Superconductor Cobaltites

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Solid State II

Outline

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- Superconductivity inCobalt Oxides
  - Structure and Phase Diagrams of
    - Na_XCoO_2
    - $Na_xCoO_2 \cdot 1.3H_2O$
  - Superconductivity in 2-D CoO Layers
- Summary

Superconductivity in Copper Oxides

- Discovered in 1986* by

    J. G. Bednorz

    K. A. Müller

  in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$

*In 1987 Müller and Bednorz were jointly awarded the Nobel Prize in physics the shortest time between the discovery and the prize award for any Nobel.

Possible High T_c Superconductivity in the Ba – La – Cu – O System

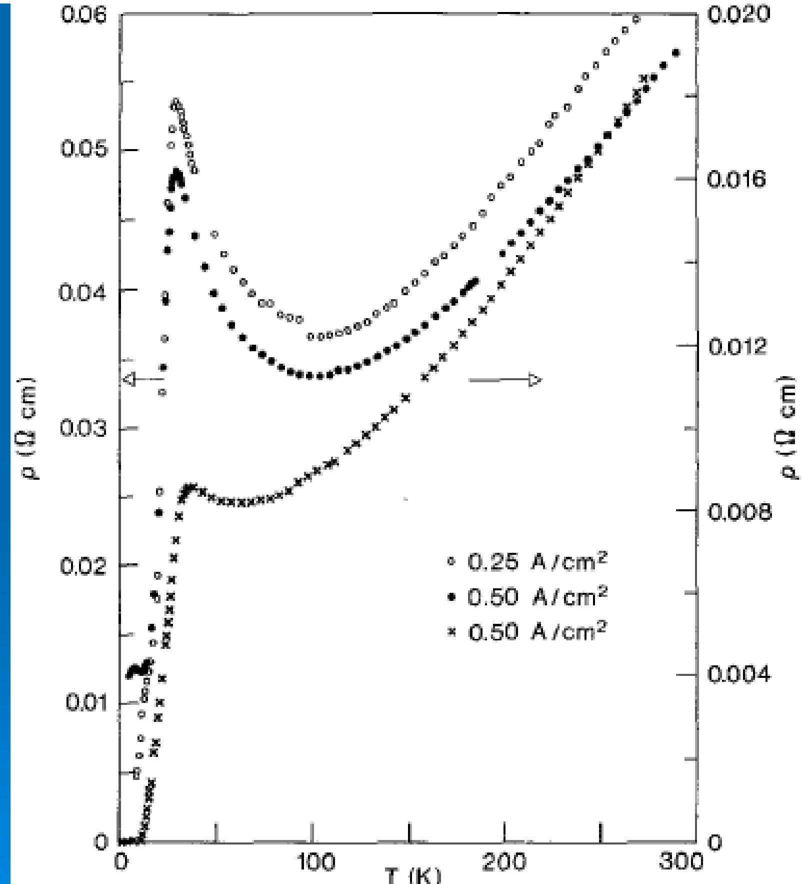
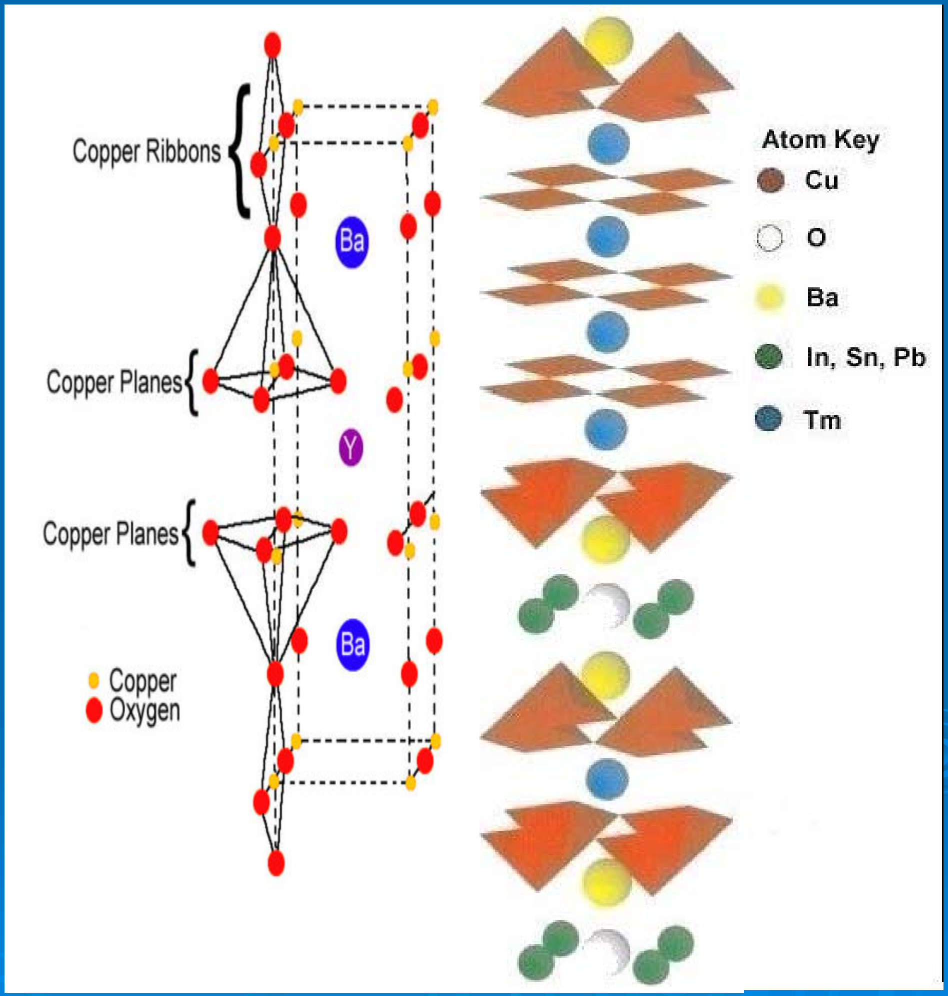


Fig. 1. Temperature dependence of resistivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$

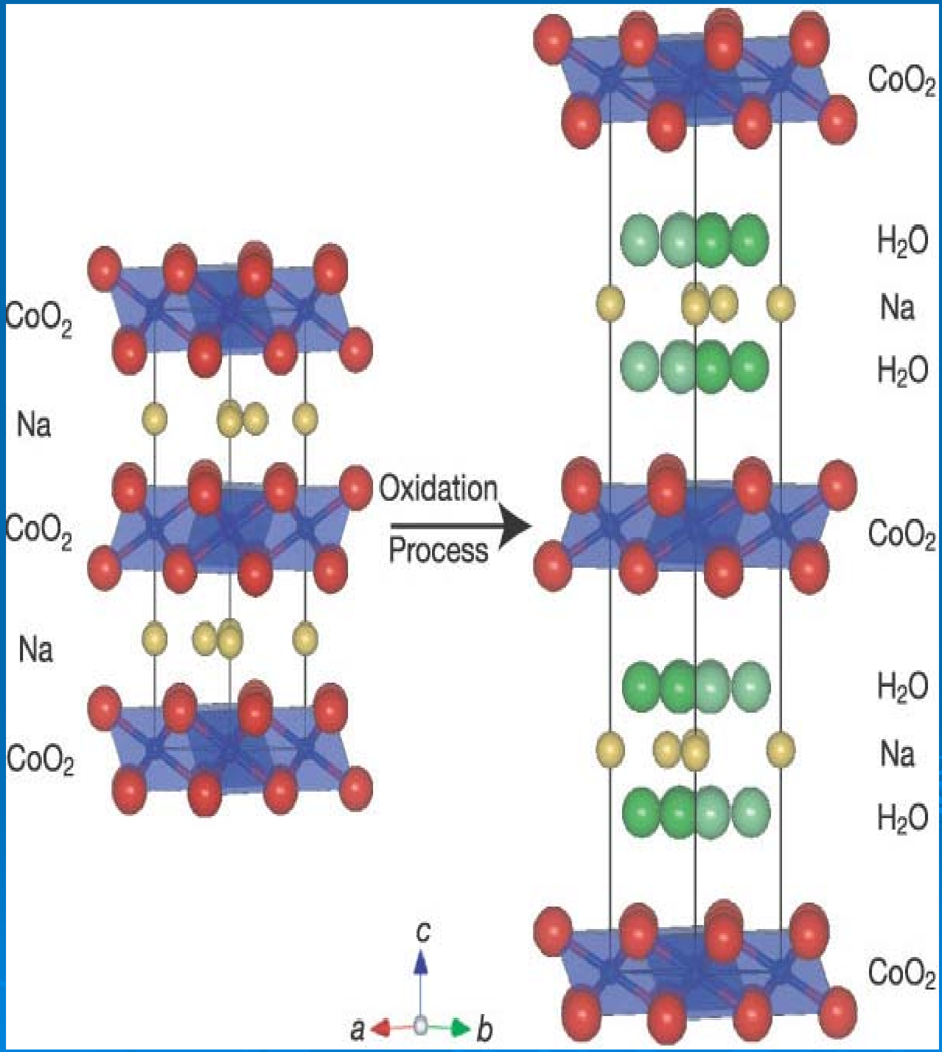
Superconductivity in Copper Oxides

- 1987
  - YBCO ($YBa_2Cu_3O_7$)
  - 92 K
- 1993
  - $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$
  - 138 K
- 2008
  - $(Sn_{1.0}Pb_{0.5}In_{0.5})Ba_4Tm_5Cu_7O_{20+}$
  - 185 K ???



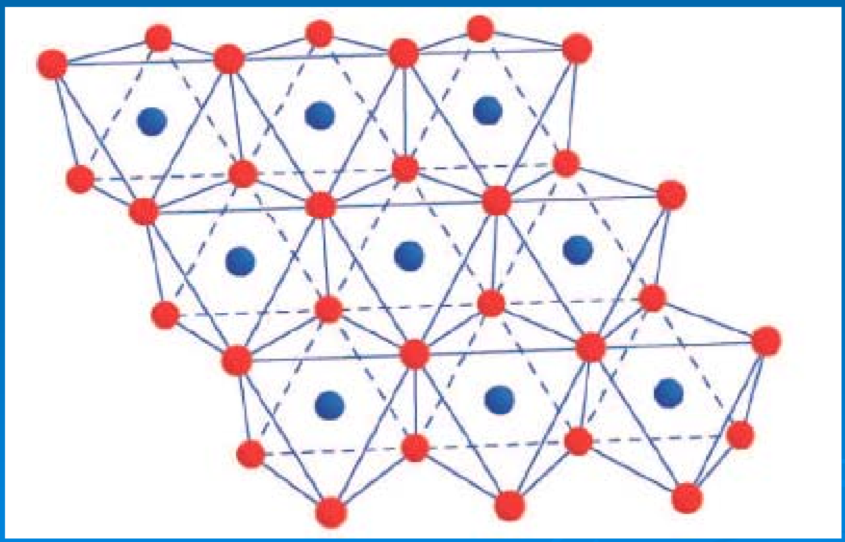
Superconductivity in Cobalt Oxides

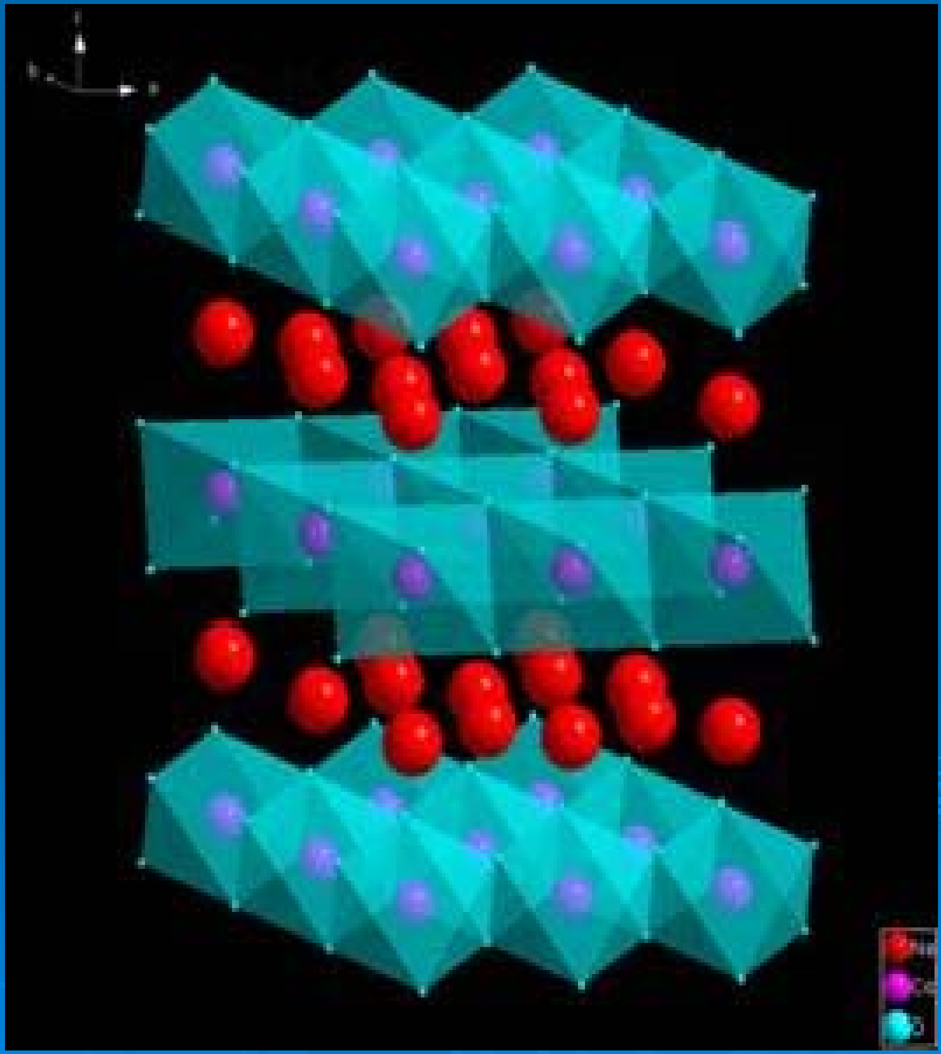
- 2003
  - Takada et. al.
  - $Na_{0.35}CoO_2 \cdot 1.3H_2O$
  - 5K



Structure of Layered Na_xCoO_2

structure consist of triangular CoO_2 layers with Na ions distributed in intervening charge reservoir layers.





Phase Diagram of Layered Na_xCoO_2

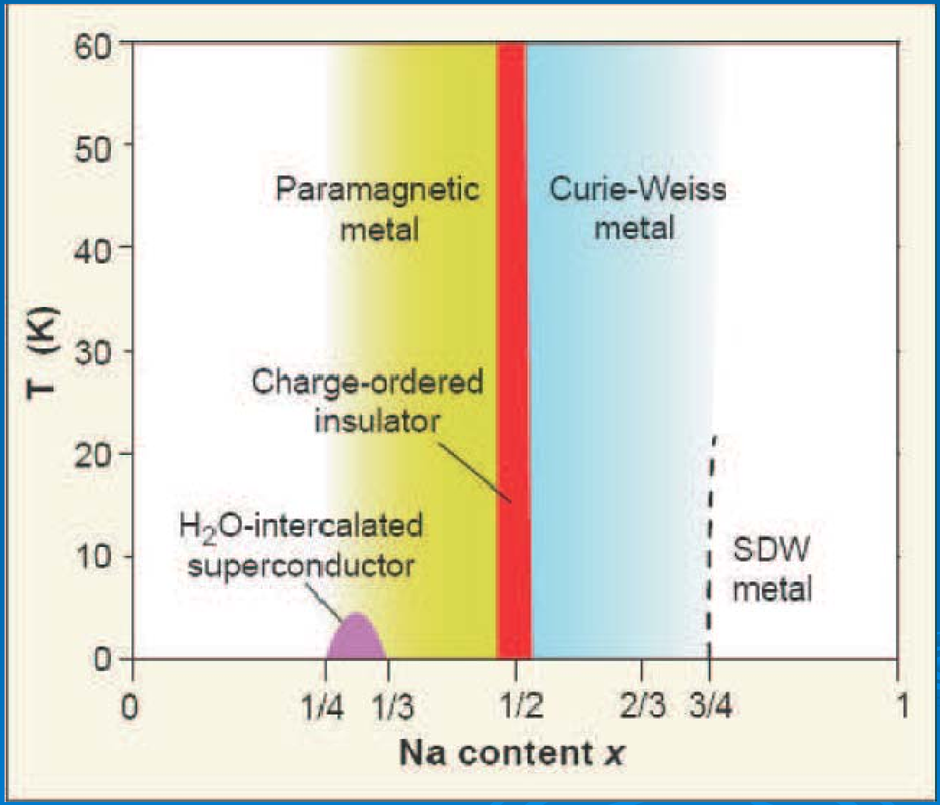
- 0.3 < x < 0.5

  Paramagnetic Metal
- x = ½

  Charge-Ordered Insulator
- 0.5 < x < 0.75

  Curie-Weiss Metal
- 0.75 < x

  Spin Density Wave Metal



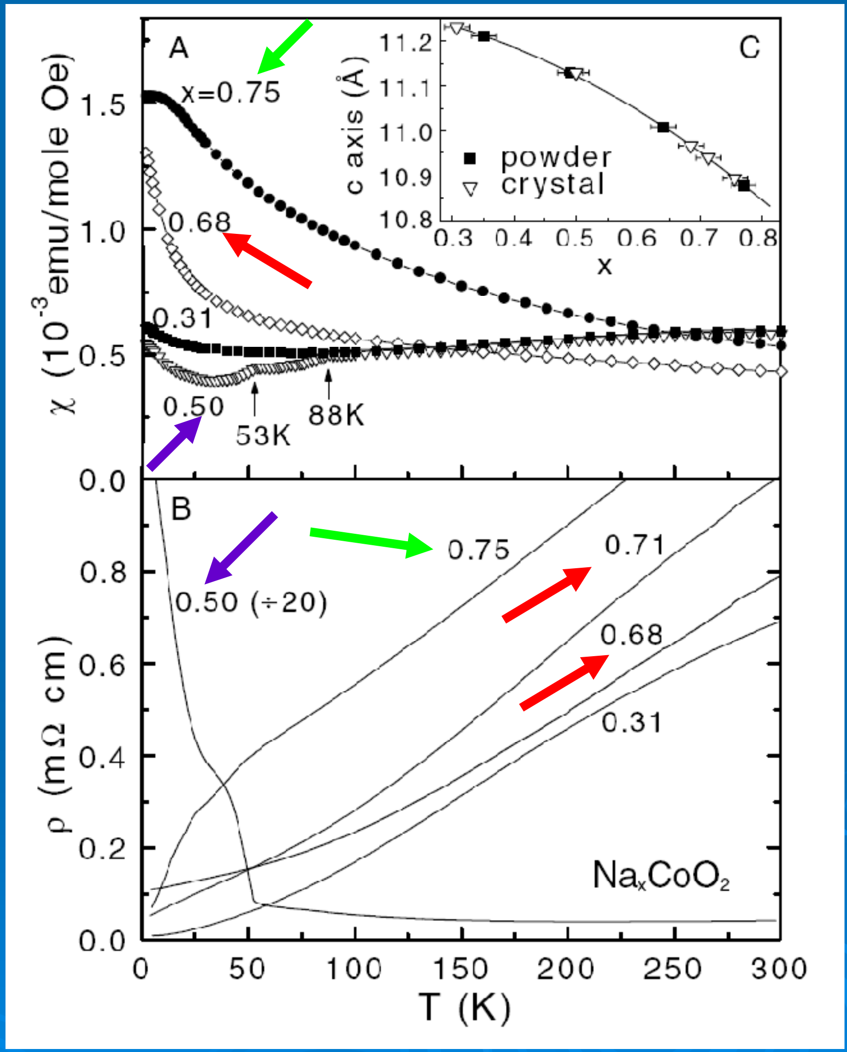
Curie-Weiss Metal
Spin Density Wave Metal

- X~2/3
  - metallic-like in charge conduction
  - insulator-like in spin alignment

  $\chi = C / (T+70)$
- X=3/4
  - Very weak magnetization

  $M \sim 0.03\mu_B$ per Co

  χ~Cont (Below 20 K)

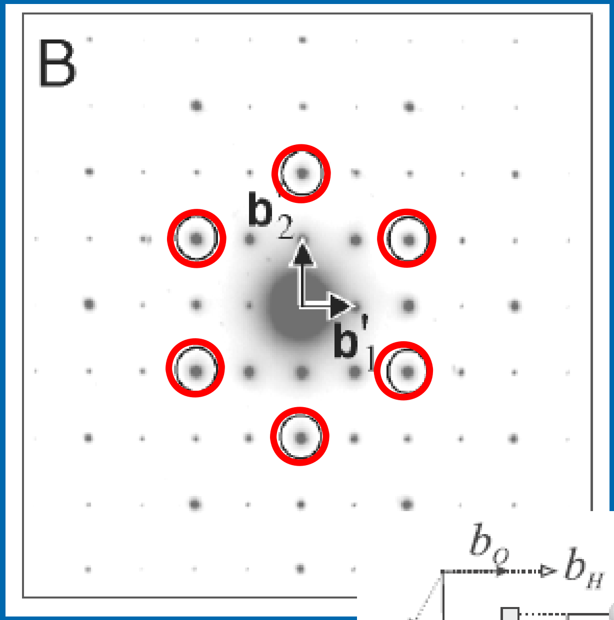


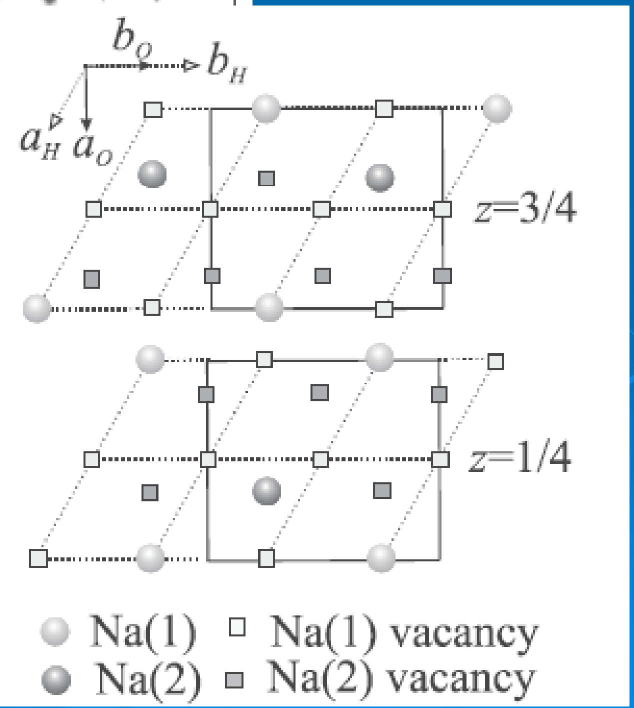
Charge-Ordered Insulator

- X=1/2
  - in-plane resistivity ρ shows a dramatic change
  - Curie-Weiss behavior in χ vanishes
  - Na superstructure

    $$a\sqrt{3}\hat{x} \quad 2a\hat{y}$$

    Bragg spots appear
  - a strong interaction between the Na ions and holes required

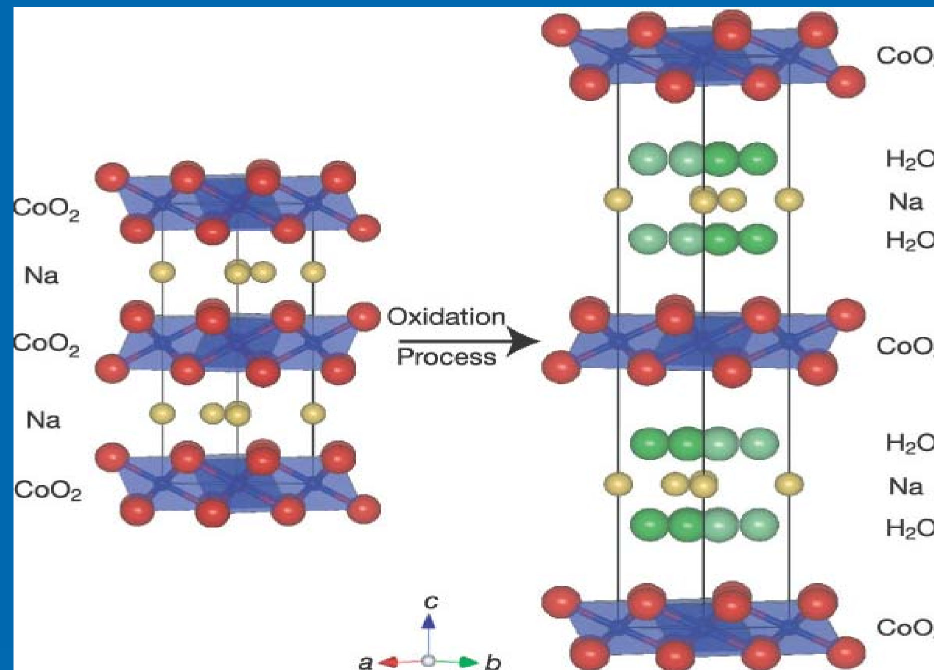


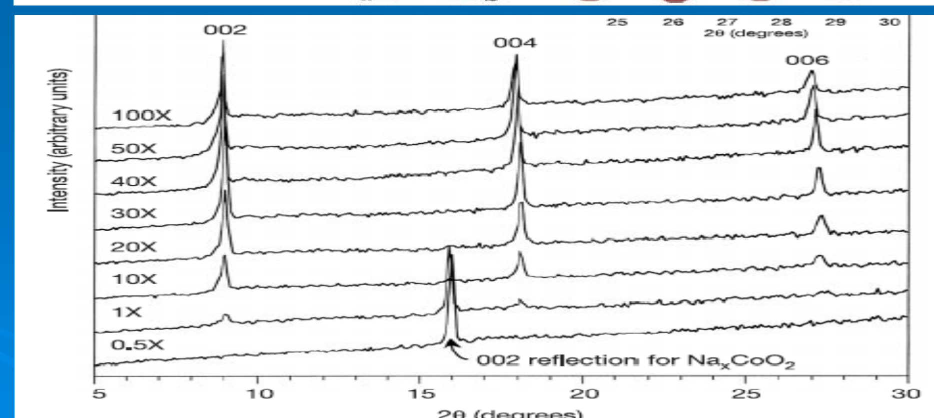


Preparation of $Na_xCoO_2 \cdot 1.3H_2O$

- Parent oxide

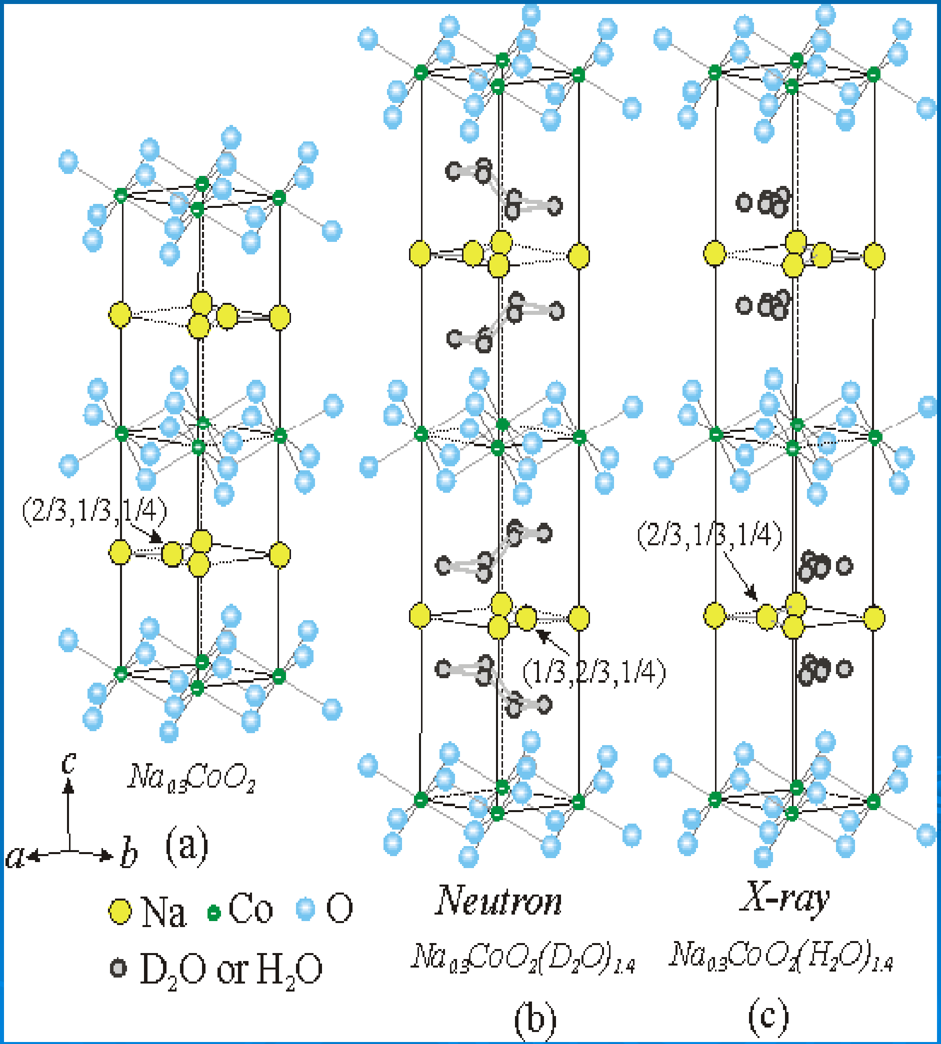
  $Na_{0.7}CoO_2$
- Na + ions are deintercalated in Br_2 solution.
- H_2O molecules intercalate between Na and CoO_2 layers.
- Distance between succeeding CoO_2 layers increased from 10.96 Å to 19.62 Å
- Optimum water content is found to be 1.3 per Co





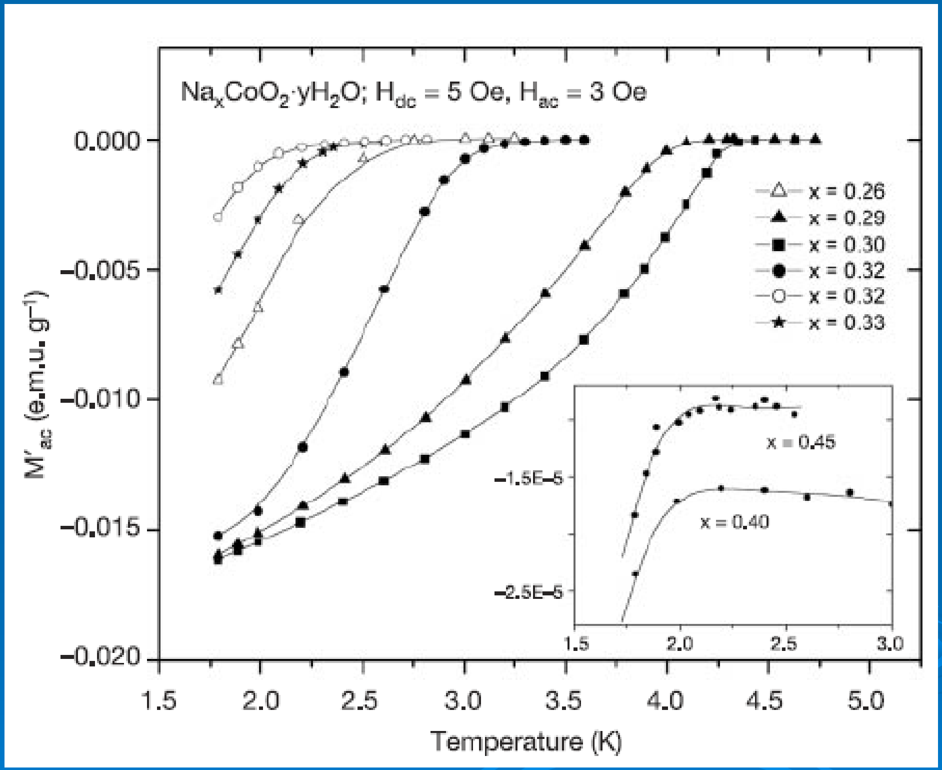
Structure of Layered $Na_xCoO_2 \cdot 1.3H_2O$

- Consists of two dimensional CoO_2 layers separated by a thick insulating layer of Na+ ions and H_2O molecules.
- CoO_2 planes
  Electronically active
- $Na_x \cdot 1.3H_2O$ layers
  Spacer
  Charge reservoir



Superconductivity phase diagram of $Na_xCoO_2 \cdot 1.3H_2O$

- a.c. susceptibility measurements are required for weakly superconducting samples.
- Single phase $Na_xCoO_2 \cdot 1.3H_2O$ has maximum Na content x~0.35
- Maximum T_C value 4.3 K is displayed by the samples with x = 0.30

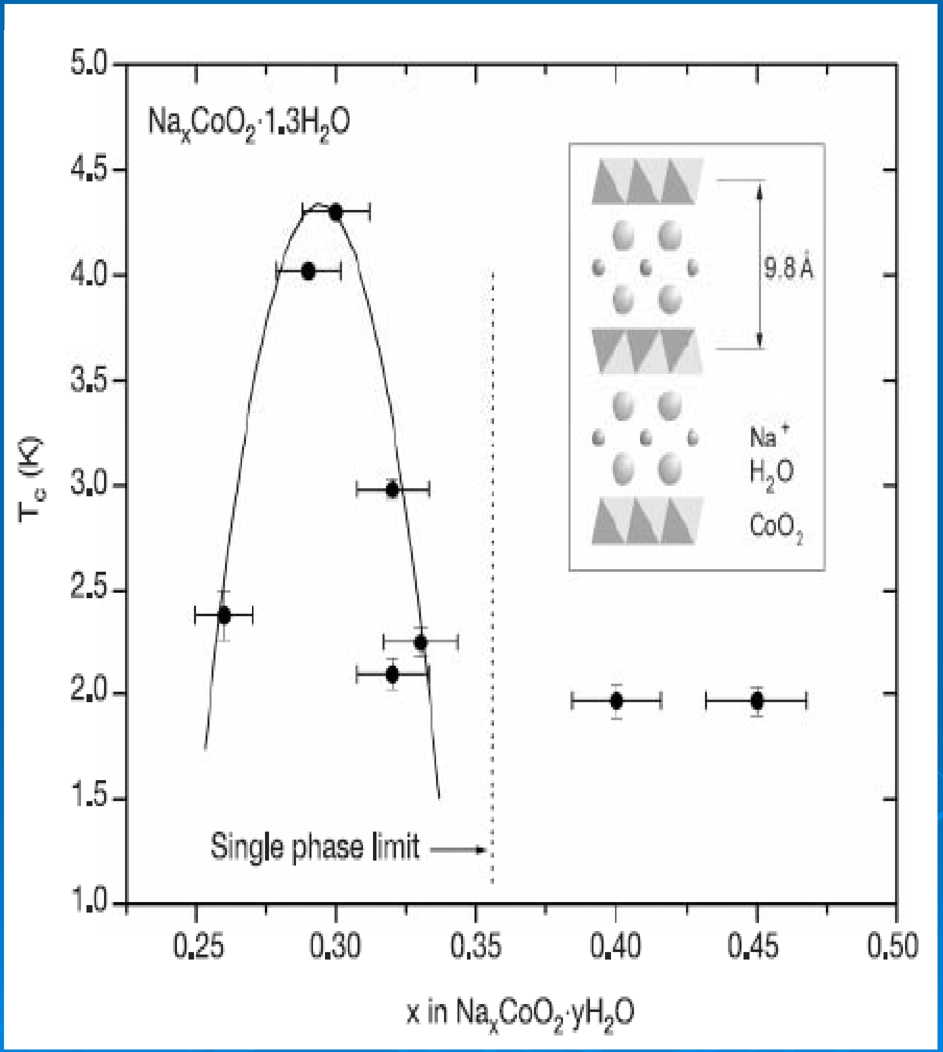


Superconductivity phase diagram of $Na_xCoO_2 \cdot 1.3H_2O$

- The optimal Na composition for the occurrence of superconductivity is x = 0.30
- x oxidation state of Co

x	oxidation state of Co
0.26	3.74+
0.30	3.70+
0.35	3.65+

- Superconductivity may occur in a narrower x interval. Samples with ideally uniform x should be prepared to test



Important observations for Cobalt oxide Superconductors

- Two dimensional character of the structure is important
  - Lower hydrates with closer CoO_2 - CoO_2 layers are not superconducting above 2 K.
  - T_C decreases under pressure
- Water molecules intercalate between Na+ ions and the Co_2 planes and therefore screen the conduction electrons from the Na potential
  - Mono-hydrates fail to superconduct

Similarities between the layered copper oxide and cobalt oxide Superconductors

- Both superconductors have transition metal oxide layers that have very weak inter-planar coupling
- Both superconductors is mixed valance

Cu^{2+} & Cu^{3+} Co^{3+} & Co^{4+}

Differences between the layered copper oxide and cobalt oxide Superconductors

- Geometry
  - nearly square-planar coordination of copper in the layers of the high-*T*c superconductors,
  - the cobalt oxide is composed of distorted edge-shared octahedra of cobalt and oxygen with cobalt-oxygen bond angles of either 81° or 99°
- Electronic structure
  - There is a strong mixing between the oxygen and transition metal levels for the copper oxides
  - there is little hybridization between the oxygen and transition metal orbitals in the layers of Na_XCoO_2

Summary & Views

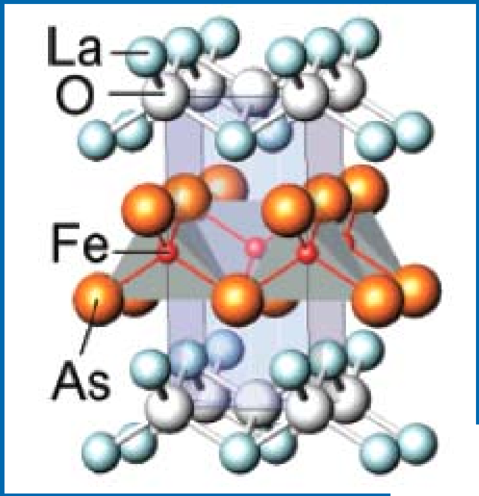
- $Na_xCoO_2 \cdot 1.3H_2O$ is (was) one of the few examples of layered transition metal oxide superconductors that do not contain copper
- Contrasts and similarities between it and copper oxides may help us to better understand the high- T_C superconductivity

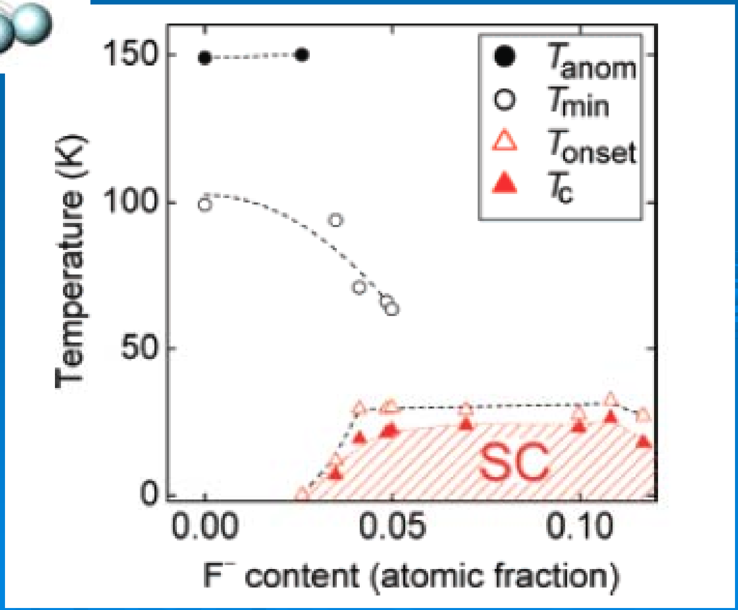
References

- Not Yet !

Iron-Based Layered Superconductors

- 2008
  - Hosomo et. al.
  - $La[O_{1-x}F_x]FeAs$ (x = 0.05-0.12)
  - 26K
- After 2 months
  - $Pr[O_{1-x}F_x]FeAs$
  - 52 K





References

- [1] J. G. Bednorz and K. A. Mller, Z. Phys. B 64, 189 (1986).
- [2] J. V. Badding, Nature Materials 2, 208 (2003).
- [3] a, *http : ==www:superconductors:org=185kpat:htm.*
- [4] P. Dai, B. C. Chakoumakos, G. F. Sun, K. W. Wong,Y. Xin, and D. F. Lu, Physica C:Superconductivity 243, 201 (1995).
- [5] K. Takada, H. Sakurai, E. T. Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature 422, 53 (2003).
- [6] Q. Huang, M. L. Foo, J. W. Lynn, H. W. Zandbergen, G. Lawes, Y. Wang, B. H. Toby, A. P. Ramirez, N. P. Ong, and R. J. Cava, J. Phys. Condens. Matter 16, 5803 (2004).
- [7] I. Terasaki, Y.Sasago, and K. Uchinokura, Phys. Rev B 56, 12865 (1997).
- [8] M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, Phys. Rev. Lett 92, 247001 (2004).

References

- [9] N. P. Ong and R. J. Cava, Science 305, 52 (2004).
- [10] H. Kojima, R. S. Tebble, and D. E. G. Williams, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences 260, 237 (1961).
- [11] Y. Wang, N. S. Rogado, R. C. Cava, and N. P. Ong, Nature 423, 425 (2003).
- [12] G. Gasparovic, R. A. Ott, J.-H. Cho, F. C. Chou, Y. Chu, J. W. Lynn, and Y. S. Lee, Physical Review Letters 96, 046403 (2006).
- [13] M. Roger, D. J. P. Morris, D. A. Tennant, M. J. Gutmann, J. P. Goff, J.-U. Hoffmann, R. Feyerherm, E. Dudzik, D. Prabhakaran, A. T. Boothroyd, et al., Nature 445, 631 (2007).
- [14] R. E. Schaak, T. Klimczuk, M. L. Foo, and R. J. Cava, Nature 424, 527 (2003).
- [15] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. AM. Chem. Soc. 130, 3296 (2008).