# Magnets without Direction

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- Introduction
- Moment Free Magnetism in one dimension
- Higher dimensional MFM
- Frustrated origins of MFM
- Interesting aspects of MFM
- Conclusions

# Acknowledgements

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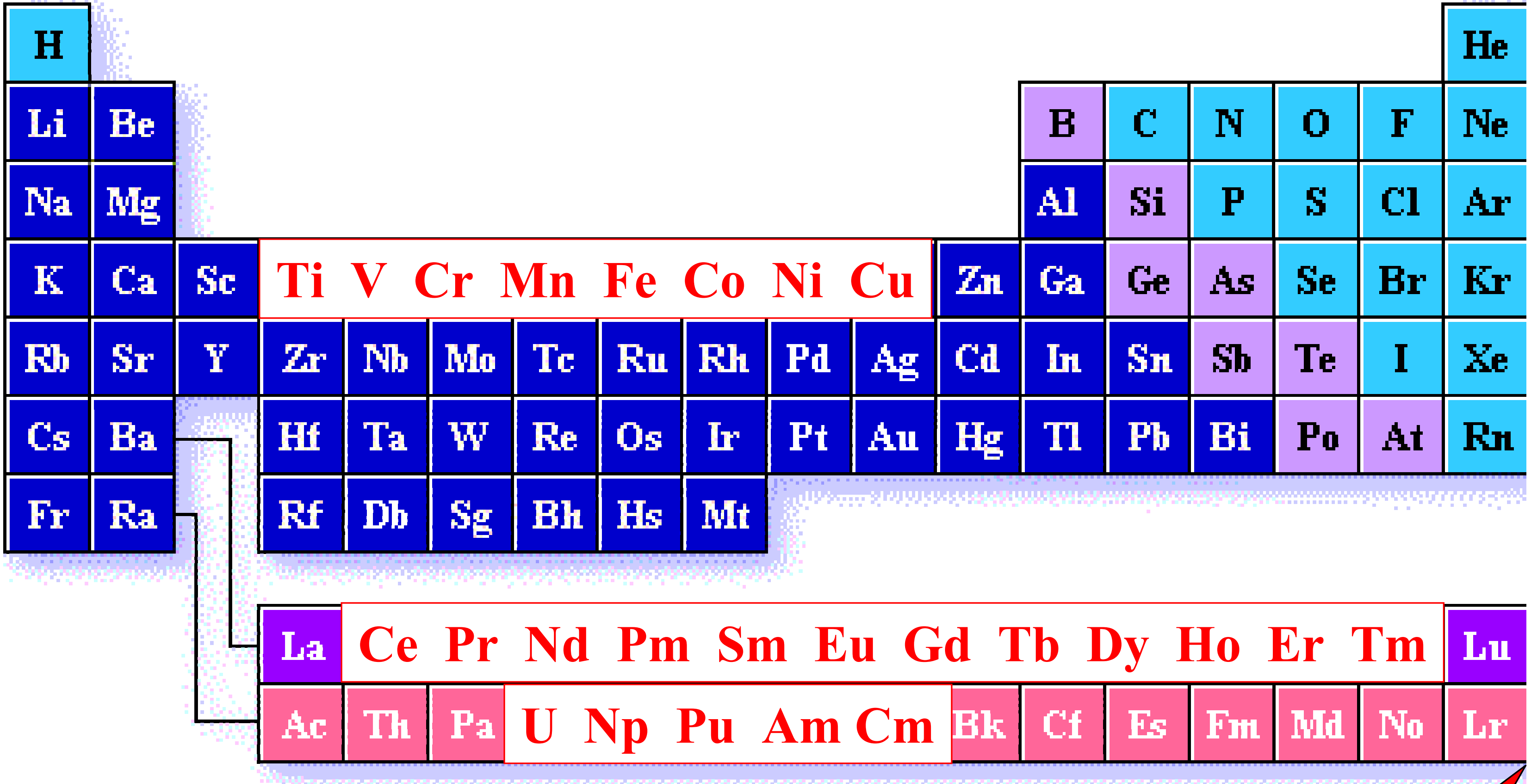
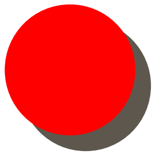
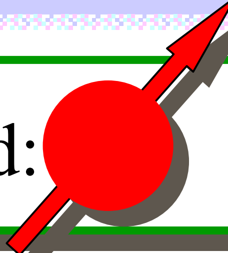
# Many electrons, few magnetic materials

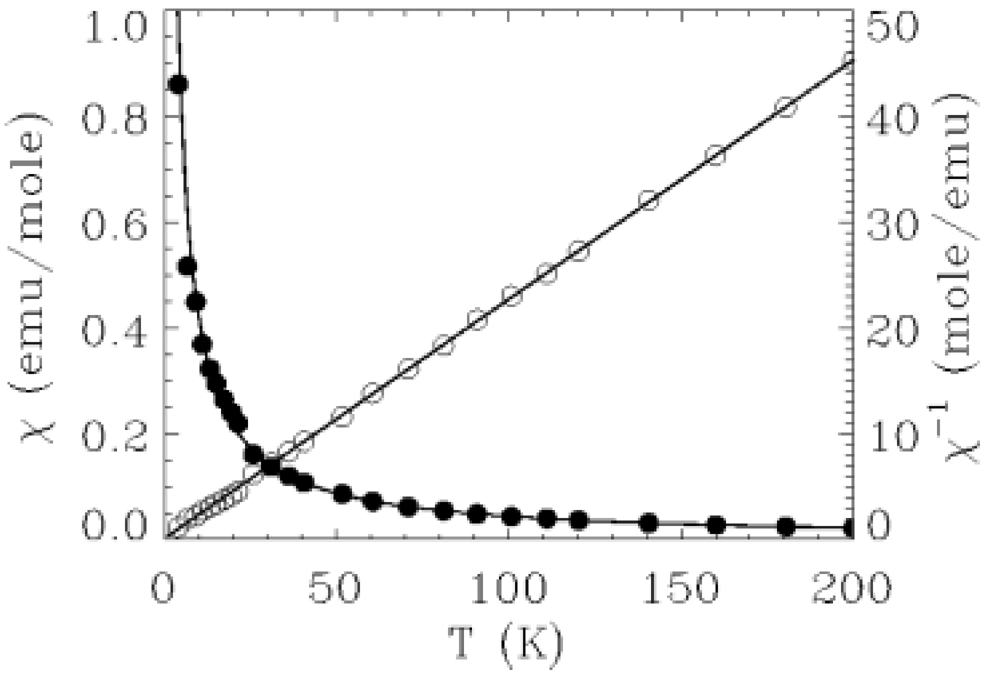



Filled shell in solid: 

Partially filled shell in solid: 

# Magnetization of Solid with unfilled Shells

$FeBr(C_{44}H_{28}N_4)$
Dilute Fe in organic matrix



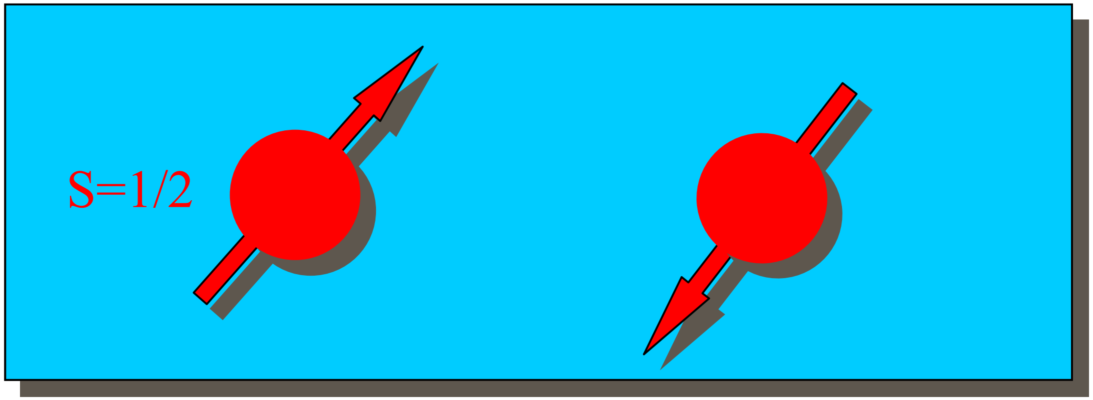

$$\mathscr{H} = -g\mu_B \mathbf{H} \cdot \sum_j \mathbf{S}_j$$

$$\mathbf{M} = \frac{g\mu_B}{V} \sum_j \langle \mathbf{S}_j \rangle$$

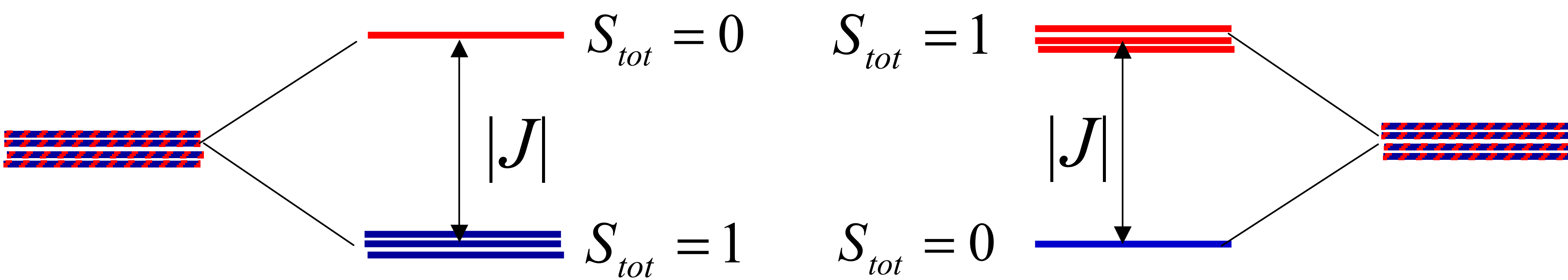
$$\boldsymbol{\chi} = \frac{\partial \mathbf{M}}{\partial \mathbf{H}}$$

"Brownian" spin dynamics suppresses χ as 1/T

# Coulomb + Pauli = Heisenberg




Coulomb interactions plus Pauli principle split 4-fold spin degeneracy




The level scheme is reproduced by Heisenberg Exchange Hamiltonian

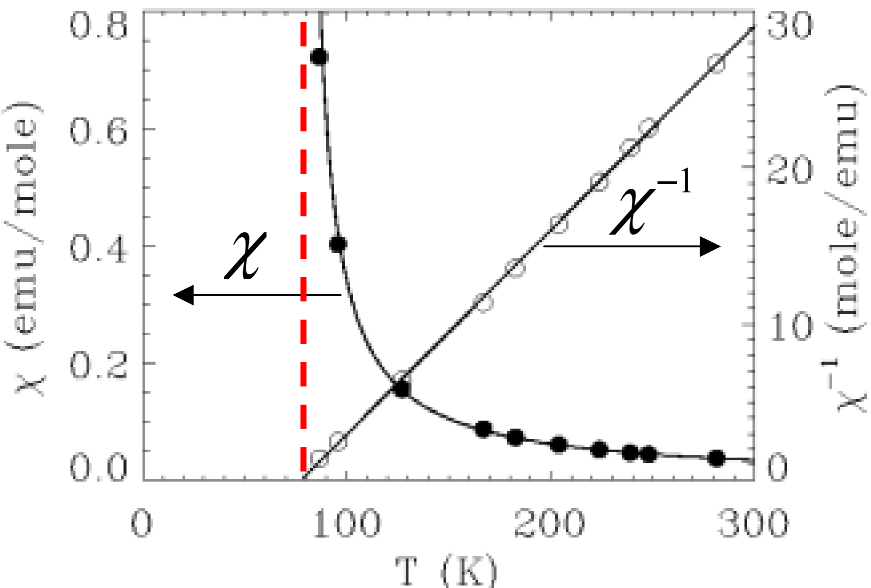
$$\mathscr{H} = J\,\mathbf{S}_i \cdot \mathbf{S}_j$$

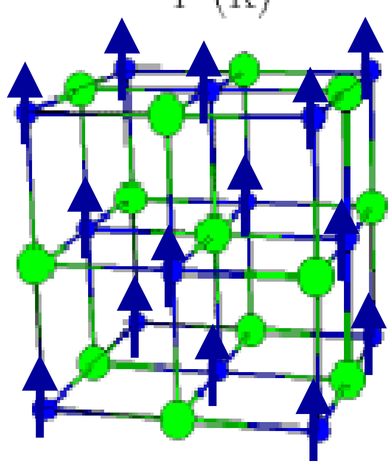
Triplet gnd. State: $J < 0$

Singlet gnd. State: $J > 0$

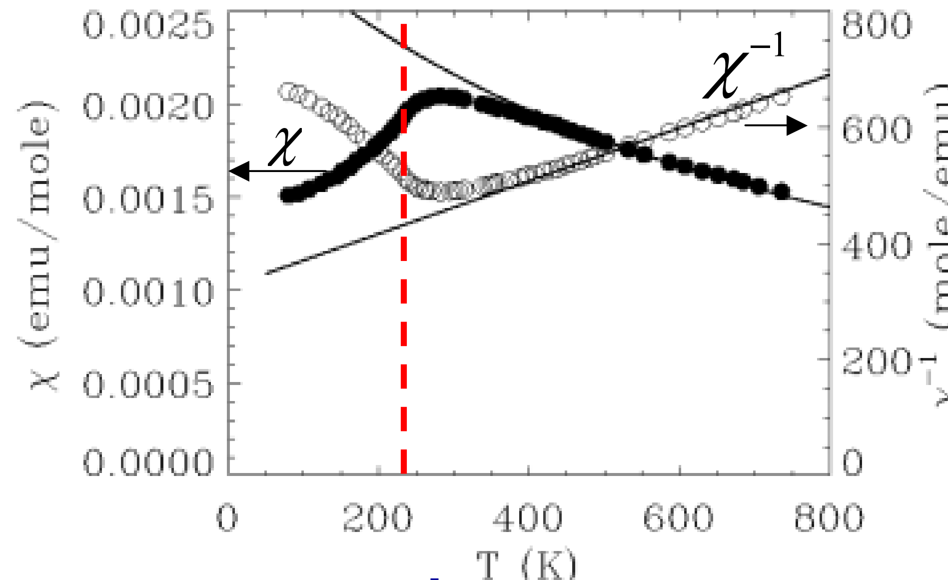
# Interactions orient moments

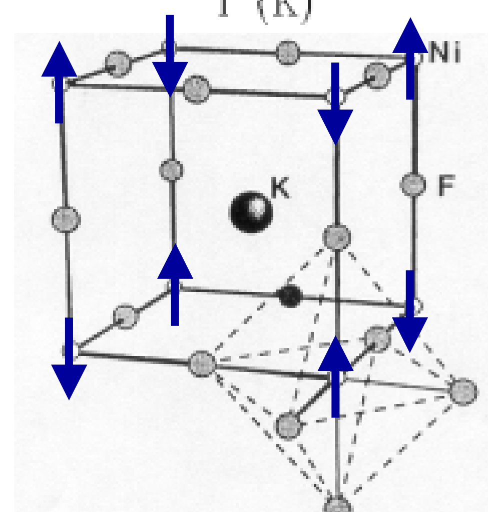
## Ferromagnetic EuO



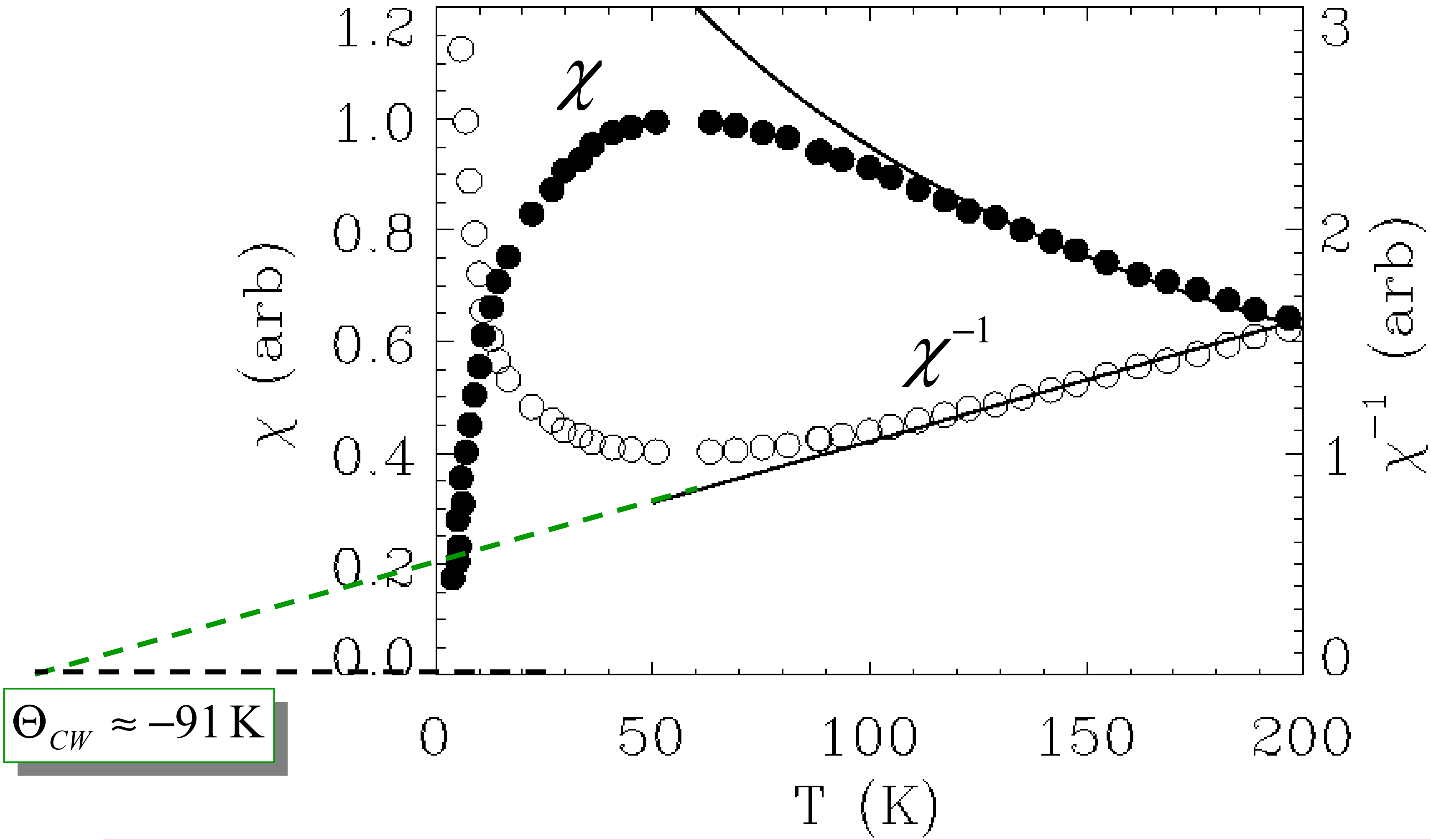



## Antiferromagnetic $KNiF_3$



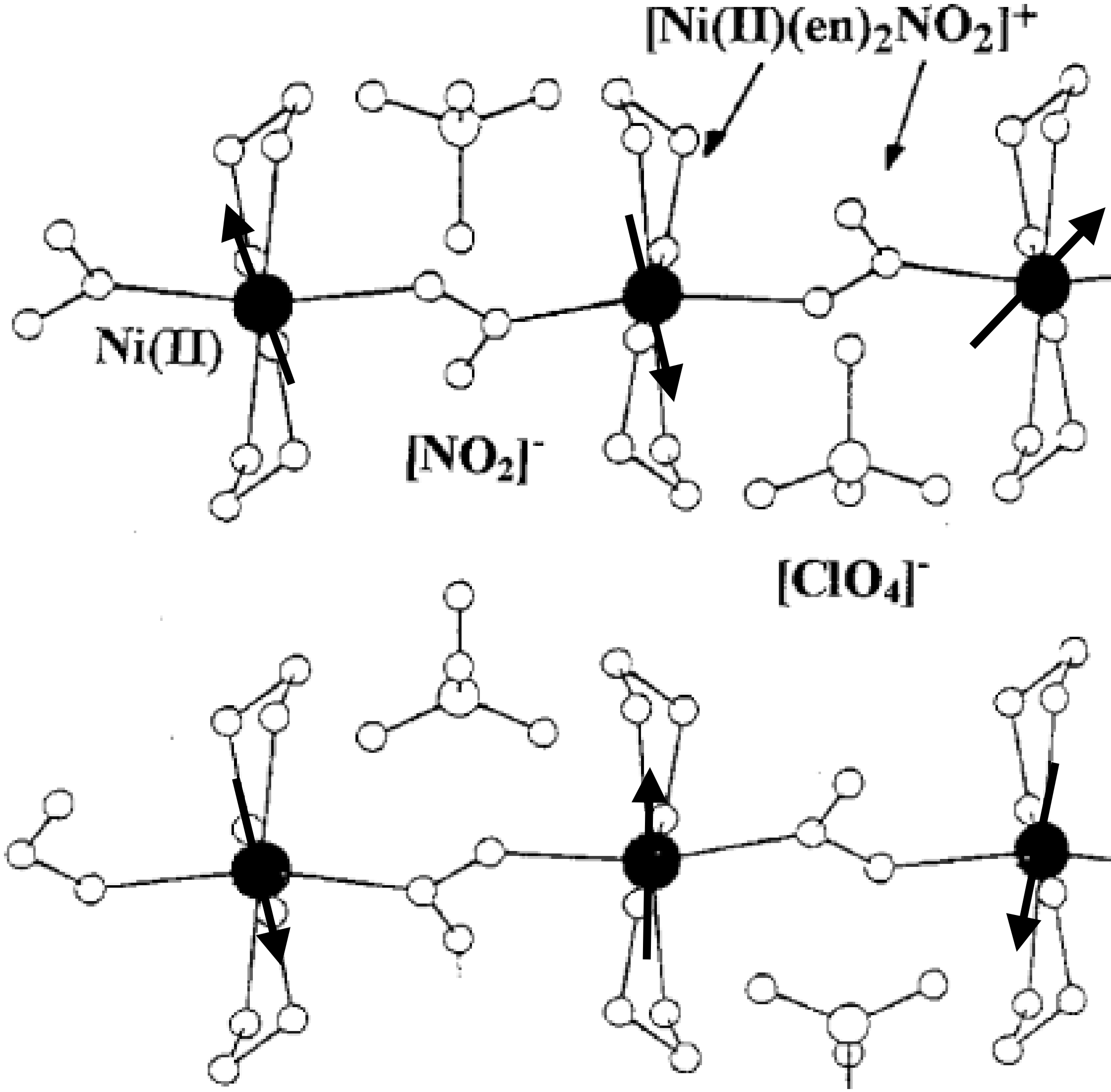



# Unconventional magnetism in NENP




- Negative Curie Weiss temperature indicates AFM interactions
- No phase transition and $\chi \rightarrow$ small for $T \rightarrow 0$

# A can of magnetic worms




Magnetic interactions link spins in chains

Ensemble of Quasi-one-dimensional Antiferromagnets chains

NENP=$Ni(C_2H_8N_2)_2NO_2ClO_4$

# When is magnetism unconventional?

Consider the state of things at T=0

| | |
|---|---|
| Conventional: | $\left\|\langle \mathbf{S} \rangle\right\| \approx S$ |
| Unconventional: | $\left\|\langle \mathbf{S} \rangle\right\| << S$ |

$\langle \delta S \rangle = S - \langle S^z \rangle$ is a measure of <u>how</u> unconventional.

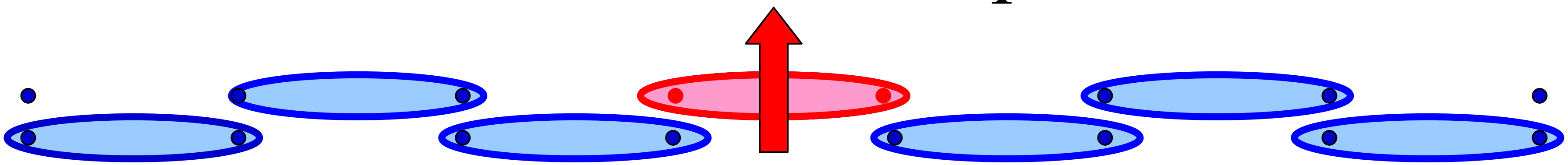
We can calculate $\langle \delta S \rangle$ assuming that it is small

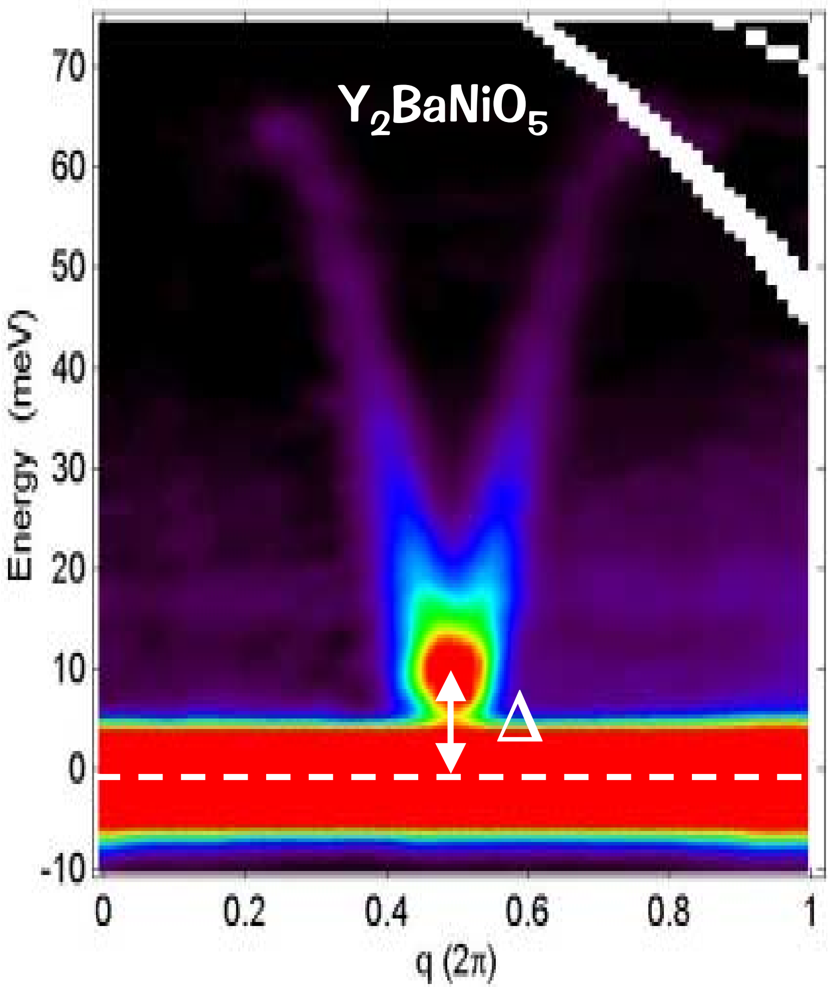
$$\langle \delta S \rangle \approx \frac{1}{2S}\frac{1}{N}\sum_{\mathbf{R}} \langle S^-_{\mathbf{R}} S^+_{\mathbf{R}} \rangle = \frac{1}{2S}\int \frac{d^D\mathbf{Q}}{v_{BZ}} \frac{g^{-+}(\mathbf{Q})}{\hbar\omega(\mathbf{Q})}$$

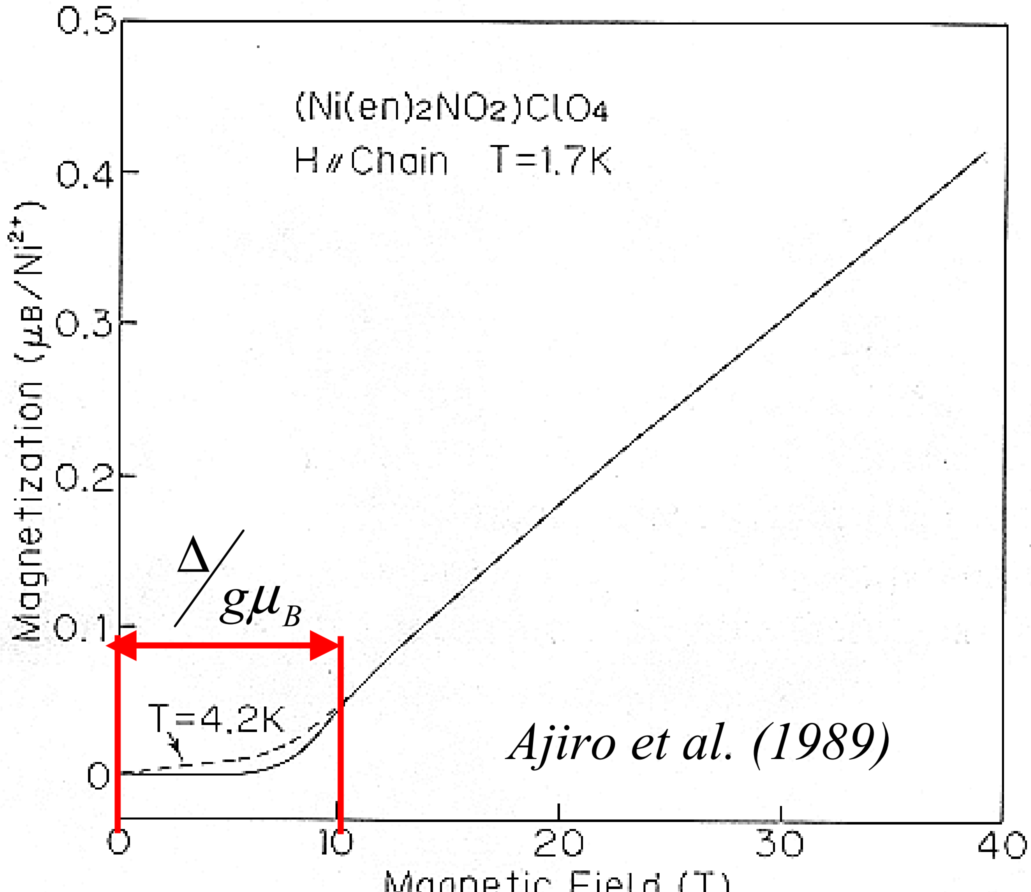
$\langle \delta S \rangle$ "diverges" when dimensionality of **Q**-space where $\omega(\mathbf{Q}) = 0$ is $\geq D-1$

$\langle \delta S \rangle \to \infty$ for
- D=1 soft points
- D=2 soft lines
- D=3 soft planes

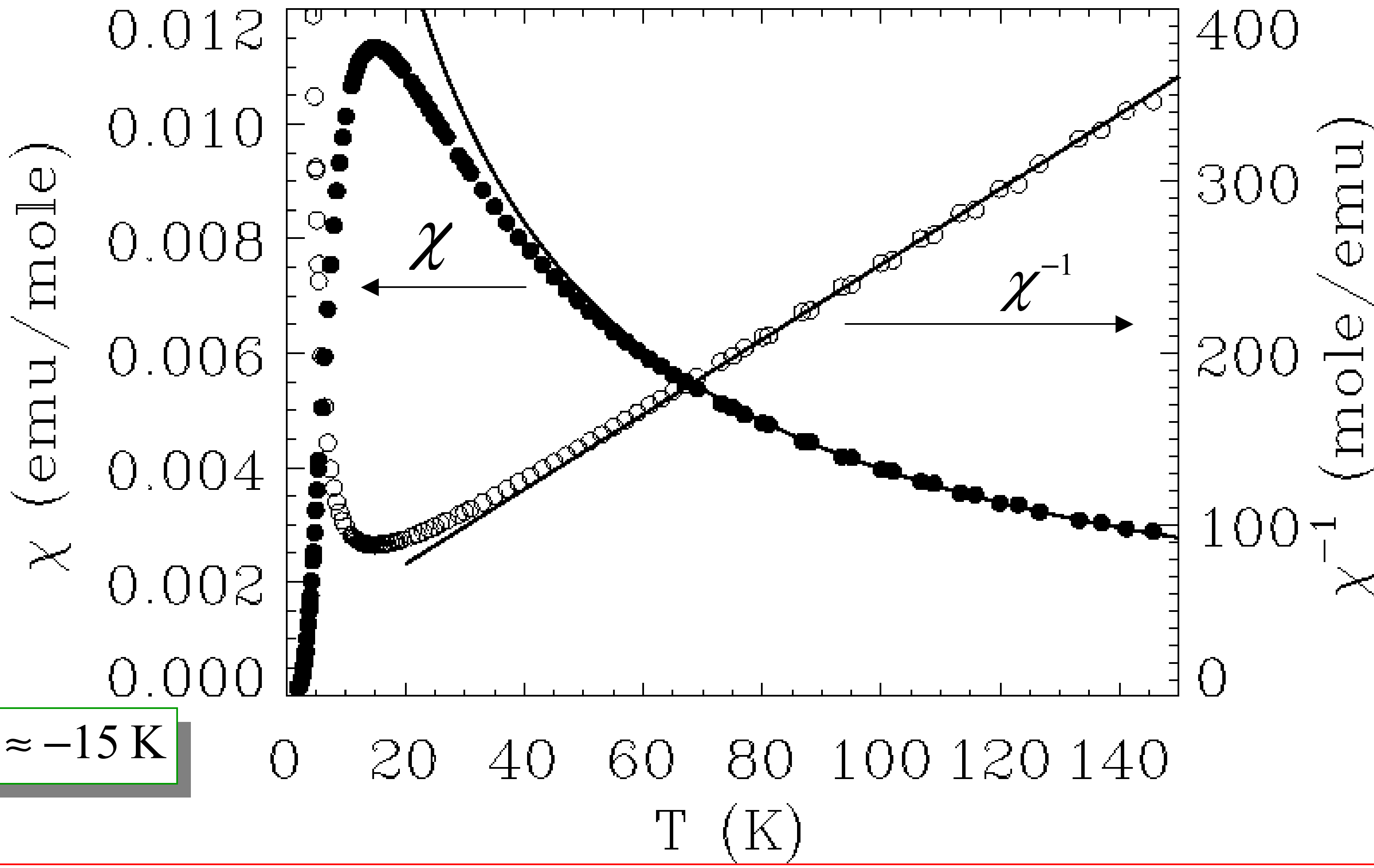
# Moment Free Magnetism averts infrared catastrophe





# Unconventional magnetism in PHCC

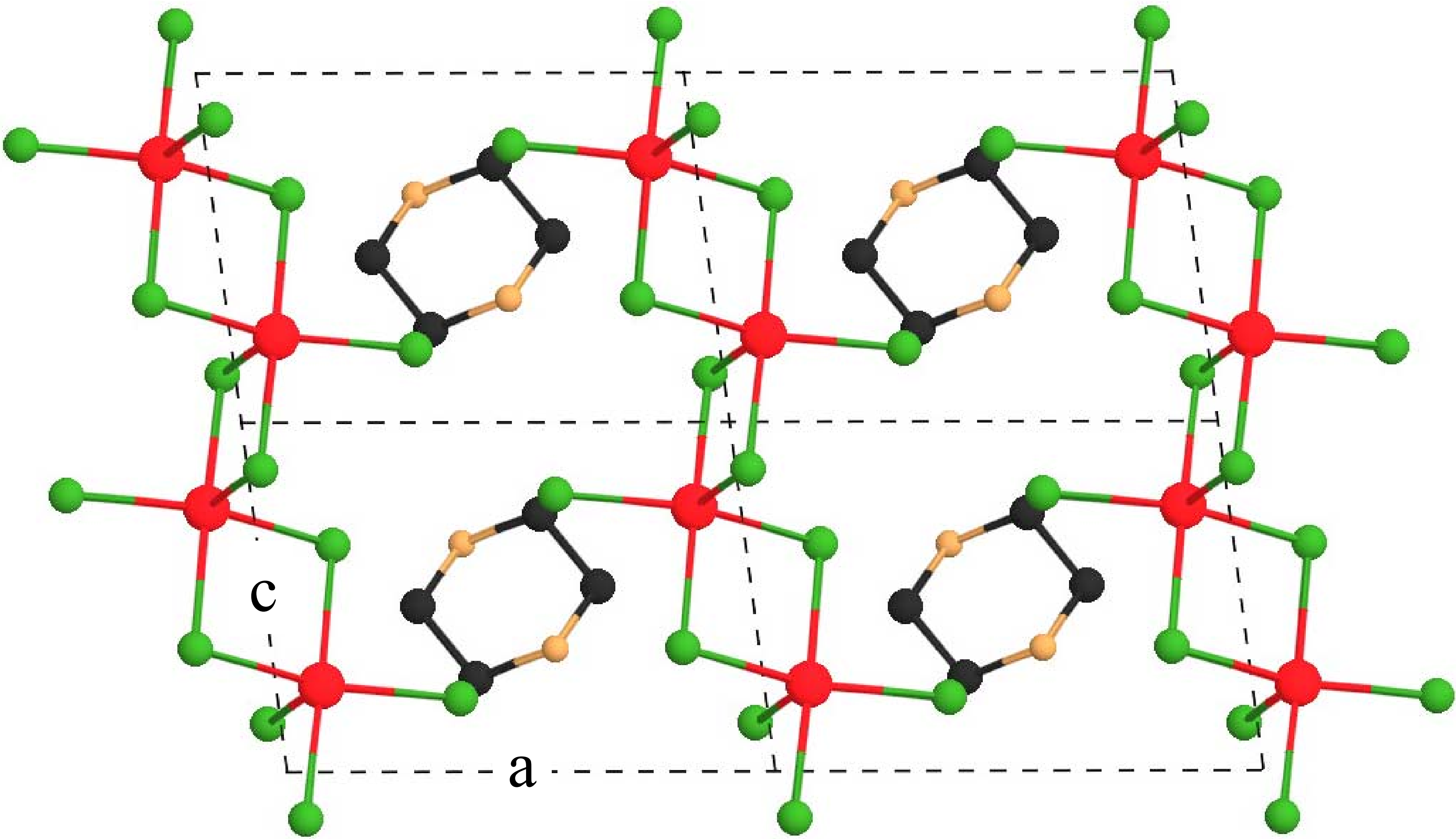



$\Theta_{CW} \approx -15\ \mathrm{K}$

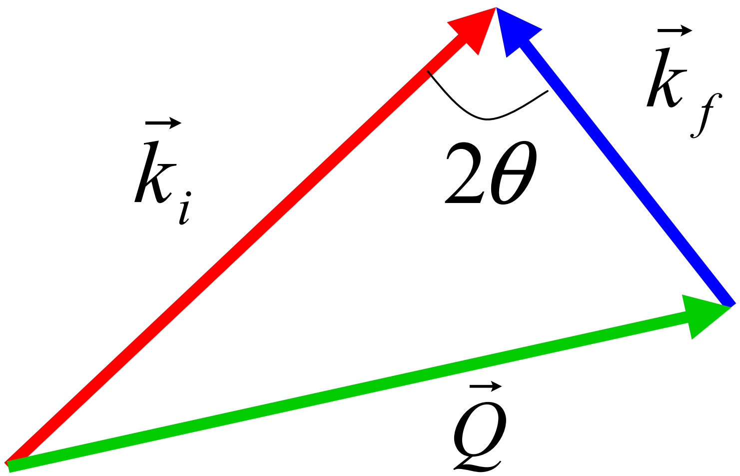
- Negative Curie Weiss temperature indicates AFM interactions
- No phase transition and $\chi \to 0$ for $T \to 0$

# Structure also "consistent" with spin chain

$C_4H_{12}N_2Cu_2Cl_6$



# Magnetic Neutron Scattering




$$\vec{Q} = \vec{k}_i - \vec{k}_f$$

$$\hbar\omega = E_i - E_f$$

The scattering cross section is proportional to the Fourier transformed dynamic spin correlation function

$$\mathbf{S}^{\alpha\beta}(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int dt\, e^{-i\omega t}\,\frac{1}{N}\sum_{\vec{R}\vec{R}'} e^{i\vec{Q}\bullet(\vec{R}-\vec{R}')} < \mathrm{S}^{\alpha}_{\vec{\mathrm{R}}}(t)\,\mathrm{S}^{\beta}_{\vec{R}'}(0) >$$

Fluctuation dissipation theorem:

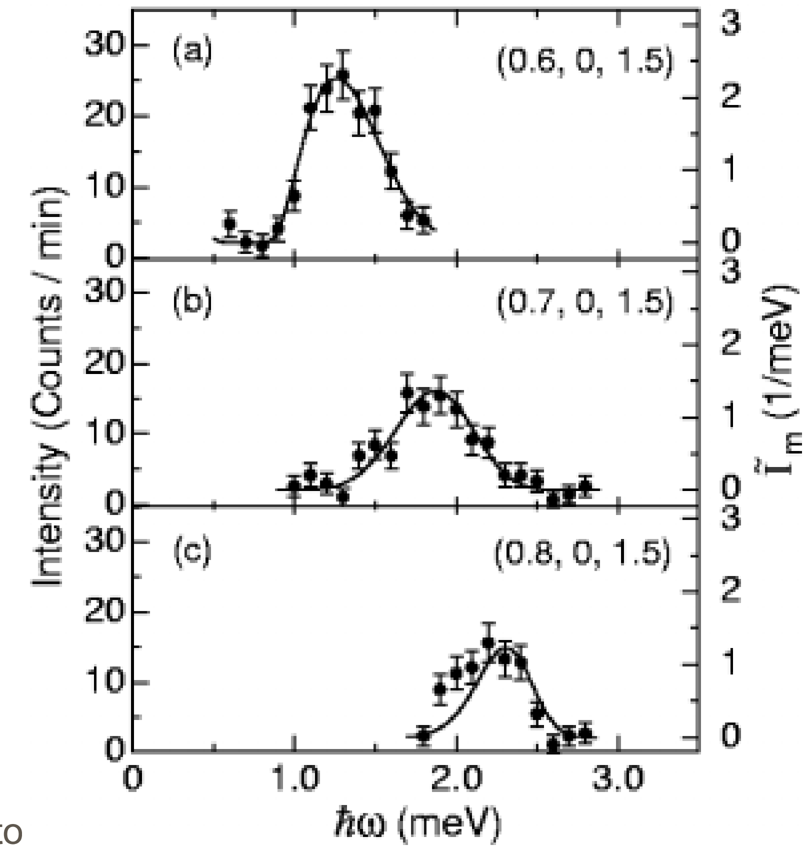
$$\chi''(Q,\omega) = (g\mu_B)^2\,\pi\left(1 - e^{-\beta\hbar\omega}\right)\mathbf{S}(Q,\omega)$$

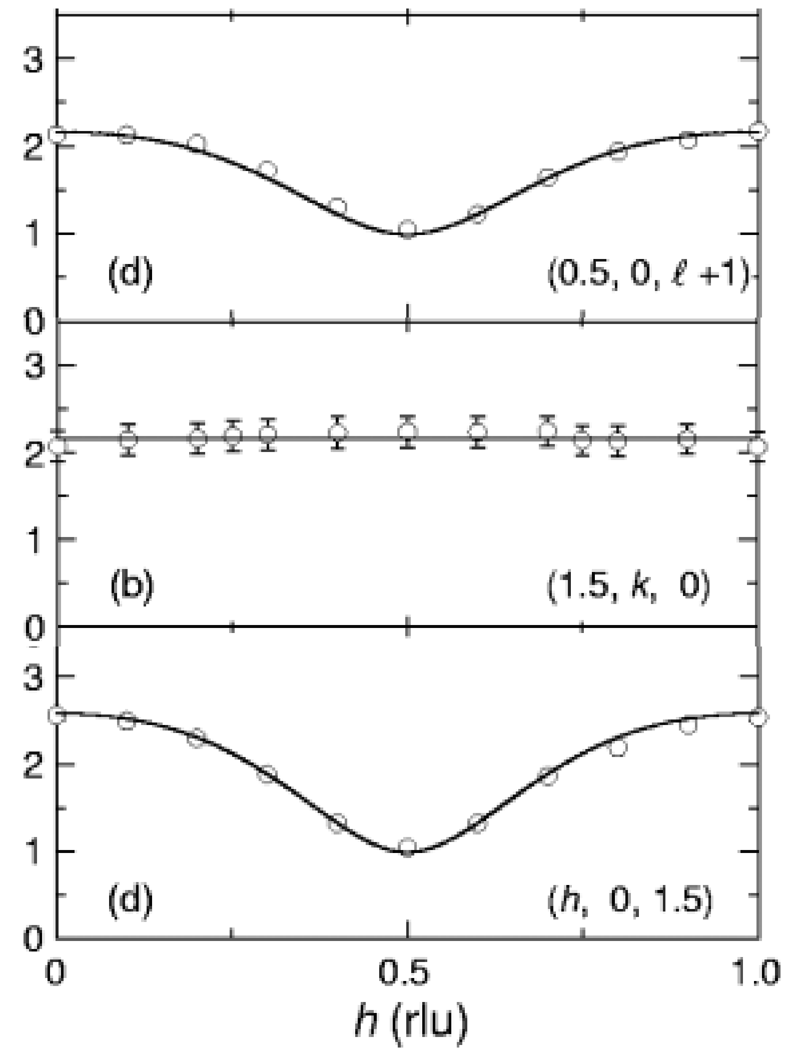
SPINS Cold neutron triple axis spectrometer at NCNR

# PHCC is magnetically two dimensional

Dispersion ⊥ to "chains"

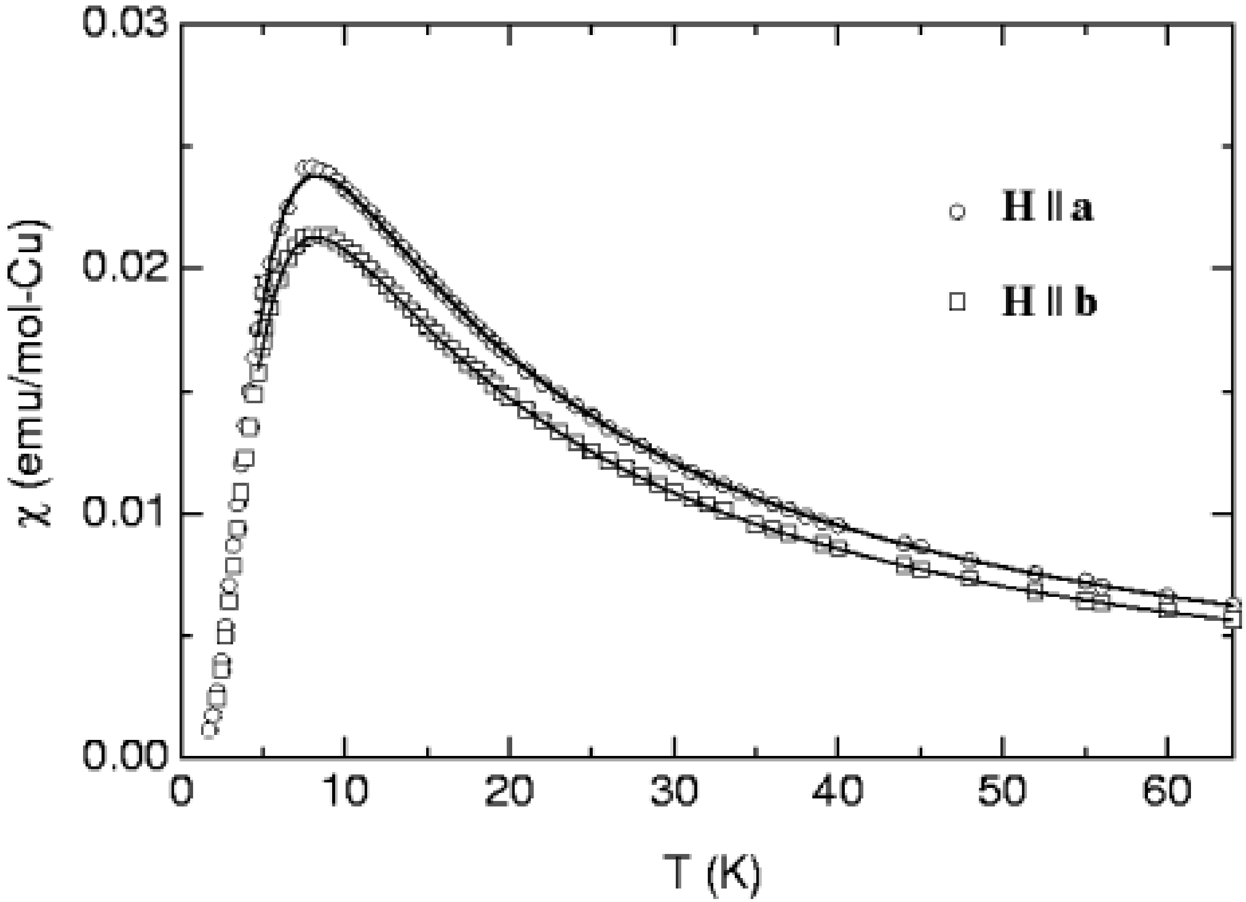
Not chains but planes

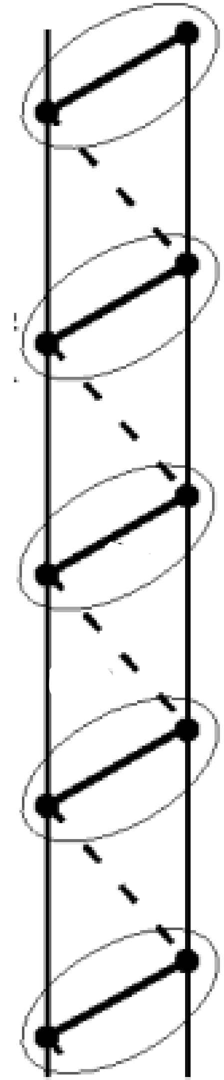



Georgeto

# Unconventional magnetism in CuHpCl

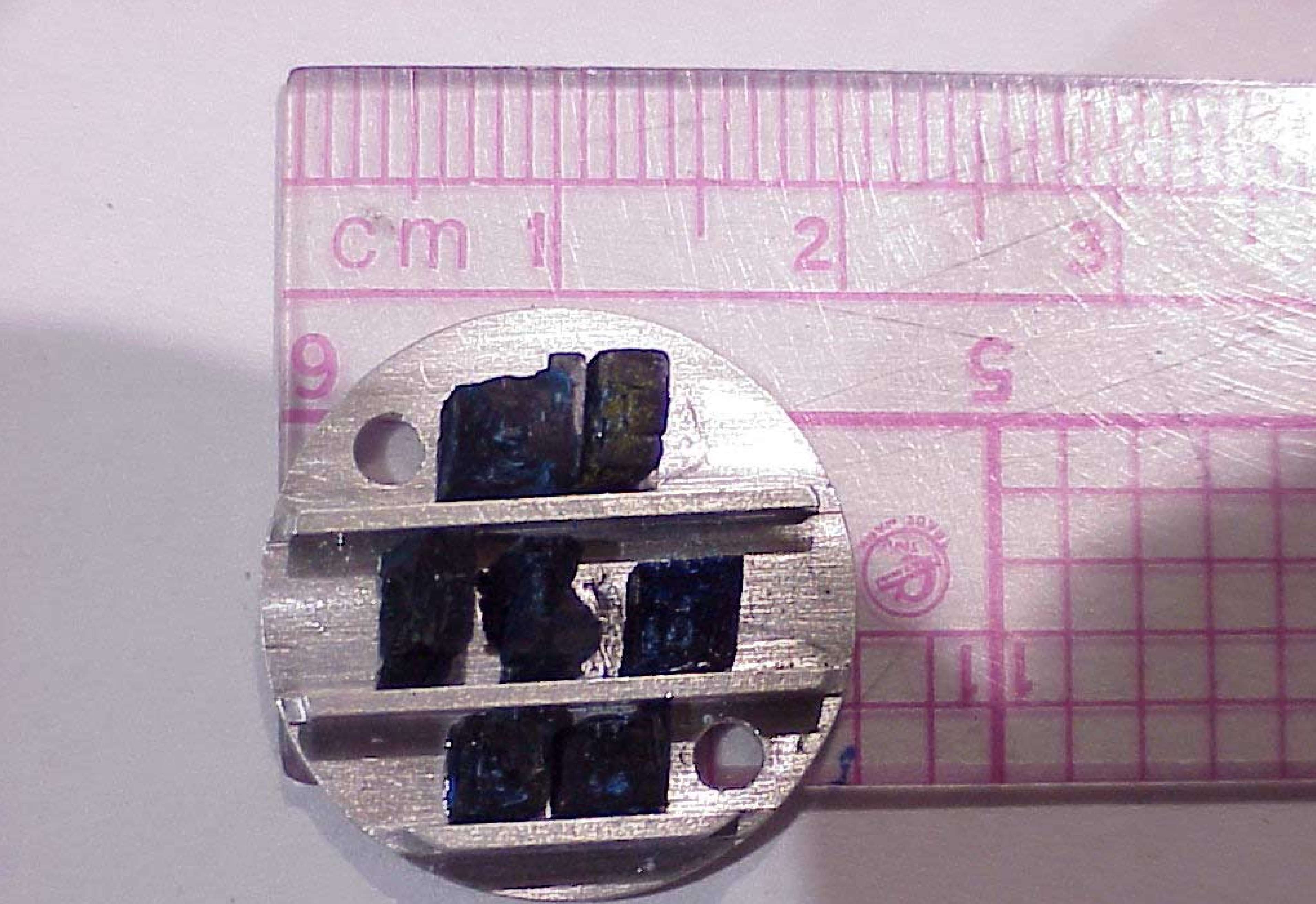


Putative Spin ladder model for CuHpCl

- Negative $\Theta_{CW}$ indicates AFM interactions
- No phase transition and $\chi \rightarrow 0$ for $T \rightarrow 0$
- Spin ladder model consistent with $\chi(T)$

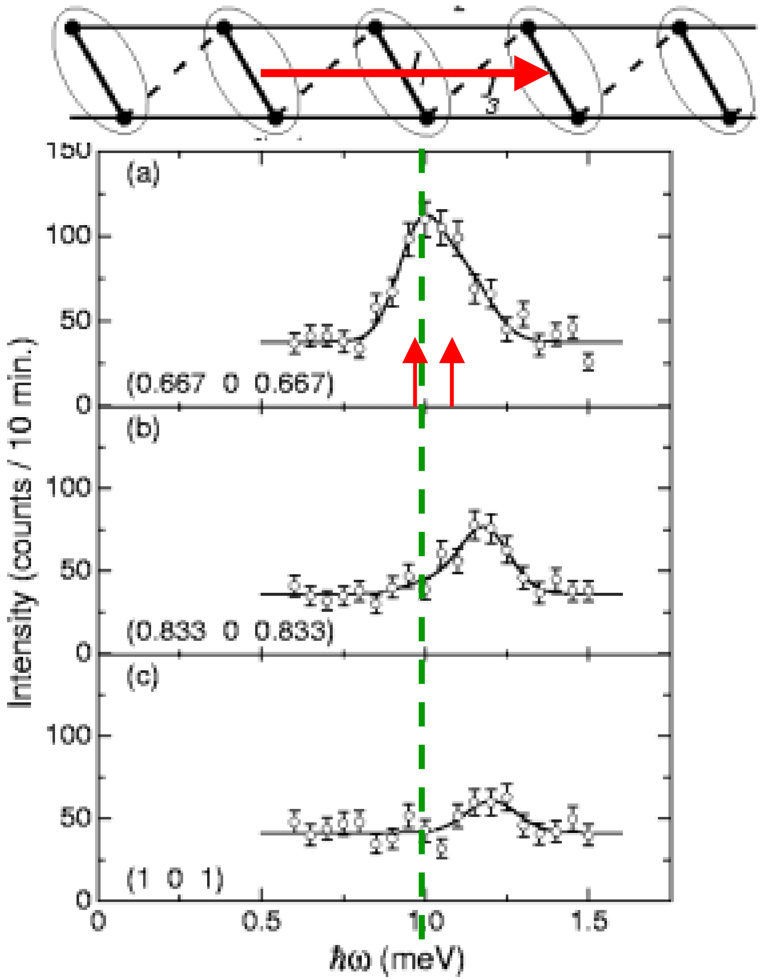
George



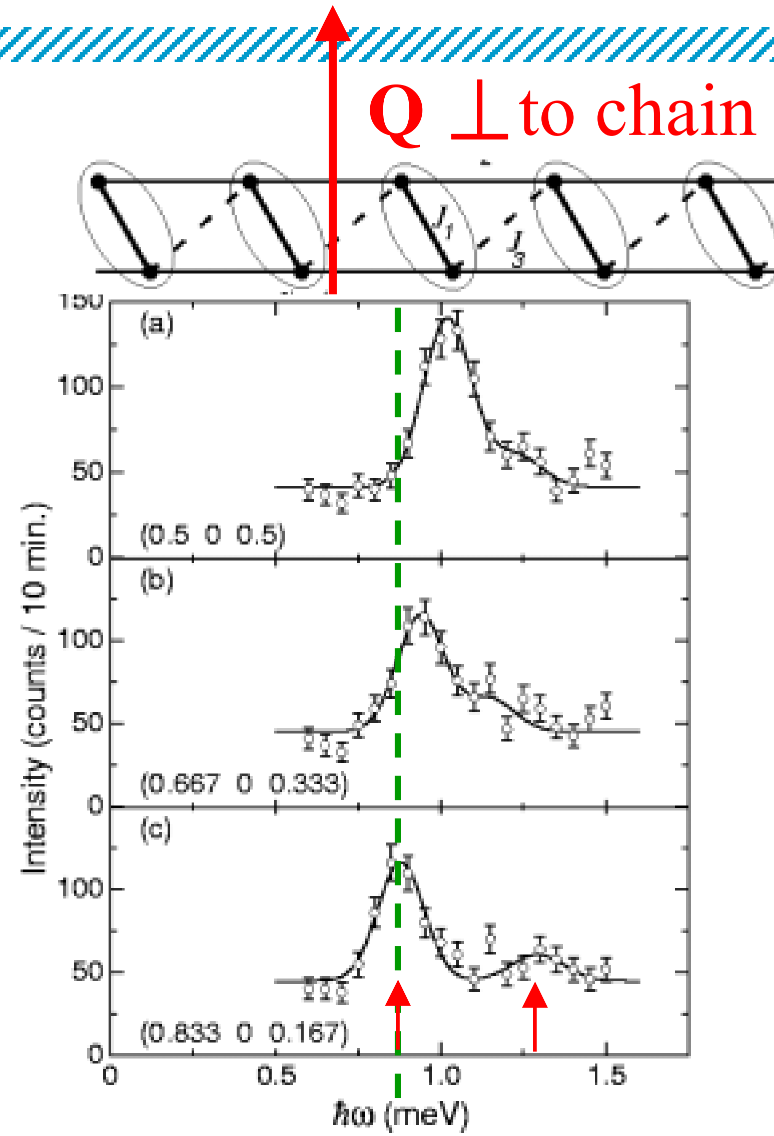

CuHpCl hydrogenous single crystals

# ….But there is dispersion ⊥ to "ladder"

**Q** // to chain



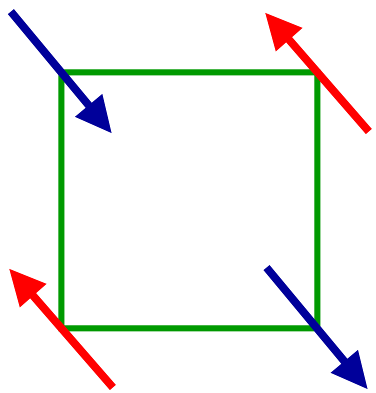

**Q** ⊥ to chain

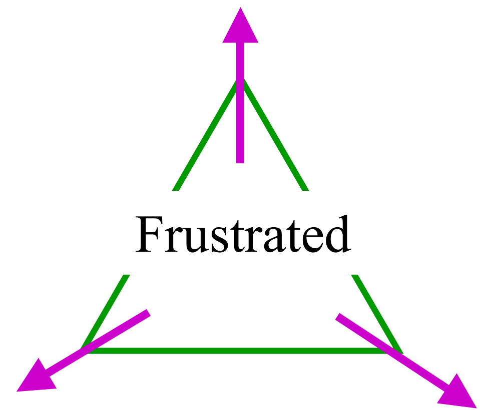



….and there are two modes when ladder gives only one

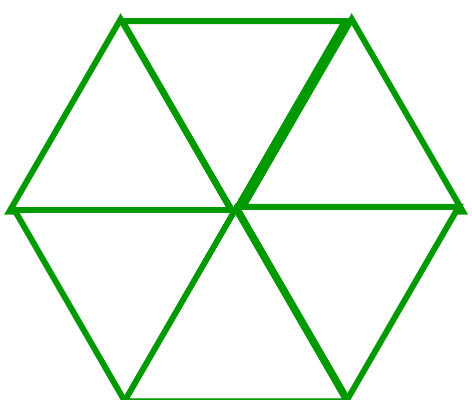
# A frustrated route to Moment Free Magnetism?

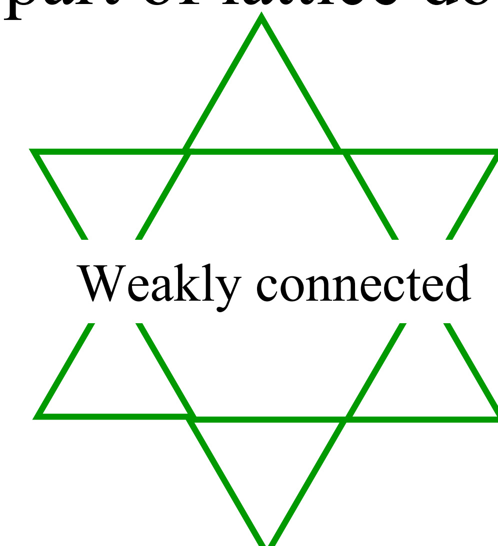
Magnetic Frustration: All spin pairs cannot simultaneously be in their lowest energy configuration






Weak connectivity: Order in one part of lattice does not constrain surrounding spins





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# Neutrons can reveal frustration

The first $\omega$-moment of scattering cross section equals "Fourier transform of bond energies"

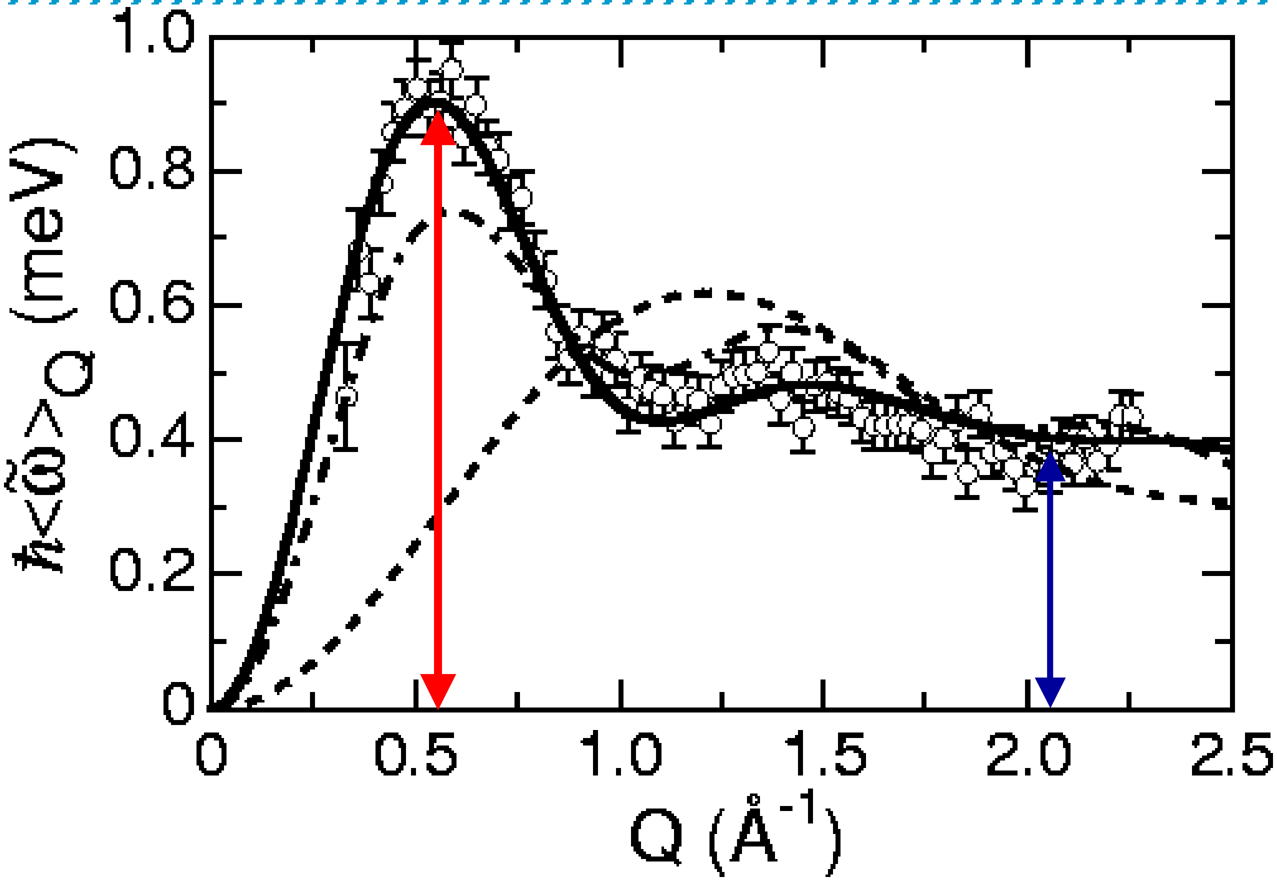
$$\hbar^2 \int \omega \, d\omega \, \mathcal{S}(\mathbf{Q},\omega) = -\frac{1}{3}\frac{1}{N}\sum_{\mathbf{rd}} J_{\mathbf{d}} < \mathbf{S}_{\mathbf{r}} \cdot \mathbf{S}_{\mathbf{r+d}} > \left(1 - \cos \mathbf{Q}\cdot\mathbf{d}\right)$$

For a powder sample we know only $Q = |\mathbf{Q}|$

$$\hbar^2 \int \omega \, d\omega \, \mathcal{S}(Q,\omega) = \boxed{-\frac{1}{3}\frac{1}{N}\sum_{\mathbf{rd}} J_{\mathbf{d}} < \mathbf{S}_{\mathbf{r}} \cdot \mathbf{S}_{\mathbf{r+d}} >}\left(1 - \frac{\sin Qd}{Qd}\right)$$

- high $Qd$ plateau measures ground state energy
- negative terms are "frustrated bonds"
- bond energies are small if $J_{\mathbf{d}}$ and/or $< \mathbf{S}_{\mathbf{r}} \cdot \mathbf{S}_{\mathbf{r+d}} >$ small

# Neutrons reveal frustration in CuHpCl

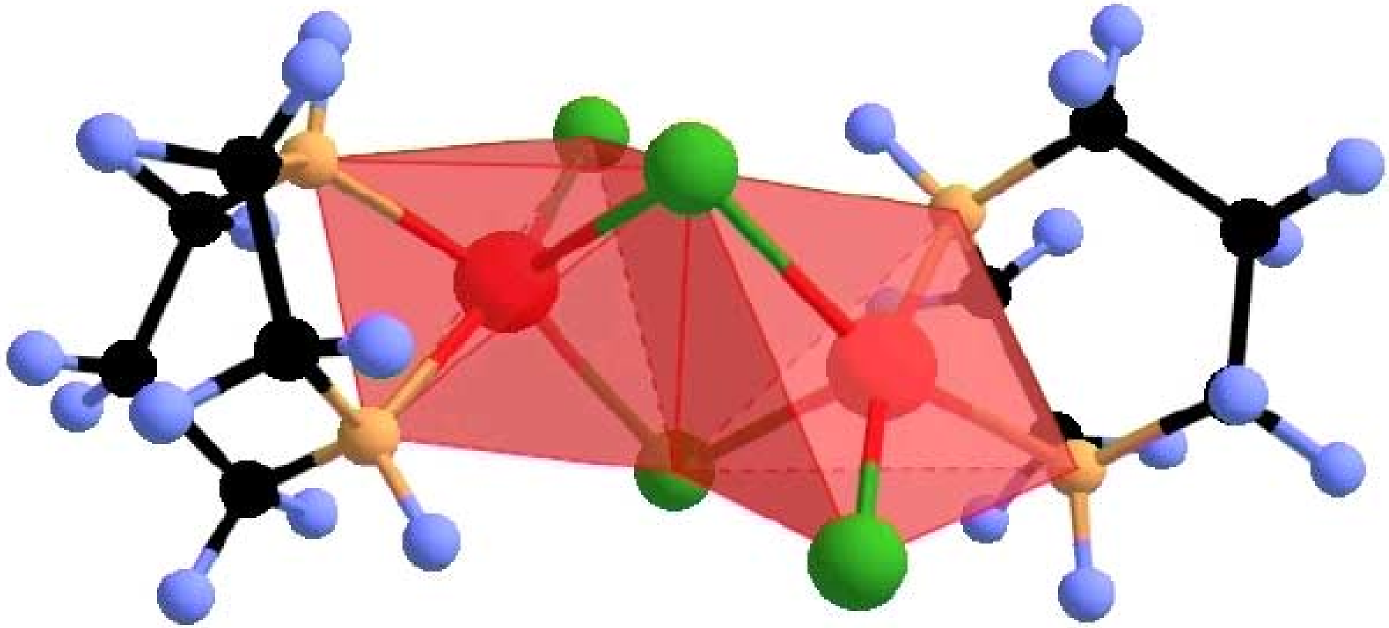



Peak to plateau ratio $> \max\left[1-\frac{\sin x}{x}\right] = 1.217$

→ Mixed signs for bond energies → Frustration

# Structure of CuHpCl

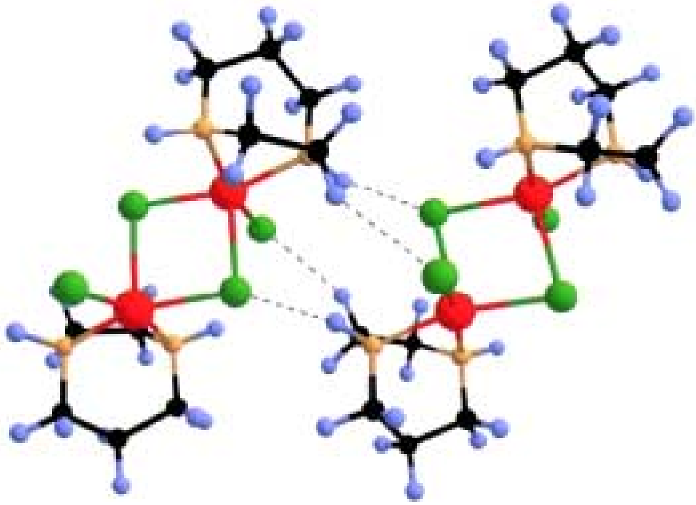
CuHpCl is hydrogen bonded crystal of $Cu_2(C_5H_{12}N_2)_2Cl_4$

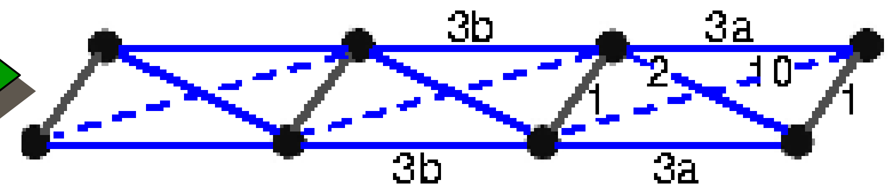


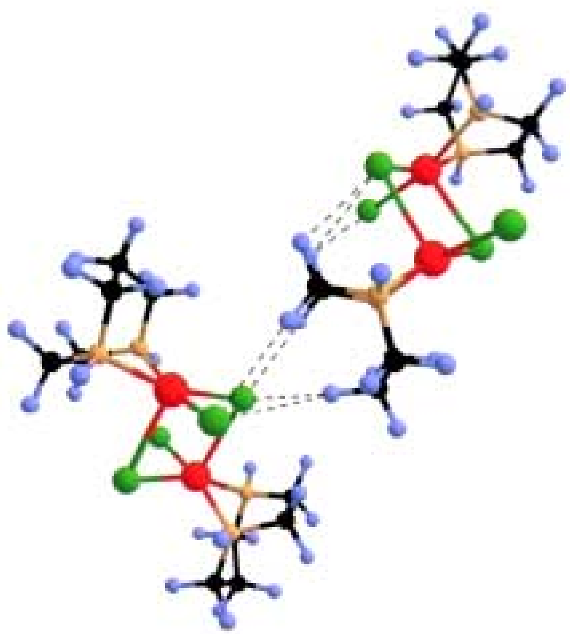
Molecules possess approximate centro symmetry

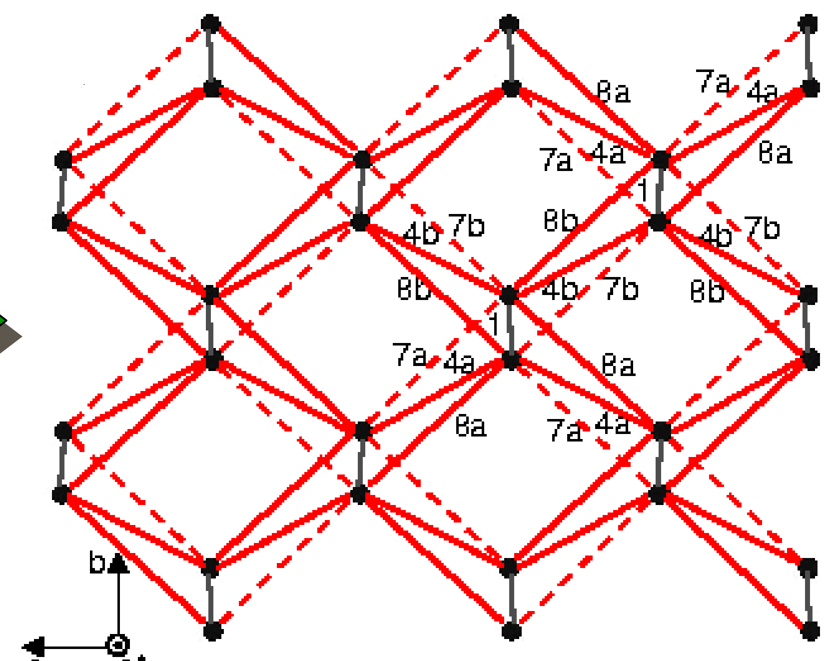
Exchange interaction within molecule $|J|<1$ meV

# Two lattices from H-bond exchange

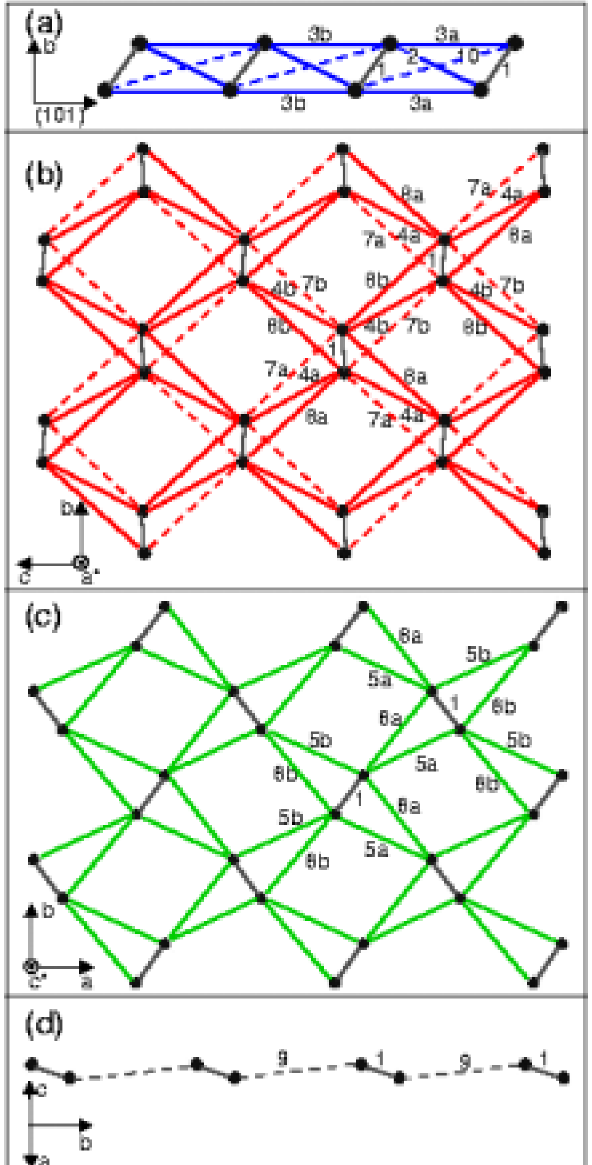


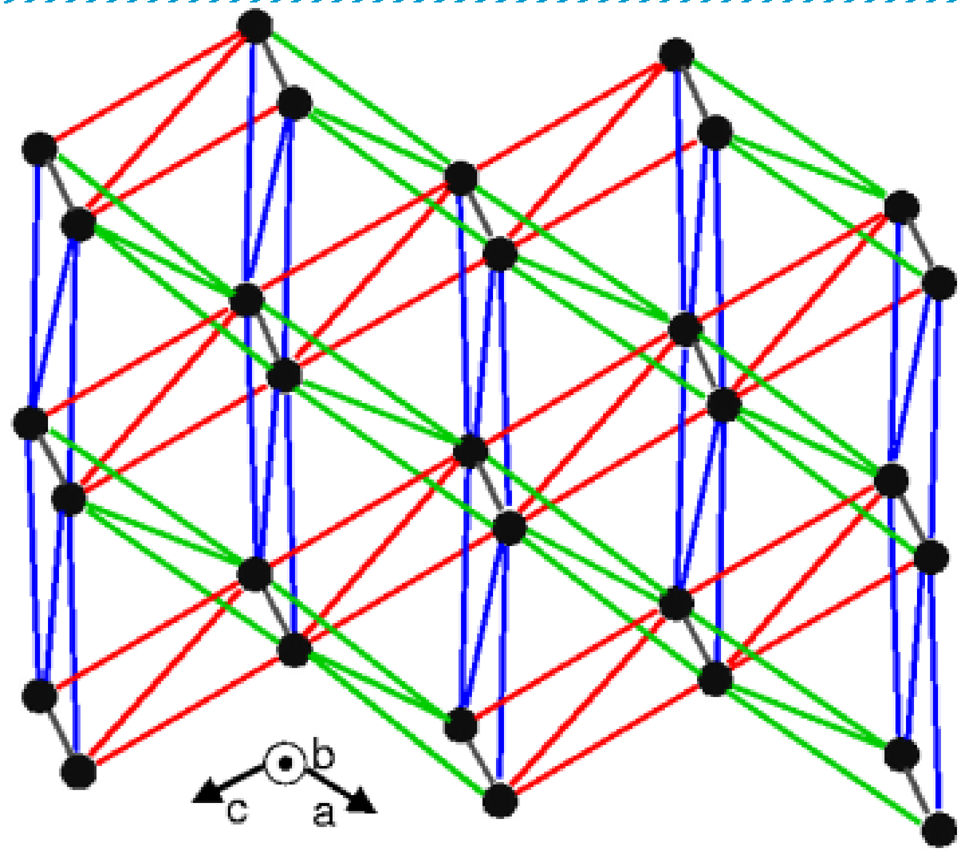




# Building an enigma

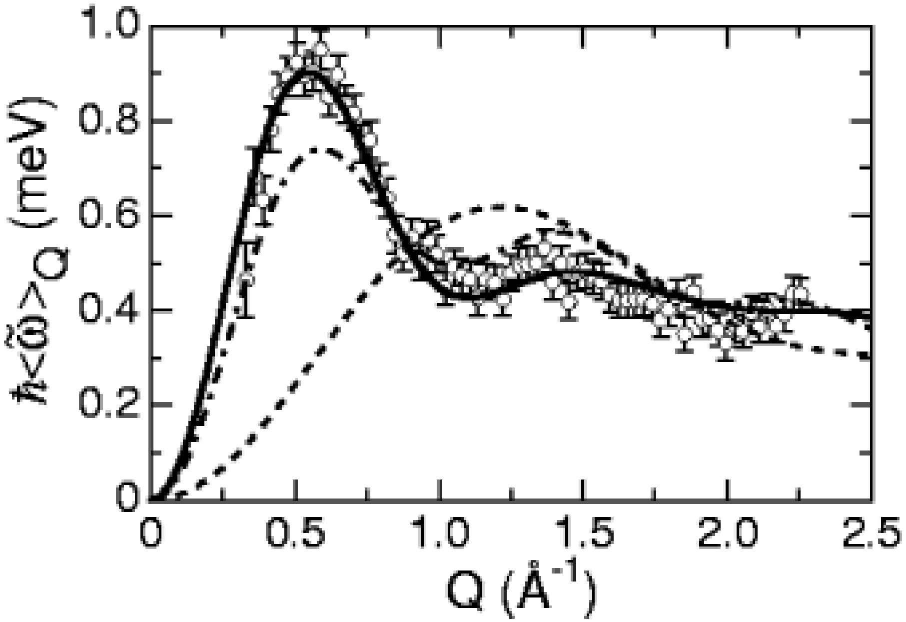


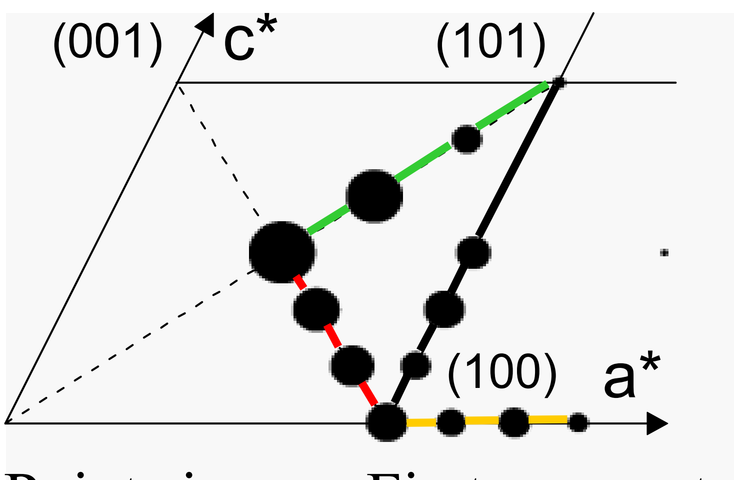




Dispersion throughout a-c plane

Spin liquid on 3-dimensional lattice

# Detailed bond energy distribution




Point size ∝ First moment

| Bond ID | $J_{\mathbf{d}}\langle \mathbf{S}_{\mathbf{0}} \cdot \mathbf{S}_{\mathbf{d}} \rangle$ (meV) |
|---|---|
| 1 | 0.42(3) |
| 2 | 0.06(4) |
| 3 | -0.29(3) |
| 4 | -0.18(1) |
| 5 | 0.06(2) |
| 6 | -0.05(4) |
| 7 | -0.09(7) |
| 8 | -0.15(3) |
| 9 | 0.1(2) |
| 10 | 0.01(5) |

# Frustrated three dimensional spin liquid

| Bond ID | $J_d \langle \mathbf{S}_0 \cdot \mathbf{S}_d \rangle$ (meV) |
|---|---|
| 1 | 0.42(3) |
| 2 | 0.06(4) |
| 3 | -0.29(3) |
| 4 | -0.18(1) |
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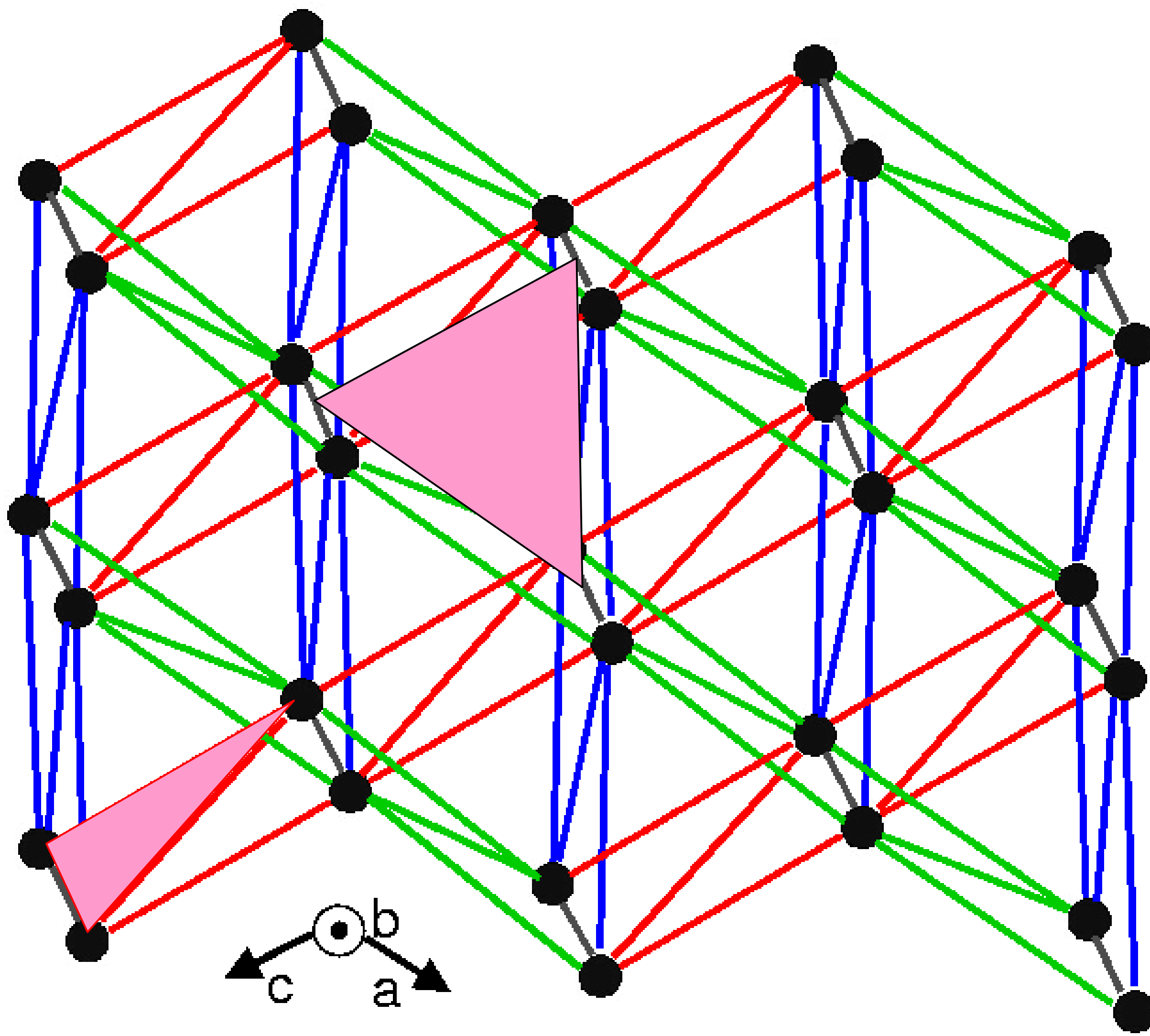
| 6 | -0.05(4) |
| 7 | -0.09(7) |
| 8 | -0.15(3) |
| 9 | 0.1(2) |
| 10 | 0.01(5) |

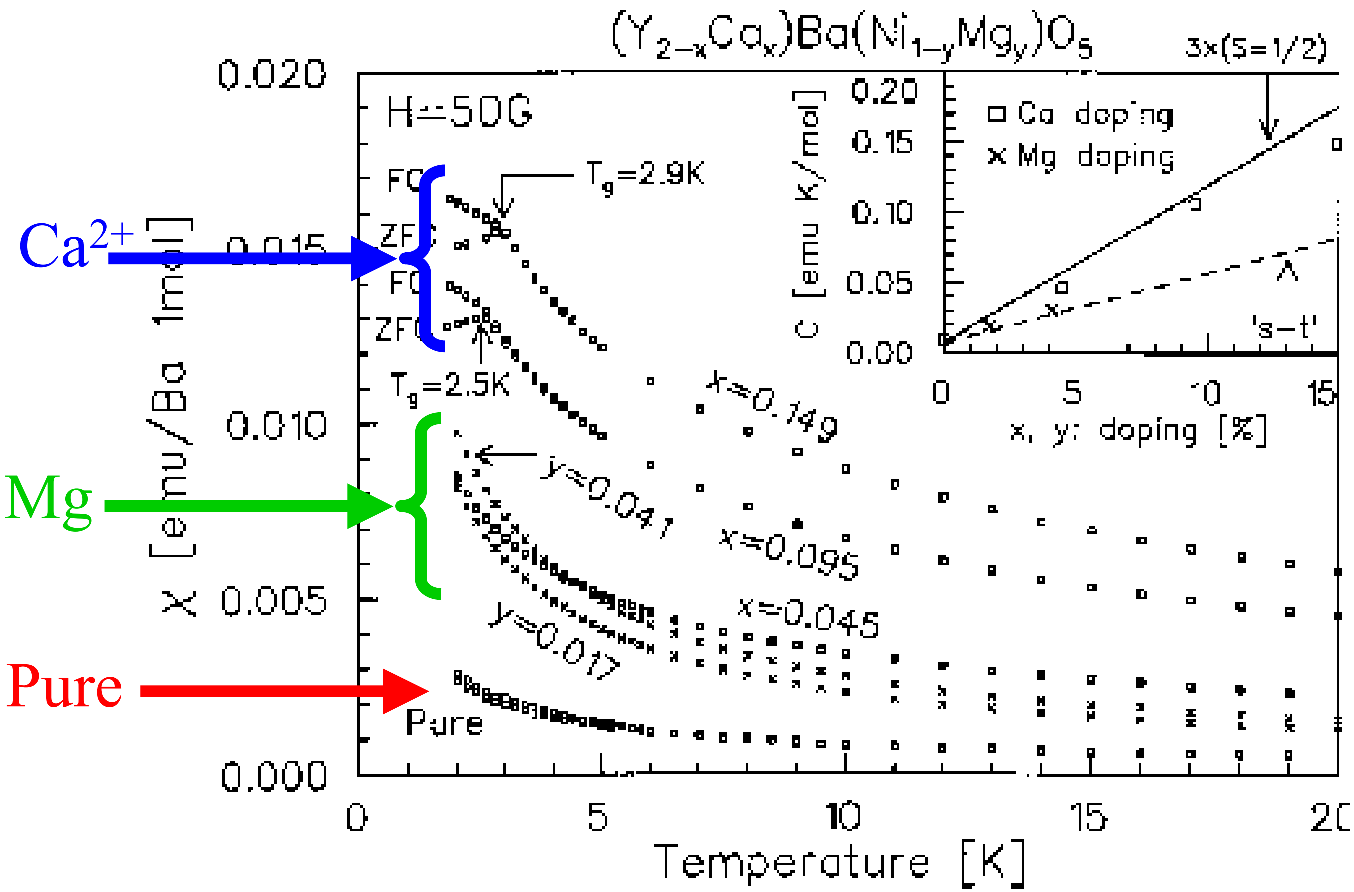


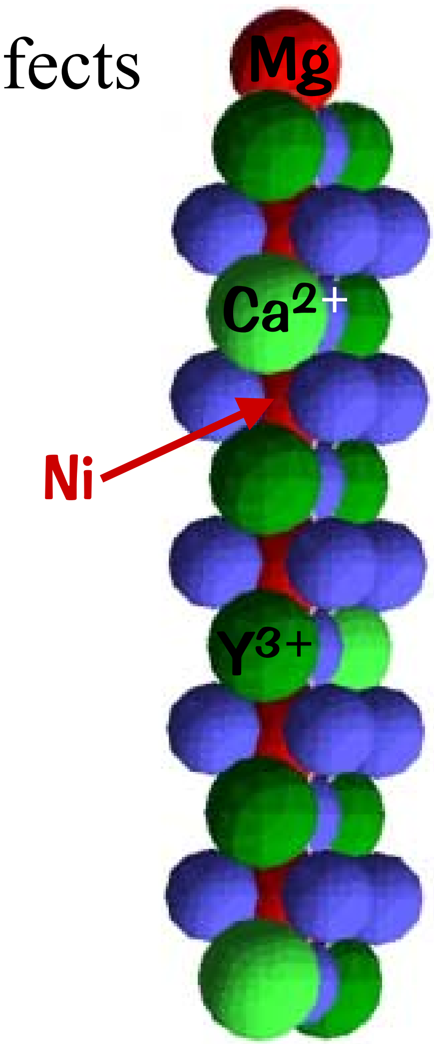
# Significance of findings so far

- Neutron scattering required to classify quantum spin liquids
- Systems thought to be one dimensional may represent a richer class of materials
- Experimental realizations of spin liquids were sought, not found, in symmetric frustrated magnets
- Perhaps spin liquids are more common in complex geometrically frustrated lattices

# Impurities in a quantum spin liquid

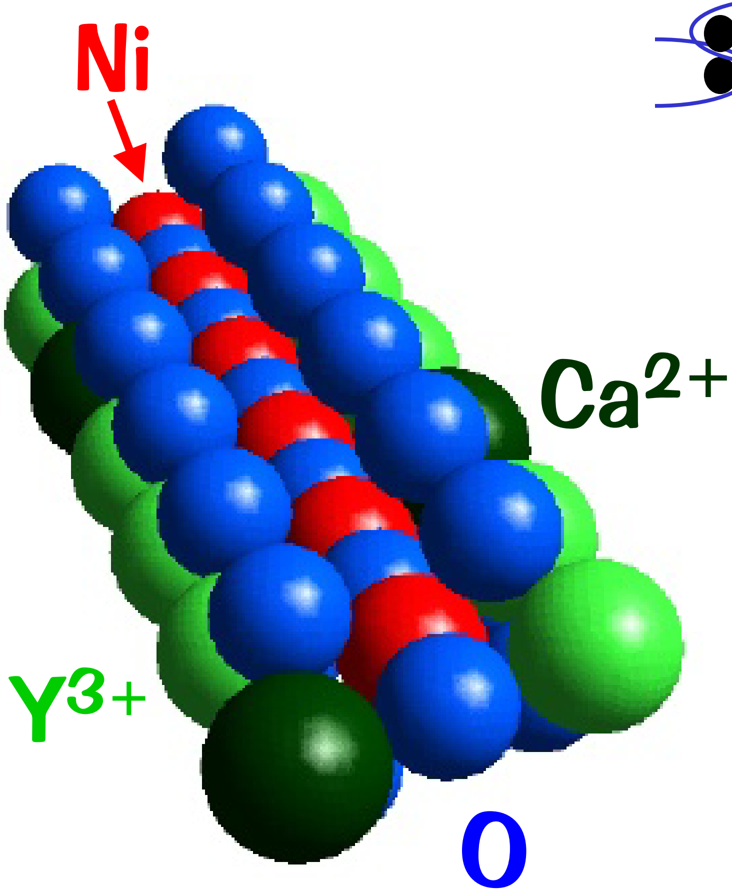
- $Mg^{2+}$ on $Ni^{2+}$ sites → finite length chains
- $Ca^{2+}$ on $Y^{3+}$ sites → mobile bond defects

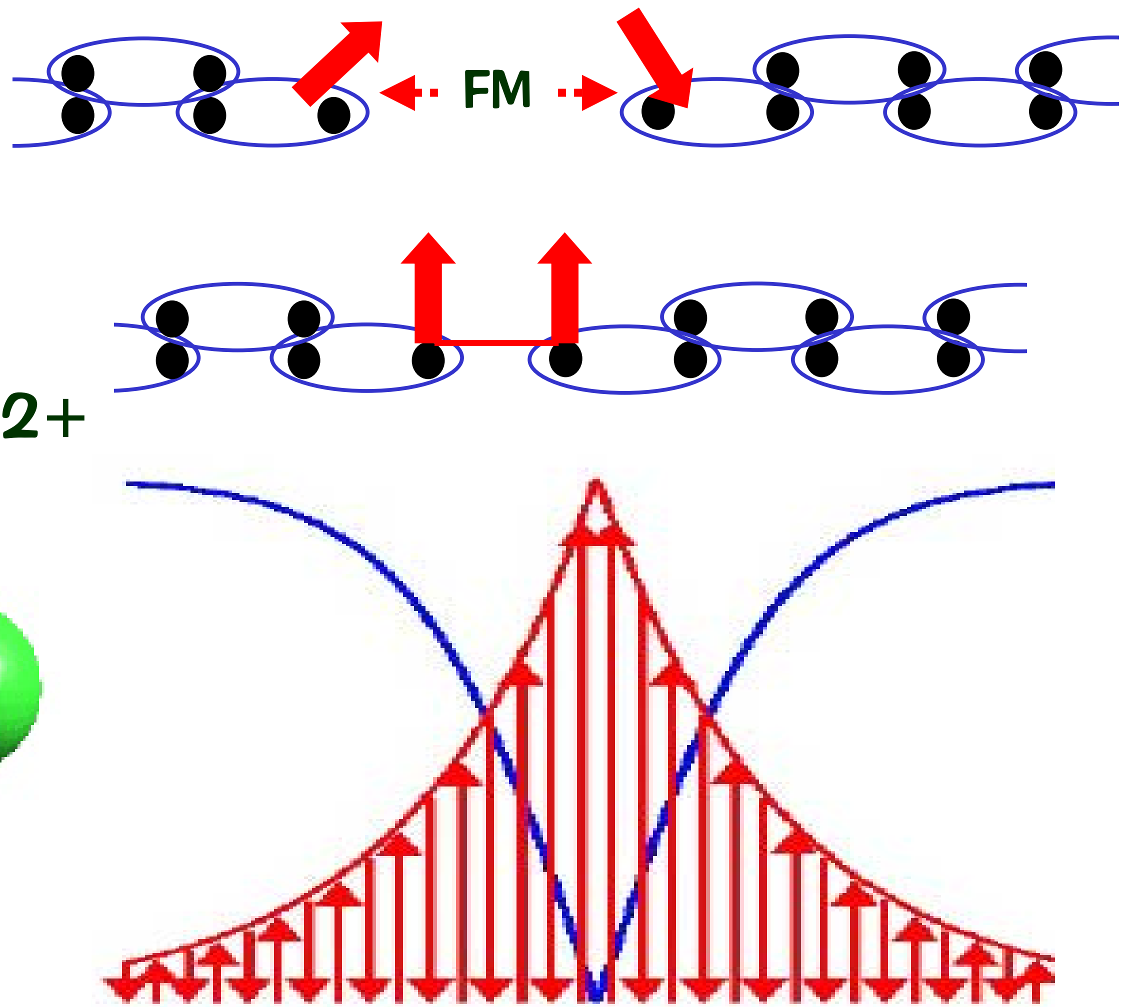



*Kojima et al. (1995)*

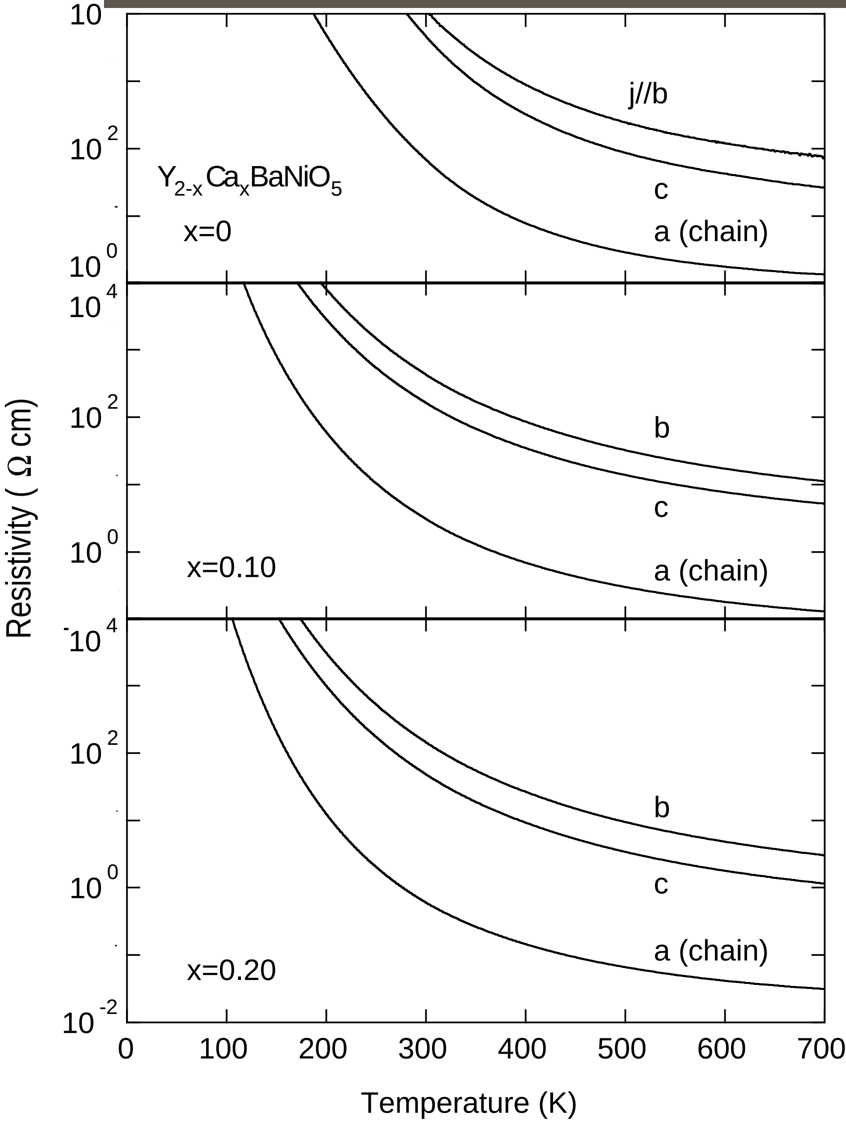
# Holes dressed by spin polarons



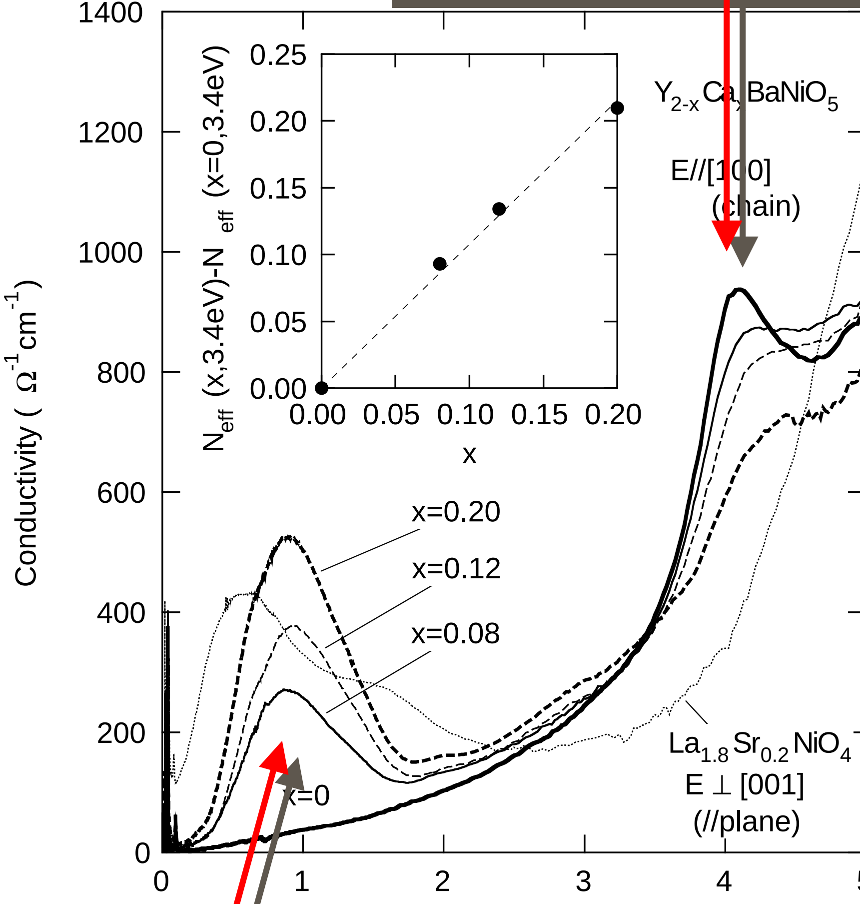



# Transport in Ca doped $Y_2BaNiO_5$

1D conductivity, no Charge ordering




Charge Transfer excitation

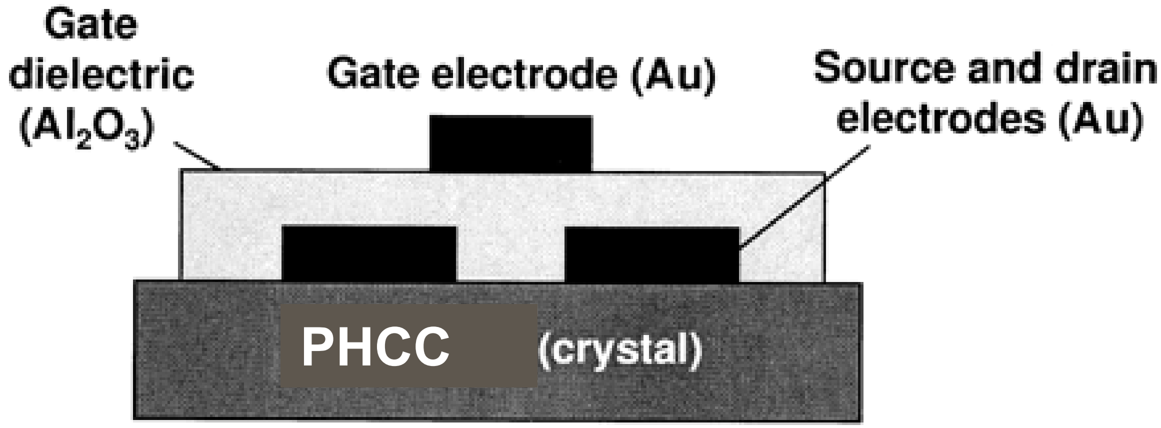



Charge polaron

*T. Ito et al. Submitted to PRL (2001)*

# Holes in a quantum spin liquid

- Experiments in one dimensional spin liquids show holes dressed by spin polaron
- However, impurities localize charge in one dimension
- Some organic materials can be doped and conduct in Field Effect Transistors [Schon et al. Science (2000)]




- If this were possible for organo-metallic spin liquids, could have fascinating correlated metals.

# Conclusions

- Spin systems with a gap can be mistaken for being quasi-one-dimensional
- Two and three dimensional moment free magnetism found in PHCC and CuHpCl
- Neutron scattering reveals frustrated bonds in the corner-sharing triangular clusters of these materials
- <u>Hypothesis:</u> Moment free magnetism may be a common state of interacting spin systems with triangular motif and weak connectivity
- <u>Idea:</u> Interesting transport properties may exist if the materials can be doped