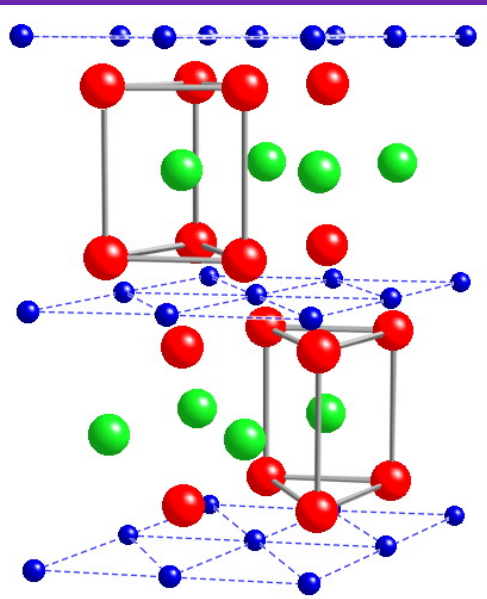
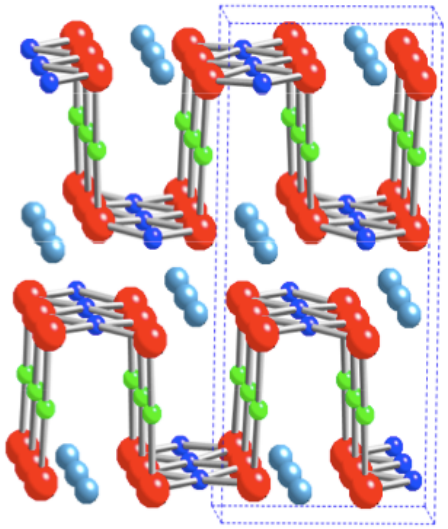
Cation, charge and spin defect orderings in Na_xCoO_2 and $LiCu_2O_2$





Outlines

- Review of Na_xCoO_2 studies so far
- Na vacancy ordering and its impact
- Review of QM frustrated 1d Heisenberg system
- Nonmagnetic spin defect impact on $LiCu_2O_2$

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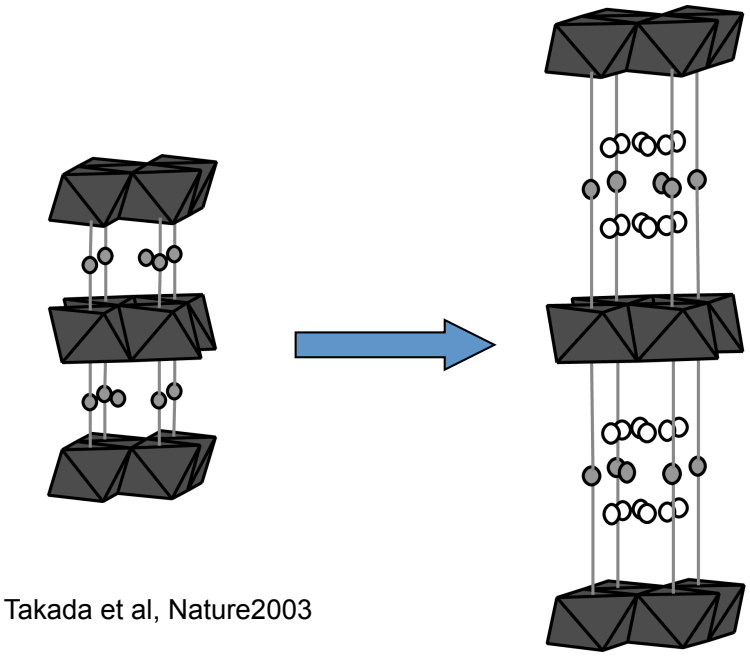
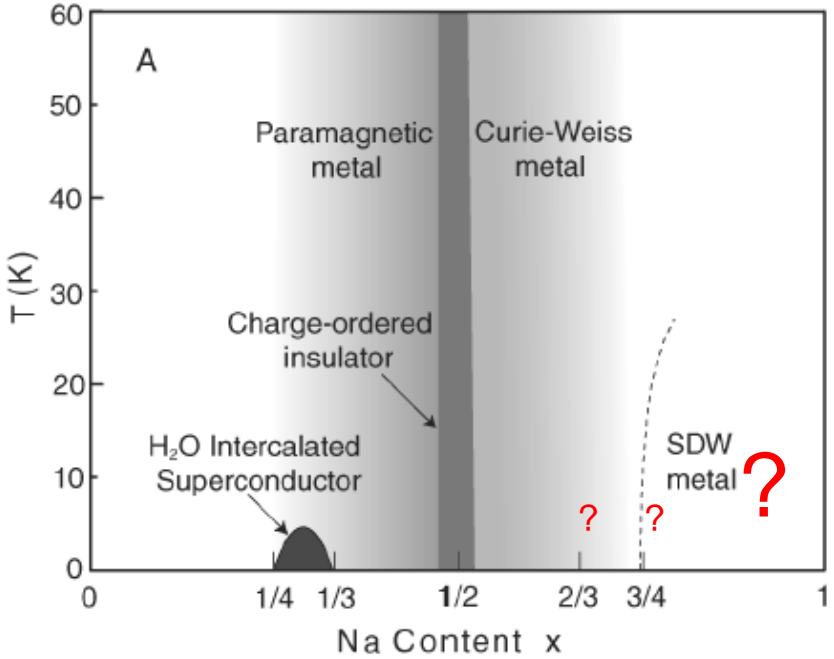
Center for Condensed Matter Sciences
National Taiwan University

Why Na_xCoO_2?

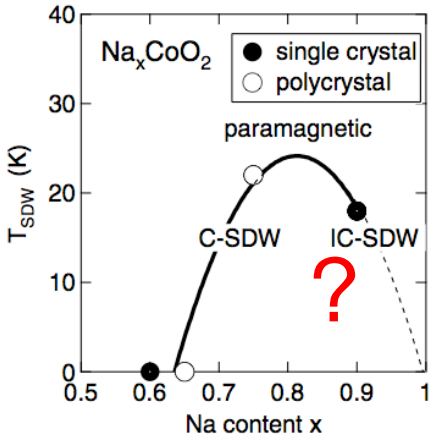


Takada et al, Nature2003



Foo et al., PRL 2004

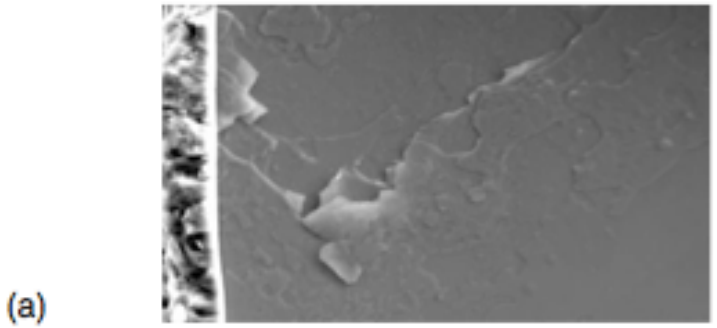
- high thermoelectric power: $ZT = \frac{S^2 \sigma T}{k}$
- superconductivity: ~4.5K
- similar to battery cathode material Li_xCoO_2
- spin, charge and ion orderings and frustration in low-d QM system
- Curie-Weiss metal and MIT transition

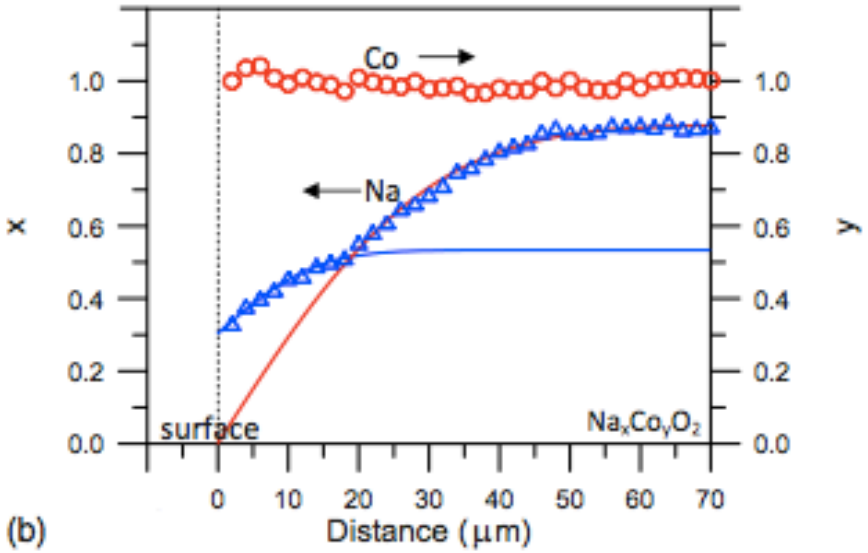


Sugiyama et al., PRL2004

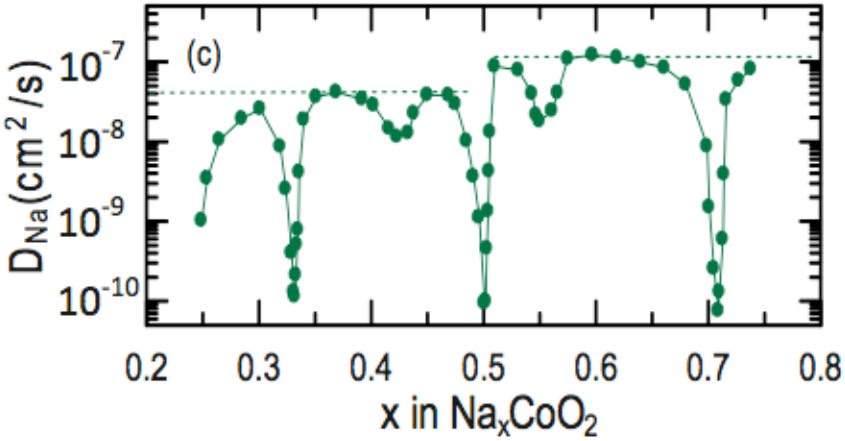
Diffusion of Na in Na_xCoO_2

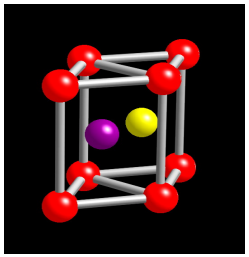
Self diffusion

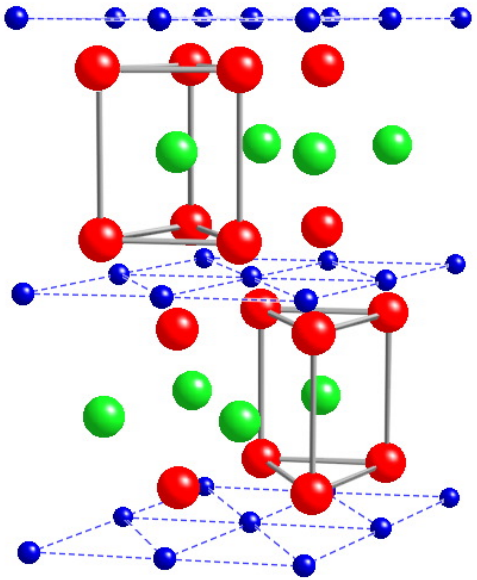




Potentiostatic intermittent titration technique

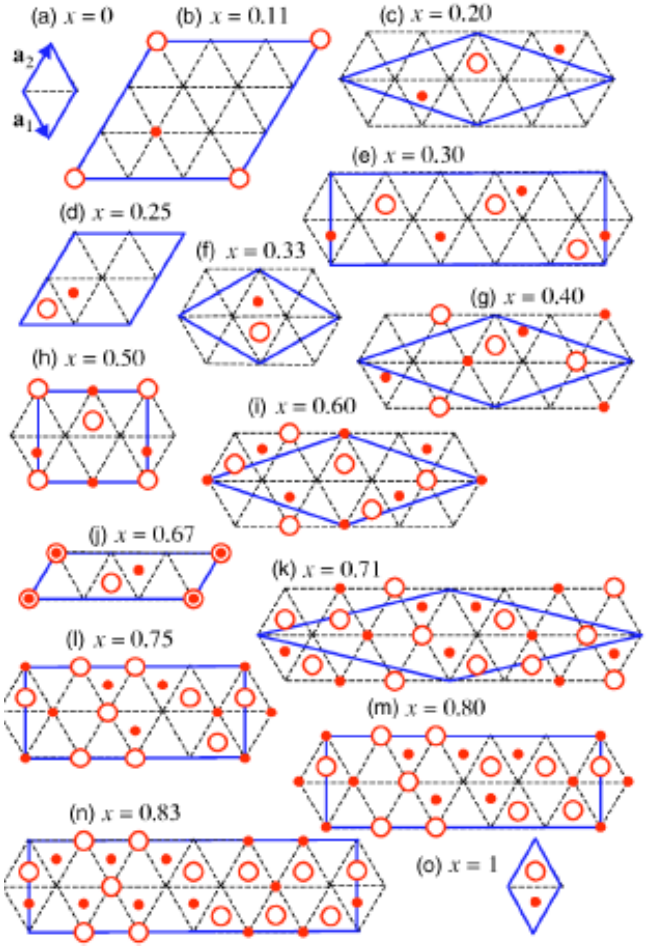






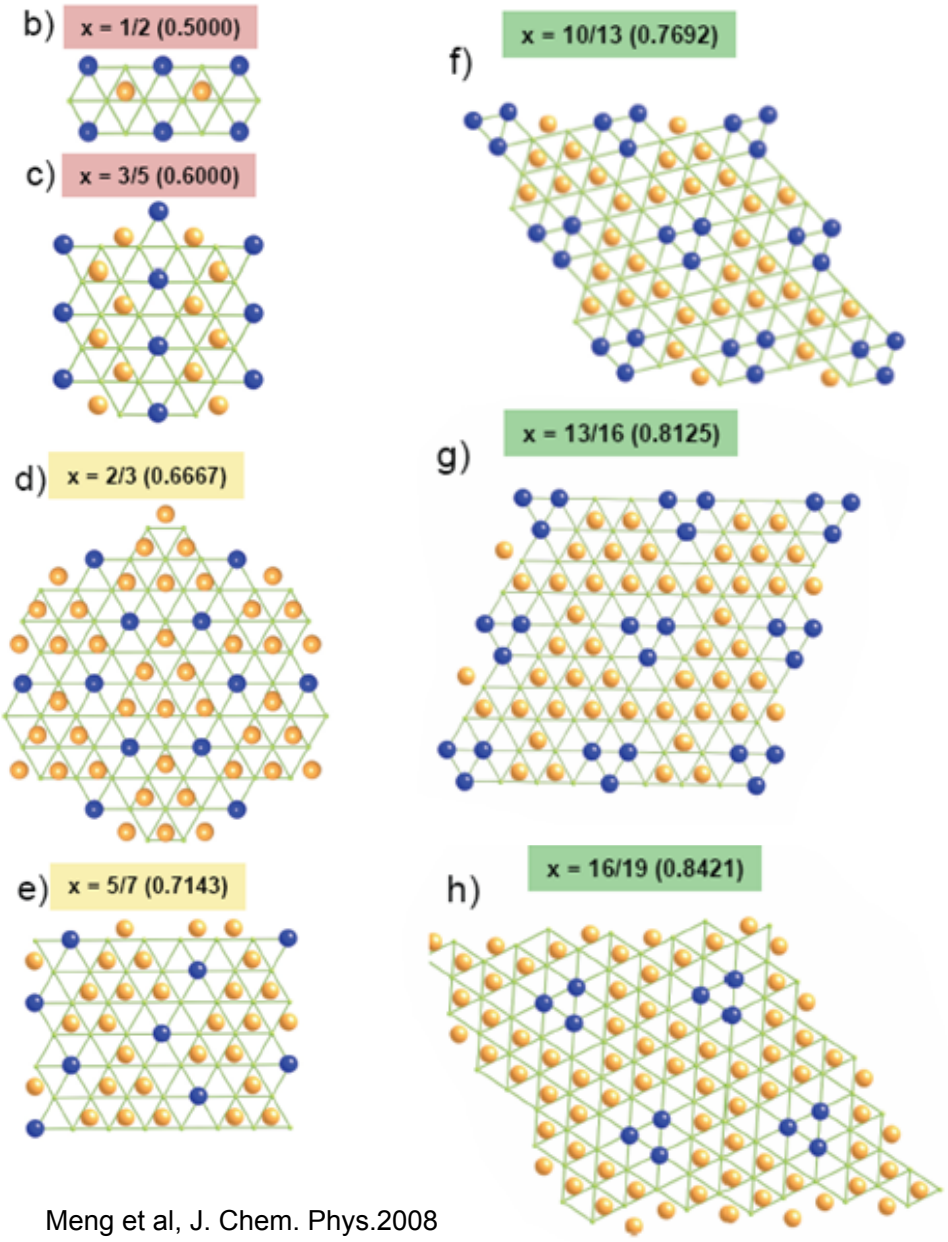
Shu and Chou, PRB2008

some predicted Na orderings



Zhang et al. PRB2005

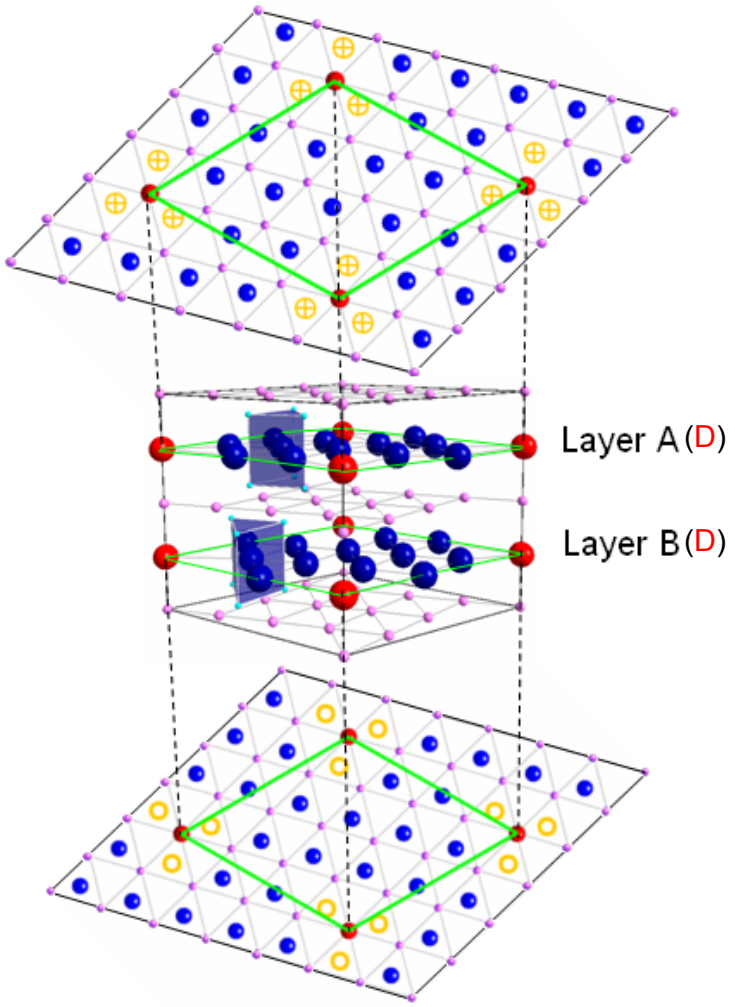
- screened Coulomb interaction among Na
- 2/3 not commensurate ?
- DFT+GGA+U



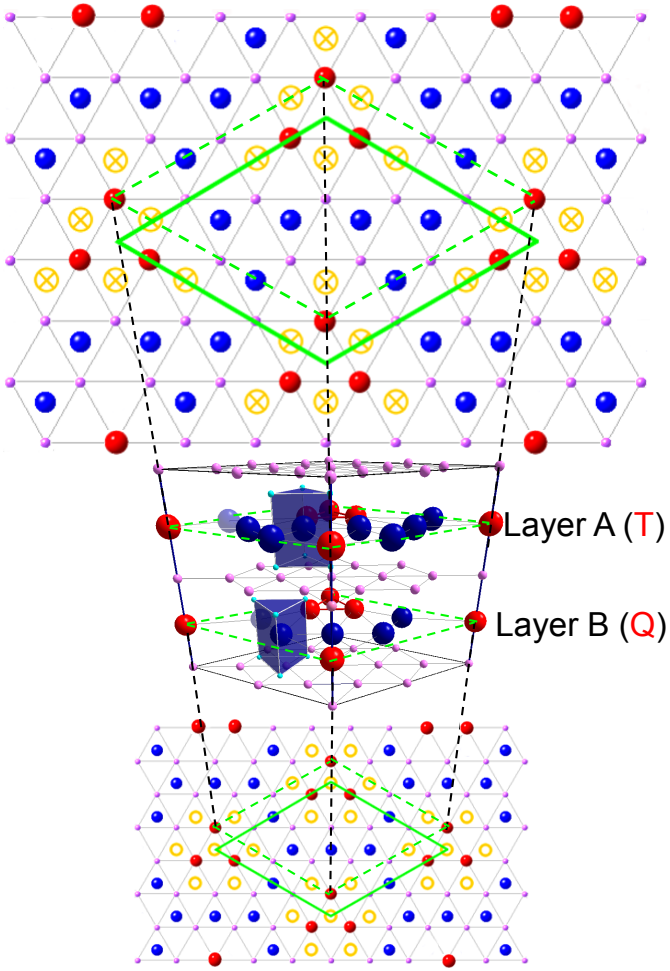
Meng et al, J. Chem. Phys.2008

$Na_{0.84}CoO_2$ and $Na_{0.71}CoO_2$ superlattices

½(11/13+11/13) = 0.846



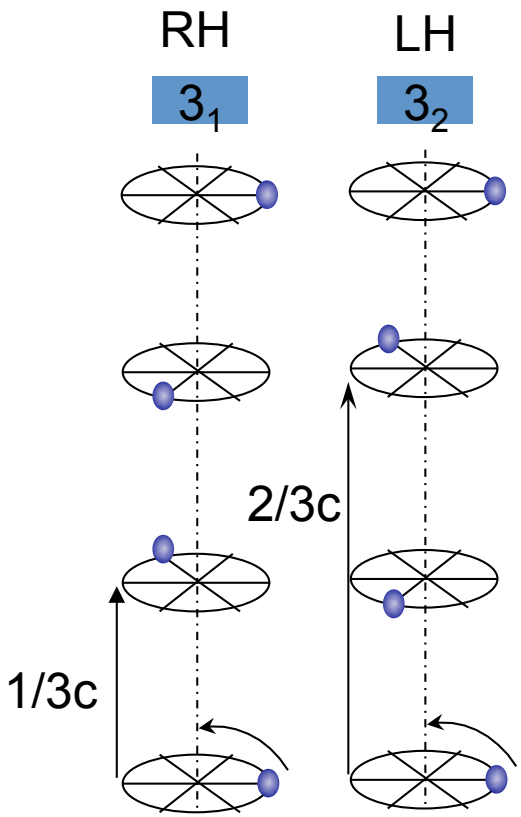
½(9/12+8/12) = 0.708

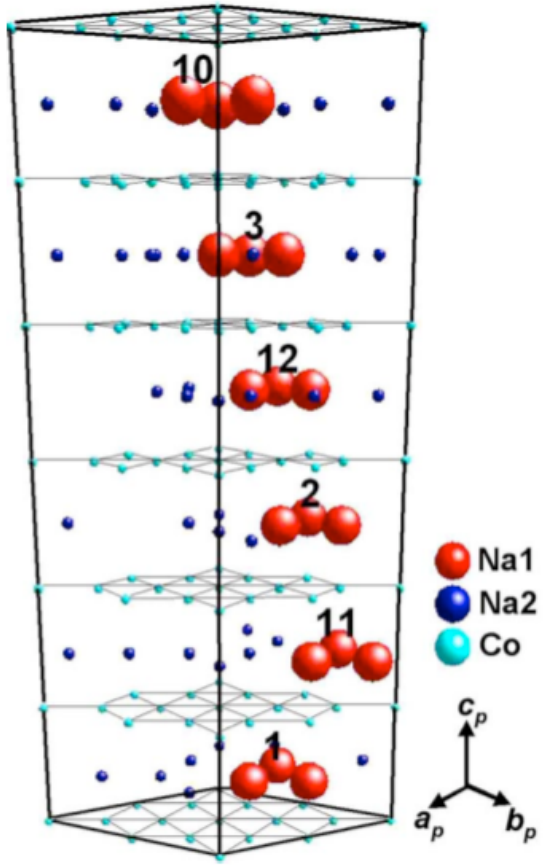


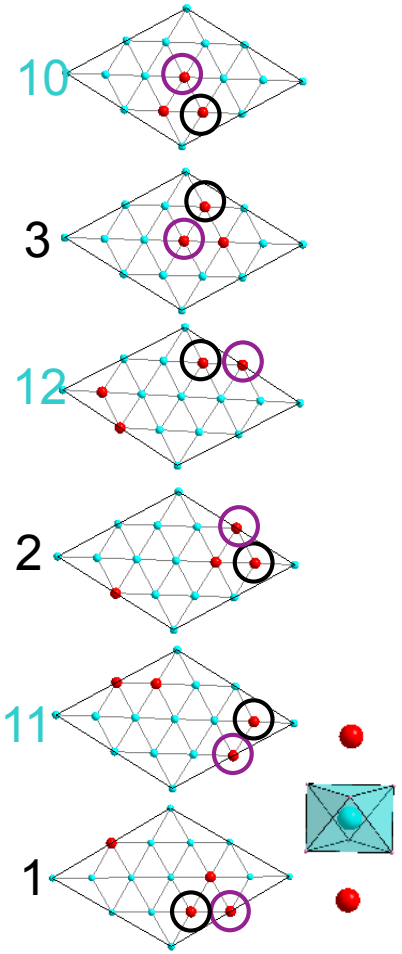
- Partially localized and itinerant doped carriers ➔ Curie-Weiss metal

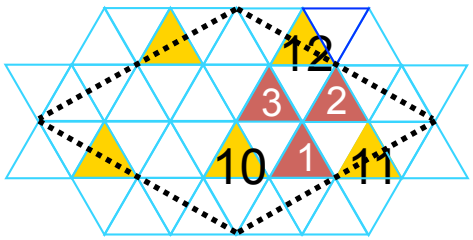
3c stacking and RH chirality

- 3c stacking
- trimer stability
- trimer chain along c
- chirality: RH or LH



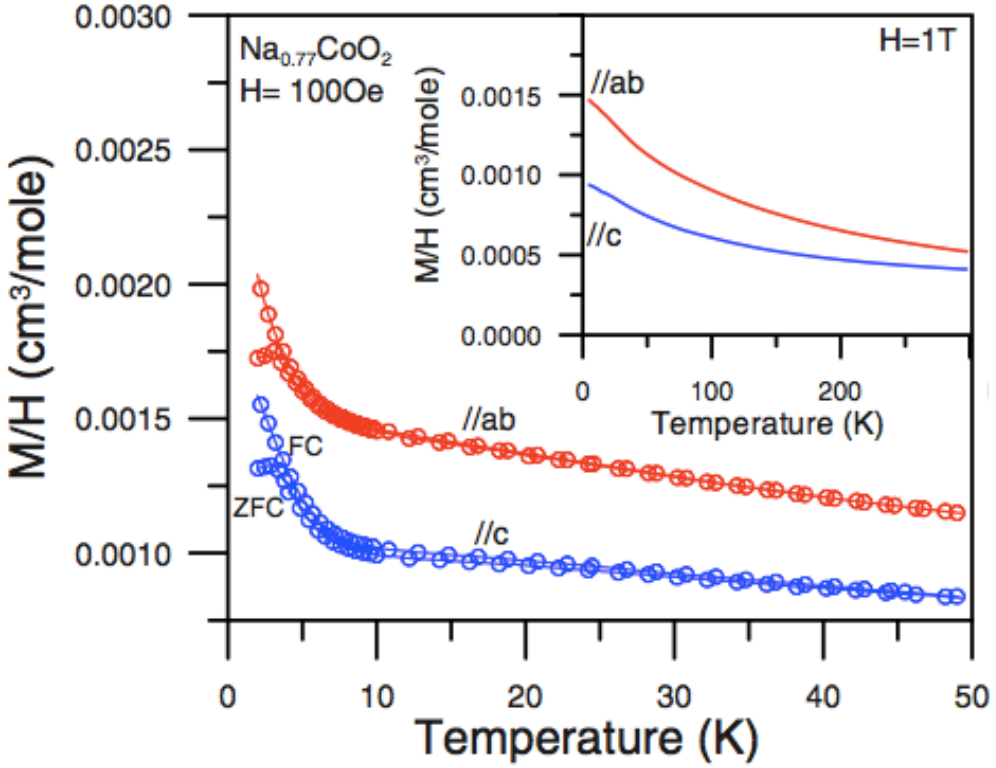


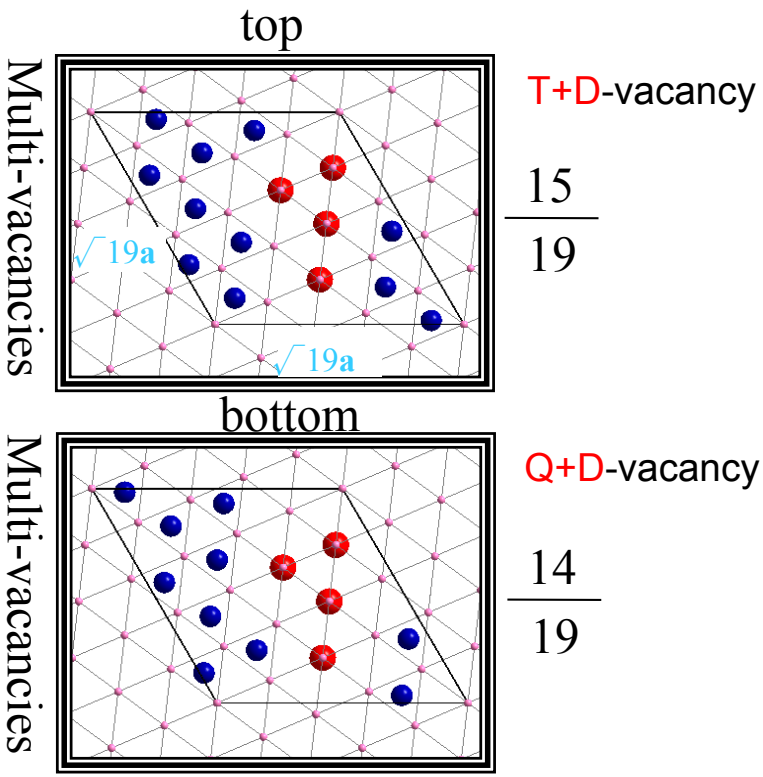




Huang et al., PRB2009

One more: $Na_{0.77}CoO_2$ superstructure

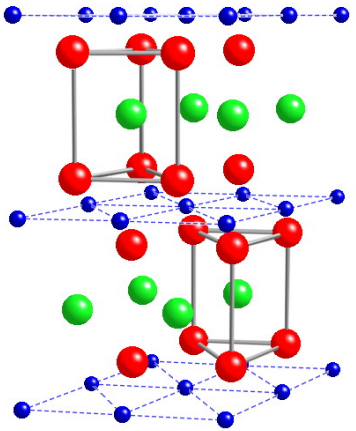




- largest superlattice √19a found
- spin glass transition T_g ~ 3K
- frustrating and random attachment

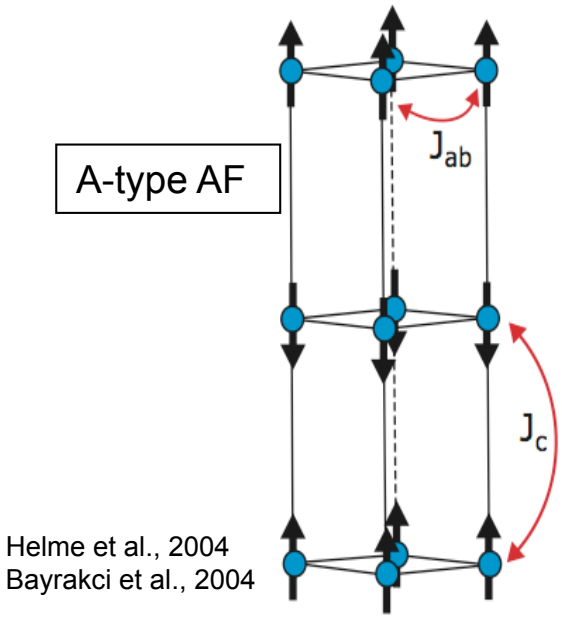
$$x = 1 - \frac{1}{2}\left(\frac{4+5}{19}\right)$$

$$\sqrt{19}a \times \sqrt{19}a \times 3c$$

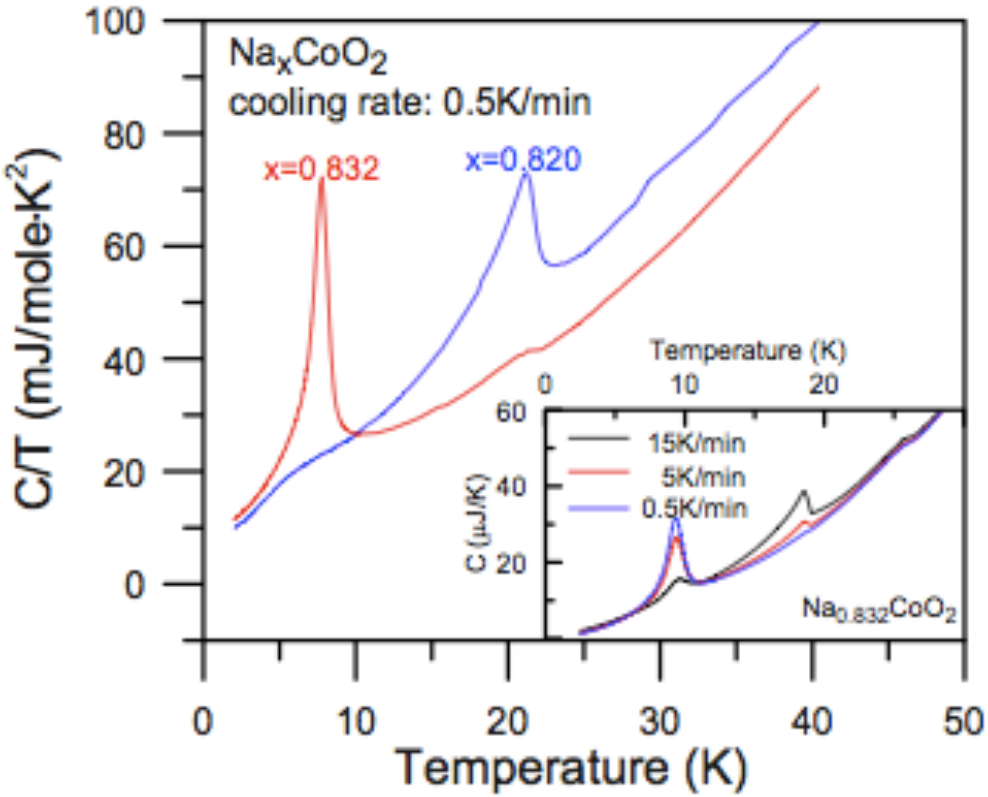


Huang et al. PRB2009

A-type AF and its cooling rate dependence



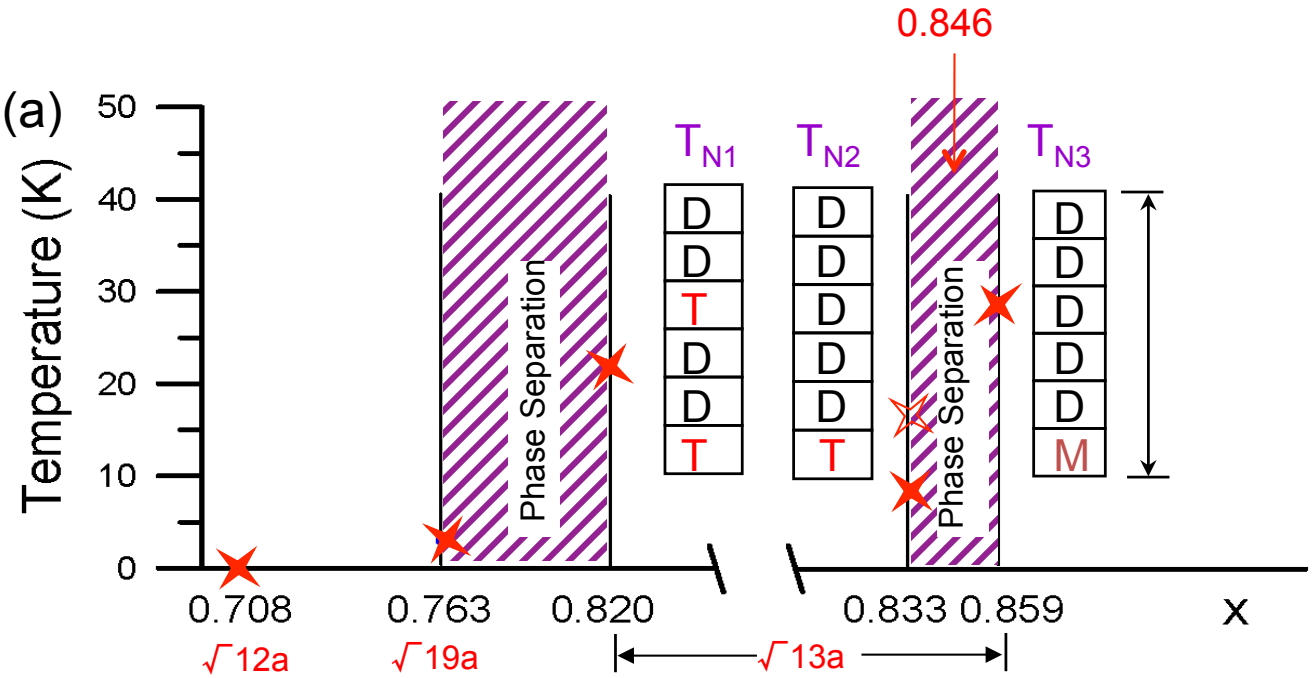
Helme et al., 2004
Bayrakci et al., 2004



For x = 1 - 2/13 ~ 0.84 of di-vacancy ordering

- 1/13 localized?
- Heisenberg AF ground state?
- Kondo insulator ground state?
- in-plane Stoner mechanism FM: exchange vs. kinetic energy
- Interlayer coupling – A-type AF

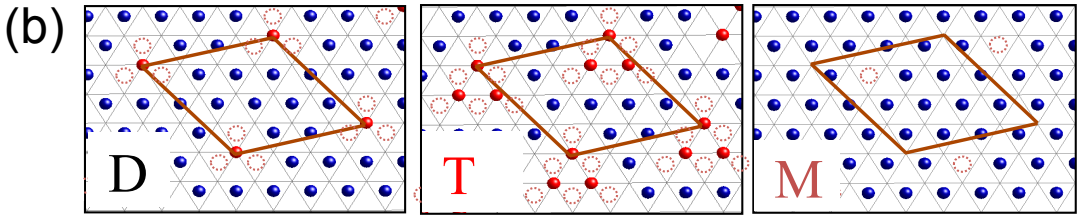
Phase Diagram and Staging



$\sqrt{13}a \times \sqrt{13}a \times 3c$

Ideal superlattice x=1-2/13=0.8462

1 Na/supercell ➔(1/13)/6=0.0128
Add extra 1 Na2 ➔0.846+0.0128*1=0.859(√13)
Take off 1 Na2 ➔ 0.846-0.0128*1= 0.833 (√13)
Take off 2 Na2 ➔ 0.846-0.0128*2= 0.820 (√13)
Take off 3 Na2 ➔ 0.846-0.0128*3= 0.808 (mix)
Take off 4 Na2 ➔ 0.846-0.0128*4= 0.795 (mix)
Take off 5 Na2 ➔ 0.846-0.0128*5= 0.782 (mix)
Take off 6 Na2 ➔ 0.846-0.0128*6= 0.769 (???)
0.763 (√19)

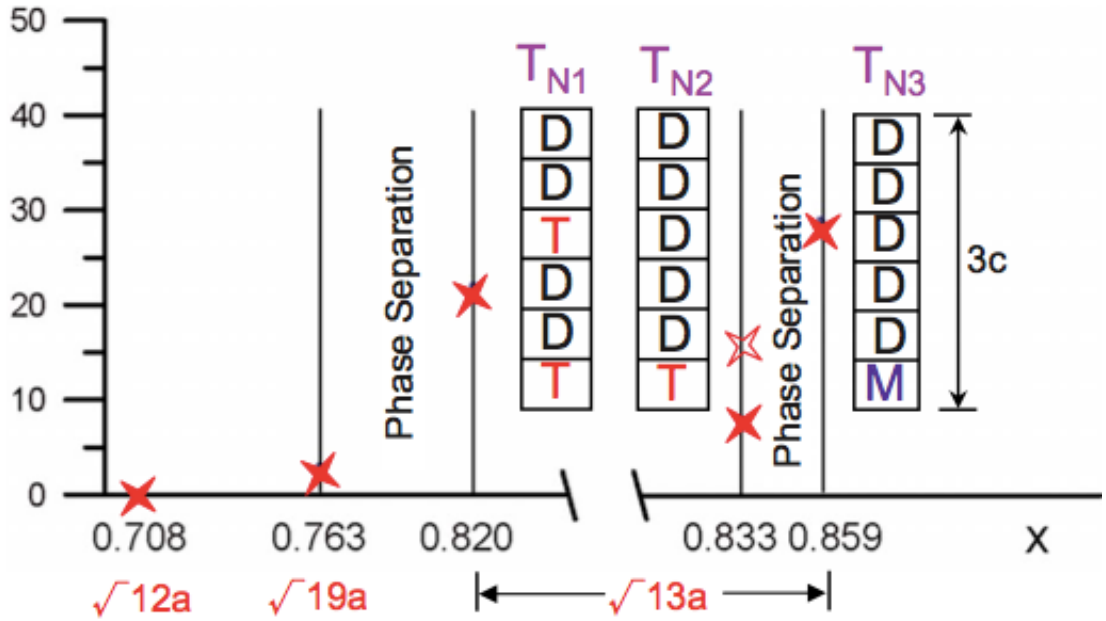


- Staging model of interlayer coupling
- in-layer itinerant FM Stoner mechanism
- inter-layer AF localized spins
- rate dependent T_N of A-AF

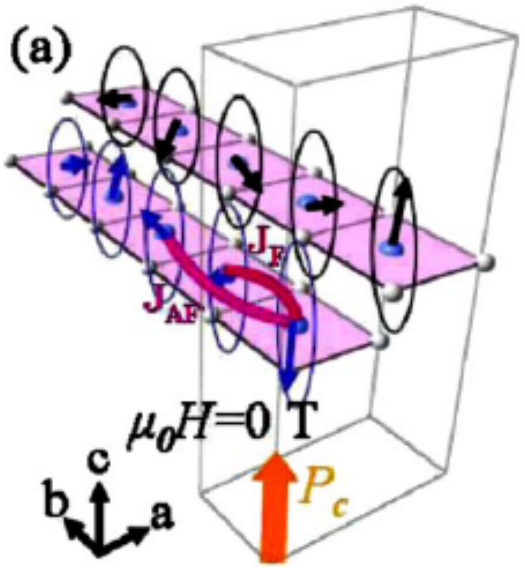
Shu et al., PRB2009

Summary of Na_xCoO_2

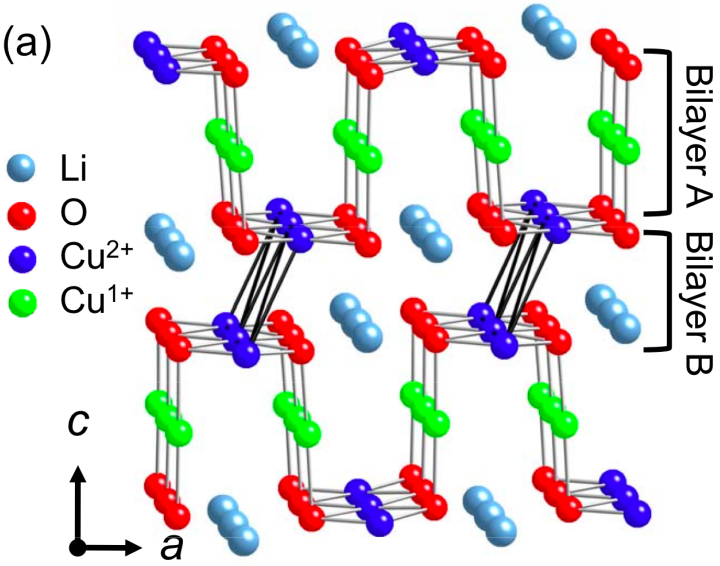
- Na ordering and partial localization – reconstructed FS
- Phase separation and staging phenomena
- Electronic origin of Na ordering
- Novel quantum spin liquid in $Na_{0.71}CoO_2$
- Na trimer stability
- Discrete T_N's , staging and revised phase diagram

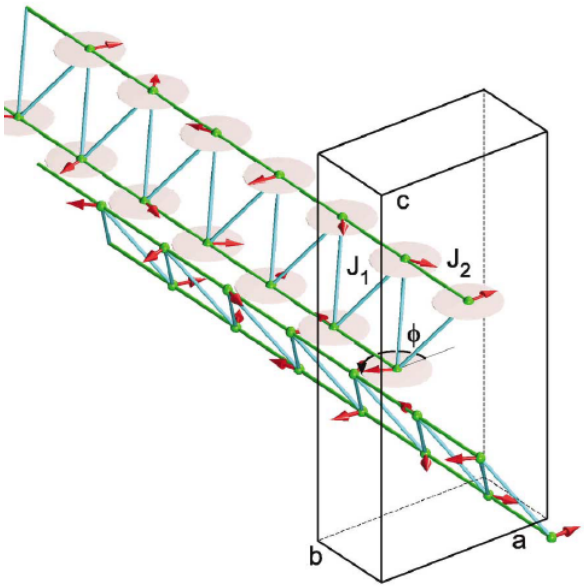


What's so interesting in $LiCu_2O_2$?



Park *et al*. PRL 98,057601(2007)





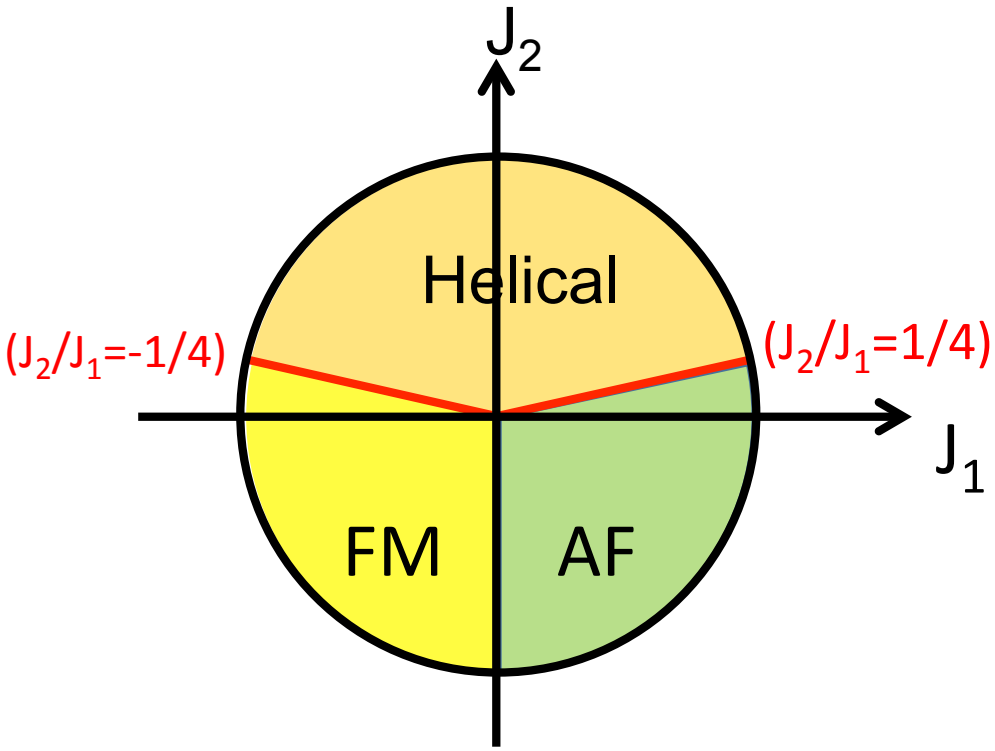
Masuda *et al*. PRL 92,177201(2004)

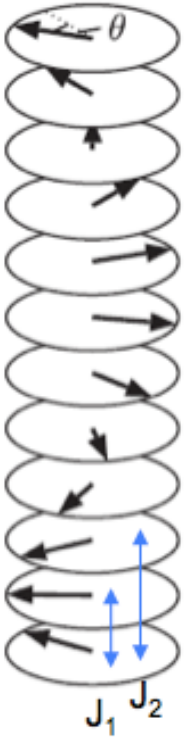
- multiferroics
- helical spin ordering
- Li nonstoichiometry
- severe twinning
- QM fluctuation
- interchain coupling
- inconsistent spin spiral planes
- incomplete interpretation on the origin of P

$$\mathbf{P} \propto \mathbf{Q} \times (\mathbf{S}_i \times \mathbf{S}_{i+1})$$

- IC spiral modulation ζ = 0.174
- pitch angle 2πζ = 62.6°

Classical helical ordering





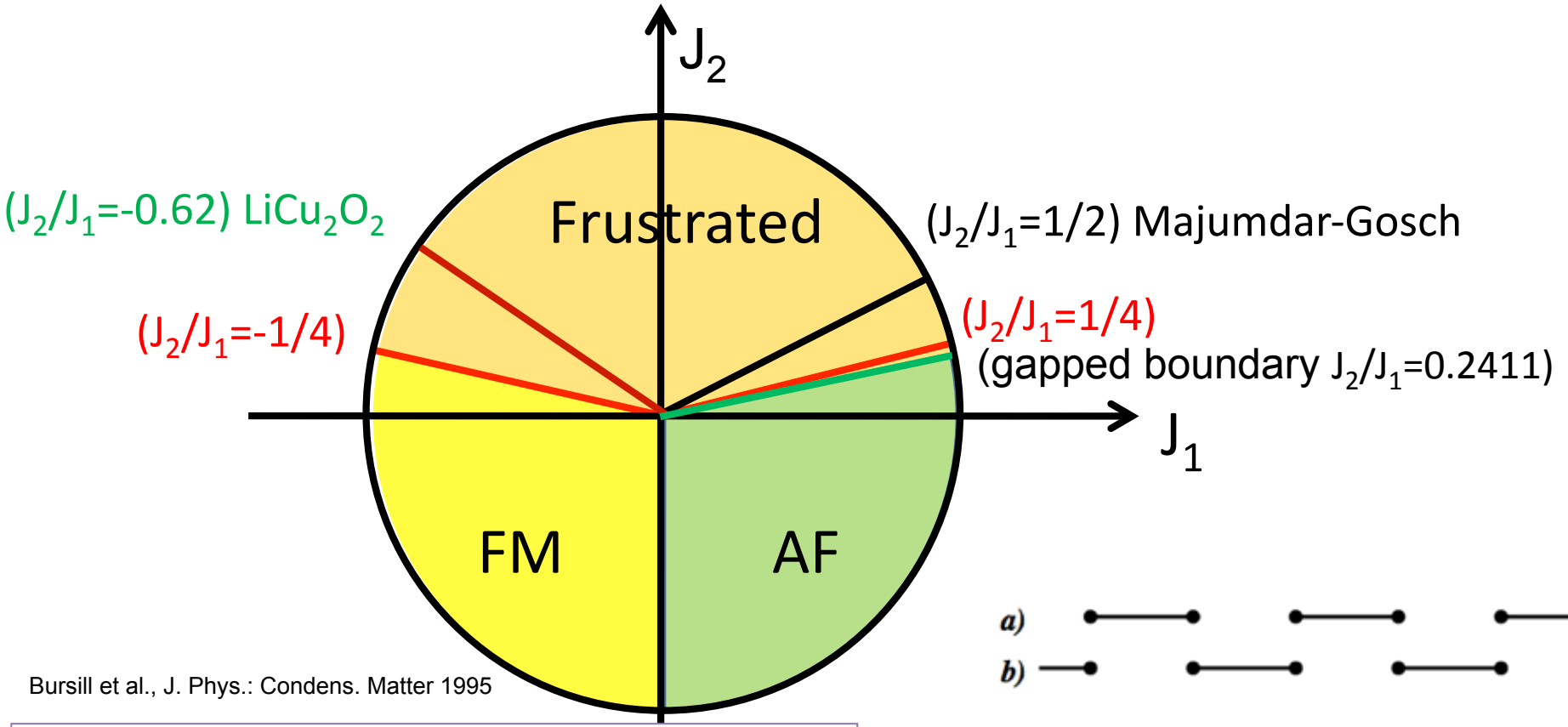
$$H = J_1 \sum (\mathbf{s}_i \cdot \mathbf{s}_{i+1}) + J_2 \sum (\mathbf{s}_i \cdot \mathbf{s}_{i+2})$$

$$E = -2NS^2(J_1 \cos\theta + J_2 \cos 2\theta),$$

$$(J_1 + 4J_2 \cos\theta) \sin\theta = 0.$$

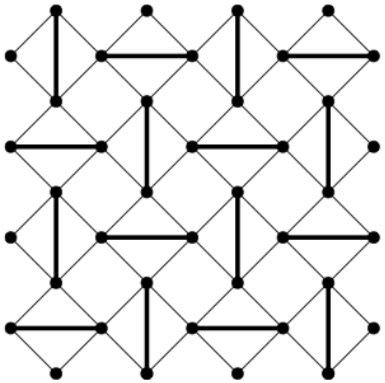
$$\theta = 0 \text{ or } \theta = \pi \quad \text{or} \quad \cos\theta = -\frac{J_1}{4J_2}.$$

Frustration in 1d QM Heisenberg system



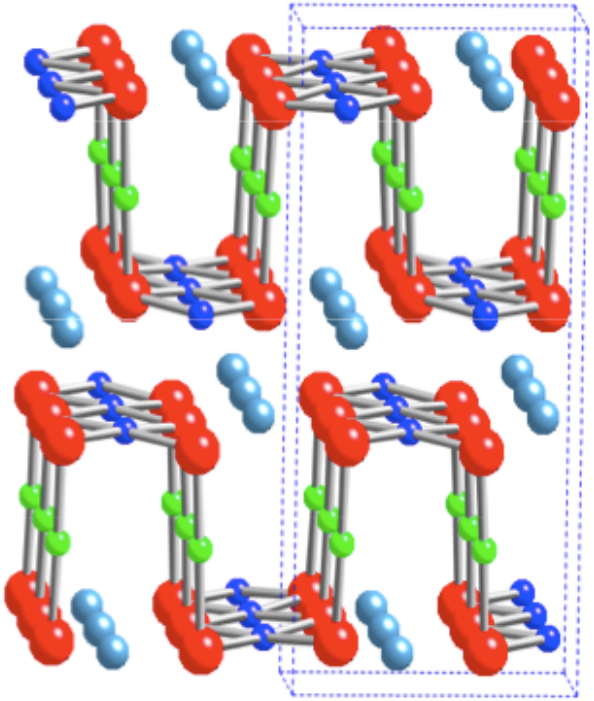
Bursill et al., J. Phys.: Condens. Matter 1995

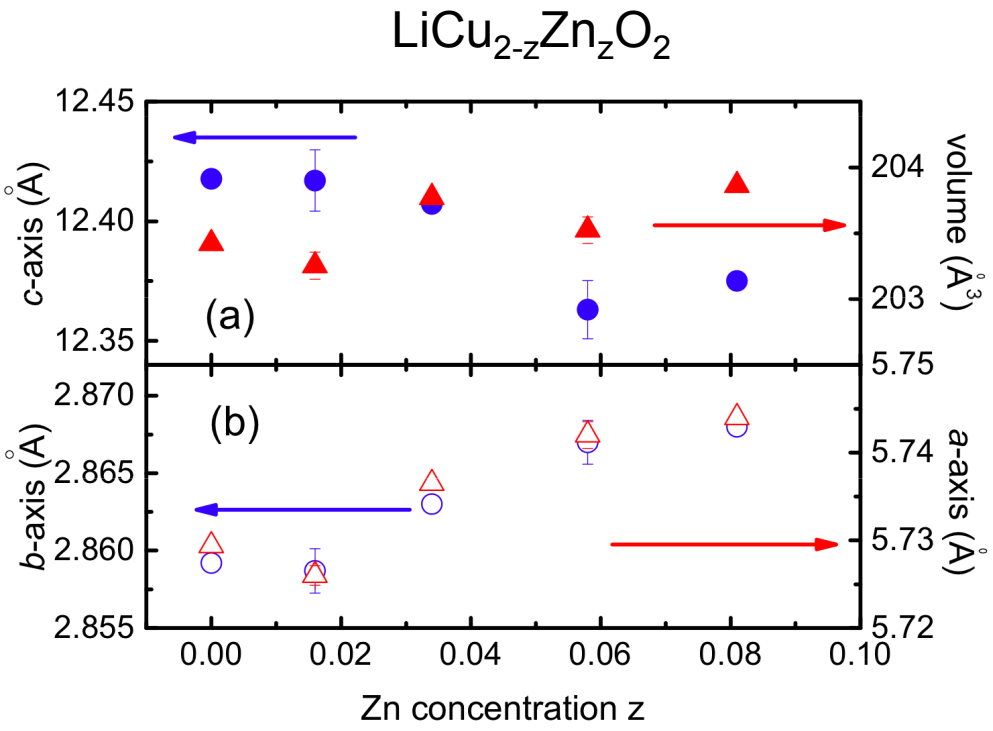
$$H = J_1 \sum (\mathbf{s}_i \cdot \mathbf{s}_{i+1}) + J_2 \sum (\mathbf{s}_i \cdot \mathbf{s}_{i+2})$$



- edge-sharing CuO_2 chain
- α_c=0.2411 separates gapped and gapless states
- Majumdar-Ghosh 2-fold degenerate dimer ground state
- complex periodicity when approaching FM critical point

Zn substitution site and structure change





- Ionic radius:

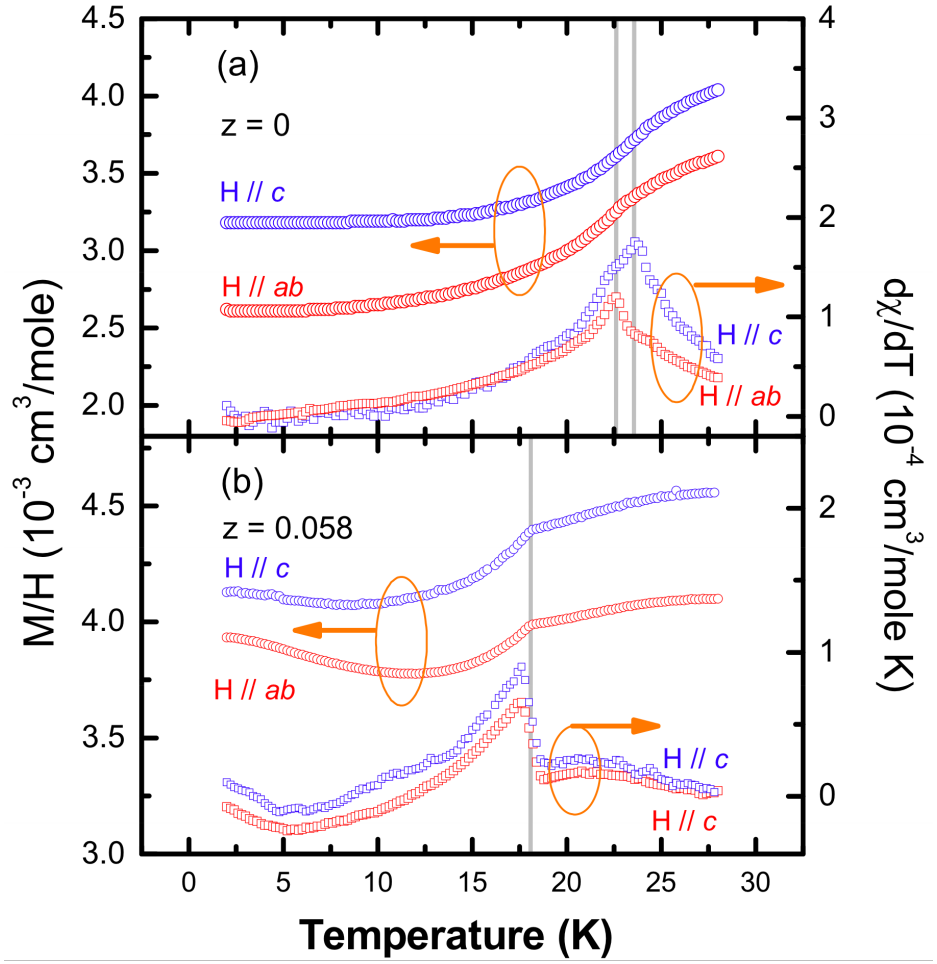
Cu^{2+} = 0.71 A (CN=4)

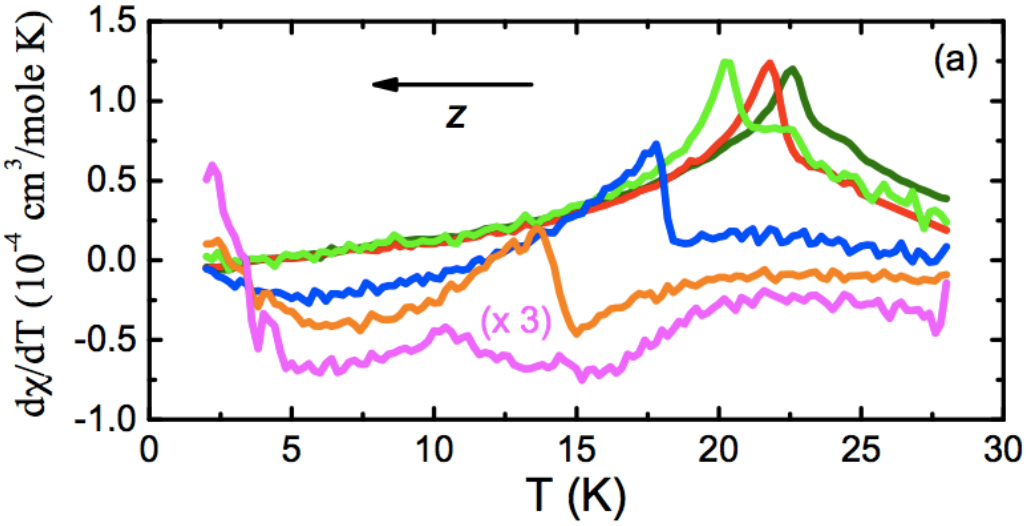
Zn^{2+} = 0.74 A (CN=4)

Cu^{+} = 0.60 A (CN=2)

- no signature of superlattice or structure change
- significantly reduced c-axis and slightly enlarged ab

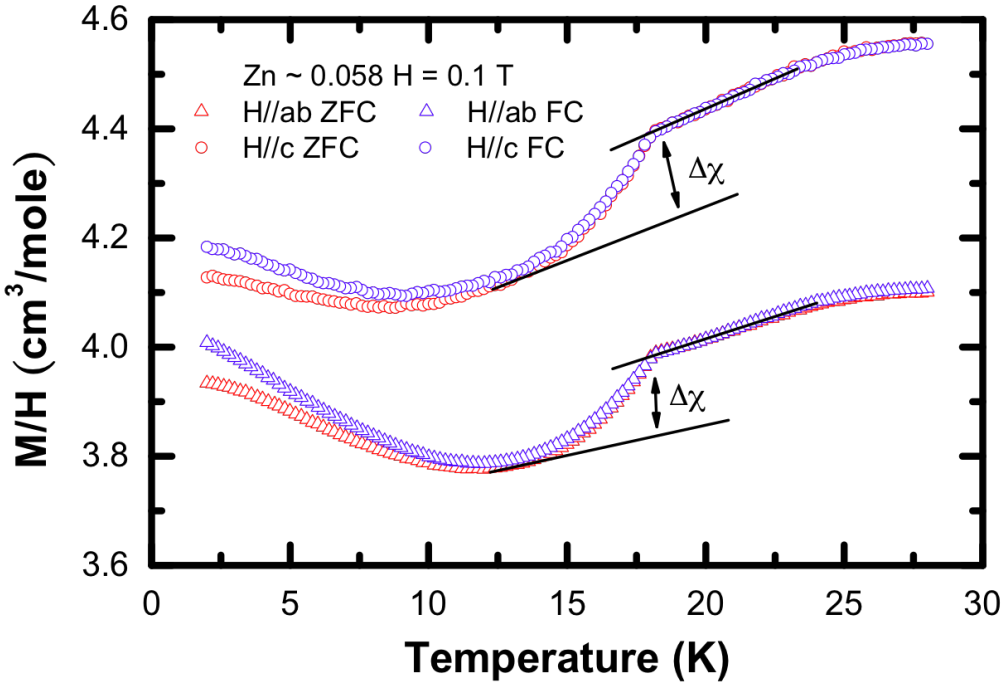
Zn substitution: magnetic property change

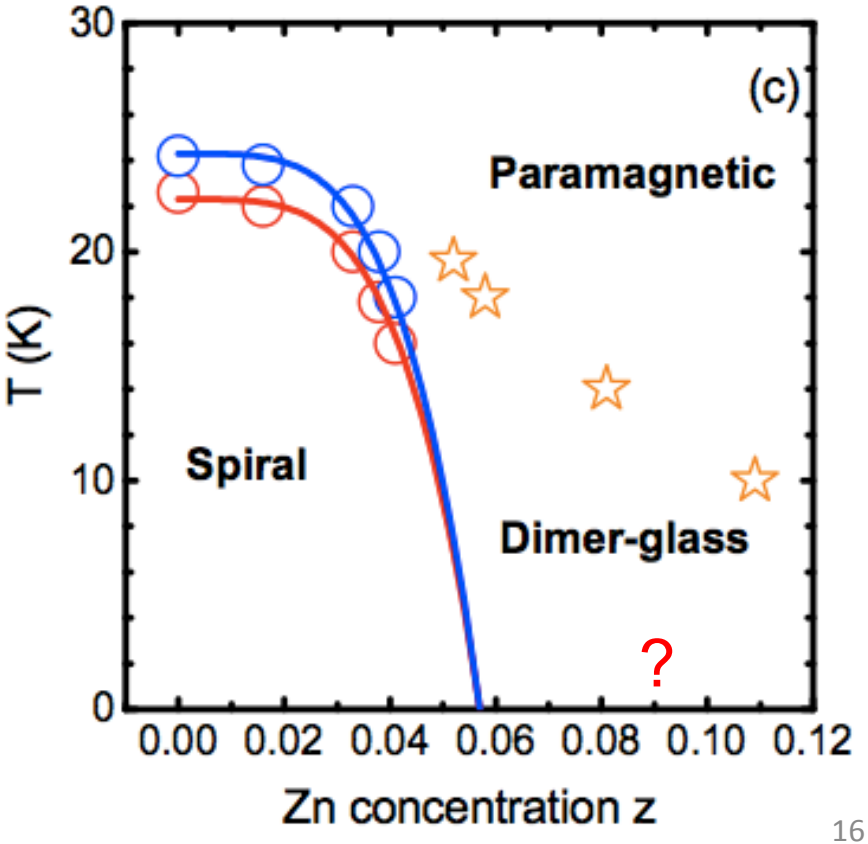




- reduced helical ordering < 5%
- novel magnetic transition > 5%
- spin glass? spin gap? AF?

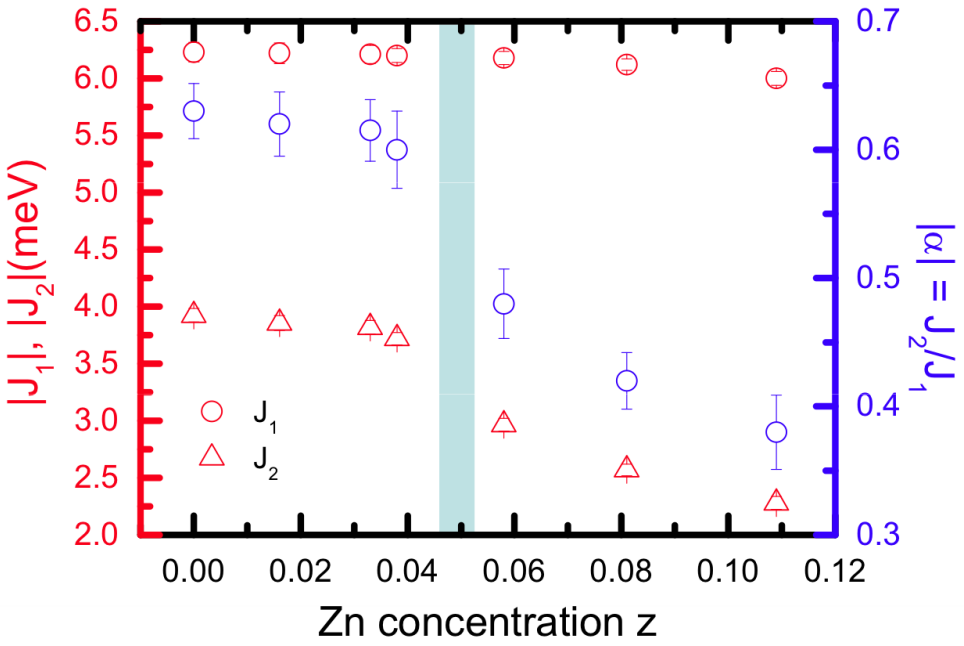
Spin glass or partial spin gap opening?





- spin glass < 5K ?
- antiferromagnetic ordering?
- partial spin gap : $\Delta\chi/\chi(T_c)$~ z, phase separation?
- spin-phonon coupled isolated dimer?
- or dimer without translational symmetry breaking?

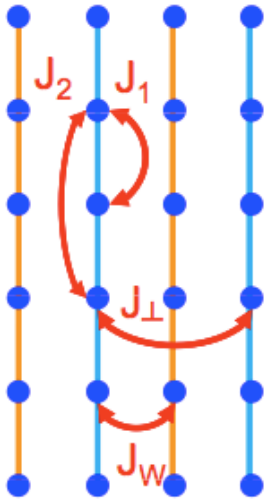
χ(T) fitting: HTSE and N=16-ring

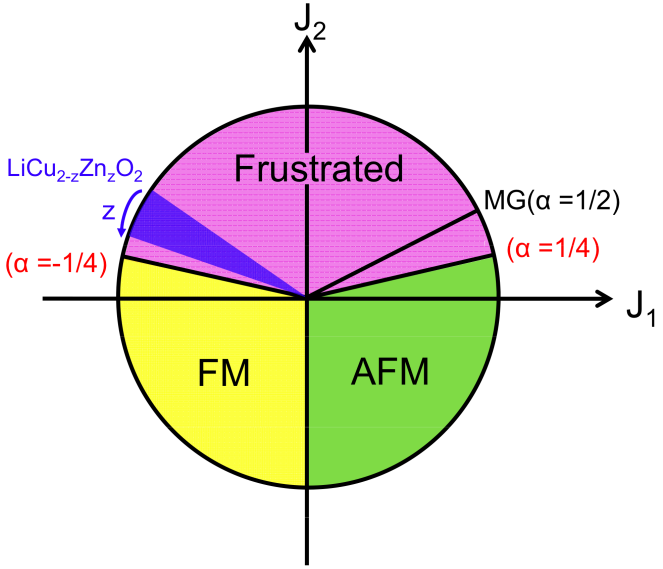


- High temperature series expansion
- N=16 ring exact diagonolization
- nearly constant J_1 and significantly reduced J_2

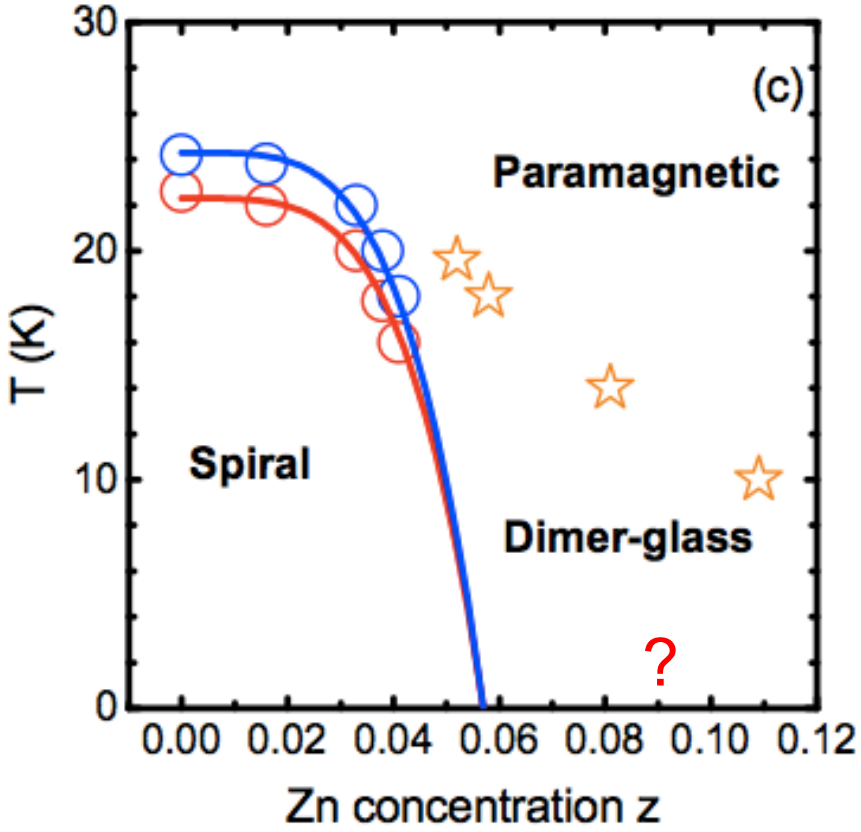
$$H = J_1 \sum (\mathbf{s}_i \cdot \mathbf{s}_{i+1}) + J_2 \sum (\mathbf{s}_i \cdot \mathbf{s}_{i+2})$$

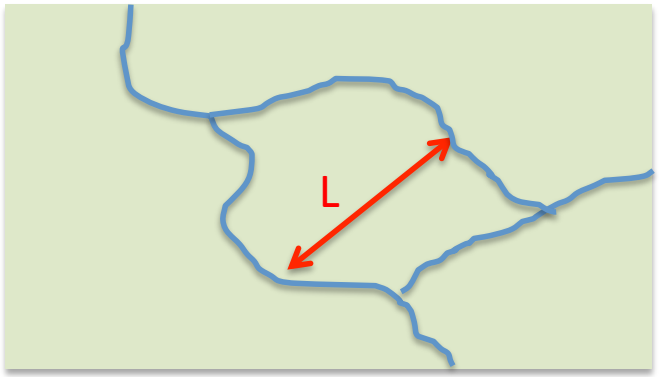
$$\chi = \frac{1}{T} \sum_{n,k} a_{n,k} \alpha^k (\beta J)^n$$





Finite size effect?





Finite size effect

$$1-\frac{T_c(x)}{T_c(0)}=\left(\frac{x}{x_c}\right)^n \propto L^{\frac{-1}{\nu}}$$

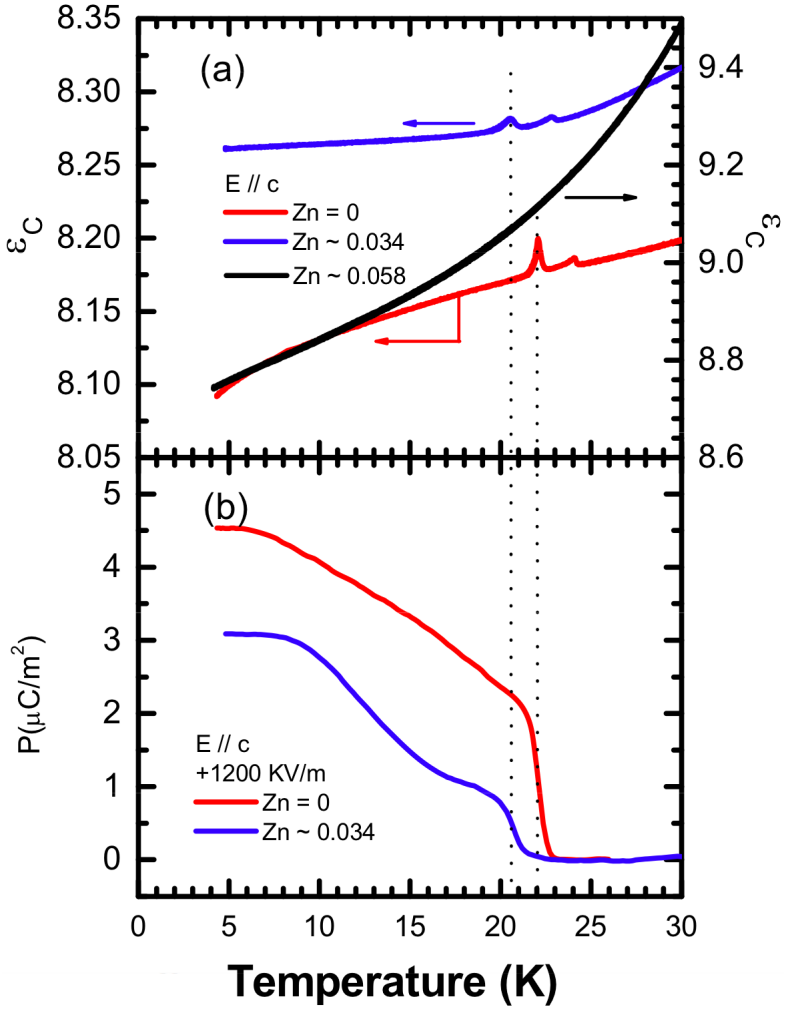
$$\Rightarrow L \propto x^{-n\nu}$$

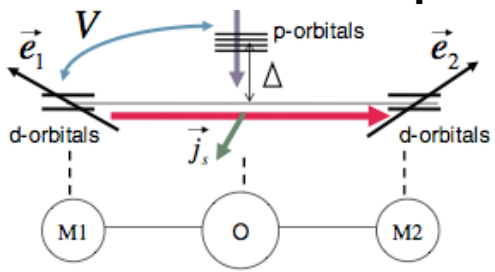
with n=4, ν = ½:

$L \sim 1/x^2$

- helical ξ_{ab} ~ 1200 A for $LiCu_2O_2$
- 5% Zn: L ~ 1000-2000 A
- helical ordered finite size domain boundaries formed with isolated spins?
- mesoscopic phase separation?
- soliton-like spin transport and localization?

Electric polarization

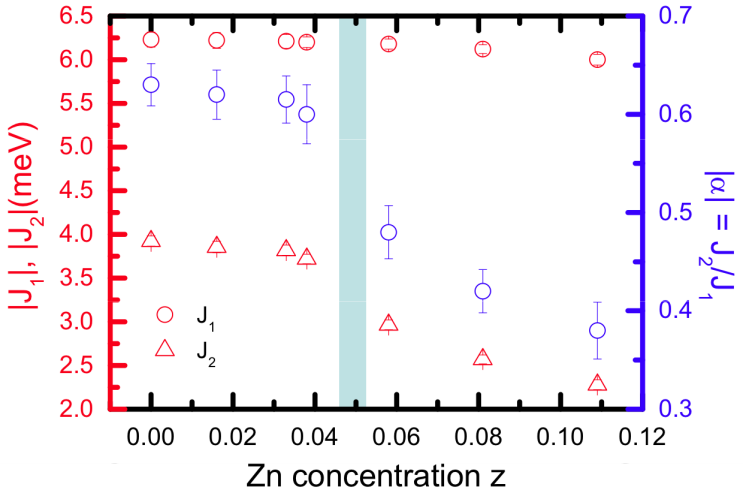


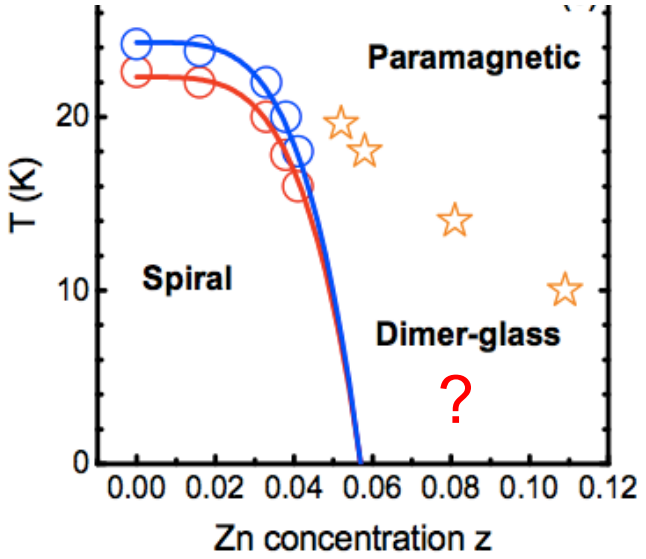


Katsura et al., PRL2005

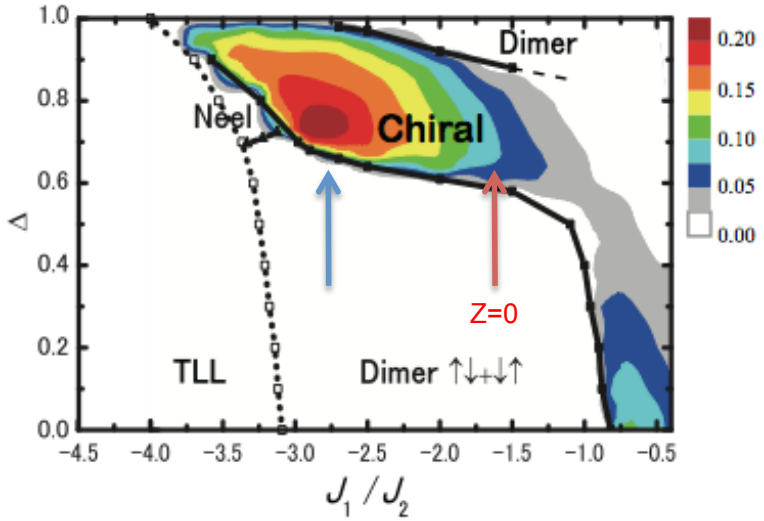
$$\mathbf{P} \propto \mathbf{Q} \times (\mathbf{S}_i \times \mathbf{S}_{i+1})$$

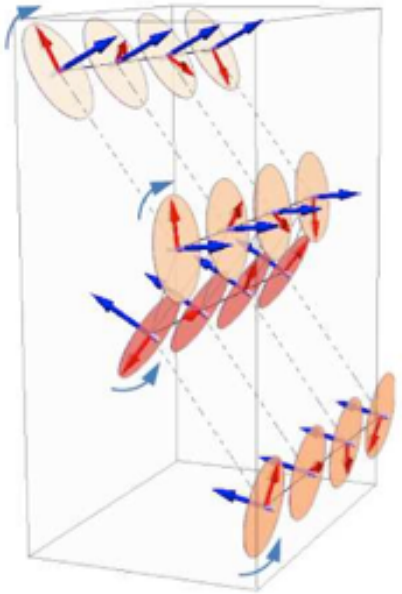
- reduced P at low Zn
- quenched P for lacking of helical LRO

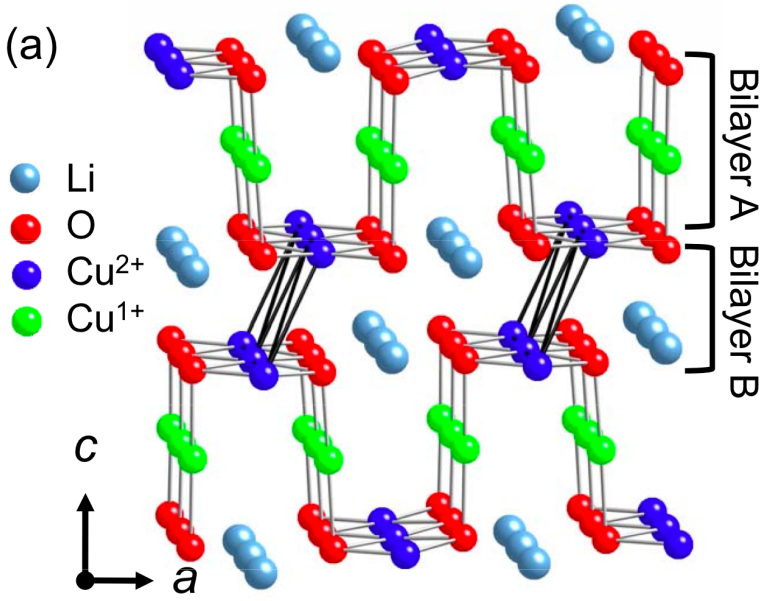




Dimers, really possible?







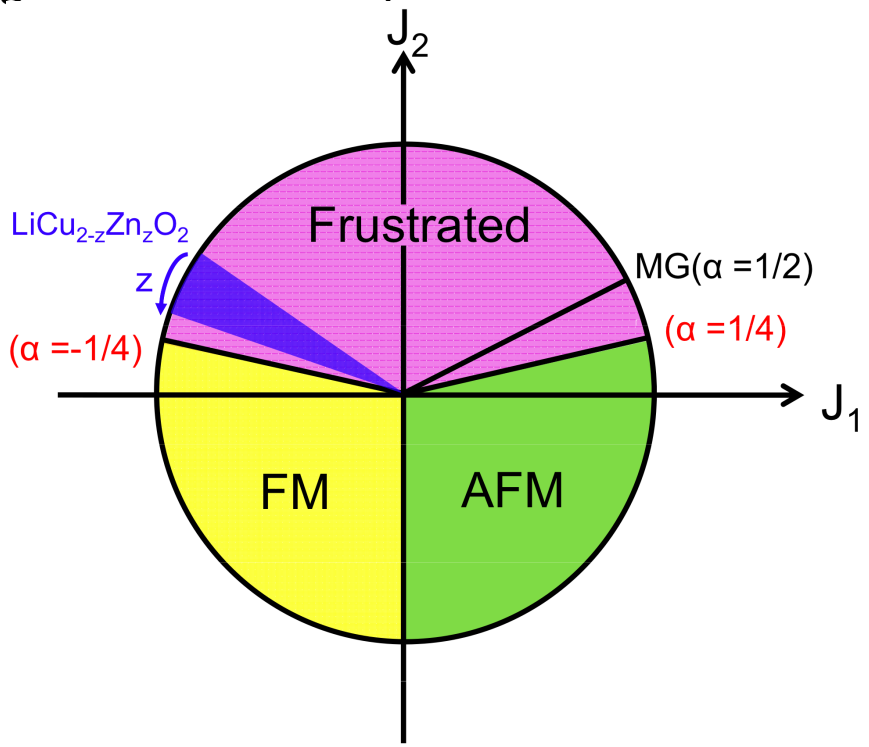
- easy plane anisotropy
- iTEBD: DMRG algorithm on infinite system
- 4 sets of D plus interlayer DM interaction
- finite vs. infinite chain

$$H_{1D} = \sum_{m=1,2} J_m \sum_j \left(S_j^x S_{j+m}^x + S_j^y S_{j+m}^y + \Delta S_j^z S_{j+m}^z \right)$$

Furukawa et al., arXiv:1003.3940

Summary of $Li_xCu_2O_2$

- Li vacancy coupled to the IC helical spin ordering?
- Nonmagnetic doping effect: possible isolated dimers of spin-Peierls character
- microscopic phase separation of spin-assisted origin?
- phase diagram: finite size effect, domains and dimer clusters
- reduced P and quenched P due to inhomogeneous helical spin modulation



Collaborators

Na_xCoO_2:

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- M. W. Chu – TEM/XRD
- W. W. Pai - STM
- Y. K. Kuo – Cp, Seebeck
- J. Y. Lin – Cp
- W. L. Lee – Hall, MR
- D. J. Huang – RISXS

- P. A. Lee - theory
- Y. S. Lee - neutron
- T. Imai – NMR
- P. Lemmens – Raman
- L. Balicas – SdH
- H. S. Sheu –XRD

$Li_xCu_2O_2$:

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