (manganites), Davis (STM in HTc)
  - PLD technique (deffects, domains, etc)
- **Insulators** that become metals upon doping (even strongly correlated ones)

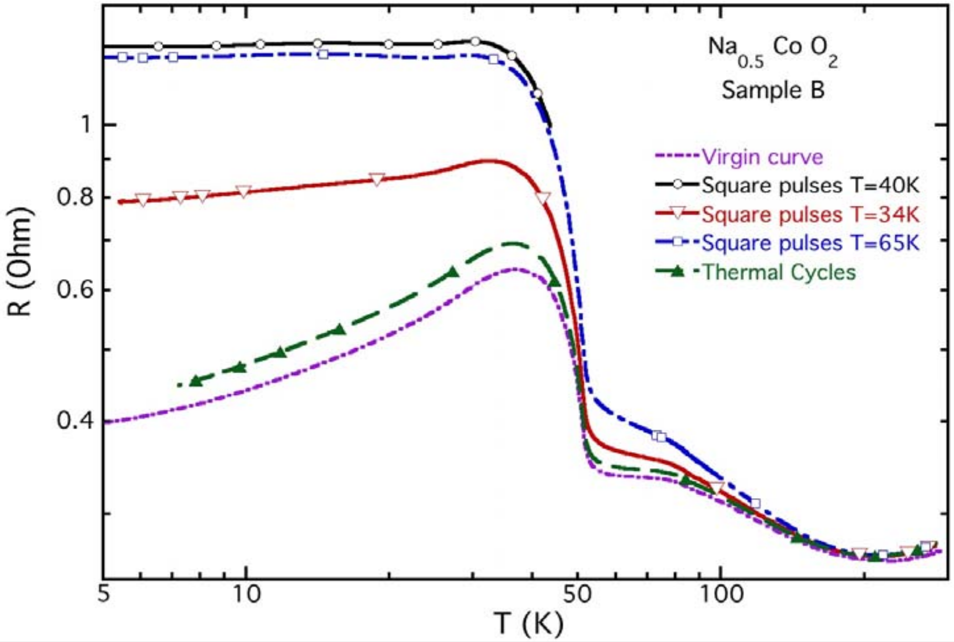


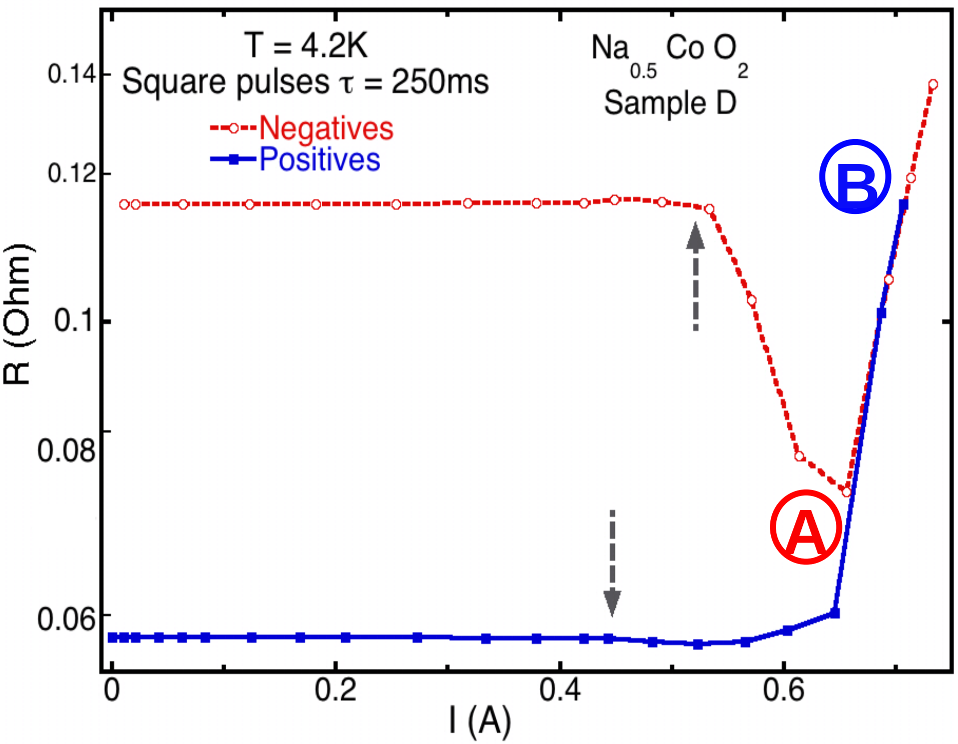


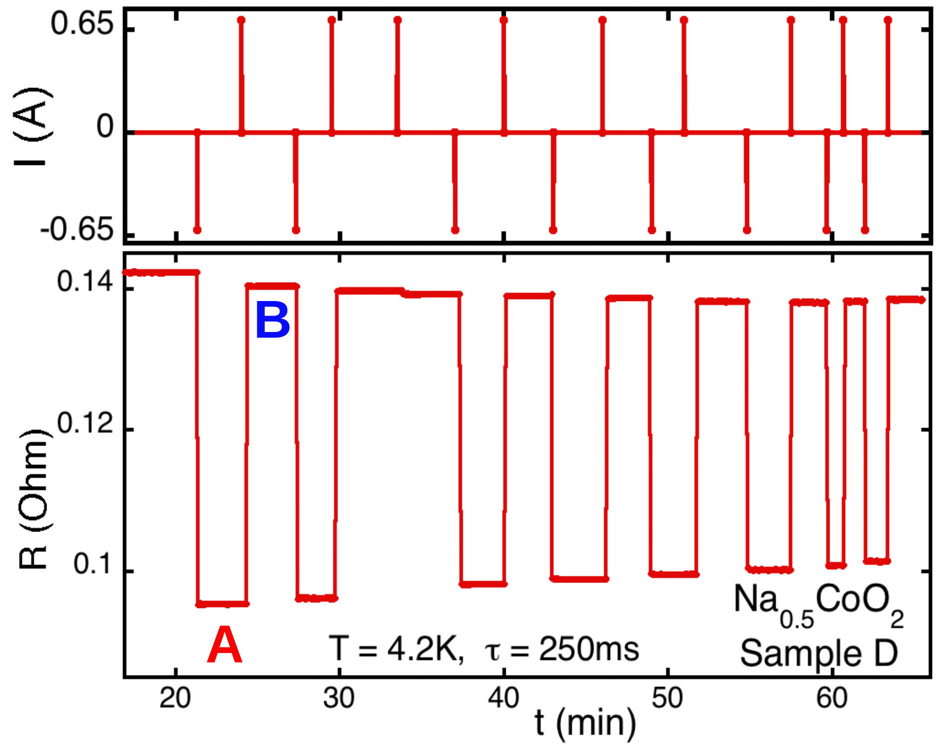
Parameters of the model:

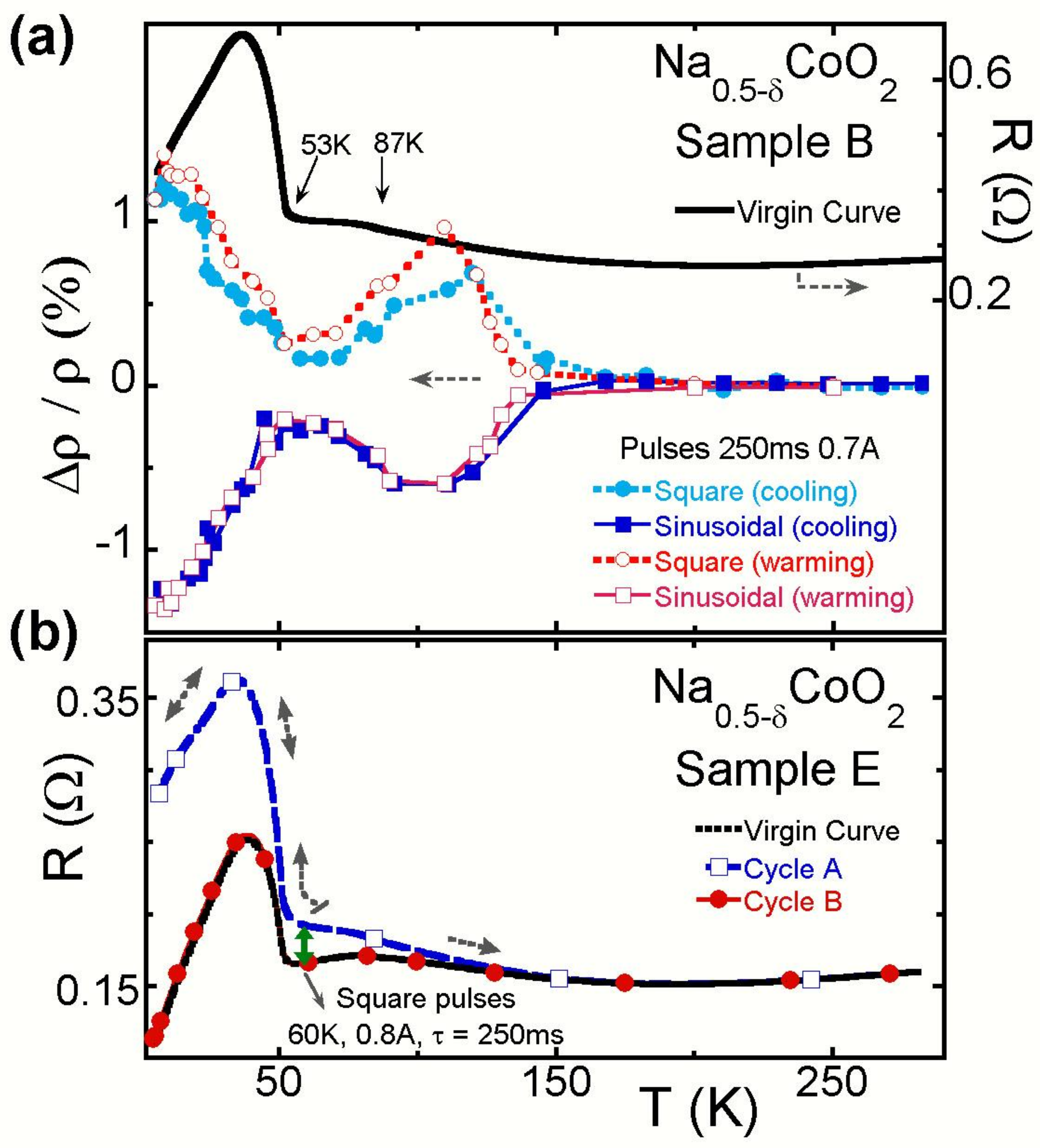
- $p_{AB} = \gamma_{AB} N_B [1 - n(B)] f_{AB}(V)$
- $\Gamma_{ET} = \Gamma_{BE} << \Gamma_{TM} = \Gamma_{MB}$, $\Gamma_{AB} = <\gamma_{AB}>$

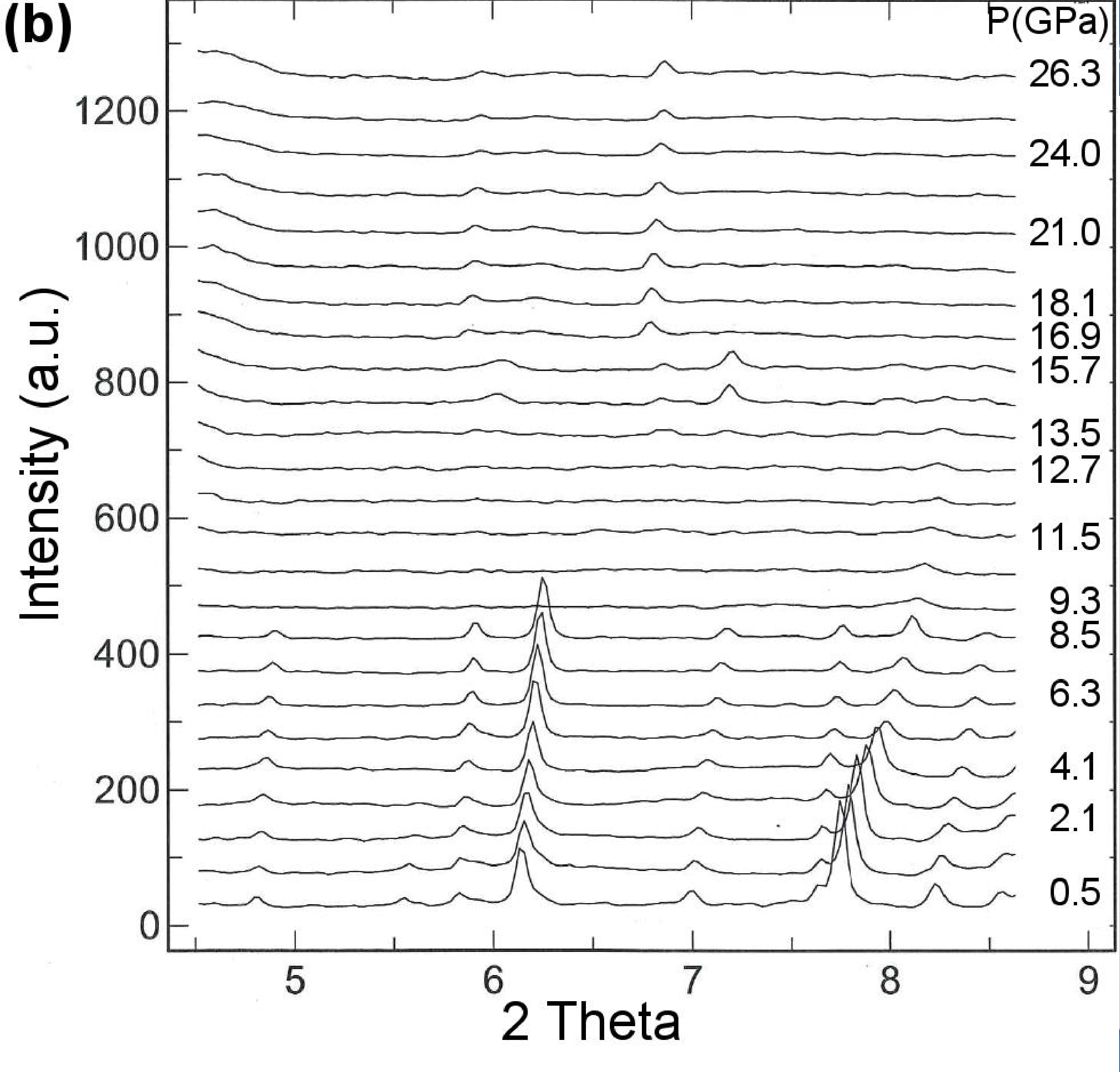

Na0.5CoO2
P = 1GPa
Single crystal
(Sample A)
Cycle
14
12
7
6
5
3
2
dR / dT
Cycle #2
T (K)
R (Ohm)
T (K)

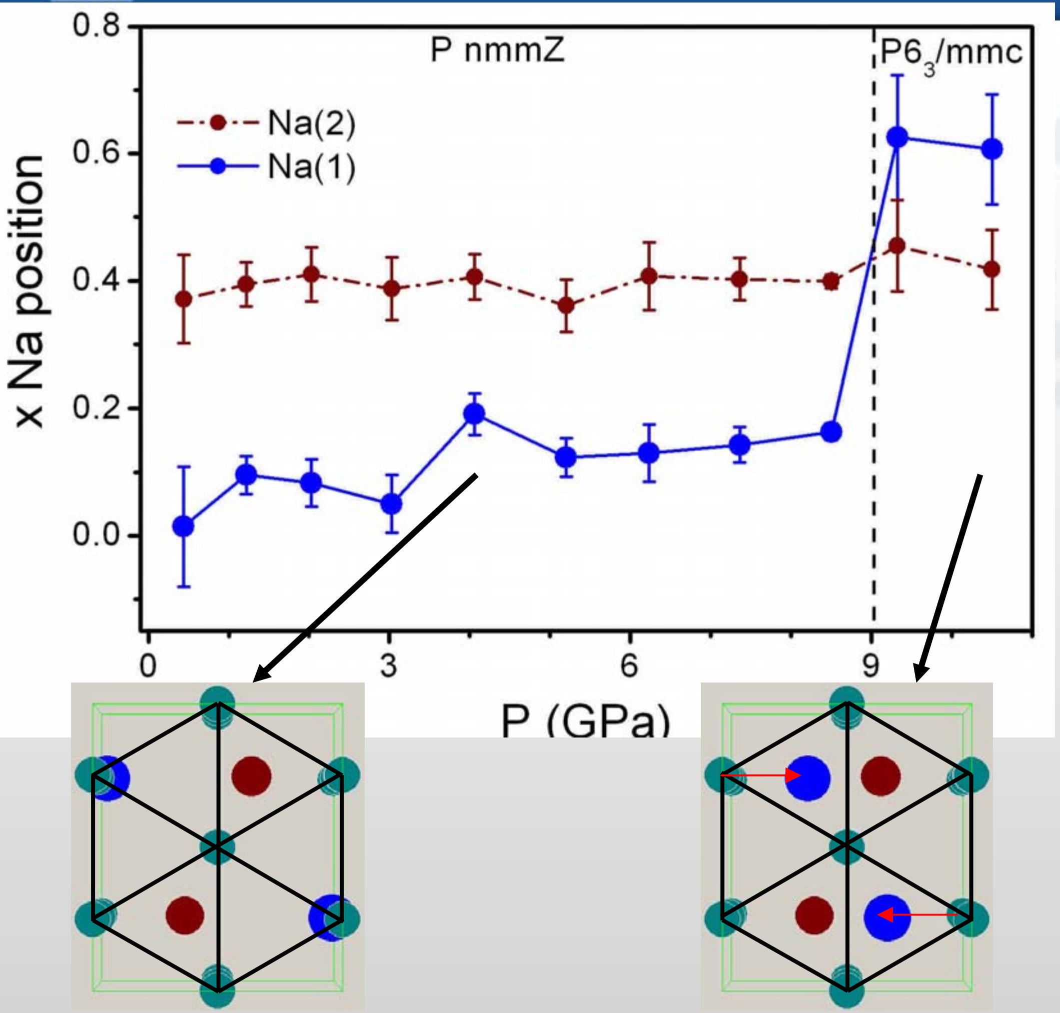

Na0.5 Co O2
Sample B
Virgin curve
Square pulses T=40K
Square pulses T=34K
Square pulses T=65K
Thermal Cycles
R (Ohm)
T (K)


T = 4.2K
Square pulses τ = 250ms
Na0.5 Co O2
Sample D
Negatives
Positives
B
A
R (Ohm)
I (A)


I (A)
B
A
R (Ohm)
T = 4.2K, τ = 250ms
Na0.5CoO2
Sample D
t (min)


(a)
$Na_{0.5-\delta}CoO_2$
Sample B
53K
87K
Virgin Curve
Pulses 250ms 0.7A
Square (cooling)
Sinusoidal (cooling)
Square (warming)
Sinusoidal (warming)
Δρ / ρ (%)
R (Ω)
1
0
-1
0.6
0.2
(b)
$Na_{0.5-\delta}CoO_2$
Sample E
Virgin Curve
Cycle A
Cycle B
Square pulses
60K, 0.8A, τ = 250ms
R (Ω)
0.35
0.15
50
150
250
T (K)

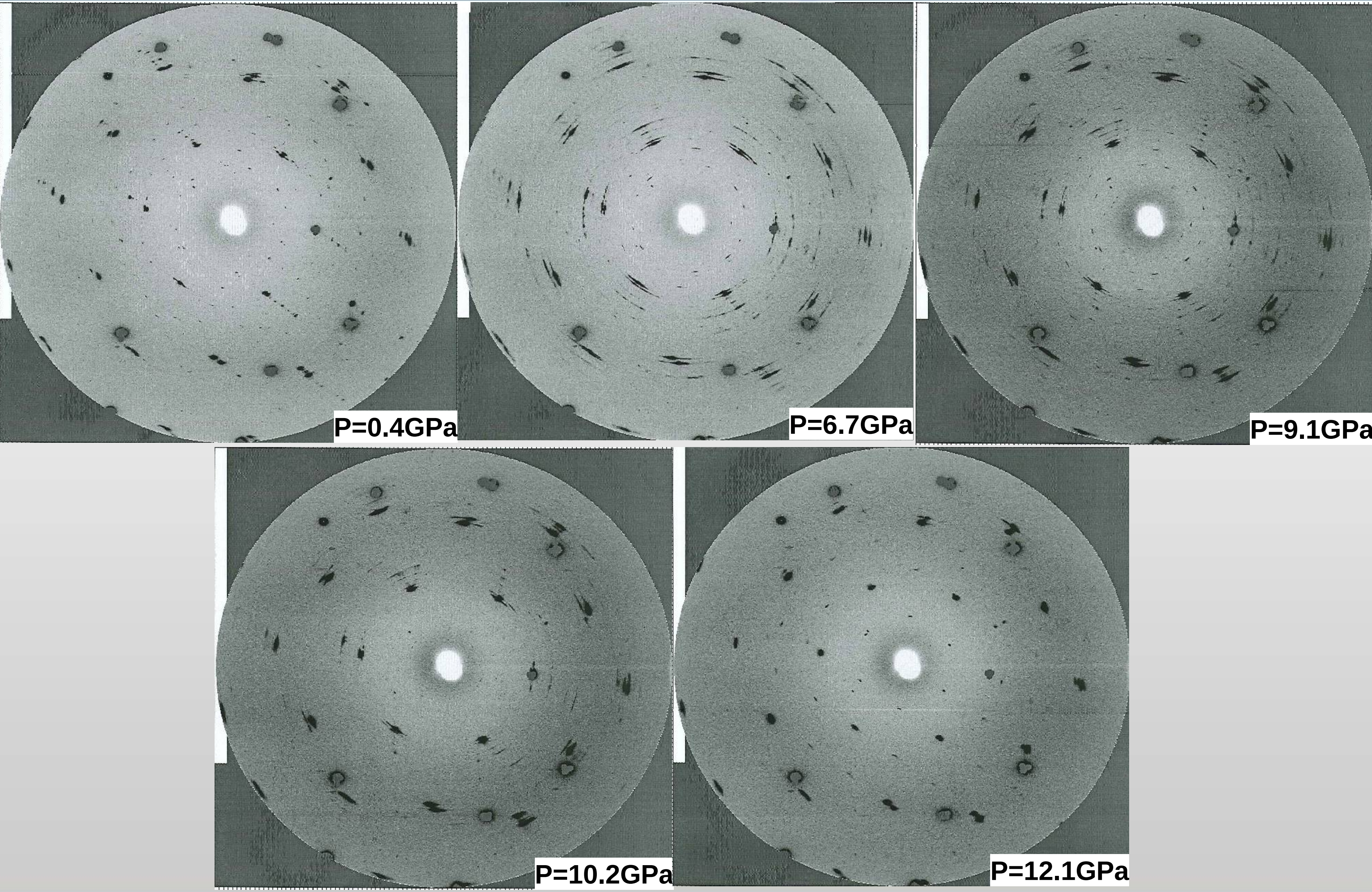

(b)
P(GPa)
26.3
24.0
21.0
18.1
16.9
15.7
13.5
12.7
11.5
9.3
8.5
6.3
4.1
2.1
0.5
1200
1000
800
600
400
200
0
Intensity (a.u.)
5
6
7
8
9
2 Theta

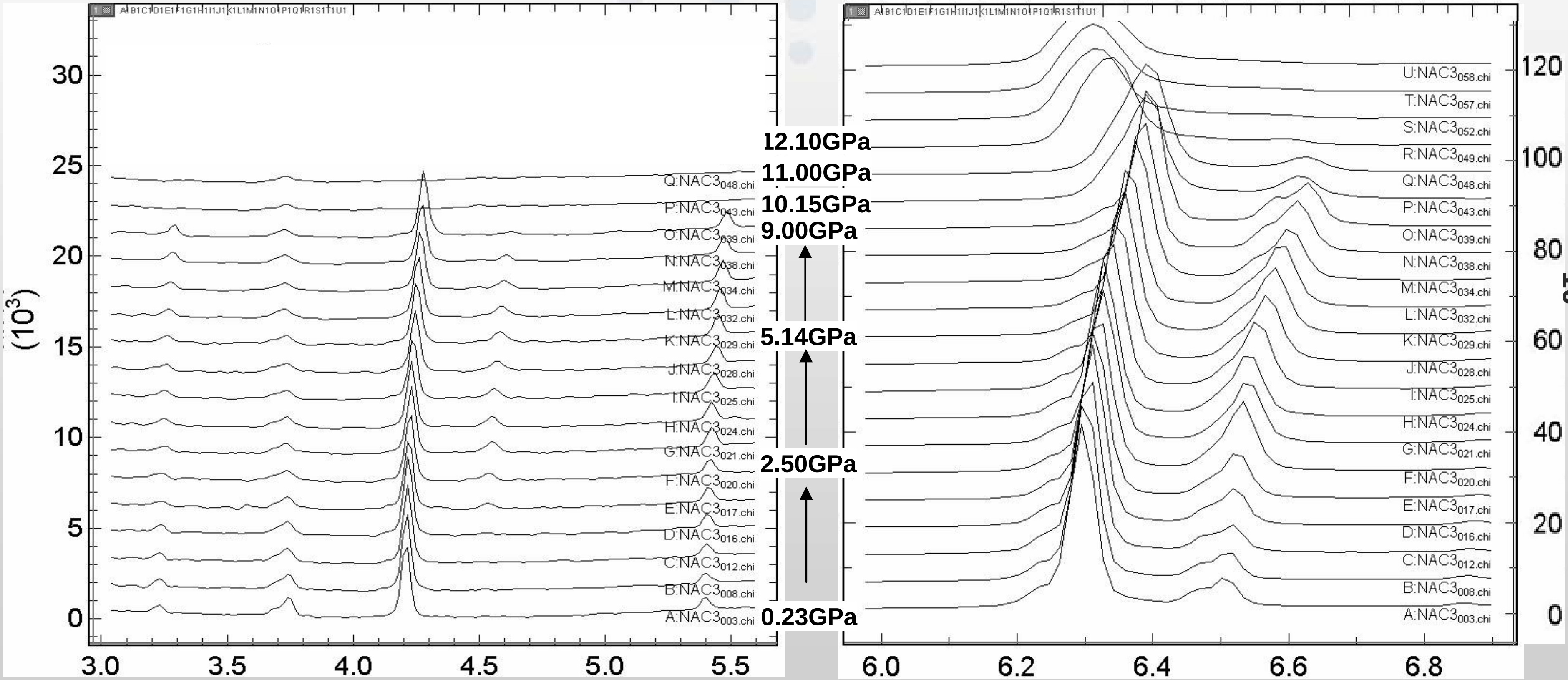


Pressure induces transition from:

- **Na(1) to Na(2) position**
- **Orthorhombic to hexagonal phase**

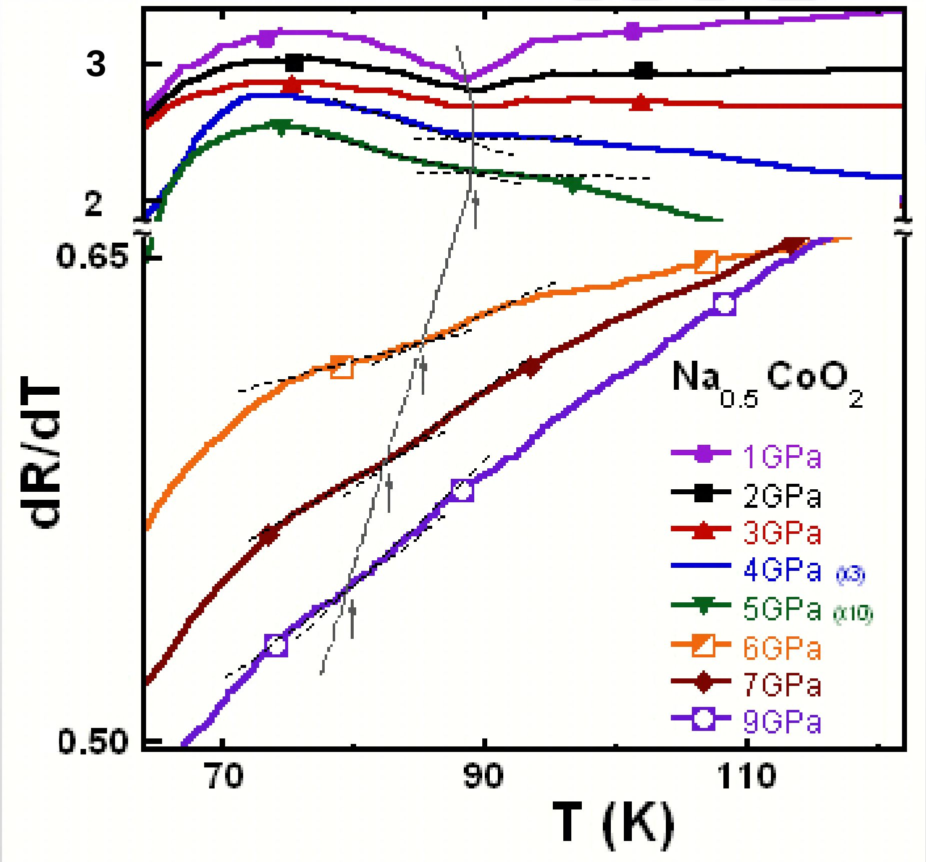
$Na_{0.5}CoO_2$ Single Crystal

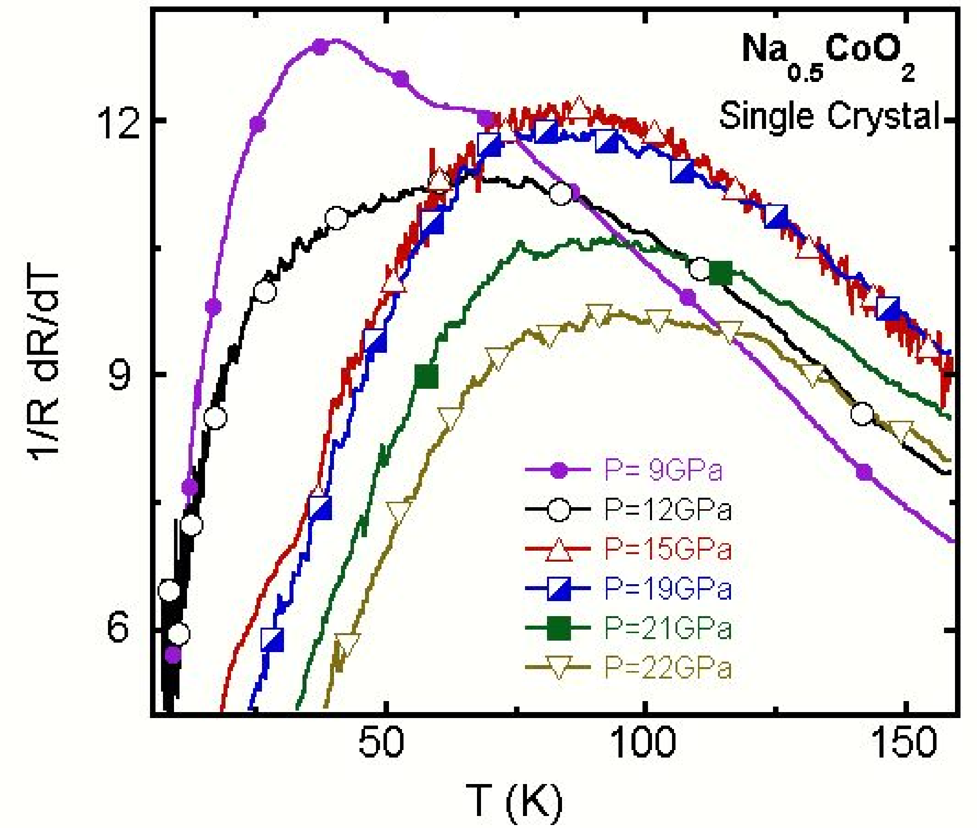




12.10GPa
11.00GPa
10.15GPa
9.00GPa
5.14GPa
2.50GPa
0.23GPa
(10^3)
10^3
Q:NAC3048.chi
P:NAC3043.chi
O:NAC3039.chi
N:NAC3038.chi
M:NAC3034.chi
L:NAC3032.chi
K:NAC3029.chi
J:NAC3028.chi
I:NAC3025.chi
H:NAC3024.chi
G:NAC3021.chi
F:NAC3020.chi
E:NAC3017.chi
D:NAC3016.chi
C:NAC3012.chi
B:NAC3008.chi
A:NAC3003.chi
U:NAC3058.chi
T:NAC3057.chi
S:NAC3052.chi
R:NAC3049.chi

Results: Transport





P<9GPa • **Pressure dependence of T_M**

P>15GPa: • **Different behavior of 1/R dR/dT**